Synthesis, Crystal Structure and Physico−Chemical Studies on Thienyl−Substituted Alkoxides of the Rare Earth Metals

Dissertation

Zur Erlangung des Grades
des Doktors der Naturwissenschaften
der Naturwissenschaftlich−Technischen Fakultät III
Chemie, Pharmazie, Bio− und Werkstoffwissenschaften
der Universität des Saarlandes

von

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Saarbrücken
2009

Tag des Kolloquiums:	16. 07. 2009
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Die vorliegende Arbeit entstand in der Zeit vom Oktober 2004 bis Juli 2009 in der Anorganischen Chemie der Universität des Saarlandes in Saarbrücken (Deutschland) unter Anleitung von Herrn Prof. Dr. Dr. h. c. Michael Veith und in der UTINAM der Universität des Franche−Comté (Frankreich) unter Anleitung von Herrn Prof. Dr. Michael Knorr.

Ich danke meinen verehrtenen Doktorväter, Herrn Prof. Dr. Dr. h. c. Michael Veith und Herrn Prof. Dr. Michael Knorr, recht herzlichen für die interessante Themenstellung und großzügige Förderung dieser Arbeit. Ihre hilfreichen Ratschläge und ihre ständige Diskussionsbereitschaft während der Durchführung haben maßgeblich zum Gelingen der vorliegenden Arbeit beitragen.

Allen Mitarbeiterinnen und Mitarbeitern des Instituts für Anorganische Chemie und des UTINAM, insbesondere dem AK Veith und Knorr, die auf verschiedenste Weise zum Gelingen dieser Arbeit beigetragen haben, sei recht herzlich gedankt.

Herrn H.D.R. Dr. Laurent Guyard, bin ich besonders dankbar für die wertvollen Ratschläge, die Diskussionsbereitschaft, sowie für seine Geduld, und auch für das gewissenhafte Korrekturlesen.

Herrn Dr. Volker Huch bin ich besonders dankbar für die Durchführung der Röntgenanalysen, für die wertvollen Ratschläge und die Diskussionsbereitschaft und auch für das gewissenhafte Korrekturlesen. Weiterhin danke ich Herrn Dr. Michael Zimmer für die Aufnahme der NMR−Spektren am 400er. Frau Helga Feuerhake und Frau Susanne Harling gelten mein Dank für die Durchführung der Elementaranalysen.

Des Weiteren möchte ich mich bei Prof. Dr. Claudia Wickleder und Dr. Hailing Cui (Universität Siegen, Deutschland) und Dr. Abderrahim Khatyr (Universität Besançon, Frankreich) für die Lumineszenzmessung.

Aber auch bei meiner Familie, und meinen Freunden, auch wenn sie wenig mit der eigentlichen chemischen Arbeit zu tun haben, möchte ich mich bedanken, da sie mir den nötigen Rückhalt gegeben haben.

J’exprime tous mes remerciements à toutes les personnes qui, de près ou de loin, m'ont supportée, encouragée, aidée tout au long ces années que j'ai investies dans cette recherche et dans la rédaction de cette thèse.
Je tiens à remercier tous mes amis de Besançon, de Moselle, de Saarbrücken, …
Merci à ma famille de m’avoir soutenue.
Merci à « l’équipe des pas prêts »: Valérie (à la soupe, jamais de la vie, tu rêves !!!) et son compagnon Patrick (promis, je vais suivre des cours d’informatique…), Richard (le coach; même pas cap…), Eve et Stéphane (si si, un jour tu verras…), et Vincent (notre clown de service; j’attends encore ton gâteau…).

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Table of Abbreviations

A	A: Ampere
B	bpm: 2,2’–bipyrimidine
C	CN: Coordination Number Cp: cyclopentadienyl Cp*: pentamethylcyclopentadienyl CV: cyclovoltametry
D	d: doublet / day dd: doublet of doublet DR: Diffuse Reflection
E	E: potential E_{pa}: anodic peak potential E_{pc}: cathodic peak potential EI: Electronic Ionisation *et al.*: and others (latin: et alii or et alteri)
F	FAB: Fast Atom Bombardment FWHM: Full Width at Half Maximum
G	g: gram
H	h: hour HH: Head–Head HOMO: Highest Occupied Molecular Orbital HT: Head–Tail Hz: hertz
I	I: intensity IR: infrared ITO: Indium Tin Oxide
J	*J*: coupling constant / resulting quantum number
L	LED: Light−Emitting Diode LUMO: Lower Unoccupied Molecular Orbital
M	m: multiplet M: metal / mol.L^{-1}

	MAS: Magic Angle Spinning mg: milligram mmol: millimol MRI: Magnetic Resonance Imaging
N	NIR: Near Infrared NLO: Non Linear Optical nm: nanometer NMR: Nuclear Resonance Magnetic
O	OM: Molecular Orbital
P	PCP: paracyclophane ppm: 10^{-6} part per million PT: polythiophene py: pyridine PATs: polyalkylthiophenes
R	R: organic function / reflexion indice RE: Rare Earths ref: reference
S	s: singlet / second
T	t: triplet T: thiophene 2T: bithiophene 3T: terthiophene thf: tetrahydrofuran tta: 2−thenoyltrifluoroacetonate
U	UV: ultra violet UV−Vis: ultra violet−visible spectroscopy
V	V: Volt
X	X: halogen
°	degree
°C	degree Celcius
Å	Ängström
δ	δ: chemical shift (NMR)

λ	λ: wavelength λ_{abs}: absorption wavelength λ_{em}: emission wavelength λ_{ex}: excitation wavelength
$\bar{\nu}$	number of waves

Table of Compounds

$HO–C(C_8H_5S_2)_3$	**1**	*sh2294*
$HO–C(C_4H_3S)_3$	**2**	*sh2302*
$HO–C(C_{14}H_{11}S_2)$	**3**	
$HO–C(C_{16}H_{13}S)$	**4**	
$HO–C(C_{17}H_{15}S)$	**5**	
$HO–C(C_{17}H_{15}S)$	**6**	
$HO–C(C_{14}H_{11}S_2)$	**7**	
$HO–C(C_{16}H_{13}S)$	**8**	
$Y[OC(C_8H_5S_2)_3]_3(thf)_2$	**9**	*sh2375*
$\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf	**10**	*sh2385*
$Er[OC(C_8H_5S_2)_3]_3(thf)$	**11**	
$\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf	**12**	*sh2389*
$[NaOC(C_4H_3S)_3]_4(thf)_2$	**13**	*sh2386*
$\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene	**14a**	*sh2438*
$\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf	**14b**	*sh2349*
$Sn[OC(C_4H_3S)_3]_2(thf)$	**15**	*sh2400*
$Y[OC(C_4H_3S)_3]_3(thf)_2$	**16a**	*sh2359*
$\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene	**16b**	*sh2443*
$Y[OC(C_4H_3S)_3]_3(py)_2$	**17a**	*sh2344*
$\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene	**17b**	*sh2437*
$\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf	**18**	*sh2390*
$\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf	**19**	*sh2557*
$Er[OC(C_4H_3S)_3]_3(thf)_3$	**20**	
$[KOC(C_{14}H_{11}S_2)]_4(thf)_3$	**21**	*sh2680*
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$	**22**	
$\{Nd[OC(C_{14}H_{11}S_2)]_3(thf)_3\}$ • thf	**23**	*sh2595*
$Er[OC(C_{14}H_{11}S_2)]_3(thf)$	**24**	
$\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf	**25**	*sh2565*
$\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene	**26**	*sh2579*
$\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene	**27**	*sh2620*

$\{Nd[OC(C_{16}H_{13}S)]_3(thf)_3\} \bullet thf$	**28**	*sh2591*
$\{Sm[OC(C_4H_3S)_3]_3(thf)_3\} \bullet thf$	**29**	*sh2605*
$Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$	**30**	
$[KOC(C_{17}H_{15}S)]_4(thf)_2$	**31**	*sh2656*
$[NaOC(C_{17}H_{15}S)]_4(thf)_2$	**32**	
$\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\} \bullet toluene$	**33**	*sh2667*
$\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\} \bullet toluene$	**34**	*sh2703*
$Er[OC(C_{17}H_{15}S)]_3[HOC(C_{17}H_{15}S)]$	**35**	
$Er[OC(C_{17}H_{15}S)]_3[HOC(C_{17}H_{15}S)]$	**36**	
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$	**37**	
$\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\} \bullet ½ toluene$	**38**	*sh2737*
$Y[OC(C_{14}H_{11}S_2)]_3(py)_2$	**39**	
$Nd[OC(C_{14}H_{11}S_2)]_3(thf)_3$	**40**	
$[NaOC(C_{16}H_{13}S)]_4(thf)_2$	**41**	
$Y[OC(C_{16}H_{13}S)]_3(py)_2$	**42**	
$\{Nd[OC(C_{16}H_{13}S)]_3(thf)_3\} \bullet thf$	**43**	*sh2698*
$Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$	**44**	

Zusammenfassung

Die vorliegende Dissertationschrift behandelt die Synthese, kristallographische Charakterisierung, sowie elektrochemische als auch photophysikalische Untersuchung von Thiophene−substituierten Methoxiden der Alkalimetalle, Sn(II) und Selten Erden.

Der erste Teil ist der Synthese, NMR− sowie der Kristallstruktur−Untersuchung der neuen Verbindungen gewidmet. Um strukturelle und stereoelektronische Effekt bezüglich der Molekülgeometrie miteinander korrelieren zu können, wurde eine ausgedehnte Serie von Metall−Alkoxiden dargestellt. Es wurden folgende zwei Parameter variiert: die Natur des Liganden, und die Natur des Metallzentrums. Zwei unterschiedliche Syntheserouten wurden ausgelotet: die Salz−Metathese und die Reaktion des Metallamids mit dem Alkohol.

Der zweite Teil umfasst die electrochemischen Eigenschaften der neuen Verbindungen. Die zyklischen Voltamogramme werden durch die Oxidationwelle der Thiophengruppen bestimmt. Jedoch lässt sich weder eine Reduktion noch Oxidation der Metallzentren nachweisen. Im Gegensatz zu den anderen Verbindungen führt das wiederholte Durchlaufen der Redoxpotentiale von $HO–C(C_8H_5S_2)_3$ (**1**), $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf (**10**) und $Er[OC(C_8H_5S_2)_3]_3(thf)$ (**11**) zur Ausbildung von Polymerfilmen.

Der dritte Teil beschreibt die Lumineszenz–Eigenschaften der neuen Verbindungen. Die UV−Vis Absorptionsspektren werden von den organischen Liganden ($\pi \rightarrow \pi^*$ Übergänge der Aromaten) dominiert. Die Emissionsspektren der Natrium, Kalium und Yttrium−Verbindungen zeigen breite Banden, welche den $\pi^* \rightarrow \pi$ Übergängen der aromatischen Liganden zugeordnet werden. Zudem belegen die Lumineszenzspektren der Nd^{3+} und Sm^{3+} Alkoxide einen Energietransfer (“Antenneneffekt“) vom Liganden hin zum Lanthanid−Zentrum.

Abstract

The present work focuses on the synthesis, crystal structure determination, electrochemical and luminescence studies of thienyl–substituted methoxides of alkali, tin(II) and rare earth metals.

The first part is devoted to the synthesis, NMR and crystallographic investigations of the new products. To correlate structural and stereoelectronic effects on the molecular geometry, a series of rare earth metal alkoxides was prepared. They were synthesized by varying two parameters: the nature of the ligand, and the nature of the metal centre. Two alternative synthetic pathways leading to alkoxides have been investigated: the salt metathesis reaction and the reaction between the metal silyl amides and the carbinols.

The second part deals on the electrochemical properties of the novel compounds. The CVs are dominated by the oxidation wave of the thiophene groups. No reduction or oxidation of the metal centres has been noticed. Contrarily to the other compounds, the repetitive cycling of potentials of $HO–C(C_8H_5S_2)_3$ (**1**), $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf (**10**) and $Er[OC(C_8H_5S_2)_3]_3(thf)$ (**11**) leads to the formation of polymeric film.

The third part concerns the luminescence properties of the novel compounds. The UV−Vis absorption spectra are dominated by the organic ligands ($\pi \rightarrow \pi^*$ transitions of the aromatic groups). The emission spectra of the potassium, sodium and yttrium compounds reveal broad bands attributed to the $\pi^* \rightarrow \pi$ transitions of the aromatic ligands. Furthermore, the luminescence spectra of the Nd^{3+} and Sm^{3+} alkoxides exhibit an energy transfer (“antenna effect”) from the ligand to the lanthanide centre.

Résumé

Ce travail porte sur la synthèse, la détermination des structures cristallographiques, l'étude des propriétés électrochimiques et la luminescence de méthoxydes contenant des groupements thiophéniques de métaux alcalins, d'étain(II) et de terres rares.

La première partie est consacrée à la synthèse et aux études RMN et cristallographiques des nouveaux composés. Afin de corréler les effets structuraux et stéréoélectroniques sur la géométrie moléculaire, une série d'alcoxydes métalliques a été préparée. Ils ont été synthétisés en variant deux paramètres: la nature du ligand et la nature du centre métallique. Deux voies de synthèse ont été envisagées: la réaction de métathèse et la réaction entre les amidures métalliques et les carbinols.

La seconde partie traite des propriétés électrochimiques des composés. Les voltammogrammes cycliques sont dominés par la vague d'oxydation des unités thiophéniques. Aucune réduction ou oxydation due aux centres métalliques n'a été constatée. Contrairement aux autres composés, après cyclage de la rampe de potentiels, la formation d'un film électroactif a été observée dans le cas des produits $HO–C(C_8H_5S_2)_3$ (**1**), $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\} \bullet 4\,thf$ (**10**) et $Er[OC(C_8H_5S_2)_3]_3(thf)$ (**11**).

La troisième partie concerne les propriétés de luminescence des produits. Les spectres d'absorption UV−Vis sont dominés par les ligands organiques (transitions $\pi \rightarrow \pi^*$ des groupements aromatiques). Les spectres d'émission des composés du potassium, sodium et yttrium révèlent de larges bandes attribuées aux transitions $\pi^* \rightarrow \pi$ des groupements aromatiques. En outre, les spectres de luminescence des alcoxydes de Nd^{3+} et de Sm^{3+} mettent en évidence un transfert d'énergie (effet d'antenne) entre le ligand et le lanthanide.

Chapter 1 Introduction

Part 1 Aims of this Study

During the last decade, the synthesis and photophysical investigations of trivalent rare earth compounds have received a great deal of attention.[1] Indeed, these types of materials have found a lot of applications, for example as optical signal amplifiers,[2] lasers,[3] or as luminescence probes in biological systems.[4] Unfortunately, trivalent lanthanide ions have an intrinsic small molar absorption coefficient in the UV−Vis−NIR spectrum due to their parity forbidden *intra*−configurational *4f*−*4f* transitions. However, upon coordination with organic ligands acting as “antenna”, absorbing and transmitting energy to the rare earth ion and thus increasing their luminescence efficiency, lanthanide compounds appear to be promising candidates.[5] The choice of the ligand for complexation plays a key role in constructing efficient luminescence lanthanides complexes. Two common requirements for selecting a ligand for coordination with lanthanide ions are the metal binding strength and ultraviolet (UV) absorption properties of ligands. Among several categories of ligands, nitrogen– and oxygen–donor groups have been utilized in the sensitization of lanthanide luminescence. In particular, bidendate aromatic amines, carboxylic acids and β–diketonates are known to provide energy transfer to lanthanides ions.[6] However, to date only few examples of lanthanide complexes bearing sulphur moieties have been reported[7] probably due to the generally lower stability and the mismatch between a soft sulfur–donor ligand and a hard lanthanide metal ion. In particular, those containing thienyl rings have been barely explored, although their transition metal counterparts have been investigated in detail.[8] This interest stems from the fact that thiophene derivatives are quite attractive as organic ligand systems because of their electroactive character and their rich−electron system. A further aspect is the ease of electropolymerisation of thienyl precursors by voltametric methods, thus allowing the formation of polymer films which can be conducting or not.[9] Moreover, poly−compounds involving thiophene unit have attracted much attention as components of electronic devices.[10]

The Besançon research group has a long−standing tradition and experience on the design of novel sulphur−rich compounds (dithiolenes, tetrathiafulvalenes, polythioethers and thiophene derivatives) and the study of their physico−chemical properties (NLO, luminescence, redox−activity, electropolymerization). Since the research group of Prof. Veith has the know−how in the preparation of lanthanide compounds and the handling of even quite moisture sensitive metal alkoxides including their structural characterization, the objective of this Ph.D. work was to combine these complementary competences in order to design novel lanthanide complexes bearing thienyl ligands. The strategy that we have chosen is to develop suitable tertiary alcohols with thienyl substituent; capable to be bonded on rare earth metal centres through a covalent M−O−R bond, leading to coordination compounds with singular redox and luminescence properties.

Our objective is triple:

1) Synthesize and characterize new rare earth functionalized alkoxides containing thienyl substituents.
2) Study the electrochemical properties of these compounds, the formation of polymeric films and to correlate the influence of the different organic ligands and metal used.
3) Study the luminescence properties of the lanthanide alkoxides and the influence of the thienyl groups and lanthanides on the antenna effect.

1 Synthesis and Crystal Structure Investigations of New Rare Earth Methoxides Containing Thienyl Substituents

With the aim to synthesize new rare earths alkoxides, we have chosen to study the reactivity of tertiary alcohols containing thienyl substituents (Figure 1.1) towards lanthanides and to determine their crystal structures. Their propensities to act as alkoxide ligands via covalent M–O bonding are based on the inherent weak acidity of these compounds, which therefore can be easily deprotonated. Moreover, the products obtained are assumed to be very suitable for the elaboration of efficient luminescent materials due to the electron−rich system and the lack of high phonon[i] groups like OH or NH in the ligands, which would lead to some quenching processes also in the case of lanthanide ions emitting in the NIR range.

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[i] Phonons are a quantum mechanical version of a special type of vibrational motion, known as normal modes in classical mechanics, in which each part of a lattice oscillates with the same frequency.

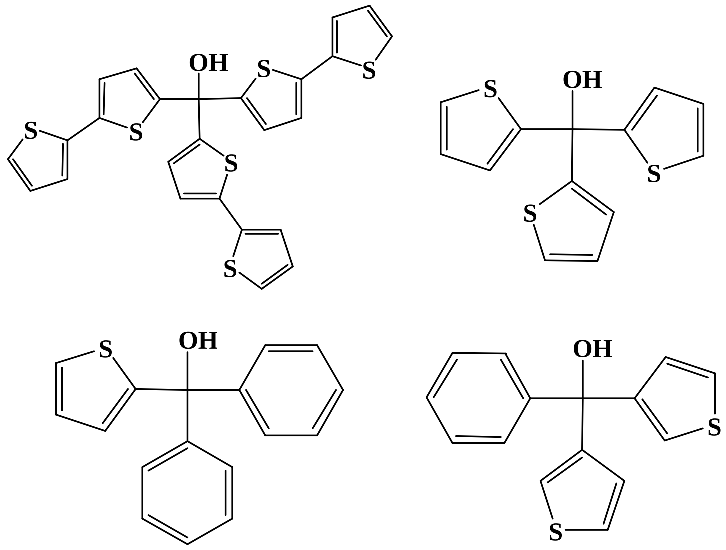


Figure 1.1. Examples of organic ligands used.

To correlate structural and steric effects on the molecular geometry, a series of rare earth methoxides containing thienyl substituents was prepared. They were synthesized by varying two parameters: i) the nature of the alkoxothiophene ligand, and ii) the nature of metal centre. Two way of synthesis have been studied: the reaction between the metal silyl amides and the carbinols, and the salt metathesis reactions. These works will be developed in Chapter 2.

2 Electrochemical Studies of Metal Methoxides Containing Thienyl Substituents

Thiophene derivatives are electrochemically oxidable. In Chapter 3, we will present the redox properties of the star–shaped molecules and the metal alkoxides. We will study the influence of two parameters on these properties: i) the organic ligand: the longer of the thienyl chains, the number of thienyl and phenyl groups present in the molecule, the functionalization of the thienyl moieties and their attached position; ii) the nature of the metal centre.

3 Luminescence Studies of Metal Methoxides Containing Thienyl Substituents

In Chapter 4, we will discuss about the luminescence properties of the products. The organic ligands, alkali metal alcoholates and the yttrium alkoxides are investigated to get some informations about the position of the electronic excited states of the bonded ligands. Then, we will present the luminescence properties of the lanthanide alkoxides and study the influence of the organic ligands and the metal centre used on the "antenna effect".

Part 2 Chemistry, Properties and Applications of Thiophenes, Oligothiophenes and Polythiophenes

1 Thiophenes and Oligothiophenes

1.1 Thiophenes

Thiophene is a 1–heterocyclopenta–2,4–diene, a heterocyclic compound (Figure 1.2). It contains a sulphur heteroatom carrying formally two non−bonding doublets. This system contains π–delocalized electrons forming an aromatic structure of 6 electrons. The aromatic structure of thiophene is similar to that of the cyclopentadienyl anion. This latter can be considered as a butadiene bonded to a negatively charged carbon and in which the negative charge is delocalized over the 5 carbons. In its stead, the thiophene skeleton contains a neutral atom carrying free electronic pairs which are delocalized in a similar manner, thus providing the two electrons necessary to satisfy the Hückel rule's of $4n + 2$ electrons. As can be seen in Scheme 1.1, to optimize the orbital overlap, the heteroatom is considered to be sp^2 hybridized; one electronic pair making part of the delocalized π−system is situated in the p orbital lobe. The second electronic pair is formally localized in sp^2 hybrid orbital in a coplanar mode, and therefore does not participated in an efficient overlap with the π−conjugated ring system.

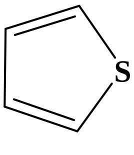
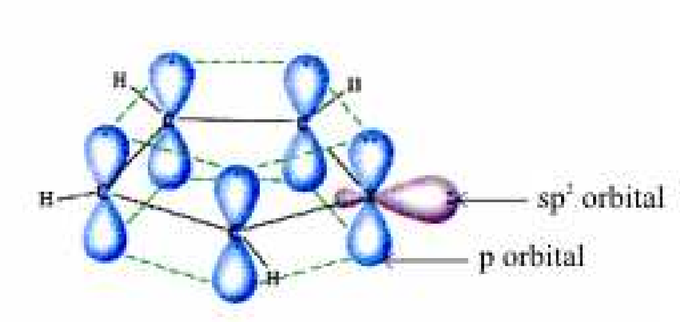


Figure 1.2. Thiophene molecule.



Scheme 1.1. Atomic orbitals of thiophene.

Thiophene was discovered as a contaminant in benzene.[11] It was observed that isatin[ii] forms a blue dye if it is mixed with sulphuric acid and crude benzene. The formation of the blue indophenin was long believed to be a reaction with benzene. Victor Meyer was able to isolate the substance responsible for this reaction from benzene. This new heterocycle compound was indeed thiophene.[12] Thiophene and its derivatives occur in petroleum, sometimes in concentrations up to 1–3 %.

Several types of nomenclature have been established for the thiophenes and the thiophene derivatives. Short notations like the original proposed by Bredt[13] and later on by Steinkopf[14] were later followed by the general and more convenient abbreviations T and nT. However, only the much more complicated systematic nomenclature allows to precise denotation of linkages between rings and positions or substituents. The numbering scheme of thiophene and 2,2'–bithiophene is given in Figure 1.3.

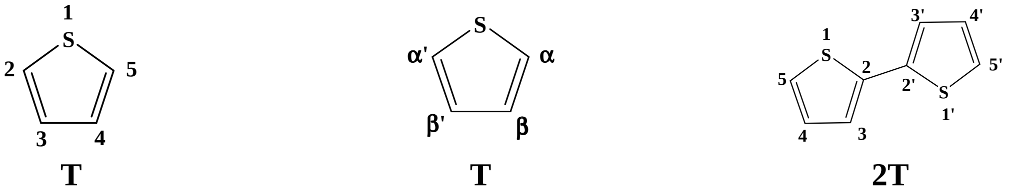


Figure 1.3. Nomenclature of thiophene T and of 2,2'–bithiophene 2T.

Thiophene is considered as an aromatic compound, although theorical calculations suggest that the degree of aromaticity is less than the degree of aromaticity of benzene. As a consequence of its aromaticity, thiophene does not exhibit the properties seen for conventional thioethers.

Although the sulphur atom itself is relatively unreactive, the flanking carbon centres, the 2– and 5–positions, are highly susceptible to attack by electrophiles. For examples, halogens give initially 2–haloderivatives followed by 2,5–dihalothiophene. Perhalogenation is easily accomplished to give C_4X_4S (X = Cl, Br, I).[15]

Thiophene is also readily lithiated with *n*–butyl lithium to give 2–lithiumthiophene, which is a good precursor to a variety of derivatives, including thienyl.[16]

[ii] Isatin or 1H–indole–2,3–dione is an indole derivative.

1.2 Oligothiophenes: Definition and Generalities

An oligothiophene is a delocalized π–system consisting of a limited number of monomer units (n < 10), adopting an anti–conformation (Figure 1.4).

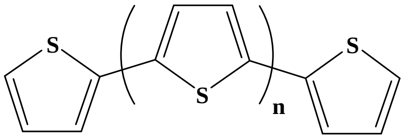


Figure 1.4. Representation of an oligothiophene.

The conjugated oligothiophenes are, like thiophene−based polymers, materials which are exhaustively studied since many years, since they can serve as model compounds for the polymer investigations. Indeed, oligothiophenes are easier to be investigated than polythiophenes. The first oligothiophenes, perfectly defined, have been isolated in 1947 by Zechmeister *et al.*.[17] Since, they have been synthesized by different ways such as coupling reactions,[18] for example (see section 2. Polythiophenes). The polymerisation of thiophene derivatives containing more than 6 non–substituted cycles is difficult due to their insolubilities. However, it is not necessary to place a substituent on each cycle to increase the solubility (contrarily to the polymers). The smaller terms (up to 6 monomeric units) can be polymerized.[19] The derivatives with 11 or 12 thiophenic cycles exhibit electric conductivities comparable to that of polythiophenes.[19a]

1.3 Applications

1.3.1 Luminescence Properties of Thiophenes, Thiophene Derivatives and Oligothiophenes

In absorption and fluorescence spectroscopy, two important types of frontier orbitals are considered: the Highest Occupied Molecular Orbitals (HOMO) and the Lowest Unoccupied Molecular Orbitals (LUMO). Both of these refer to the ground state of the molecule. The different luminescent mechanisms in organic compounds have been summarized in the Perrin–Jablonski diagram (Figure 1.5). It shows the possible processes such as photon absorption, internal conversion, fluorescence, intersystem crossing, phosphorescence, and delayed fluorescence and triplet–triplet transitions.

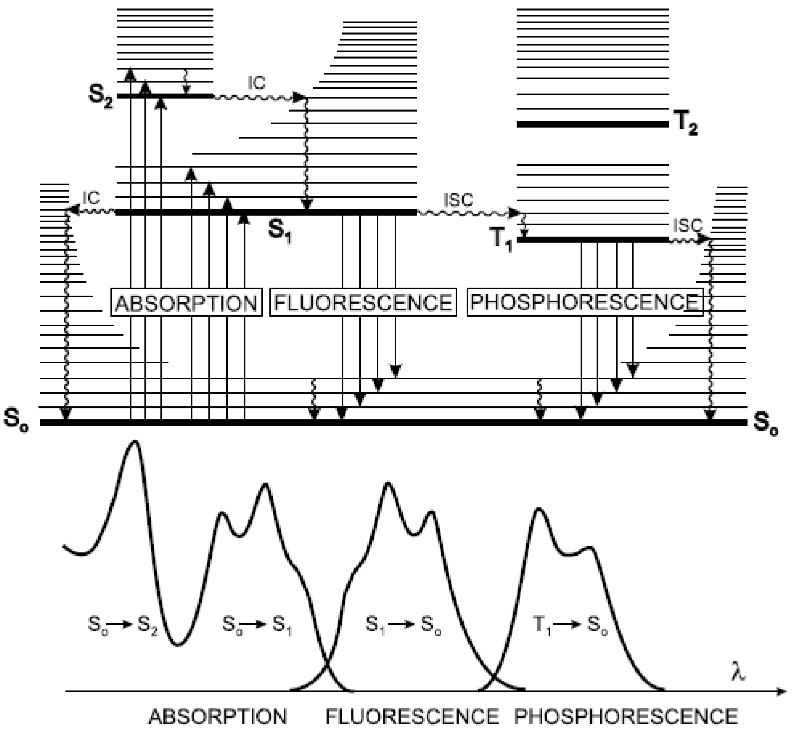


Figure 1.5. Perrin–Jablonski diagram and illustration of the relative positions of absorption, fluorescence and phosphorescence spectra. The singlet electronic states are denoted S_0 (fundamental electronic state), S_1; S_2; . . . and the triplet states, T_1; T_2; . . . : Vibrational levels are associated with each electronic state.

The internal conversion is a non–radiative transition between two electronic states of the same spin multiplicity. From S_1, internal conversion to S_0 is possible but is less efficient than conversion from S_2 to S_1, because of the much larger energy gap between S_1 and S_0. Therefore, internal conversion from S_1 to S_0 can compete with emission of photons (fluorescence) and intersystem crossing to the triplet state from which emission of photons (phosphorescence) can possibly be observed. Emission of photons accompanying the $S_1 \rightarrow S_0$ relaxation is called fluorescence. It should be emphasized that, (apart from a few exceptions), fluorescence emission occurs from S_1 and therefore its characteristics (except polarization) do not depend on the excitation wavelength (provided of course that only one species exists in the ground state).

In solution at room temperature, non–radiative de–excitation from the triplet state T_1, is predominant over radiative de–excitation called phosphorescence. In fact, the transition $T_1 \rightarrow S_0$ is forbidden (but it can be observed because of spin–orbit coupling), and the radiative rate constant is thus very low. During such a slow process, the numerous collisions with solvent molecules favour intersystem crossing and vibrational relaxation in S_0. On the contrary, at low temperatures and/or in a rigid medium, phosphorescence can be observed. The lifetime of the triplet state may, under these conditions, be long enough to observe phosphorescence on a time–scale up to seconds, even minutes or more. The phosphorescence spectrum is located at wavelengths higher than the fluorescence spectrum because the energy of the lowest vibrational level of the triplet state T_1 is lower than that of the singlet state S_1.

Thiophenes, thiophene derivatives and oligothiophenes are electron−rich systems via their *π*–rings, and therefore can act as chromophores. Their absorption and excitation spectra are dominated by the $\pi \rightarrow \pi^*$ transitions and the emission spectra by the $\pi^* \rightarrow \pi$ transitions. Becker *et al.*[20] have studied the absorption and emission spectra of nT (Table 1.1) and shown that the increase of thienyl units in the oligothiophenes causes a red−shift of the transitions due to a more important conjugation inside the molecules.

	T	**2T**	**3T**	**4T**	**5T**	**6T**	**7T**
Abs. Max. [nm]	231	303	354	392	417	436	441
Em. Max. [nm]		362	426	478	482	502	522

Table 1.1. Shift of the maxima in the electronic spectra of unsubstituted nT in dioxane at room temperature.

One of the strategies to increase the luminescence properties of compounds containing thienyl substituents consists to attach a paracyclophane unit (PCP) on the heterocycle. The orbital overlap between the two rings of the PCP is quite more important and can possibly lead to an electronic connection between appropriately substituents on both rings. In addition, although cyclophanes usually have an electron–rich character, this may be adjusted by the choice of appropriate substituents on both rings. This research axis has been developed in the Besançon laboratory by Guyard *et al.*.[21] For example, they have synthesized new cyclophane–derivatized oligothiophenes (Figure 1.6), and demonstrated that for 4 or 6 thienyl units, the molecules display a strong fluorescence and should be promising compounds for LED devices.

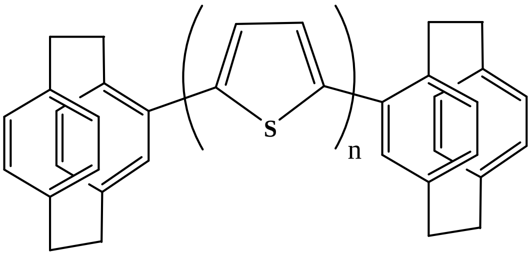


Figure 1.6. New cyclophane–derivatized oligothiophenes. n = 2, 3, 4, 6.

1.3.2 Optical Applications: the Push–Pull Molecules

Another interest of these thiophene derivatives or oligothiophenes lies in these non–linear optical properties. According to the works of Davydov *et al.*[22] there is a direct correlation between the NLO properties of organic materials and their electronic structure. In the 80's Zyss[23] has shown that optimized candidates for strong NLO behaviour are molecules possessing a donor group connected to an attractive group via a *π*–delocalisable electron spacer (Scheme 1.2). Indeed, the effect of the second order in NLO originates from the intramolecular interactions between a donor and an acceptor (charge transfer between two groups of opposite nature).

Donor——$\boxed{\pi\text{–conjugated system}}$——Acceptor

Scheme 1.2. Schematic representation of a push–pull molecule.

Push–pull molecules containing thienyl derivatives or oligothiophenes have been investigated in previous works in the laboratory.[9a, 24] From the theoretical studies which are rendered the principal factors to develop attractive NLO properties, some chromophores have been synthesized and their NLO properties investigated (Figure 1.7).

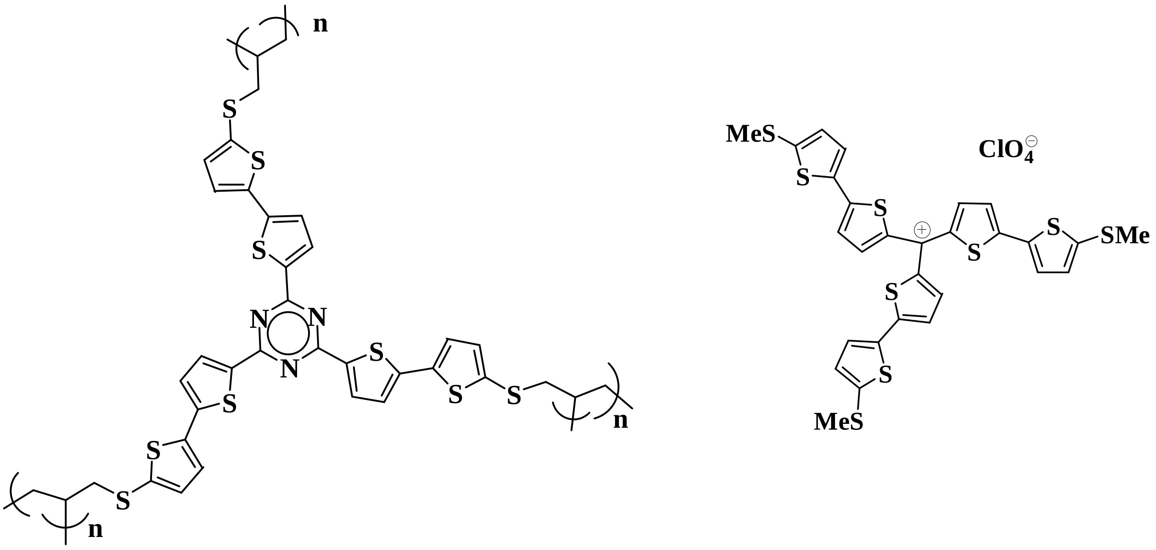


Figure 1.7. Examples of Push–Pull molecules studied in the Besançon laboratory.

1.3.3 Coordination Chemistry of Thiophenes, Thiophene Derivatives and Oligothiophenes

1.3.3.1 Transition Metals

As explained above, thiophene derivatives and oligothiophenes are attractive materials because of their potential applications in the field of electronic and optoelectronic devices. Incorporation of transition metals with their large varieties of ligand environments and oxidation states is expected to increase the molecular hyperpolarizability and to enhance the already appealing NLO properties of these compounds.[25] Several types of metal–complexes interacting with thiophene−type ligands have been studied: the π–complexes, the cleaving of C–S bonds from thiophenes and the functionalization of the heterocycles to allow for the appropriate ligated groups to be bonded to the terminal rings.

1.3.3.1.1 The π–Coordination

The reactions of the Cp*M units with thiophene derivatives can lead to π metal–arenes with varying coordination modes. For example, Angelici *et al.*[26] have elaborated one system in which a new mode of thiophene ligand bonding is observed (Figure 1.8). Another research group's, Graf *et al.*,[27] has synthesized $[(\mathrm{CpRu})_x(\eta^y,\eta^z\text{–oligothiophene})](\mathrm{PF}_6)_x$ and studied the influence of the ruthenium on the properties of the terthiophene array (Figure 1.8).

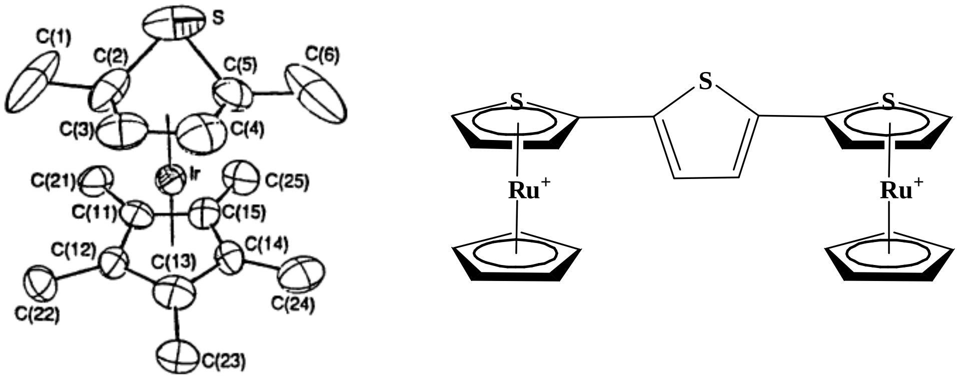


Figure 1.8. Examples of π–coordination.

1.3.3.1.2 The Cleaving of C–S Bonds from Oligothiophenes

Organometallic complexes with thienyl ligands can be obtained by exploiting the electron–rich metal fragments ability to cleave C–S bonds of thiophenes in regioselective manner.[28] This approach allows a one–pot access to new structural motifs in which oligothiophenes may act as spacers between metal centres. In this category, we can cite the [MeC(CH_2PPh_2)$_3$]Rh{η^3–SC[5–(2,2':5',2''–terthienyl)]=CHCH=CH_2} (Figure 1.9).[29]

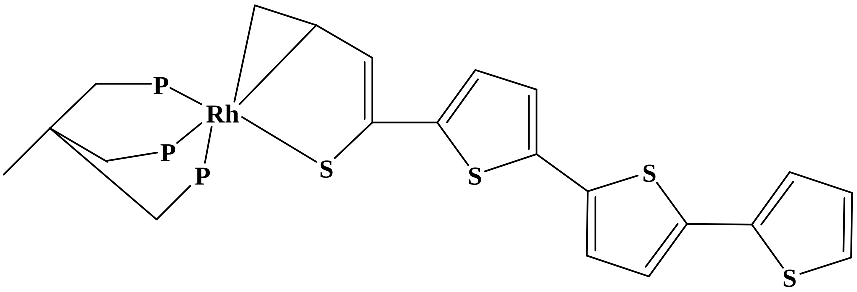
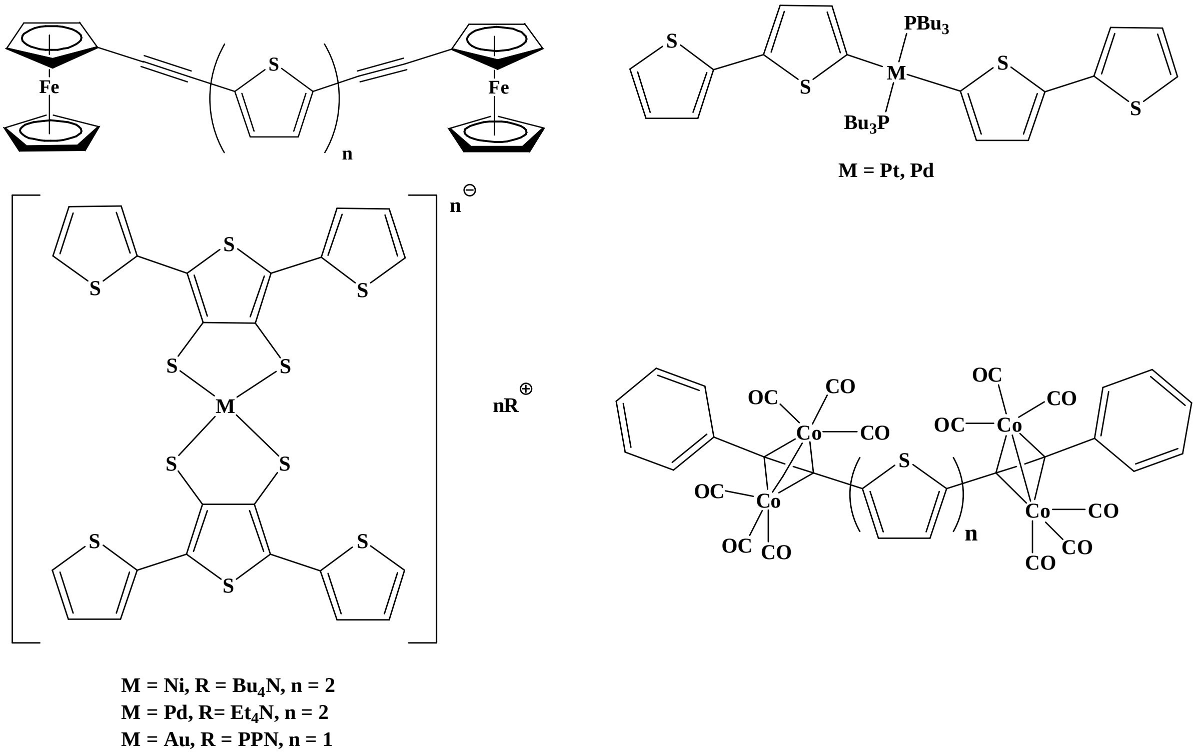


Figure 1.9. [MeC(CH_2PPh_2)$_3$]Rh{η^3–SC[5–(2,2':5',2''–terthienyl)]=CHCH=CH_2}.

1.3.3.1.3 The Functionalization of the Heterocycles to Allow for the Appropriate Ligated Groups to Be Bonded to the Terminal Rings

This domain of research is very large. Thiophenes or oligothiophenes have been first functionalized by lithium, ethylene function(s), sulphur atom(s), carboxylic acid, etc...[30] and then react with metal derivatives to form the desired complexes (Figure 1.10).



M = Ni, R = Bu$_4$N, n = 2
M = Pd, R= Et$_4$N, n = 2
M = Au, R = PPN, n = 1

Figure 1.10. Examples of metal complexes containing thiophene or oligothiophene derivatives.

1.3.3.2 Rare Earths

Lanthanides complexes containing thiophene or oligothiophene derivatives have been less explored than theses transition metal analogs.[7] But the chemistry of such complexes is receiving more and more attention because of their applications as luminescence materials, for example. Thiophene or oligothiophenes functionalized by amine, carboxylate, nitrobenzoate, benzoic acid, isophlatic acid, β–diketonate, etc… are used as ligands in lanthanide complexes (Figure 1.11).[8a, 31]

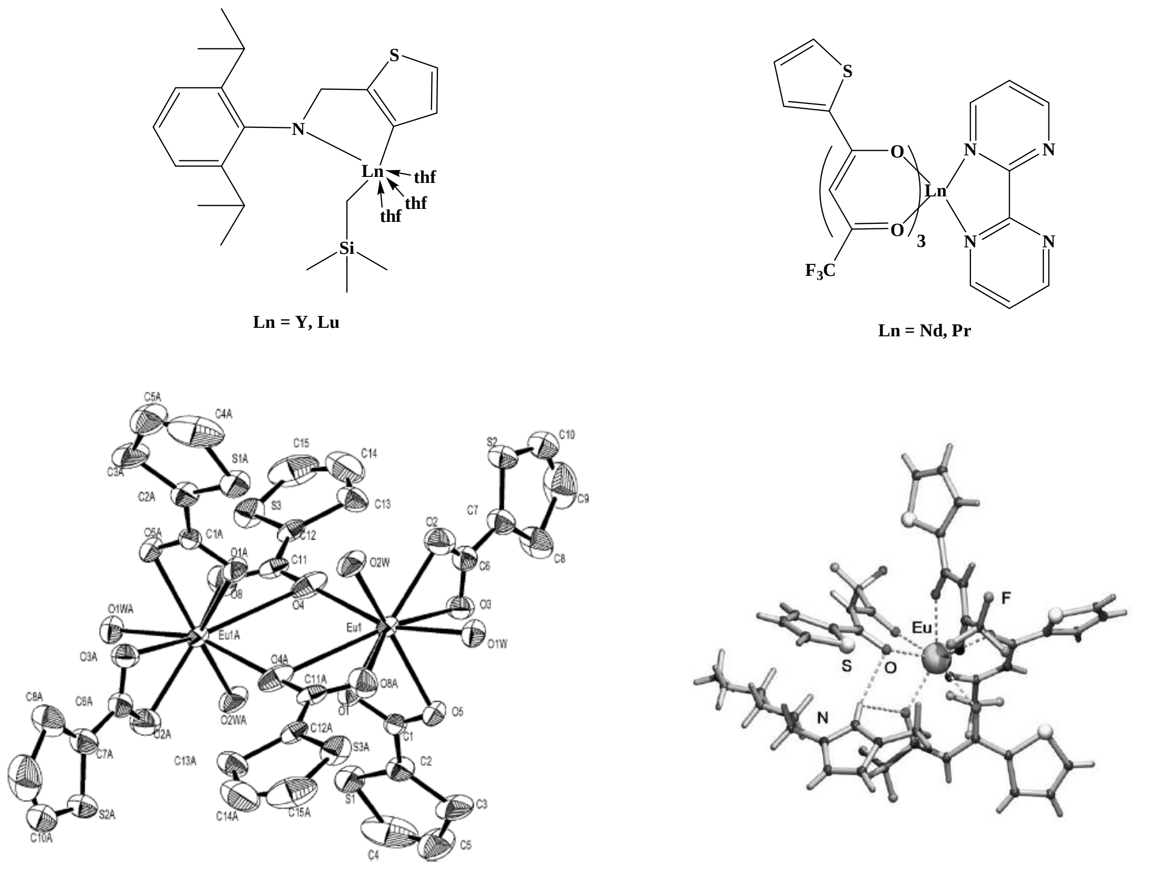


Figure 1.11. Examples of lanthanide complexes containing thiophene or oligothiophene derivatives.

2 Polythiophenes

2.1 Generalities

Since the first synthesis of polythiophene during the purification process of thiophene with sulphuric acid in 1883,[11] the interest to study the intrinsic properties of these materials has considerable grown.[32] However, efficient and rational synthesis of these polymeric materials was only achieved in the 80's years. One of the first chemical preparation of unsubstituted polythiophene (PT) was reported in 1980 by the group of Yamamoto[33] and the group of Lin.[34] They are used a metal–catalyzed coupling reaction with the 2,5–dibromothiophene in the presence of Mg and Ni(bipy)Cl_2. One of the advantages of theses polymers is the π–conjugation along the chain in which the thiophene units are connected at the 2,5– positions. Nevertheless, some minor defaults such as the 2,4– or the 2,3–couplings, lead to a loss of conjugation, decreasing the conductivity and of NLO properties.[35]

2.2 Regioregularity

As many other linear polyaromatic compounds, the polythiophenes are almost insoluble in organic solvents due to the rigidity of their skeletons. Therefore, it is difficult to characterize them. To avoid this problem, lateral flexible chains containing at least 4 carbon atoms can be attached at the –3 and/or –4 position of each monomeric unit.[36] This chemical modification allows solubilising the polymers chains even in usual organic solvents.

Different regioisomers could be obtained by the introduction in position –3 (Figure 1.12): i) Head–Tail (HT), ii) Head–Head (HH), iii) random configuration.

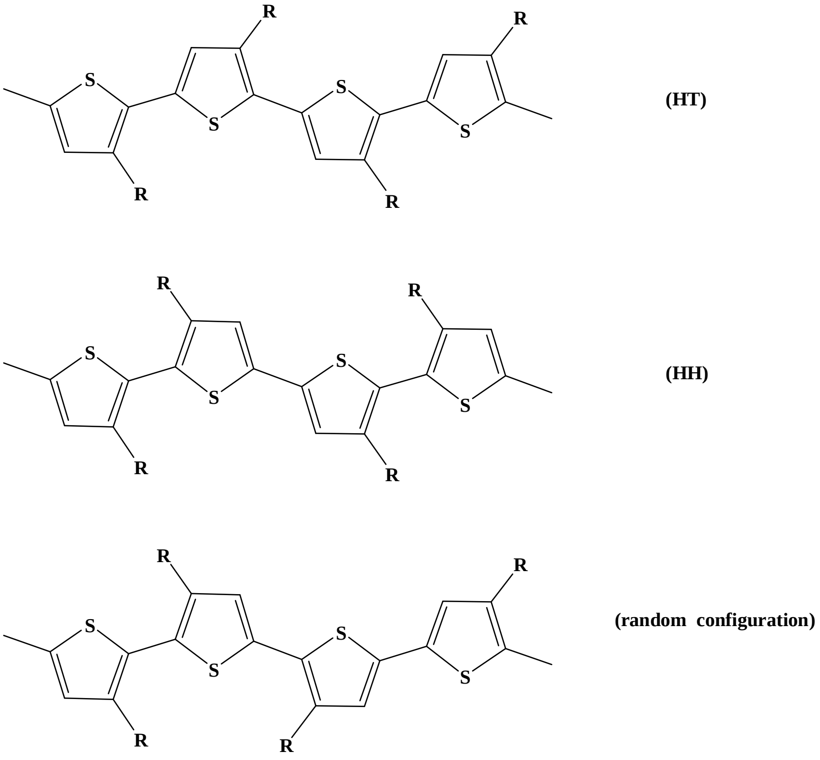


Figure 1.12. Representation of the regioisomers.

The coplanearity in the HH–polymers is notably decreased leading to a loss of conductivity. However, no drop of conductivity is observed in the case the HT–polymers. The investigations on the regioregular polymers have shown that the percentage of crystallinity increases with the regioregularity. Moreover, the cristallinity of the lateral chain is necessary for the development of optimum physico–chemical properties of the polymer. In the case of the random configuration–polymer, the optimal lengths of the lateral chain to obtain good conductivities and good NLO properties are in the range between 7 to 9 carbon atoms.[37] To further improve the solubility and the percentage of crystallinity, it is possible to add another lateral chain at the –4 position. This substitution pattern limits *α–β* coupling and therefore reduces defaults inside the polymer chains. However, this substitution causes a loss of coplanearity. The presence of one or two alkoxy substituents can reduce the loss of conjugation since the oxygen atoms bonded to the thiophene unit is sterically less hindered, thus limiting the loss of coplanearity.[38]

To prepare polythiophenes, three methods are in general used: i) the electrochemical coupling, ii) the oxidative coupling, iii) the organometallic coupling.

2.3 Electrochemical Carbon–Carbon Coupling

The synthesis of polythiophenes by electrochemical oxidation has received a great deal of attention since the first results obtained by Diaz.[39] Nevertheless, the mechanism is not yet exactly understood, but by analogy with electropolymerization of polypyroles,[40] the following sequence it is in general assumed. In the first step, the radical cation is formed after oxidation. In the second step, a coupling reaction between two radical cations takes place leading after rearomatization to bithiophene (Figure 1.13). Then, the bithiophene unit is oxidised and coupled with another radical cation of thiophene forming a terthiophene.

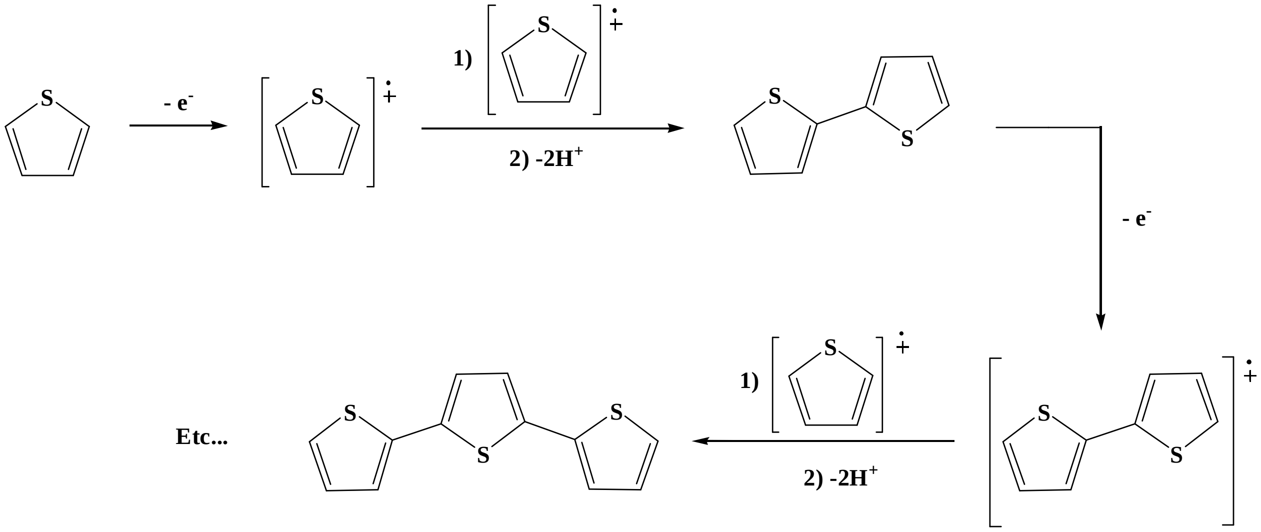


Figure 1.13. Formation of polythiophenes by electrochemical coupling.

The oxidation potentials of the oligomers forming during the oxidation process have lower values than the starting monomer; therefore they are more easily to oxidize. The polymer formed is deposited on the electrode or on a surface of semi–conducting substrates. This method has the advantage to form quite stable films. This type of polymerization has been applied for the synthesis of non–substituted polythiophenes,[41] for some soluble poly(3–alkythiophenes)[42] and for polymers containing oxygen atom(s) in the lateral chain (Figure 1.14) (methoxy, ether).[43] In all cases, the polymers obtained possess a "random configuration". These compounds exhibit conductivities about 1000 $S.cm^{-1}$. A transparent conducting polymer has been also obtained by electropolymerization of 3,4–ethylenedioxythiophene.[44]

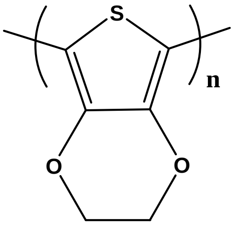


Figure 1.14. Poly(3,4–ethylenedioxythiophene).

Even water soluble polythiophenes can be synthesized after introduction of an ionic group in the lateral chain.[45] If thiophenes are disubtituted at the 2,5–positions with silyl groups, the polymerization takes place with elimination of the silyl groups.[46]

2.4 Oxydative Carbon–Carbon Coupling

Yoshino and Sugimoto[47] have reported in 1986 a very simple method to prepare polyalkylthiophenes (PATs). The monomer, 3–alkylthiophene is dissolved in chloroform and oxidatively polymerized in the presence of $FeCl_3$,[40] $MoCl_5$ or $RuCl_3$.[48] In general, the $FeCl_3$ method is the most often used to prepare PATs.[49] One advantage of this route is to generate exclusively 2,4–coupling in PATs.

2.5 Organometallic Carbon–Carbon Coupling

Another variation to synthesize polythiophenes is the carbon–carbon coupling reaction catalyzed by organometallic nickel or palladium complexes. These species are generated *in situ* during the reaction with an organomagnesium compound giving rise to the oligomers or polymers. For example, in the 80's, a new synthetic way consisting in the reaction of 2,5–dibromothiophene with magnesium in presence of a nickel catalyst led to formation of a polymeric material.[50] Mc Cullough *et al.*[51] have prepared the regioregular "head–tail" 3–alkylpolythiophene via the polymerisation of 2–bromomagnesio–5–bromo–3–alkylthiophene. The regioregularity of these compounds are excellent (98 % of "head–tail"), and they possess better conductivity and optical properties compared to non–regioregular materials. Another variation consists to replace Mg by Zn. For example, in the presence of $NiCl_2$(dppp) as catalyst, formation of regioregular "head–tail" polymer has been reported.[52]

2.6 Applications of Polythiophenes in Material Sciences

Many applications have been suggested for the conducting polythiophenes: as examples can be cited, the utilization as transistors,[53] the conception of electroluminescent compounds, photovoltaic cells, photochemical films, NLO materials,[54] batteries and diodes. Two types of applications for conducting polymers can be considered: i) static applications (electric conductivity), ii) dynamic applications (modification of optical properties and conduction due to the application of electric potential or environmental stimulus). For the static applications, we can cite the polymer blend Baytron P. containing the poly(3,4–ethylenedioxythiophene)–poly(styrene sulfonate) (Figure 1.15) utilized for electrostatic coating. This material can be used in dynamic applications when electrochemical potential is applied to the polymeric film. Its interesting electrochemical properties are employed for the production of mirrors which become opaque or reflective during the application of an electric current.[55]

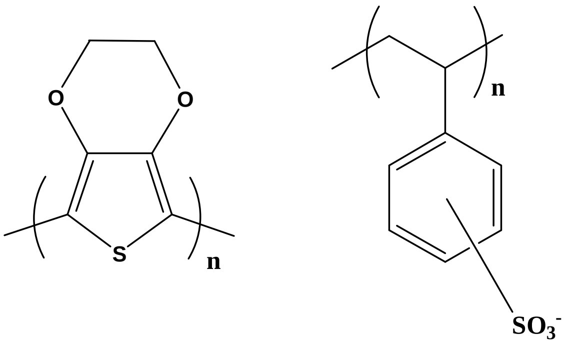


Figure 1.15. Poly(3,4–ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT PSS).

The use of polythiophene in sensing devices for biomedical applications or for the detection of metallic ions is also emerging.[56] In this regard, previous studies in our laboratories have demonstrated that poly{[5−(2’,2−dithienyl]methanol} (Figure 1.16) deposited on a ITO surface is a promising coating material for the grafting of latex particles.[57]

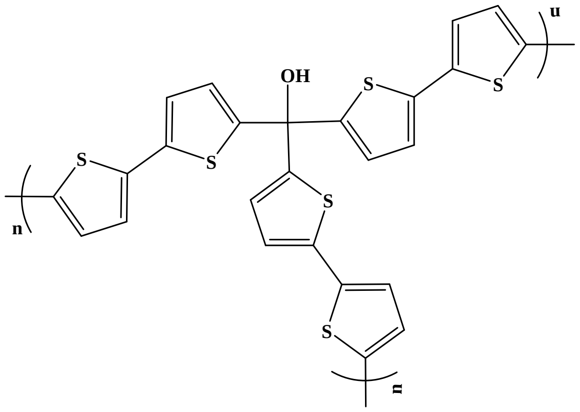


Figure 1.16. Poly{[5−(2’,2−dithienyl]methanol}.

Another strategy to obtain conducting polymers with intriguing electronic properties consists to attach one PCP molecule on the thiophene units. This axis of research has been first developed in our laboratory by Guyard *et al.*,[9b, 21, 58] and further improved by Salhi *et al.* with their studies of the influence of the PCP trans–annular interactions on the polymer properties.[59] The polymeric PCP−functionalized thiophene films (Figure 1.17) deposited on an ITO electrode are electro–active and electro–chrome and exhibit a colour change from orange–yellow to black after oxidation.[9b, 58] These films present also fluorescence properties.[59] The presence of PCP trans–annular interactions increases the charge delocalization along the polymeric chain. These electronic properties are tempting to envisage their incorporation in materials for the elaboration of LEDs or for efficient organic molecules for ONL.

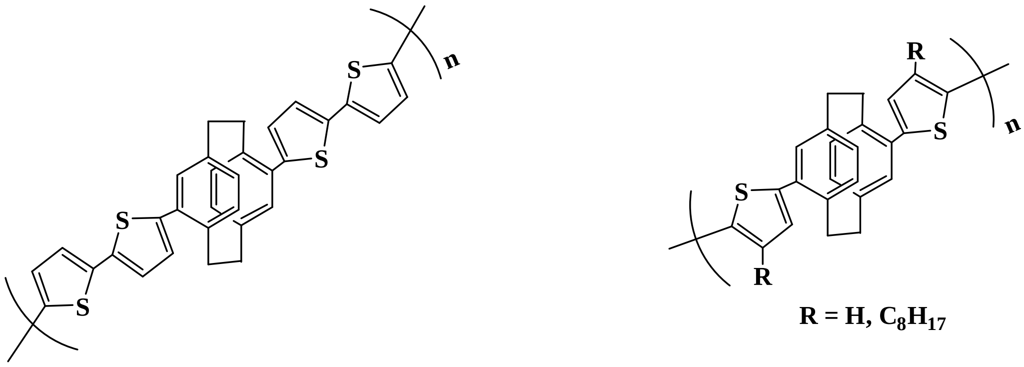


Figure 1.17. Examples of polymers of oligothiophenes functionalized by PCP developed in our laboratory.

Part 3 Chemistry, Properties and Applications of Rare Earth Metals

1 Generalities

The rare earth elements comprise all the lanthanides (or lanthanoid according IUPAC) series as well as the metals scandium ^{21}Sc and yttrium ^{39}Y. Together with the elements included between the actinium ^{89}Ac and the lawrencium ^{103}Lw, which are called actinides, the lanthanides form the totality of the *f*–block metals. Note that lutetium is a *d*−block lanthanoid. The lanthanides are divided in two categories: the ceric group: from the lanthanum ^{57}La to the samarium ^{62}Sm, and the yttric group: from the europium ^{63}Eu to the lutetium ^{71}Lu. Since the chemical properties of the lanthanides, yttrium and scandium are very similar, they can be treated together in practice. Within this manuscript, the terms “lanthanide” and “rare earth” are used together to describe this block metal.

Rare Earths in the Nature

Two trends emerge from the data presented in Table 1.2. Firstly, the lighter rare earths are more abundant than the heavier ones; secondly, that the elements with even atomic number are more abundant than those with odd atomic number. Overall, cerium, the most abundant lanthanide on earth, has a similar concentration comparable to that of Ni and Cu (50 ppm), whilst even Tm and Lu, the rarest lanthanides, are more abundant than Bi, Ag (0.7 ppm) or the platinum metals.

	La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Y**
Crust	35	66	9.1	40	0.0	7	2.1	6.1	1.2	4.5	1.3	3.5	0.5	3.1	0.8	31
Solar System	4.5	1.2	1.7	8.5	0.0	2.5	1.0	3.3	0.6	3.9	0.9	2.5	0.4	2.4	0.4	40.0

Table 1.2. Abundance of the lanthanide in the crust (in ppm) and in the solar system solar system (with respect to 10^7 atoms Si).[60]

The principal sources of rare earth ores (Table 1.3) are the monazite ($LnFCO_3$), the bastnasite [$(Ln, Th)PO_4$] and the xenotime [$(Y, Ln)PO_4$]. In addition to these minerals, there are Chinese rare earth reserves which amount to over 70 % of the known world total, mainly in the form of the ionic ores from southern provinces. The Chinese ores have made them a leading player in lanthanide chemistry.

%	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
Monazite	20	43	4.5	16	0	3	0.1	1.5
Bastnasite	33.2	49.1	4.3	12	0	0.8	0.12	0.17
Xenotime	0.5	5	0.7	2.2	0	1.9	0.2	4

%	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Monazite	0.05	0.6	0.005	0.2	0.002	0.1	0.02	2.5
Bastnasite	*160*	*310*	*50*	*35*	*8*	*6*	*1*	0.1
Xenotime	1	8.6	2	5.4	0.9	6.2	0.4	60.0

Table 1.3. Typical abundance of the rare earths in ores (italic values are in ppm).[60]

2 Physical and Chemical Properties

2.1 Electron Configuration

Lanthanides are elements in which the *4f* orbitals are, in general, partially or completely filled, along with the actinides they are the only elements having *f* electrons. The contracted nature of the *4f* orbitals and their small overlap with the ligand atom orbitals attaches a predominantly ionic character to lanthanoid−ligand atom bonds in complexes. In other words, these electrons are hardly available to contribute to covalent bonding. The representation of these seven *4f* orbitals is given in Figure 1.18.

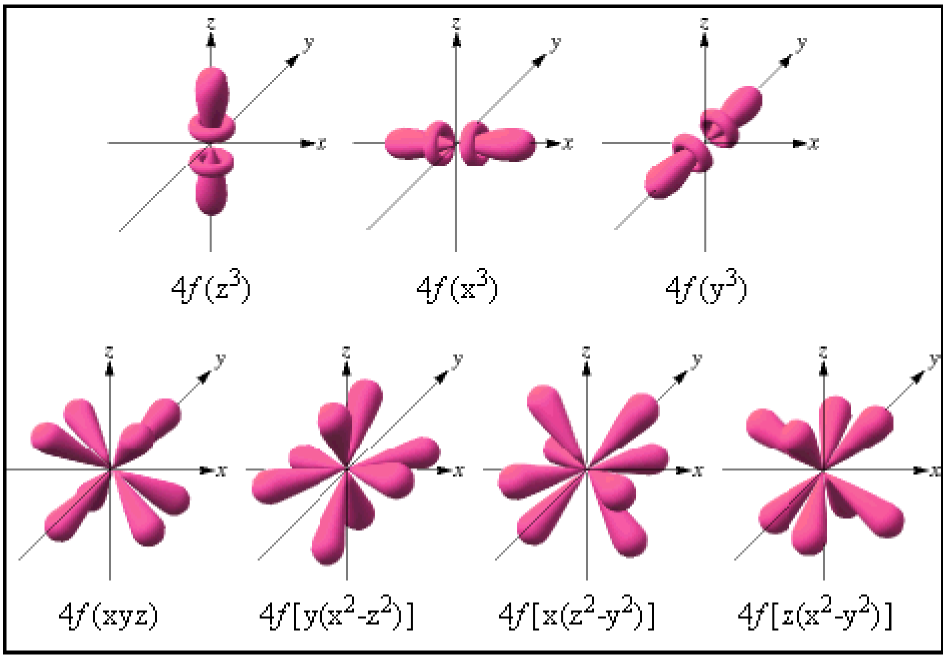


Figure 1.18. *4f*–orbital representation.[61]

In the lanthanide series, the electron configuration varies from [Xe]$4f^{0}5d^{1}6s^{2}$ to [Xe]$4f^{14}5d^{1}6s^{2}$ achieved by successive filling of the *4f* orbitals (Table 1.4). Note that, in the case of La and Ce the *4f* orbitals have not contracted sufficiently to bring the energy of the 4f electrons below that of the *5d* electrons; for Gd the effect of the half–filled *4f* sub–shell dominates, explaining the presence of the *5d* electron; in the case of Lu the *4f* sub–shell is entirely filled with 14 electrons, one *5d* electron is present. In contrast, for these elements yttrium and scandium have the electron configuration [Kr]$4d^{1}5s^{2}$ and [Ar]$3d^{1}4s^{2}$, respectively, no *f* orbitals are presents.

The oxidation state +3 predominates all the rare earth series (Table 1.4). For the lanthanides, this finding can be explained by the fact that the *f* electrons are core electrons. This most stable oxidation state +3 encountered for all the lanthanide series results from the loss of *6s* and *5d* electrons. Some lanthanides may have another oxidation state (Table 1.4) such as +2 (Sm^{2+}, Eu^{2+} and Yb^{2+}) and +4 (Ce^{4+}, Pr^{4+} and Tb^{4+}). This behaviour is due to the contribution of empty, half–filled or totally–filled *f* orbital to the stability of the considered ions. As can seen from Table 1.4, all the rare earths in cationic form are paramagnetic, with the exception of lanthanum(III), lutetium(III), yttrium(III) and scandium (III).

Rare Earths (Z)	Name	Electron configuration	Oxidation states	Electron configuration of + 3 oxidation states
La (57)	Lanthanum	[Xe]$5d^1 6s^2$	**3**	[Xe]
Ce (58)	Cerium	[Xe]$4f^1 5d^1 6s^2$	**3**–4	[Xe]$4f^1$
Pr (59)	Praseodymium	[Xe]$4f^3 6s^2$	**3**–4	[Xe]$4f^2$
Nd (60)	Neodymium	[Xe]$4f^4 6s^2$	2–**3**–4	[Xe]$4f^3$
Pm (61)	Promethium	[Xe]$4f^5 6s^2$	2–**3**	[Xe]$4f^4$
Sm (62)	Samarium	[Xe]$4f^6 6s^2$	2–**3**	[Xe]$4f^5$
Eu (63)	Europium	[Xe]$4f^7 6s^2$	2–**3**	[Xe]$4f^6$
Gd (64)	Gadolinium	[Xe]$4f^7 5d^1 6s^2$	**3**	[Xe]$4f^7$
Tb (65)	Terbium	[Xe]$5f^9 6s^2$	**3**–4	[Xe]$4f^8$
Dy (66)	Dysprosium	[Xe]$4f^{10} 6s^2$	2–**3**–4	[Xe]$4f^9$
Ho (67)	Holmium	[Xe]$4f^{11} 6s^2$	2–**3**	[Xe]$4f^{10}$
Er (68)	Erbium	[Xe]$4f^{12} 6s^2$	**3**	[Xe]$4f^{11}$
Tm (69)	Thulium	[Xe]$4f^{13} 6s^2$	2–**3**	[Xe]$4f^{12}$
Yb (70)	Ytterbium	[Xe]$4f^{14} 6s^2$	2–**3**	[Xe]$4f^{13}$
Lu (71)	Lutetium	[Xe]$4f^{14} 5d^1 6s^2$	3	[Xe]$4f^{14}$
Y (39)	Yttrium	[Kr]$4d^1 5s^2$	**3**	[Kr]
Sc (39)	Scandium	[Ar]$3d^1 4s^2$	**3**	[Ar]

Table 1.4. Electron configurations and oxidation states of rare earths (bold values are the most probable oxidation states).[62]

2.2 Nature of the Metal–Ligand Bonding

2.2.1 The HSAB Principle

The concept of chemical hardness has been created by Pearson in 1963[63] using the interaction between a Lewis acid A and a Lewis base B (Equation 1.1).

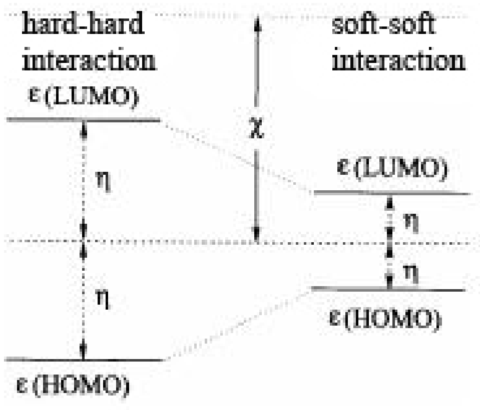
$$\mathrm{A} + :\mathrm{B} \rightleftharpoons \mathrm{A} : \mathrm{B}$$

Equation 1.1. Lewis acid–base reaction. A stands for a Lewis acid or an acceptor of electrons and B for a base or a donor of electrons.

Pearson has classified the acids and bases in two categories according to their polarizabilities (reductive ability, unsaturated degree):

- the hard acids and the hard bases which are hardly polarisable
- the soft acids and the soft bases, which are easily polarisable.

He has postulated that the Lewis acids form preferentially coordination bonding with the same nature of ligand: it is the HSAB principle (Hard and Soft Acids and Bases): the hard acids interact more strongly with the hard bases, the soft acid with the soft bases. The interactions hard acid–hard base are principally ionic (distant levels of energy) and the soft acid–soft base are in majority covalent (nearby levels of energy). When using the concept of molecular orbitals, an acid A is a molecule having the LUMO and a base B is a molecule having the HOMO as frontier orbitals. The resulting A–B entity is stable, this formation corresponding to a lowering of the global energy of the system. The bonding orbital is occupied by the two electrons arising from the base and the antibonding orbital is empty. The Schema 1.3 shows a representation of the interactions between the hard acid/hard base couple and the soft acid/ soft base combination.



Scheme 1.3. Scheme of molecular orbital representing the interaction between the frontier orbitals of the pairs hard–hard and soft–soft. (η = absolute hardness defined by (I – A)/2; χ = absolute electronegativity defined by (I + A)/2; I and A are, respectively, the first ionization potential and the first electronic affinity of the considered specie.

2.2.2 Case of Lanthanides

The cations of lanthanides in the oxidation state +3 have a high charge density and are few polarisable due to the low spatial extension of their *f* orbitals: therefore, they can be considered as hard Lewis acid according to the Pearson classification. They interact preferentially with ligand having hard donor atoms such as oxygen or nitrogen to form interactions with strong electrostatic character. These cations have also an important affinity towards water molecules. Organic ligands which are functionalized by an oxygen donor groups and having a charge such as carboxylate are however capable to substitute coordinated water molecules, leading to stable complexes in aqueous reaction medium. Among the neutral donors, the more polarisable amines are preferred over oxygen donors such as ethers. In comparison, carboxamide and sulfoxide donor groups interact more easily than less polar ligands as alcohols. In general, the electrostatic character of the metal–ligand interaction gives rises to labile complexes with fast kinetic of substitution. Note in some rare case, also dative interactions with a soft sulphur donors have been crystallographically evidenced.[8a]

2.3 Coordination Number and Ionic Radii

2.3.1 Coordination Number (CN)

In the case of *f*–orbitals, the non–directional lanthanide–ligand interactions are translated by extremely variable coordination numbers and associated geometries. The stereochemistry of rare earths complexes is dictated only by the steric and electrostatic features of the ligands.[64] These very hard ions are accommodated with a large number of small ligands (8–9) to satisfy their electronic requests. In other words, the steric constraints play a major effect in the coordination sphere, and a multidentate ligand can impose a very particular coordination around the central ion. In the solid state, coordination numbers between 3 and 14 are observed, the most frequent are between 7 and 12.[65]

In solution, high coordination numbers are generally observed, the most common being the coordination 8 and 9. The Ln^{3+} ions have a tendency to complete their coordination spheres with solvent molecules or anions, in particular if the number of donor site offered by the ligands is not sufficient or if their electronic densities are too weak. The coordination numbers and the ionic radii of lanthanides are closely correlated.[60] A lot of studies have shown that the average CN of aqua–complexes $[Ln(H_2O)_n]^{3+}$ is about 9, for the beginning of the lanthanide series (Ln = La–Nd), and about 8 as well for the smaller ions (Ln = Tb, Lu).[66] The lanthanides ions have the propensity to adopt to different environments and Bünzli nicknamed them “the chameleon of coordination chemistry”.[65] In the case of the yttrium, aqua–complex has been identified as $[Y(H_2O)_8]^{3+}$.

2.3.2 Ionic Radii

The *4f* series exhibit a decrease of the ionic radii when the atomic number increases (Table 1.5). This monotonous ionic radii contraction[67] can be rationalized by the increase of effective nuclear charge upon addition of an electron in the *f* orbitals which are closer to the nucleus than the more diffuse *d*–orbitals of the transition metals. The screening effect of a *4f* electron towards another valence electron is weak, leading to a progressive contraction of *5s*, *5p*, *6s* and *6p*–orbitals towards the cores.

M^{+3}	CN = 6	CN = 7	CN = 8	CN = 9	CN = 10	CN = 12
La	1.032	1.100	1.160	1.216	1.270	1.360
Ce	1.010	1.070	1.143	1.196	1.250	1.340
Pr	0.990		1.126	1.179		
Nd	0.983		1.109	1.163		1.270
Pm	0.970		1.093	1.144		
Sm	0.958	1.020	1.079	1.132		1.240
Eu	0.947	1.010	1.066	1.120		
Gd	0.938	1.000	1.053	1.107		
Tb	0.923	0.980	1.040	1.095		
Dy	0.912	0.970	1.027	1.083		
Ho	0.901		1.015	1.072	1.120	
Er	0.890	0.945	1.004	1.062		
Tm	0.880		0.994	1.052		
Yb	0.868	0.925	0.985	1.042		
Lu	0.861		0.977	1.032		
Y	0.900	0.960	1.019	1.075		
Sc	0.745		0.870			

Table 1.5. Ionic radii of rare earths (III) for different coordination numbers.[68, 69]

3 Energy levels of Ln^{3+} Ions: the Russell−Saunders Model

In the Russell–Saunders coupling scheme, the electron spins are coupled together separately from the coupling of the orbital angular momenta of the electron, and the orbital moment is unquenched. The ground state for a given lanthanide ion is unaffected by the ligands bound to it because of the shielding of the *4f* electron by the filled *5s* and *5p* orbitals.

The spins of the individual electron(s) are coupled together (added vectorially) to give the spin quantum number for the ion (*S*). The orbital angular moment (*l*) of the individual electrons are coupled similarly.

For an *f* electron, $l = 3$, so the magnetic quantum moment m_l can have any one of the seven integral values between +3 and –3. Vectorial addition of the m_l–values for the *f* electrons for the multi–electron ion affords *L*, the total orbital angular momentum quantum number. There is a weaker coupling, spin–orbit coupling, between *S* and *L*. Vector addition of L and S affords the resulting quantum number, *J*. It can have values of $(L + S)$; $(L + S) - 1$; …; $(L - S)$. For any ion, a number of electronic states are possible. The ground state can be determined using the Hund's rules:

1) The spin multiplicity $(2S + 1)$ is as high as possible.
2) If there is more than one term with the same spin multiplicity, the term with the highest *L*–value is the ground state.
3) For a shell less than half–filled, *J* for the ground state takes the lowest possible value; for a shell more than half–filled, *J* for the ground state is the highest possible;

To give an example, we work out the term symbol for the ground state of Nd^{3+} (f^3). First we complete a "box diagram", representing orbitals by boxes (7 boxes for 7 orbitals) and electrons by arrows (Figure 1.19). We put the electrons in separated orbitals when the shell is less than half–filled, i.e. choosing the maximum number of unpaired electrons, and choosing to maximize the values of m_l to give the highest *L*–value (see Hund's rule 2).

m_l	3	2	1	0	–1	–2	–3
	↑	↑	↑				

Figure 1.19. Box diagram for Nd^{3+}.

So $S = \sum ms = ½ + ½ + ½ = 3/2$, therefore $2S + 1 = 4$.

$L = \sum m_l = 3 + 2 + 1 = 6$, so it is an I state (Figure 1.20).

L	0	1	2	3	4	5	6	7
State Symbol	S	P	D	F	G	H	I	K

Figure 1.20. State symbol for different values of *L*.

J can have the values of (*L* + *S*); (*L* + *S*) – 1; ….; (*L* – *S*), so here *J* = (6 + 3/2); (6 + 3/2) – 1; (6 – 3/2). Since the shell is less than half–filled, the state with the lower *J* value is the ground state (see Hund's rule 3), so this is 9/2. The term symbol for the ground state of Nd^{3+} is $^{4}I_{9/2}$.

4 Magnetic Properties of the Rare Earths

With the exception of La^{3+} and Lu^{3+} and of course Y^{3+} and Sc^{3+}, the Ln^{3+} all contain unpaired electrons and are paramagnetic. Their magnetic properties are determined by the ground state, as the excited states are so well separated from the ground state (owing to spin–orbit coupling) and are thus thermally inaccessible. For the *3d* transition elements, the paramagnetism is determined only by the spin moment, the orbital angular contribution of magnetic moment ions has been cancelled by the interaction between the orbital field areas of ligands. In this case, the maximum of paramagnetism coincided with the maximum of unpaired electrons in the *3d* orbitals. In lanthanide ions, the spin–orbital interaction is important therefore there are high couplings between orbital angle *L* and the angular moment of spin *S*. The magnetic moment for a free ion in a *J* state is given by the Equation 1.2 in which *J* is the quantum number combined with the total kinetic moment and *g* the Landé factor is defined by the Equation 1.3.

$$\mu_{eff} = g_J \sqrt{J(J+1)}$$

Equation 1.2. Magnetic moment.

$$\vec{J} = \vec{L} + \vec{S}$$
$$|L - S| \le J \le L + S$$
$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Equation 1.3. Determination of the Landé factor.

The magnetic moment values of lanthanide ions are collected in the Table 1.6.[70]

Ln^{3+} ions	Number of *f* electrons	Ground term $^{2S+1}L_J$	g_J	Predicted μ_{eff}	Experimental $\mu_{eff}^{(a)}$
Ce^{3+}	1	$^2F_{5/2}$	6/7	2.54	2.46
Pr^{3+}	2	$^3H_4$	4/5	3.58	3.47
Nd^{3+}	3	$^4I_{9/2}$	8/11	3.62	3.52
Pm^{3+}	4	$^5I_4$	3/5	2.68	–
Sm^{3+}	5	$^6H_{5/2}$	2/7	0.84	1.58
Eu^{3+}	6	$^7F_0$		0	3.54
Gd^{3+}	7	$^8S_{7/2}$	2	7.94	7.90
Tb^{3+}	8	$^7F_6$	3/2	9.72	9.60
Dy^{3+}	9	$^6H_{15/2}$	4/3	10.65	10.30
Ho^{3+}	10	$^5I_8$	5/4	10.61	10.40
Er^{3+}	11	$^4I_{15/2}$	6/5	9.60	9.40
Tm^{3+}	12	$^3I_6$	7/6	7.56	7.00
Yb^{3+}	13	$^2F_{7/2}$	8/7	4.53	4.30

Table 1.6. Electronic properties of Ln^{3+} (μ_{eff} and g_J are calculated in ground state with the Equations 1.2 and 1.3). The magnetic moments are expressed in Bohr magnetons. (a): values observed for crystal system of $[Ln_2(SO_4)_3 \cdot 8H_2O]$.[68, 71]

The experimental and calculated magnetic moment values of Sm^{3+} and Eu^{3+} ions are different. At room temperature, these ions present a small population degree of one or more smaller exited electronic levels. For Sm^{3+}, we must consider the first excited level $J = 7/2$ and for Eu^{3+}, the excited proximity level $J = 1$ and $J = 2$ explains this difference.

5 Optical Properties

The Laporte rules (or parity rule), is an spectroscopic selection rule named after Otto Laporte and excludes the electronic transitions involving an electron redistribution within the same sub–level, in other words between the orbitals having the same symmetry properties towards an inversion centre. This rule originates from a quantum mechanical selection rule, which states that during an electron transition, parity should be inverted. Therefore, the *p–p*, *d–d* and *f–f* transitions are forbidden. The spin rule prohibits the transition implying a spin change. The optical transitions of electric dipole type take place among the *4f* levels, so they are not allowed by the Laporte and spin rules. Ln^{+3} ions have exited states resulting from intern *4f–4f* electronic transitions conferring to the metal centre interesting spectroscopic properties. The *4f* electrons do not fully take part in chemical bonding and are involved as core electrons, therefore fine absorption and emission bands are observed. Moreover, as the *4f–4f* transitions are forbidden, these bands have a weak transition probability ($\epsilon \leq 1\ \mathrm{mol}^{-1}.\mathrm{cm}^{-1}$). In comparison, broad and intense bands are often observed for *d*–*d* transitions of the *d*–block metals. The lanthanide ion levels in solution, shown in Figure 1.21, have been established from the literature data.[2, 72] As can be seen, lanthanide ions possess luminescent and non−luminescence level. When the energy gap between lower energy luminescence level and the higher luminescence level coincides with one or more vibrational energy quanta of one solvent molecule or a function of the organic ligand (OH or NH, for example), a non−radiative de−excitation of the excited state can take place instead of the luminescence desired.

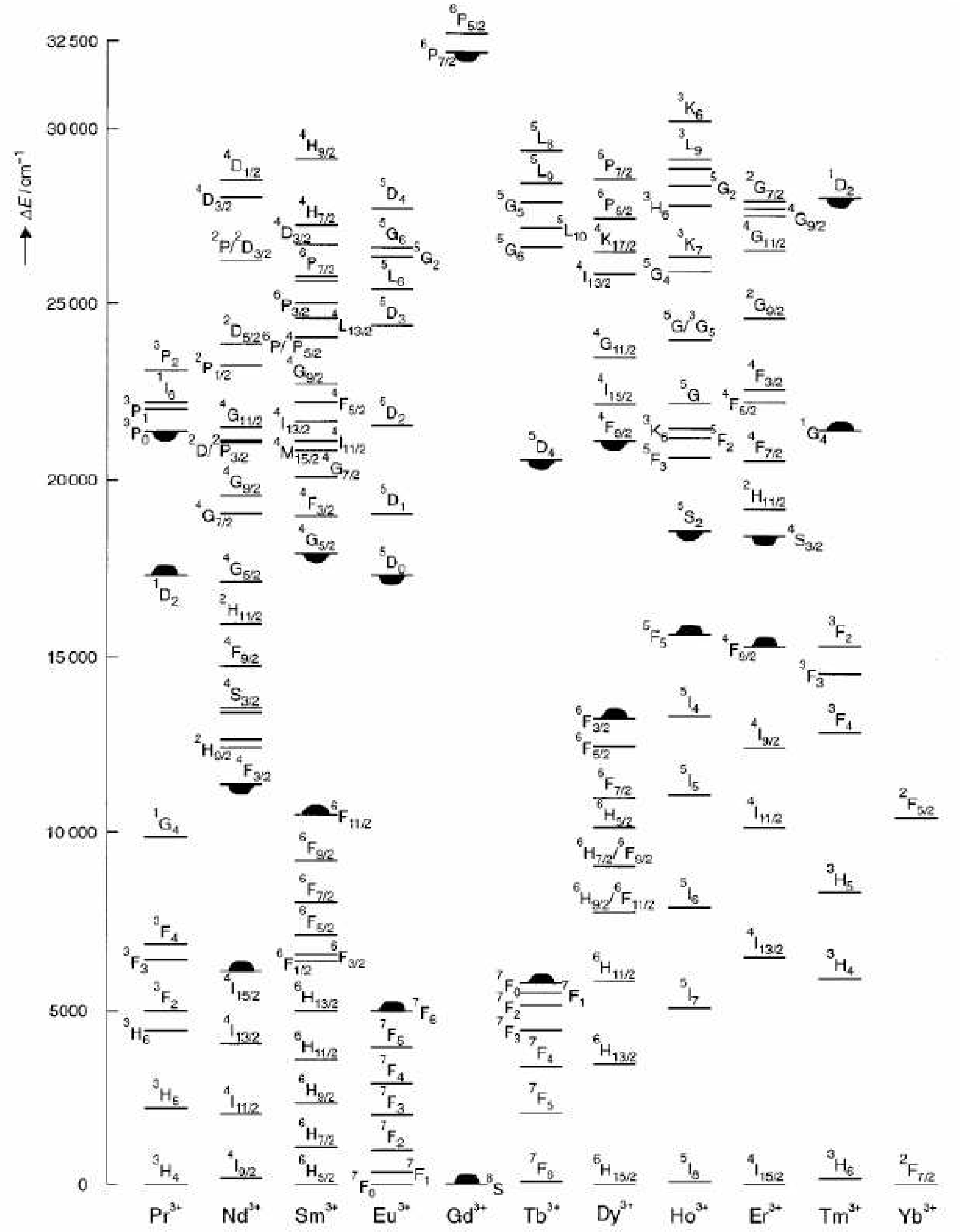


Figure 1.21. Energy diagram of lanthanide ions in aqueous solution. The lowest luminescence level (▼), and the highest non−luminescence level (▲) are represented.[2, 72a]

6 Electrochemical Properties

As explained above, the lanthanide ions may adopt different oxidation states. Their redox potentials are listed in Table 1.7.[73]

	$E^0_{\mathrm{Ln4+/Ln3+}}$	$E^0_{\mathrm{Ln3+/Ln2+}}$
La		–2.94
Ce	1.70	–2.92
Pr	3.40	–2.84
Nd	4.60	–2.62
Pm	4.90	–2.44
Sm	5.30	–1.50
Eu	6.40	–0.34
Gd	7.90	–2.85
Tb	3.30	–2.83
Dy	5.00	–2.56
Ho	6.20	–2.79
Er	6.10	–2.87
Tm	6.10	–2.22
Yb	7.1	–1.18
Lu	8.5	

Table 1.7. Standard electrode potentials of the Ln^{4+}/Ln^{3+} and Ln^{3+}/Ln^{2+}.[73]

Relatively few reports about the electrochemical properties of lanthanide complexes have been reported.[74] Nevertheless, the studies have shown the difficulty to reduce or oxidize these ions by voltammetry methods. Indeed, as can be seen in Table 1.7, only the potentials of Ce^{4+}/Ce^{3+}, Sm^{3+}/Sm^{2+}, Eu^{3+}/Eu^{2+} and Yb^{3+}/Yb^{2+} are in an electrochemically accessible range. To illustrate the redox process of lanthanide ions, we present here some examples extracted from the literature. Blatt *et al.*[74a] have investigated the electrochemical properties of $Eu[N(SO_2CF_3)_2]_3(H_2O)_3$ and $Sm[N(SO_2CF_3)_2]_3(H_2O)_3$ and the CV have shown the reversible reduction and oxidation of the lanthanides ions (Figure 1.22 and Figure 1.23).

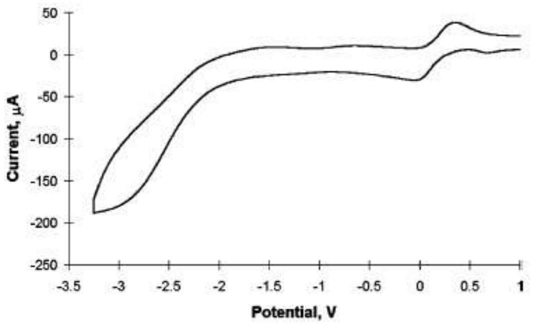


Figure 1.22. Cyclic voltammogram of $Eu[N(SO_2CF_3)_2]_3(H_2O)_3$ in $[Me_3NnBu]–[TFSI]$, 1.44×10^{-1} mol L^{-1}, 300 mV s^{-1}. Pt electrode surface area = 0.0314 cm^2.[74a]

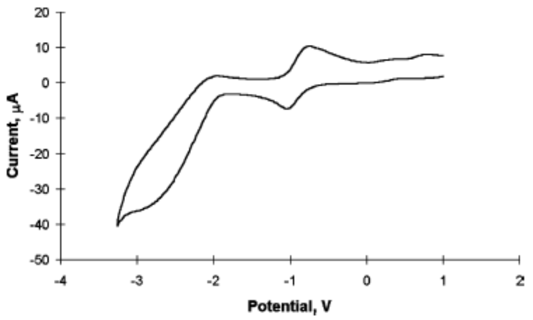


Figure 1.23. Cyclic voltammogram of $Sm[N(SO_2CF_3)_2]_3(H_2O)_3$ in $[Me_3NnBu]–[TFSI]$, 2.2 $\times 10^{-1}$ mol L^{-1}, 100 mV s^{-1}. Pt electrode surface area = 0.0314 cm^2.[74a]

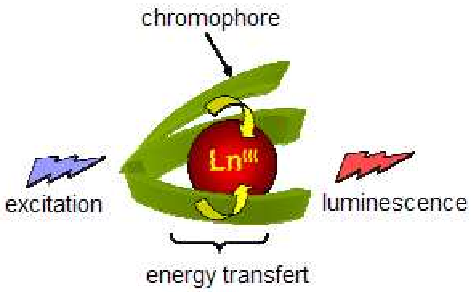
As already discussed above, thiophene derivatives are electrochemically active. Sultan *et al.*[31b] have studied the redox activity of some lanthanide complexes containing these thiaheterocycles, such as $[Ln(tta)_3]_x$bpm (Ln = Tb, Er, Pr, Nd and Eu, x = 1 or 2, tta = 2−thenoyltrifluoroacetonate, bpm = 2,2’–bipyrimidine). The redox chemistry of the homodinuclear complexes of terbium, erbium and the praseodymium and neodymium monometallic complexes reveal only the irreversible reduction of the orbitals localized on the tta ligands whereas the studies of the europium homodinuclear complex show a redox activity of the metal.

7 Applications

7.1 Luminescence Materials

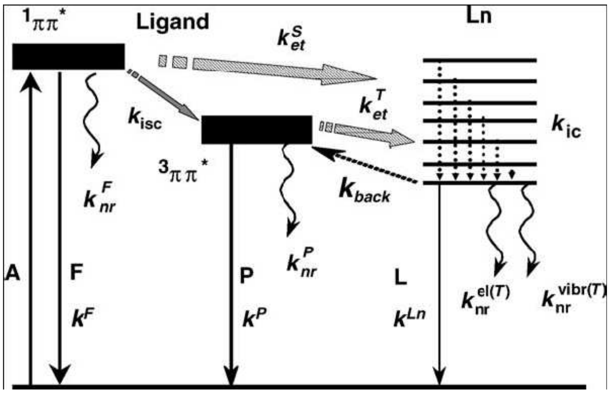
7.1.1 The Antenna Effect

As explained above, the lanthanide *f–f* transitions (electric dipole transitions) are “Laporte–forbidden”, therefore the generation of fluorescence from the lanthanide ion being difficult. Direct excitation of the lanthanide ion can be achieved, but this only becomes practical with use of lasers or at high ion concentrations. However, such disadvantages can be overcome by using sensitization techniques (Scheme 1.4).[2, 5, 75] This involves using indirect excitation of the lanthanide ion with a sensitising chromophore (often termed as an antenna)[76] usually through an intramolecular energy transfer process.[2, 5, 77] The antenna needs to be close in proximity to the lanthanide ion, which is achieved through coordination of the lanthanide to a ligand containing an antenna.



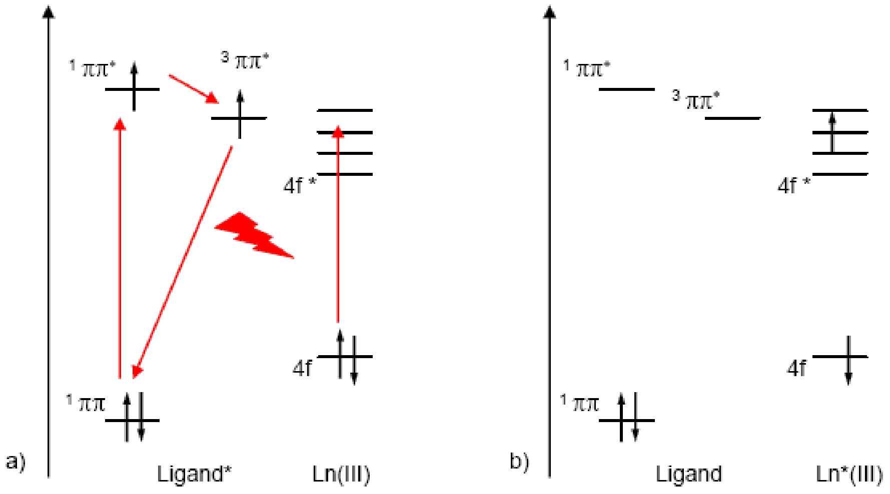
Scheme 1.4. Schematic representation of antenna effect leading to a luminescence lanthanide chelate.

The energy transfer succession is represented in the Schema 1.5. Being nearby the lanthanide ion via a ligand, the chromophore absorbs the incident light ($\pi \rightarrow \pi^*$) populating these excited singlet states. The lanthanide ion supports the intersystem crossing $^1\pi\pi^* \rightarrow {}^3\pi\pi^*$ (weak atom effect), allowing to populate the triplet excited states of the chromophore. The energy is transferred to the excited states of the lanthanide via the $^3\pi\pi^*$ states. This phenomenon can lead to the luminescence from radiative de−excitation.



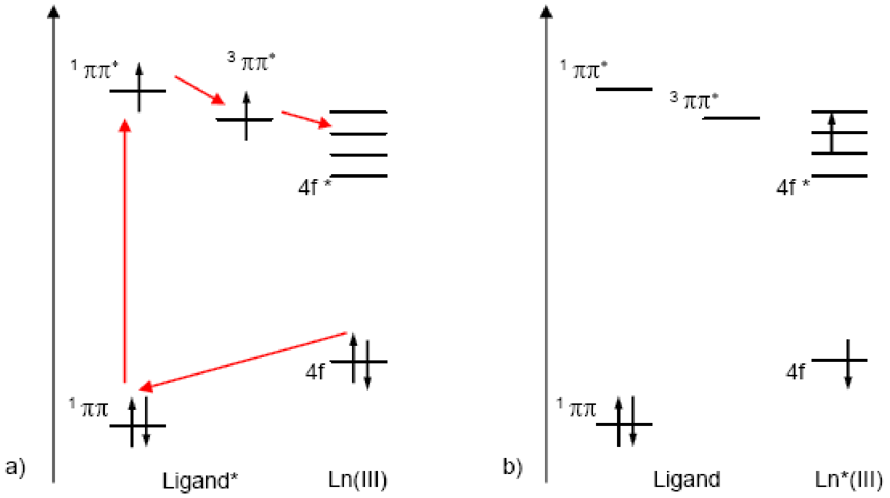
Scheme 1.5. Simplified diagram showing the energy migration paths in a Ln^{+3} complex[78] [$^1\pi\pi^*$stands for singlet state; $^3\pi\pi^*$ for triplet state, *A* for absorption, *F* for fluorescence, *P* for phosphorescence, *L* for luminescence (either fluorescence or phosphorescence), *isc* for intersystem crossing; *nr* for nonradiative, *ic* for internal conversion, *et* for energy transfer, *back* for back transfer, *T* for temperature–dependent, *el* for electronic and vibr for vibrational].

There are a lot of discussions[79] about the energy transfer of the excited triplet states toward the excited states of the lanthanide. Some mechanisms have been proposed by Förster[80] and Dexter.[81] The Förster mechanism's[82] (Scheme 1.6) describes a non−radiative energy transfer through the space, resulting from a dipole–dipole coulomb interaction between a donor (the chromophore) and an acceptor (the lanthanide). The donor deactivation produces an electric field (a transitional dipole), which leads to a dipolar oscillation of the acceptor and enables to populate these excited states. This is a “through space” process that does not require physical contact between the sensitizer and the acceptor, the lanthanide ion.



Scheme 1.6. Föster mechanism’s: a) before, b) after ligand desexcitation.

The Dexter energy transfer (Scheme 1.7) involves an exchange interaction requiring a mutual electronic exchange between the antenna and the metal–centre acceptor.[81] Energy transfer occurs through the overlapping orbital of the antenna and the metal ion and hence requires physical contact between the two components.



Scheme 1.7. Dexter mechanism’s a) before b) after ligand desexcitation.

The principal difference between these two models is the interaction distances. The Dexter mechanism is effective only for very short distances (< 10 Å) because a pronounced orbital covering is required, whereas the Förster mechanism applies to longer distances and is depending on spectral covering of donor emission spectrum and acceptor absorption spectrum.

7.1.2 Examples of Luminescence with Thiophene−Substituted Ligands

Recent studies have shown that thiophene derivatives could be good candidates as sensitising chromophore.[31b, 31d−i] Sultan *et al.*[31b] have reported on luminescence investigations of homodinuclear lanthanoid complexes (Er^{3+}, Eu^{3+}, Tb^{3+}, Nd^{3+} and Pr^{3+}), bridged by 2,2'–bipyrimidine or 2,3–bis(2–pyridyl)pyrazine and 2−thenoyltrifluoroacetonate (Figure 1.24).

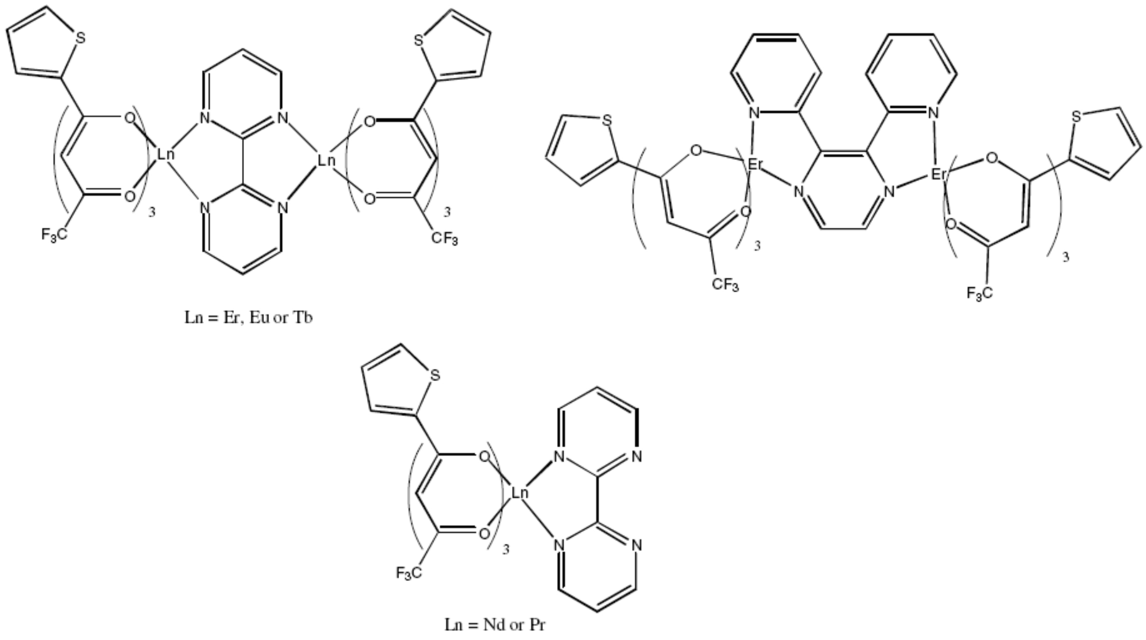


Figure 1.24. Lanthanides complexes studies by Sultan *et al.*.[30b]

The emission spectra upon an excitation at the tta ligand indicate an electronic communication between the metal centre through the bridging ligands (Figure 1.25).

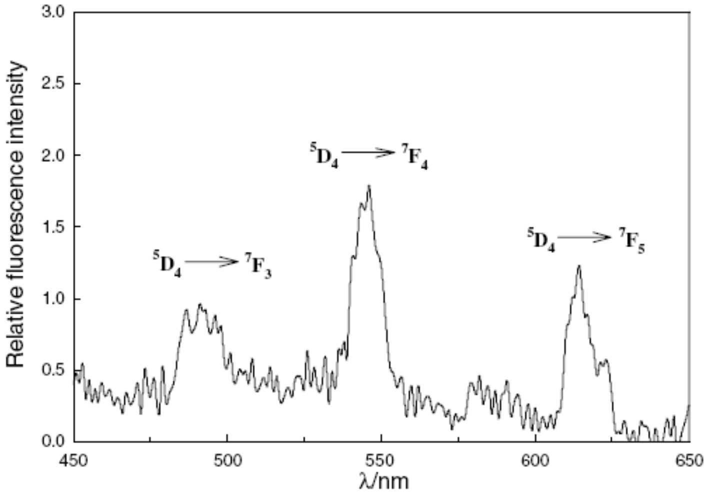


Figure 1.25. The emission spectrum of the terbium homodinuclear complex in methanol solution.[30b]

7.1.3 Applications of Luminescence to Sensory Probes

The use of lanthanide complexes is considerable as probes for the presence of particular cations and anions, oxygen, etc., with obvious potential in biological, clinical and environmental applications. For example, luminescence of the Eu^{3+} complex of the tentradentate tris(2–pyridylmethyl)amine ligand with R = CH_3 (Figure 1.26) shows a particular sensitivity for nitrate (over other ions such as chloride, sulphate and acetate), greatest enhancement of the luminescence spectrum being for the “hypersensitive” $^5D_0 \rightarrow {}^7F_2$ transition at 618 nm, as might be excepted.[83] The terbium complex, in contrast, exhibits greatest sensitivity for chloride. Using the achiral ligand (R = H) reveals similar selectivity for these anions, but with rather less sensitivity.

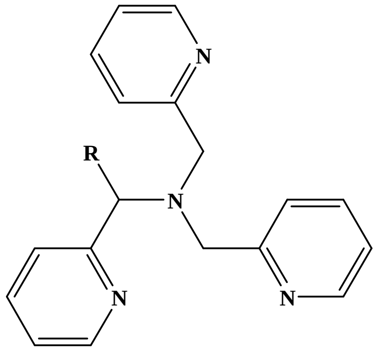


Figure 1.26. A tris(2–pyridylmethyl)amine ligand, R = CH_3, H.

Gunnlaugsson *et al.*[84] have synthesized a terbium complex (Figure 1.27) which is a molecular logic gate corresponding to a two–input INHIBIT function. The output (a terbium emission line) is observed only when the “input”, the presence of proteins and the absence of oxygen, are both satisfied.

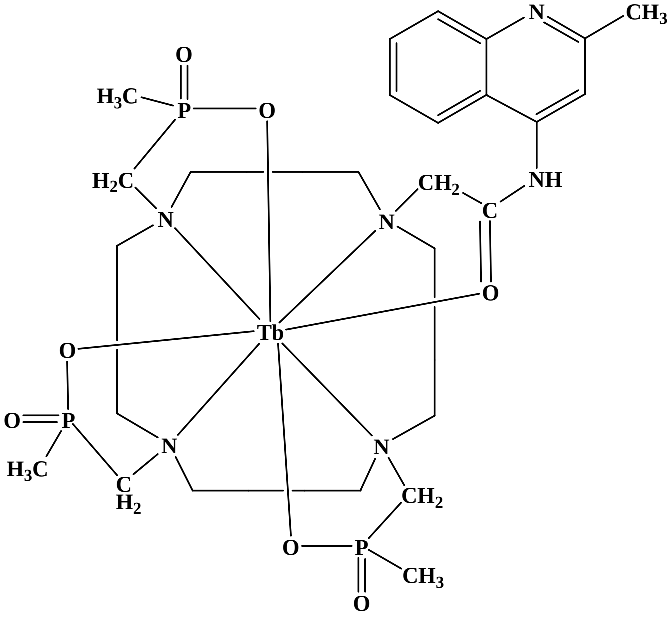


Figure 1.27. A terbium complex: a molecular logic gate.

7.1.4 Fluorescence and TV

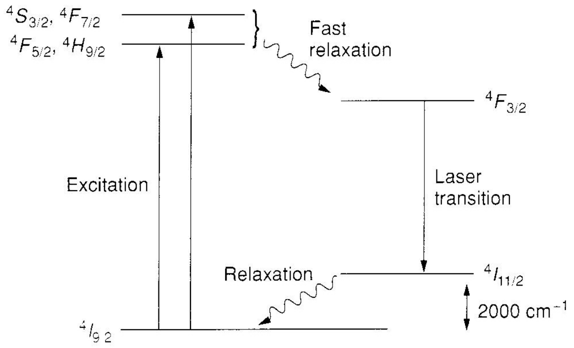
Colour television and similar displays are the largest commercial market for lanthanide phosphor, with over 100 million tubes manufactured a year. About 2 grams of phosphor is used in each tube. The lanthanide involvement in a traditional colour TV tube works along these lines. There are three electron guns firing electron beams at the screen from subtly different angles (using as a “mask” of some kind) to hit clusters, each comprising three phosphor “dots”, each “dot” emitting a different primary colour, the “mask” aligned so the appropriate electron gun fires at its matching phosphor. For many years, the red–emitting phosphor has used a Eu^{3+} material, originally Eu^{3+}:YVO_4,[85] more recently Eu^{3+} in Y_2O_2S[86] or Eu^{3+}:Y_2O_3.[87] They are employed in preference to broad band emitters like Ag:Zn,CdS[88] as although they are energetically less efficient, these “narrow–band” lanthanide phosphors are brighter (and also match the eye’s colour response better). Green light is obtained from either Cu,Al:Zn,CdS [89] or Ce^{3+}:CaS [90] and Eu^{2+}:$SrGa_2S_4$ [91] (these are “broad band emitters”). Development of materials for alternative flat–screens proceeds apace.

7.1.5 Lighting Applications

There is an intense interest in using rare earths in lighting applications. The co–called tricolour lamps use three narrow–band lanthanide light–emitting materials with maxima around 450, 540 and 610 nm; such as $Eu^{2+}:BaMgAl_{10}O_{17}$, $(Ce,Gd,Tb)MgB_5O_{10}$, and $Eu:Y_2O_3$, respectively. This gives a good colour rendering at high efficiency. An UV emitter containing $Eu^{2+}:SrB_4O_7$ could have an unusual application such as insect traps.

7.1.6 Lasers

Various lanthanide ions can be used in lasers (Light Amplification by Stimulated Emission of Radiation), different ions operating at different frequencies. The most popular is the neodymium laser, most usually using Nd^{3+} ions in yttrium aluminium garnet (YAG; $Y_3Al_5O_{12}$). Such a laser functions by increasing light emission by stimulating the release of photons from excited Nd^{3+} ions (in this case). A typical device consists of a YAG rod a few cm long (containing about 1% of neodymium in place of yttrium) that is fitted with a mirror at each end, one being a partly transmitting mirror (or a similar device). A tungsten–halogen lamp (or a similar device) is used to “pump” the system to ensure that an excess of Nd^{3+} ions is in an excited state (e. g. $^4F_{5/2}$ or $^4F_{7/2}$) so that more ions can emit electrons than can absorb; these excited ions decay rapidly (or “cascade”) to the long life–time $^4F_{3/2}$ state *non–radiatively*, so that a high proportion of Nd^{3+} ions are in this state rather than the ground state, “a population inversion” (Scheme 1.8).[92]



Scheme 1.8. “A four– level” Nd^{3+} laser.[92]

If a phonon of the correct energy (at the wavelength of the laser transition) hits a Nd^{3+} ion in the $^4F_{3/2}$ state, the Nd^{3+} ion is stimulated to release another phonon of the same wavelength, as it drops to the $^4I_{11/2}$ state. As the phonons are reflected backwards and forwards in the rod, more and more ions are stimulated into giving up photons (thus depopulating the $^4F_{3/2}$ state) and eventually the build up of photons is so great that they emerge from the rod as an intense beam of coherent monochromatic light (wavelength 1.06 μm, in the near–IR). The $^4I_{11/2}$ state is an excited level of the ground state, which is not thermally populated and so undergoes rapid relaxation to the ground state, maintaining the "population inversion" (whereupon the laser process can start again). Neodymium is thus said to act as a "four–level" laser.[92]

7.1.7 Euro Banknotes

The Euro banknotes exhibit green, blue and red luminescent bands under UV irradiation, as security measure. The red bands are doublets due to some Eu^{3+} complex, probably with a β–diketonate or some similar ligand. The green and the blue luminescence could be caused by Eu^{2+} complex.

7.2 NMR Applications

7.2.1 β–diketonates as NMR Shift Reagents

Paramagnetic lanthanide β–diketonate complexes $Ln(R^1COCHCOR^2)_3$ produce shifts in the NMR spectra of Lewis base molecules capable of forming adducts with them and are thus often referred to as Lanthanide Shift Reagent (LSRs) through all paramagnetic lanthanide complexes can exhibit shifted resonances.[93] The molecules were chosen, such us $Eu(dpm)_3$ (R^1 = R^2 = Me_3C),[94] which were quite soluble in non–polar solvents. The magnitude of the proton shifts depends upon the distance of the proton from the site of coordination to the lanthanide ion. The use of these LSRs leads to a simplification of the spectra of organic molecules without the use of high–frequency spectrometers. Nowadays, this technique is less generally used owing to the spread of high–frequency spectrometers, but chiral reagent like a lanthanide camphorate complex find applications (Figure 1.28),[95] for example when such a chiral shift reagent binds to a racemic mixture, two diasteroisomeric forms of the complex are formed, each with different peaks in the NMR spectrum; each signal can be integrated and used to calculate the enantiomeric excess, a quick way of estimating the yield of each isomer.[96]

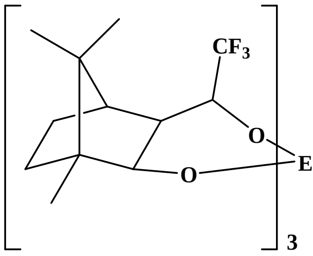


Figure 1.28. Example of a chiral shift reagent.

7.2.2 Magnetic Resonance Imaging (MRI)

The use of gadolinium complexes to assist diagnosis in this expanding area of medicine is now most important.[97] In the MRI experiment, a human body is placed on a horizontal table that is slid into the centre of the magnetic field of the MRI scanner (essentially a pulsed FT NMR spectrometer). MRI relies on detecting the NMR signals from hydrogen atoms in water molecules (which make up about 60 % of the human body) and distinguishes between water molecules in healthy and diseased tissue (since water molecules in cancerous tissue have much longer relaxation times). In this view, the choice of MRI agent is dictated by a combination of several factors: high magnetic moment, long electron–spin relaxation time, osmolarity similar to serum, low toxicity, high solubility in water, targeting tissue, coordinated water molecules, and large molecule with long rotational correction times.

Gadolinium(III) compounds are good candidates. The Gd^{3+} ion has a large number of unpaired electrons (S = 7/2) and moreover its magnetic properties are isotropic. It has a relatively long electron–spin relaxation time (~ 10^9 s). These factors are very favourable for nuclear spin relaxation.

The free Gd^{3+} (aq) ion is toxic, however, with an LD50 ~ 0.1 mmol/kg, less than the imaging dose. Gadolinium complexes are therefore used, using ligands that form a very stable *in vivo* complex. Another factor is the presence of water molecules in the coordination sphere of gadolinium, as relaxation times are shorter the nearer the water molecules are to the Gd^{3+} ions. For examples, the gadolinium complexes used is $[Gd(dtpa)(H_2O)]^{2-}$ (gadopentetate dimeglumine, Magnevist®), $[Gd(dota)(H_2O)]^{-}$ (gadoterate meglumine, Dotarem®) and $[Gd(dtpa–bma)(H_2O)]$ (gadodiamine, Omniscan®).

7.2.3 Texaphyrins

A new type of complex with a different spectroscopic application is provided by the texaphyrins, compounds of "extended" porphyrins where the ring contains five donor nitrogens (Figure 1.29). These have attracted considerable interest because these possible medicinal applications.[98]

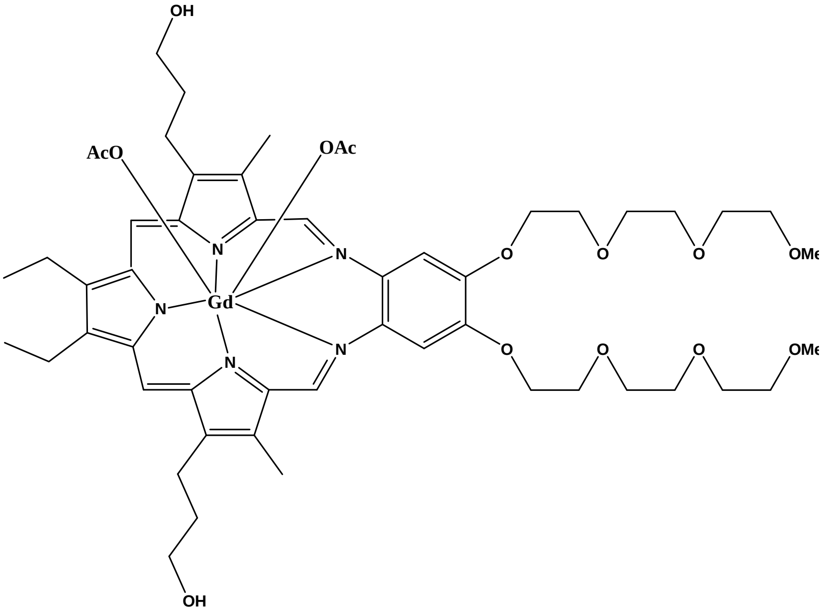


Figure 1.29. Example of a texaphyrins: the Gd–tex.

Two texaphyrins complexes are undergoing clinical trials; a gadolinium compound (Gd–tex, XCYTRIN®, Figure 1.29) is an effective radiation sensitizer for tumour cells. It assists the production of reactive oxygen–containing species, whilst the presence of the Gd^{3+} ion means that the cancerous lesions to which it localizes can be studied by MRI. It has being investigated in connection with pancreatic tumours and brain cancers. One form of the lutetium analogue (LUTRIN®) is being developed for photodynamic therapy for breast cancer, and another (ANTRIN®) is being developed for photo angioplasty, where it has potential for treating arteriosclerosis by removal of atherosclerotic plaque.

7.3 Applications of Rare Earth Reagents in Organic Synthesis

Few areas of synthesis chemistry have witnessed growth as explosive as that brought about by the application of lanthanide reagents to organic synthesis. They are employed for functional group transformations, and carbon–carbon bond forming reactions.[99]

Two metal derivatives are often used as catalyst. The first, the cerium(IV) derivatives such as $(NH_4)_2Ce(NO_3)_6$ (CAN) and $(NH_4)_2Ce(SO_4)_6$ (CAS) are utilized for oxidative reactions[100] and the cerium(III) chloride combinated with $NaBH_4$ are good reductant reagents for aldehydes and ketones (Luche protocol).[101] The second, the samarium(II) iodide can reduce for example, halogen compounds.[102] It is also used in the Barbier reactions.[103] Other rare earth complexes catalyst some reactions such as Diels–Alder, [104] Friedel–Craft, [105] Mannich [106] and polymerisation reactions.[107]

The next chapters are intended to present the synthesis, crystal structure, electrochemical and physico−chemical studies on thienyl−substituted methoxides of alkali, tin(II) and trivalent rare earth metals.

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Chapter 2 Synthesis and Crystal Structure Investigations of Metal Methoxides Containing Thienyl Substituents

Part 1 Introduction

1 Generalities

Metal alkoxides are compounds in which a metal is attached covalently to the oxygen bearing an alkyl group. To maximize the coordination number of the metals, the alkoxide oxygen bearing two non−bonding doublets can additionally bond in a dative manner to one, two or three metal centres and form M−μ−OR−M type bridges (Figure 2.1).

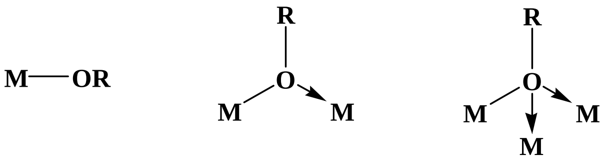


Figure 2.1. Metal alkoxides.

Alkoxides are derived from alcohols by the replacement of the hydroxyl hydrogen by a metal. The first metal alkoxide, a sodium alkoxide, was described by J. Liebig in 1837. During the last decade, some alkoxides including those of sodium, potassium, magnesium, aluminium, zirconium and titanium, even become commercially important.[1, 2, 3] The term "metal alkoxides" is preferred, although the term "metal alcoholates" is also often used. Many metal alkoxides are soluble in the corresponding alcohols. Some metal alkoxides decompose at higher temperatures to lower valence compounds, in some cases even to metal. Metal alkoxides are used for a great variety of purposes such as catalysis, with partial or complete hydrolysis, alcoholysis, or transesterification in coating for plastics, textiles, glass, metals, and additives for adhesives and paints, and for the cross−linking or hardening of natural and synthetic materials.[4, 5, 6]

2 Different Pathways for the Synthesis of Homometallic Alkoxides

2.1 Reaction between Elemental Metals and Alcohols

$$\mathbf{M + \mathit{n}\,H(OR) \longrightarrow M(OR) + \mathit{n}/2\,H_2}$$

Equation 2.1.

The direct reaction between metal and alcohol is due to the acidity of the alcohol and the electropositivity of the metal (Equation 2.1). The acidity of the alcohol depends on the alkyl function. Less electropositive metals, for example magnesium and aluminium can be brought to reaction with alcohols in the presence of a catalyst. This synthetic approach has been reported by Deacon *et al.* to prepare new lanthanide aryl oxides:[7] the elemental lanthanides being activated with mercury and treated by alcohols at high temperature to form the desired metal alkoxides.

2.2 Reaction between Metal Oxides or Metal Hydroxides and Alcohols

$$\mathbf{M_{\mathit{x}}O_{\mathit{n}} + 2\mathit{n}\,HOR \longrightarrow M_{\mathit{x}}(OR)_{2\mathit{n}} + \mathit{n}\,H_2O}$$

$$\mathbf{M_{\mathit{x}}H_{\mathit{n}} + 2\mathit{n}\,HOR \longrightarrow M_{\mathit{x}}(OR)_{2\mathit{n}} + \mathit{n}\,H_2O}$$

Equation 2.2.

The restriction of this synthesis[8] (Equation 2.2) is the formation of water molecules.

2.3 Reaction between Metal Chlorides and Alcohols

$$\mathbf{MCl_{\mathit{n}} + \mathit{x}\,HOR \longrightarrow MCl_{\mathit{n-x}}(OR)_{\mathit{x}} + \mathit{x}\,HCl}$$

Equation 2.3.

For some metals the foregoing methods (Equation 2.3) are inapplicable and the alkoxides are usually obtained via the anhydrous metal chlorides. In general, metal chlorides undergo solvation and /or partial solvolysis with the short−chain linear aliphatic alcohols, but, in no case the substitution of the chloride is complete. Formation of the metal alkoxide is then achieved by the addition of a base.[8]

2.4 Reaction between Metal Halogenides and Alkali Metal Oxides

$$\mathbf{MX}_{n} + y\,\mathbf{M'OR} \longrightarrow \mathbf{MX}_{n-y}\mathbf{(OR)}_{y} + y\,\mathbf{M'X}$$

Equation 2.4.

This reaction is also named salt elimination reaction (Equation 2.4). A lot of studies of this way of synthesis have been performed with M as lanthanides, X as chloride, iodide or bromide, and M’ as lithium, potassium or sodium.[9, 10, 11]

2.5 Reaction between Metal Amides and Alcohols

$$\mathbf{M(NR'_2)}_{n} + n\,\mathbf{HOR} \longrightarrow \mathbf{M(OR)}_{n} + n\,\mathbf{HNR'_2}$$

Equation 2.5.

This way of synthesis (Equation 2.5) is due to the propensity of the alcohol to act as a weak acid, which is entirely deprotonated in the presence of a silyl−amide group acting as a base and subsequent liberation of HNR'_2. The thus formed alkoxide ligand is then bound via covalent M–O bonding. This method has also often been used to form lanthanide alkoxides.[10, 12, 13]

2.6 Reaction between Metal Hydrides and Alcohols

$$\mathbf{MH}_{n} + x\,\mathbf{HOR} \longrightarrow \mathbf{MH}_{n-x}\mathbf{(OR)}_{x} + x\,\mathbf{H_2}$$

Equation 2.6.

The restriction of this synthesis[8] (Equation 2.6) is the accessibility of the metal hydride. This way of synthesis is applied for the group 13 elements.

2.7 Reaction between Metal Organyls and Alcohols

$$\mathbf{MR'_{\mathit{n}} + \mathit{x}\ HOR \longrightarrow MR'_{\mathit{n-x}}(OR)_{\mathit{x}} + \mathit{x}\ HR'}$$

Equation 2.7.

In general, this synthesis[8] (Equation 2.7) is used for the reaction between *n*–butyllithium and alcohols.

2.8 Insertion of Oxygen

$$\mathbf{MR_{\mathit{n}} + \mathit{n}/2\ O_2 \longrightarrow M(OR)_{\mathit{n}}}$$

Equation 2.8.

The insertion method (Equation 2.8) is also very difficult to investigate in a synthesis laboratory (all the experiments are carried under inert dinitrogen atmosphere).

2.9 Reaction between Metals Alkoxides and Alcohols

$$\mathbf{M(OR)_{\mathit{n}} + \mathit{x}\ HOR' \longrightarrow M(OR)_{\mathit{n-x}}(OR')_{\mathit{x}} + \mathit{x}\ HOR}$$

Equation 2.9.

This reaction[8, 14] (Equation 2.9) depends on the acidity of the alcohol HOR’.

3 Different Pathways for the Synthesis of Heterometallic Alkoxides

3.1 Reaction between Alkoxides

$$x\,\mathrm{M(OR)}_n + y\,\mathrm{M'(OR)}_m \longrightarrow \mathrm{M}_x\mathrm{M'}_y\mathrm{(OR)}_{xn+ym}$$

Equation 2.10.

The exchange reaction[8, 15] (Equation 2.10) between alkoxides is the principal route to form mixed alkoxides.

3.2 Metathesis Reaction with Salt Elimination

$$\mathrm{MX}_n + n\,\mathrm{M''M'(OR)}_m \longrightarrow \mathrm{MM'}_n\mathrm{(OR)}_{nm} + n\,\mathrm{M''X}$$

Equation 2.11.

This variation of the metathesis reaction (Equation 2.11) is often used when the reaction between alkoxides doesn’t work.

Part 2 Preparation of Starting Compounds

1 Organic Ligands

1.1 Presentation

To synthesize new rare earth alkoxides containing thienyl substituents, functionalized alcohols with thienyl groups or mixed carbinols bearing both aryl and thienyl units have been prepared. Recent studies performed by us on these thiophenic precursors have shown that these molecules are good candidates for thin films generated by electropolymerization and subsequent adhesion of nanoparticles.[16] It seemed therefore promising to probe whether this kind of thiophene−functionalized alcohols could be used as electrochemically active alkoxide ligands in lanthanide coordination chemistry. We report here on the preparation and the structural characterization of rare earth compounds containing this type of alkoxothiophene ligands. To correlate structural and steric effects on the molecular geometry, electrochemical and luminescence properties, a large series of rare earth methoxides containing thienyl substituents was prepared. They were synthesized by varying two parameters: i) the nature of the alkoxothiophene ligand, and ii) the nature of metal centre. The organic ligands used for this study are listed in Table 2.1.

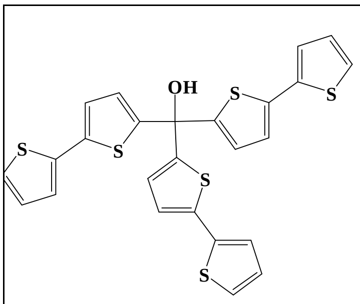
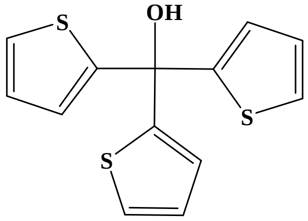
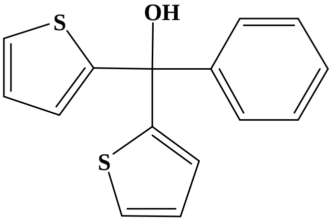
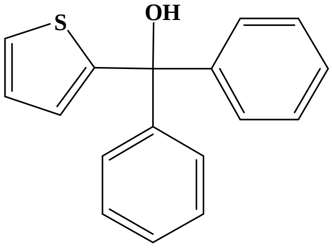
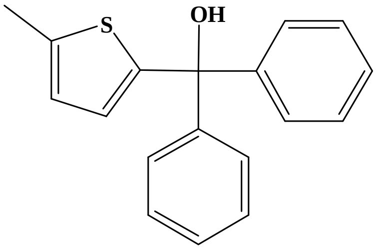
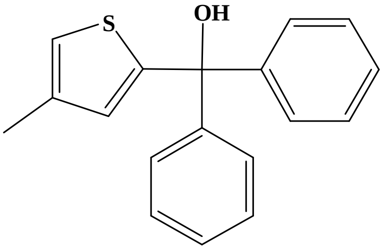
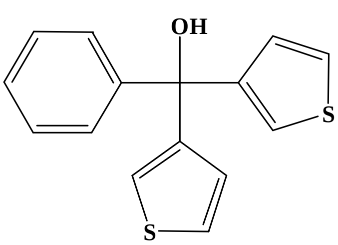
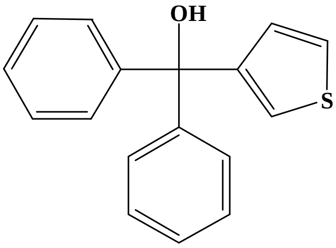
 HO–C($C_8H_5S_2$)$_3$ (**1**)	 HO–C(C_4H_3S)$_3$ (**2**)	 HO–C($C_{14}H_{11}S_2$) (**3**)
 HO–C($C_{16}H_{13}S$) (**4**)	 HO–C($C_{17}H_{15}S$) (**5**)	 HO–C($C_{17}H_{15}S$) (**6**)
 HO–C($C_{14}H_{11}S_2$) (**7**)	 HO–C($C_{16}H_{13}S$) (**8**)	

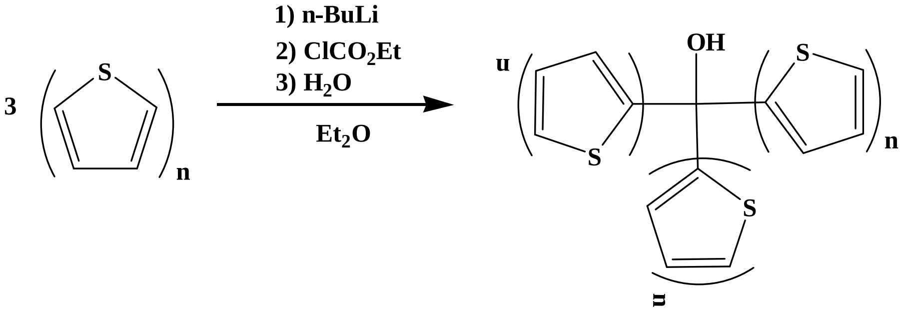
Table 2.1. Star−shaped molecules.

1.2 Synthesis and Crystal structure Determination of the Organic Ligands

1.2.1 Tris(2,2’−bithienyl−5−yl)methanol (<u>1</u>) and Tris(2−thienyl) methanol (<u>2</u>)

1.2.1.1 Synthesis

The star−shaped carbinol derivatives tris(2,2’−bithienyl−5−yl)methanol (**<u>1</u>**) and tris(2−thienyl)methanol (**<u>2</u>**) were synthesized by following procedure described. [17, 18, 19] They were obtained by a classical nucleophilic addition of three equivalents of (2−thienyl)lithium or 2,2’−bithienyl−5−yl−lithium, respectively, to ethyl chloroformate (Equation 2.12).



<u>1</u>: n = 2
<u>2</u>: n = 1

Equation 2.12. Synthesis of <u>1</u> and <u>2</u>.

These organic compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis. Furthermore, their molecular structures were determined by X–ray structure analysis for the first time and confirmed the structural proposition based on the spectroscopic data in solution.[17, 18, 19]

1.2.1.2 Crystal Structure Determination of Tris(2,2’−bithienyl−5−yl)methanol (<u>1</u>)

Colourless crystals of HO–C($C_8H_5S_2$)$_3$ (**<u>1</u>**) were obtained from a concentrated dichloromethane/petroleum benzene (3:2) solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/c in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 5.94 %. In Table 2.2 are reported the crystal data and the structure refinement for the compound and in Table 2.3 are reported some selected bond lengths and angles of interest.

Identification code	sh2294	
Empirical formula	$C_{25}H_{16}OS_6$	
Formula weight	524.74	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.217(2) Å	α= 90°.
	b = 6.059(1) Å	β= 98.82(1)°.
	c = 23.280(3) Å	γ = 90°.
Volume	2260.2(5) $Å^3$	
Z	4	
Density (calculated)	1.542 Mg/m^3	
Absorption coefficient	0.623 mm^{-1}	
F(000)	1080	
Crystal size	0.25 x 0.5 x 0.65 mm^3	
Theta range for data collection	1.27 to 23.25°.	
Index ranges	–17<=h<=17, –6<=k<=6, –25<=l<=25	
Reflections collected	26879	
Independent reflections	3243 [R(int) = 0.1379]	
Completeness to theta = 23.25°	99.7 %	
Absorption correction	None	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	3243 / 8 / 305	
Goodness–of–fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1297	
R indices (all data)	R1 = 0.1443, wR2 = 0.1765	
Largest diff. peak and hole	0.408 and –0.537 e.$Å^{-3}$	

Table 2.2. Crystal data and structure refinement for HO–C($C_8H_5S_2$)$_3$ (<u>1</u>).

O(1)–C(1)	1.440(8)	O(1)–C(1)–C(10)	104.7(5)
C(1)–C(2)	1.51(1)	O(1)–C(1)–C(2)	109.3(5)
C(1)–C(10)	1.55(1)	O(1)–C(1)–C(18)	109.8(5)
C(1)–C(18)	1.51(1)	C(18)–C(1)–C(2)	113.6(6)
		C(18)–C(1)–C(10)	111.1(6)
		C(2)–C(1)–C(10)	107.9(5)

Table 2.3. Selected bond lengths [Å] and angles [°] for HO–C($C_8H_5S_2$)$_3$ (<u>1</u>).

1.2.1.2.1 Discussion of the Molecular Structure of HO–C($C_8H_5S_2$)$_3$ (1)

A single crystal X−ray analysis of HO–C($C_8H_5S_2$)$_3$ (**1**) was carried out for unequivocal identification of the structure as shown in Figure 2.2.

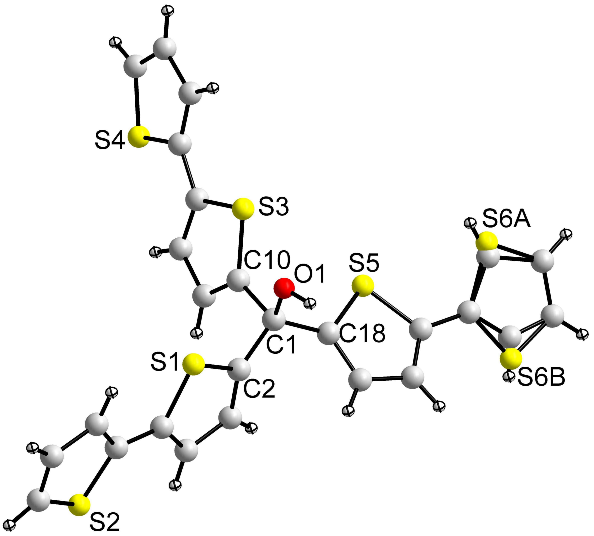


Figure 2.2. X−ray molecular structure of HO–C($C_8H_5S_2$)$_3$ (1). Carbon and hydrogen atoms are not labelled for clarity. The sulphur atom S(6) is found at two split–positions [S(6A) and S(6B)].

The geometry around the tertiary carbon centre C(1) is distorted tetrahedral. The angles O(1)−C(1)−C($C_7H_5S_2$) average 107.9(5)° and the ($C_7H_5S_2$)C−C(1)−C($C_7H_5S_2$) 110.8(6)°: this difference can be explained by the steric hindrance of the bithienyl units. The C(1)−C($C_7H_5S_2$) bond lengths are between 1.51(1) and 1.55(1) Å. The O(1)−C($C_7H_5S_2$) distance is 1.440(8) Å.

1.2.1.3 Crystal Structure Determination of Tris(2−thienyl)methanol (2)

Colourless crystals of HO–C(C_4H_3S)$_3$ (**2**) were obtained from a hexane solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/c in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 5.67 %. In Table 2.4 are reported the crystal data and the structure refinement for the compound and in Table 2.5 are reported some selected bond lengths and angles of interest.

Identification code	sh2302	
Empirical formula	$C_{13}H_{10}OS_3$	
Formula weight	278.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.147(2) Å	α= 90°.
	b = 7.424(1) Å	β= 100.24(3)°.
	c = 15.623(3) Å	γ = 90°.
Volume	1272.3(4) $Å^3$	
Z	4	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	0.561 mm^{-1}	
F(000)	576	
Crystal size	0.7 x 0.6 x 0.3 mm^3	
Theta range for data collection	1.86 to 23.93°.	
Index ranges	–12<=h<=12, –8<=k<=8, –17<=l<=17	
Reflections collected	7714	
Independent reflections	1967 [R(int) = 0.2185]	
Completeness to theta = 23.93°	99.2 %	
Absorption correction	None	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	1967 / 0 / 158	
Goodness–of–fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0567, wR2 = 0.1498	
R indices (all data)	R1 = 0.0676, wR2 = 0.1686	
Largest diff. peak and hole	0.717 and –0.376 e.$Å^{-3}$	

Table 2.4. Crystal data and structure refinement for HO–C(C_4H_3S)$_3$ (2).

O(1)–C(1)	1.440(4)	O(1)–C(1)–C(6)	110.6(3)
C(1)–C(2)	1.534(5)	O(1)–C(1)–C(2)	108.4(3)
C(1)–C(10)	1.523(5)	O(1)–C(1)–C(10)	104.9(3)
C(1)–C(6)	1.514(5)	C(6)–C(1)–C(10)	113.2(3)
		C(10)–C(1)–C(2)	108.3(3)
		C(6)–C(1)–C(2)	111.2(3)

Table 2.5. Selected bond lengths [Å] and angles [°] for HO–C(C_4H_3S)$_3$ (2).

1.2.1.3.1 Discussion of the Molecular Structure of HO–C(C_4H_3S)$_3$ (2)

A single crystal X−ray analysis of HO–C(C_4H_3S)$_3$ (2) was carried out for unequivocal identification of the structure as shown in Figure 2.3.

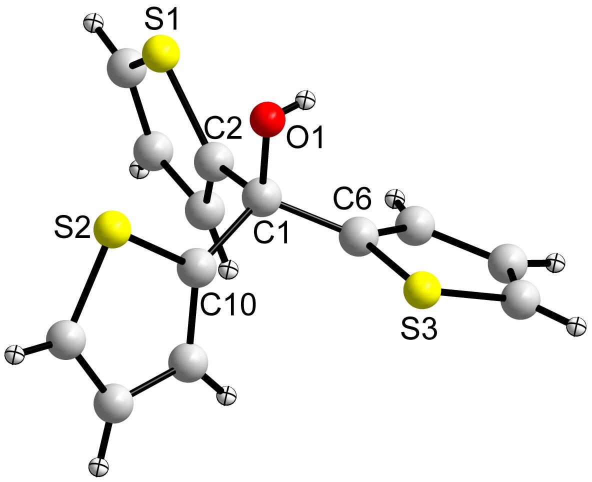
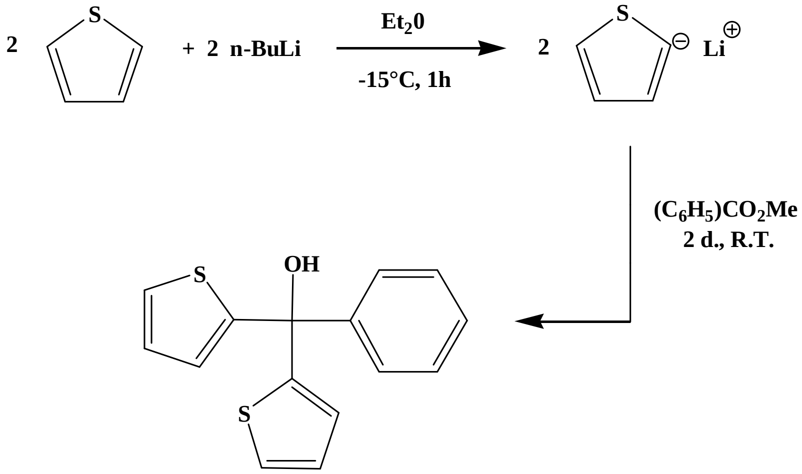


Figure 2.3. X−ray molecular structure of HO–C(C_4H_3S)$_3$ (2).

The geometry around the tertiary carbon centre C(1) is distorted tetrahedral. The angles O(1)−C(1)−C(C_3H_3S) average 107.9(3)° and the (C_3H_3S)C−C(1)−C(C_3H_3S) 110.9(3)°. In comparison with **1**, no difference of these angles has noticed. The C(1)−C(C_3H_3S) bond lengths are between 1.514(5) Å and 1.534(5) Å. The O(1)−C(C_3H_3S) distance is 1.440(4) Å.

1.2.2 Phenylbis(2−thienyl)methanol (3)

The carbinol **3** was synthesised by following the procedure described.[19] It was obtained by a classical nucleophilic addition of (2−thienyl)lithium on methyl benzoate (Equation 2.13). The solution was stirred two days at room temperature, and subsequently hydrolysed. Contrarily to the literature, where the compound was purified by chromatography using a silica column, carbinol **3** was isolated by simple washing with hexane. The compound was characterised by ^{1}H and ^{13}C NMR, IR and elemental analysis.

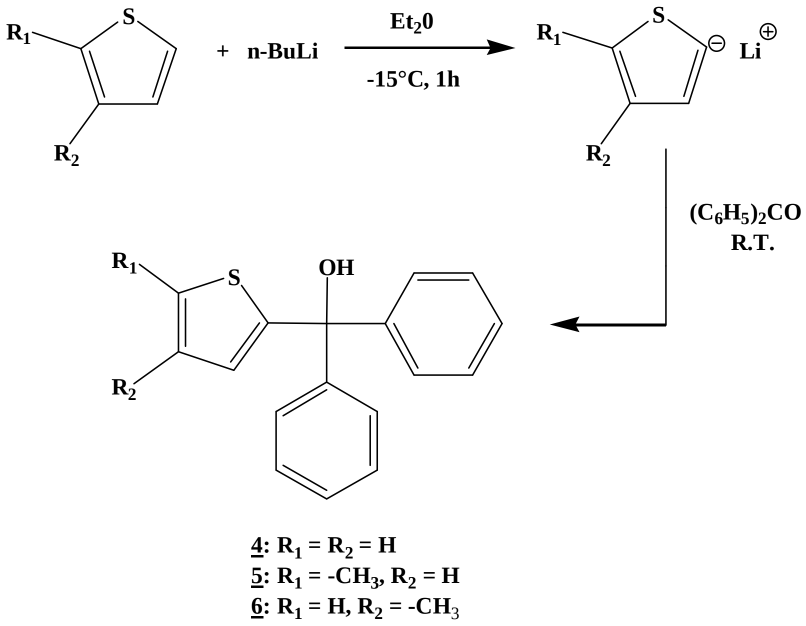


3

Equation 2.13. Synthesis of phenylbis(2−thienyl)methanol (3).

1.2.3 Diphenyl(2−thienyl)methanol (4), Diphenyl(5−methyl−2−thienyl) methanol (5) and Diphenyl(4−methyl−2−thienyl)methanol (6)

The carbinol **4** was synthesised by following the procedure described.[19] The novel compounds **5** and **6** were prepared by a similar method. They were synthesised by a classical nucleophilic addition of lithium derivatives on benzophenone (Equation 2.14). The solutions were stirred two days for **4** or overnight for **5** and **6** at room temperature, and subsequently hydrolysed. The compounds were isolated by simple washing with hexane (yields: 67 % for **5** and 56 % for **6**) and were characterised by ^1H and ^{13}C NMR, IR and elemental analysis.

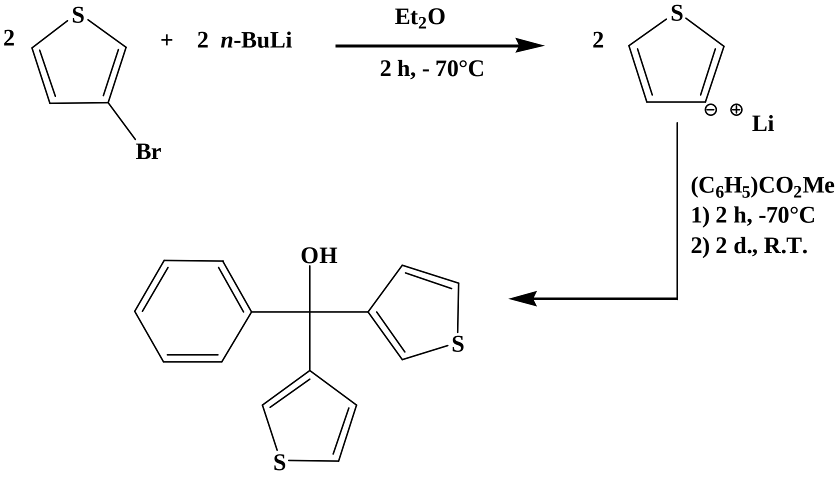


Equation 2.14. Synthesis of 4, 5 and 6.

The ^{1}H–NMR spectrum of **5** (and **6**), recorded in chloroform, displays three aromatic signals: a multiplet at 7.3 ppm (7.3 ppm) attributed to the protons of the phenyl groups, a multiplet at 6.5 ppm and a doublet at 6.4 ppm of the 4−H and the 3−H of the thienyl unit (multiplets at 6.8 and 6.4 ppm of the 5−H and the 3−H of the thienyl unit), respectively. A broad signal at 2.9 ppm (2.9 ppm) due to the alcohol function is also obtained. The latter signal, a doublet at 2.4 ppm (a multiplet at 2.2 ppm), could be assigned to the protons of the methyl group. Correspondingly, the ^{13}C–NMR spectra show the characteristic signals of the thienyl unit, the benzyl and methyl groups.

1.2.4 Phenylbis(3−thienyl)methanol (7)

The carbinol **7** was synthesised by following the procedure described.[19] It was synthesised by a classical nucleophilic addition of (3−thienyl)lithium on methyl benzoate (Equation 2.15). The solution was stirred two hours at −70°C and two days at room temperature, and subsequently hydrolysed. The compound, a white solid, was isolated by washing with hexane.



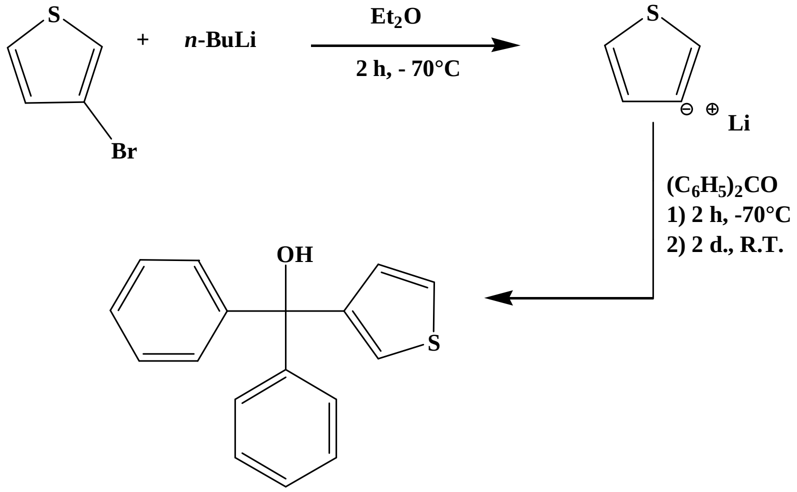
7

Equation 2.15. Synthesis of phenylbis(3−thienyl)methanol (7).

The compound was characterised by ^{1}H and ^{13}C NMR and elemental analysis.

1.2.5 Diphenyl(3−thienyl)methanol (8)

The carbinol **8** was synthesised by following the procedure described.[19] It was synthesised by a classical nucleophilic addition of (3−thienyl)lithium on benzophenone (Equation 2.16). The solution was stirred two hours at −70°C and two days at room temperature, and subsequently hydrolysed. The compound, a white solid, was isolated by washing with hexane.



8

Equation 2.16. Synthesis of diphenyl(3−thienyl)methanol (8).

The compound was characterised by ^{1}H and ^{13}C NMR and elemental analysis.

2 Synthetic Methods Studied in this Work

Two synthetic pathways leading to rare earth alkoxides have been investigated in this work: i) salt metathesis reactions between MCl_3 and carbinolates and ii) the reactions between $M[N(SiMe_3)_2]_3$ and acidic carbinols. The choice of the first method can be explained by the ability of the carbinol derivatives to form alcoholates (with sodium and potassium as counter ion in our case) and their reactivity towards MCl_3. The choice of the latter method is due to the propensity of the thienyl derivative ligands to act as alkoxide ligands via covalent M–O bonding thanks to their abilities to be easily deprotonated in the presence of a silyl–amide group acting as a base, thus liberating the volatile hexamethyldisilazane; the high solubility of silyl amides facilitating their isolation.

3 Synthesis of $M[N(SiMe_3)_2]_x$ (M = Sn, Y, Nd, Er, Sm)

The tin(II) silyl amide $Sn[N(SiMe_3)_2]_2$ was synthesized by the reaction between two equivalents of $LiN(SiMe_3)_2$ [20, 21] and one equivalent of $SnCl_2$ in diethyl ether (Equation 2.17).[22]

$$\mathbf{2\ HN(SiMe_3)_2 + 2\ \mathit{n}\text{-}BuLi \xrightarrow{\text{hexane, 24 h.}} 2\ LiN(SiMe_3)_2 + 2\ C_4H_{10}}$$

$$\mathbf{2\ LiN(SiMe_3)_2 + SnCl_2 \xrightarrow{\text{Et}_2\text{O, 2 h.}} Sn[N(SiMe_3)_2]_2 + 2\ LiCl}$$

Equation 2.17. Synthesis of $Sn[N(SiMe_3)_2]_2$.

Yttrium, neodymium, erbium and samarium silyl amides were synthesized following the procedure described in the literature (Equation 2.18).[23] The Y, Nd, Er and Sm silyl amides were obtained as clean white, blue, pale–red, and pale–blue products, respectively. The yield was found in the range from 80−85 %.

$$3\,\mathrm{LiN(SiMe_3)_2} + \mathrm{MCl_3} \xrightarrow[\text{60 °C, 42 h.}]{\text{benzene, thf}} \mathrm{M[N(SiMe_3)_2]_3} + 3\,\mathrm{LiCl}$$

Equation 2.18. Synthesis of $M[N(SiMe_3)_2]_3$ with M = Y, Nd, Er, Sm.

4 Synthesis and Crystal Structure Determination of Alcoholates Containing Thienyl Substituents

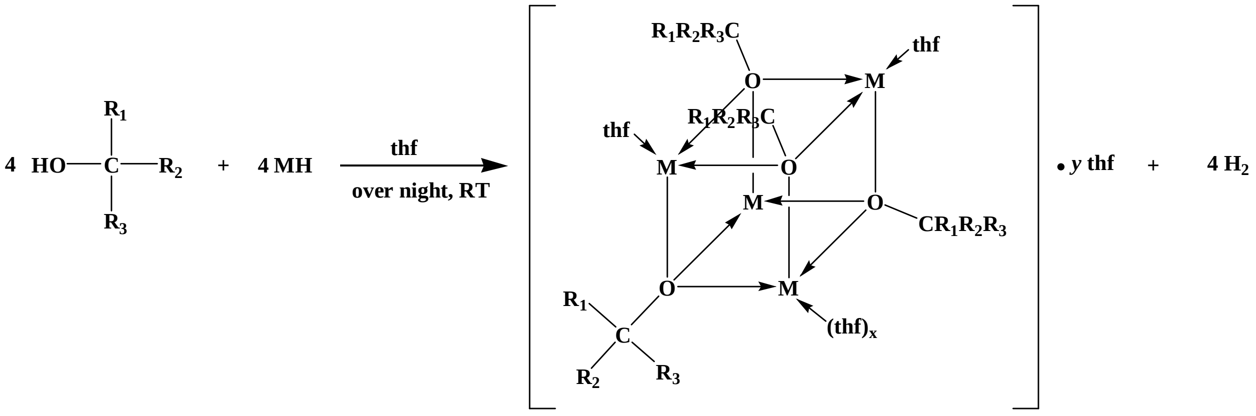
4.1 Introduction

4.1.1 Utilities of these Compounds

To investigate the synthetic potential of the salt metathesis reactions, we first were obliged to synthesize a series of alkali metal alcoholates functionalized with thienyl groups. With this objective in mind, the synthesis and structure features of some new alcoholates were studied.

4.1.2 General Synthesis

The potassium or sodium alcoholates have been synthesized at room temperature by the deprotonation of the corresponding carbinol with potassium or sodium hydride. (Equation 2.19). For all the reactions conducted overnight, a gas development was observed. The products were isolated as solids, in some case even in crystalline form.



Equation 2.19. General route of potassium or sodium alcoholates. M = K, Na; x = 0 or 1, y = 0, ½ or 1. R_1, R_2 and R_3 stand for the thienyl or/and phenyl groups.

4.2 Reactivity of HO−C(C_4H_3S)$_3$ (**2**) towards Alkali Metal Hydrides

4.2.1 Reactivity of HO−C(C_4H_3S)$_3$ (**2**) towards KH

After consumption of all the KH, concentration of the pure solution afforded colourless crystals of [KOC(C_4H_3S)$_3$]$_4$(thf)$_2$ • thf (**12**), which were grown at 5°C. Unfortunately, the yield was quite low with 20 %. The ^{1}H−NMR spectrum recorded in thf/C_6D_6 at room temperature shows three well resolved doublets of doublets at 6.9, 6.8 and 6.7 ppm in the integration ratio 12:12:12. They are attributed, respectively, to the 5−H, 3−H and 4−H protons of the thienyl units.

*4.2.1.1 Crystal Structure Determination of {[KOC(C_4H_3S)$_3$]$_4$(thf)$_2$} • thf (**12**)*

Colourless crystals of {[KOC(C_4H_3S)$_3$]$_4$(thf)$_2$} • thf (**12**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group Pccn in an orthorhombic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 9.51 %. In Table 2.6 are reported the crystal data and the structure refinement for the compound and in Table 2.7 are reported some selected bond lengths and angles.

Identification code	sh2389	
Empirical formula	$C_{64}H_{60}K_4O_7S_{12}$	
Formula weight	1482.24	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 14.246(1) Å	α = 90°.
	b = 16.743(1) Å	β = 90°.
	c = 27.707(1) Å	γ = 90°.
Volume	6608.6(6) Å^3	
Z	4	
Density (calculated)	1.490 Mg/m^3	
Absorption coefficient	0.701 mm^{-1}	
F(000)	3072	
Crystal size	0.55 x 0.3 x 0.25 mm^3	
Theta range for data collection	1.47 to 29.40°.	
Index ranges	–16<=h<=19, –23<=k<=18, –36<=l<=38	

Reflections collected	46554
Independent reflections	9114 [R(int) = 0.0290]
Completeness to theta = 29.40°	99.9 %
Absorption correction	None
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	9114 / 0 / 460
Goodness–of–fit on F^2	2.785
Final R indices [I>2sigma(I)]	R1 = 0.0951, wR2 = 0.2853
R indices (all data)	R1 = 0.1251, wR2 = 0.3074
Largest diff. peak and hole	2.130 and –1.303 e.$Å^{-3}$

Table 2.6. Crystal data and structure refinement for $\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf (12).

K(1)−O(2)	2.671(3)	K(2)−O(3)	2.687(4)
K(1)−O(1)	2.636(3)	K(2)••••K(1)	3.611(1)
K(2)−O(1)	2.652(4)	K(2)••••K(2)	3.855(2)
K(2)−O(2)	2.736(3)		
K(1)−O(2)−K(1)	87.67(9)	O(1)−K(2)−O(2)	89.7(1)
K(1)−O(2)−K(2)	87.90(9)	O(1)−K(2)−O(1)	87.1(1)
K(1)−O(1)−K(2)	90.4(1)	O(3)−K(2)−O(2)	127.4(1)
K(2)−O(1)−K(2)	92.6(1)	C(1)−O(1)−K(1)	119.1(3)
O(2)−K(1)−O(2)	91.6(1)	C(1)−O(1)−K(2)	126.6(3)
O(1)−K(1)−O(2)	91.5(1)	C(14)−O(2)−K(2)	141.3(2)
O(1)−K(2)−O(3)	118.5(1)	C(14)−O(2)−K(1)	128.5(2)

Table 2.7. Selected bond lengths [Å] and angles [°] for $\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf (12).

4.2.1.1.1 Discussion of the Molecular Structure of $\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf (12)

A single crystal X−ray analysis of $\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf (**12**) was carried out for unequivocal identification of the structure as shown in Figure 2.4.

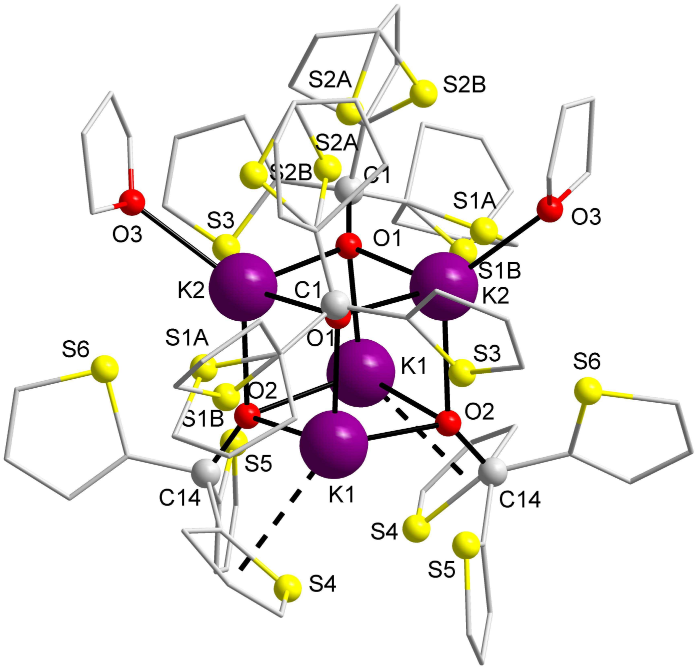


Figure 2.4. Molecular structure of {[KOC(C_4H_3S)$_3$]$_4$(thf)$_2$} • thf (12). The hydrogen atoms and the lattice tetrahydrofuran molecule are omitted for more clarity. Two thienyl groups are found in two split positions [S(1A) and S(1B), S(2A) and S(2B)].

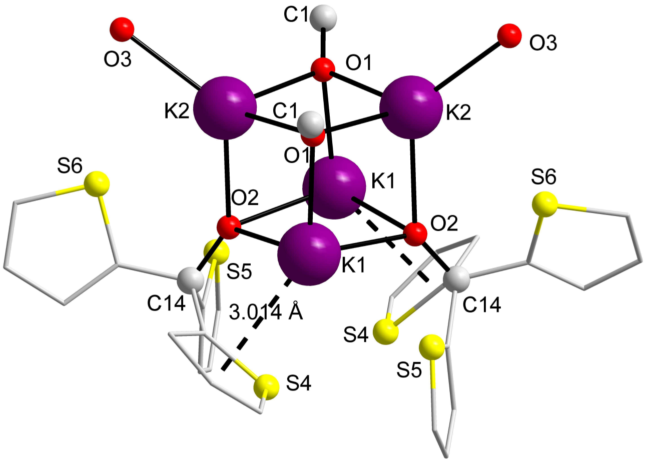


Figure 2.5. View of the distorted heterocuban core.

The crystal structure reveals a tetrameric potassium alcoholate with a distorted cubane−like K_4O_4 core, whose bond lengths are not exactly identical and angle values are around 90° (Figure 2.5). The molecule is situated on a C_2 axis in the crystal. Each potassium atom is surrounded by three tris(2−thienyl)carbinolato ligands. A tetrahydrofuran molecule is also coordinated to K(2). Another tetrahydrofuran molecule is present in the crystal lattice without interaction with the central motif. The μ_3−oxygen atom of the thienyl groups is coordinated to three alkali ions, two with a dative link and one with a covalent link. The geometry around K(1) is trigonal pyramidal and these for K(2) tetrahedral. This molecular structure is in accordance with those found for $[K(\mu_3\text{−DPE})(thf)]_4$ or $[K(\mu_3\text{−DPE})(py)]_4$ • 2 py.[24] In contrast latter examples not all the potassium atoms are ligated to a solvent molecule. A closer view to the surrounding of K(1) shows that the thienyl rings shielding the metal in a π−ligand manner (Figure 2.5). The $K\text{−}OC(C_4H_3S)_3$ distances average 2.673(4) Å and are in the range reported for $[K(\mu_3\text{−DPE})(thf)]_4$ [2.641(0) and 2.720(2) Å] and $[K(\mu_3\text{−DPE})(py)]_4$ • 2 py [2.653(8) Å].[24] The K−O bond lengths between K(2) and the oxygen atom of the tetrahydrofuran molecule of 2.687(4) Å are in agreement with those observed for $[K(\mu_3\text{−DPE})(thf)]_4$ [2.720(2) Å].[24] The K(2)····K(2) and K(2)····K(1) distances of 3.855(2) and 3.611(1) Å, respectively, are indicative for the absence of an interaction between the potassium atoms. The O(1)−K(2)−O(1) or angles of 87.1(1)° are more acute than those found for O(2)−K(1)−O(2) of 91.6(1)°. The same observation are made for the angles O(1)−K(2)−O(2) [89.7(1)°] and O(1)−K(1)−O(2) [91.5(1)°]. Indeed, the presence of the two solvent molecules coordinated only with two potassium leads to a deformation of the heterocuban core, thus inducing these variations of angles.

4.2.2 Reactivity of $HO\text{−}C(C_4H_3S)_3$ (**2**) towards NaH

After consumption of all the NaH, concentration of the pure solution afforded colourless crystals of $[NaOC(C_4H_3S)_3]_4(thf)_2$ (**13**), which were grown at 5°C. Unfortunately, the yield was quite low with 20 %. This very low yield is due to the difficulty to obtain good quality of crystals.

The ^1H−NMR spectrum recorded in thf/C_6D_6 at room temperature shows three well resolved doublets of doublets at 6.9, 6.8 and 6.7 ppm, each integrating for 12H, and attributed to the 5−H, 3−H and 4−H of the protons of the thienyl units, respectively.

4.2.2.1 Crystal Structure Determination of [NaOC(C_4H_3S)$_3$]$_4$(thf)$_2$ (13)

Colourless crystals of [NaOC(C_4H_3S)$_3$]$_4$(thf)$_2$ (**13**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group monoclinic in a C2/c crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 10.52 %. In Table 2.8 are reported the crystal data and the structure refinement for the compound and in Table 2.9 are reported some selected bond lengths and angles of interest.

Identification code	sh2386	
Empirical formula	C60 H52 Na4 O6 S12	
Formula weight	1345.70	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.189(2) Å	α = 90°.
	b = 13.343(1) Å	β = 119.97(1)°.
	c = 22.976(1) Å	γ = 90°.
Volume	6158.8(5) $Å^3$	
Z	4	
Density (calculated)	1.451 Mg/m^3	
Absorption coefficient	0.504 mm^{-1}	
F(000)	2784	
Crystal size	0.4 x 0.28 x 0.22 mm^3	
Theta range for data collection	1.83 to 34.67°.	
Index ranges	–36<=h<=36, –21<=k<=21, –36<=l<=36	
Reflections collected	105170	
Independent reflections	12917 [R(int) = 0.0356]	
Completeness to theta = 34.67°	97.5 %	
Absorption correction	Multiscan	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	12917 / 0 / 360	
Goodness–of–fit on F^2	2.755	
Final R indices [I>2sigma(I)]	R1 = 0.1052, wR2 = 0.2969	
R indices (all data)	R1 = 0.1603, wR2 = 0.3197	
Largest diff. peak and hole	4.195 and –2.547 e.$Å^{-3}$	

Table 2.8. Crystal data and structure refinement for [NaOC(C_4H_3S)$_3$]$_4$(thf)$_2$ (13).

Na(1)−O(2)	2.323(2)	Na(1)••••Na(1)	3.068(2)
Na(1)−O(1)	2.302(2)	Na(2)••••Na(2)	3.256(2)
Na(2)−O(1)	2.488(2)	Na(1)••••Na(2)	3.290(1)
Na(2)−O(2)	2.286(2)	Na(1)−S(3)	2.875(2)
Na(2)−O(3)	2.325(3)		
Na(1)−O(1)−Na(1)	95.45(8)	O(1)−Na(1)−O(1)	95.45(8)
Na(1)−O(1)−Na(2)	87.00(8)	O(2)−Na(2)−O(2)	88.79(8)
Na(2)−O(2)−Na(2)	91.21(8)	O(2)−Na(1)−O(1)	92.10(8)
Na(2)−O(2)−Na(1)	85.86(8)	C(1)−O(1)−Na(1)	125.1(2)
O(2)−Na(2)−O(1)	93.99(8)	C(14)−O(2)−Na(2)	132.2(2)

Table 2.9. Selected bond lengths [Å] and angles [°] for $[NaOC(C_4H_3S)_3]_4(thf)_2$ (13).

4.2.2.1.1 Discussion of the Molecular Structure of $[NaOC(C_4H_3S)_3]_4(thf)_2$ (13)

A single crystal X−ray analysis of $[NaOC(C_4H_3S)_3]_4(thf)_2$ (**13**) was carried out for unequivocal identification of the structure as shown in Figure 2.6.

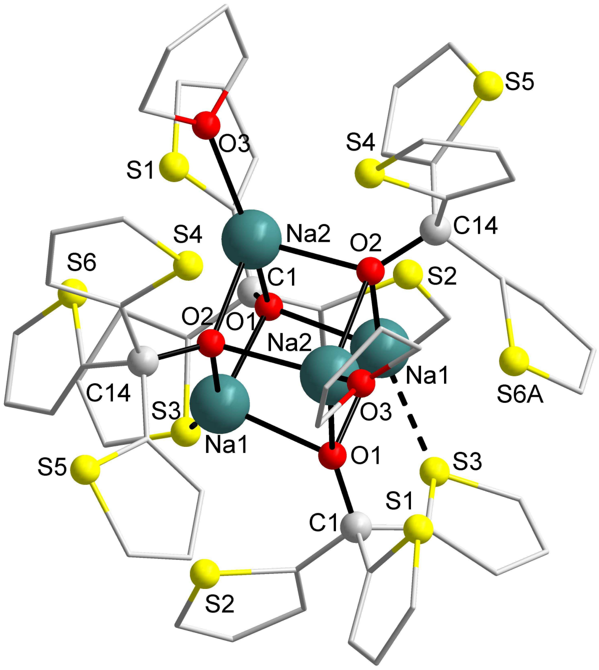


Figure 2.6. Molecular structure of $[NaOC(C_4H_3S)_3]_4(thf)_2$ (13). Hydrogen atoms are omitted for more clarity.

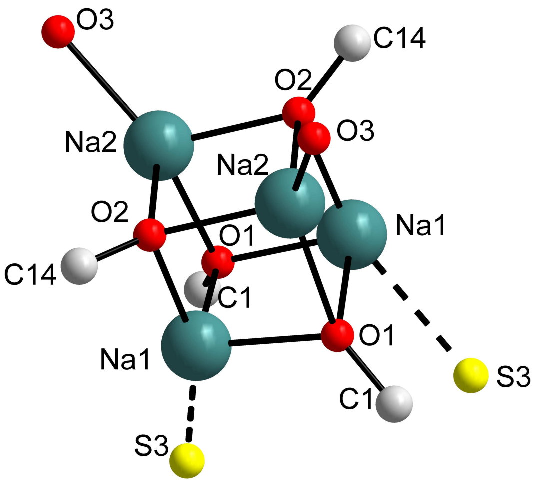


Figure 2.7. Environment around the sodium atoms.

As in the case of the potassium analogue **12**, the molecular structure reveals a tetramer in a distorted cubane arrangement (Figure 2.7). The molecule is situated on a *C*$_2$ axis in the crystal. In contrast to {[KOC(C_4H_3S)$_3$]$_4$(thf)$_2$} • thf (**12**), the Na(1) atoms are surrounded by the three tris(2−thienyl)methanolato ligands and additionally ligated by a sulphur atom of the thienyl groups S(3), with a Na(1)−S(3) distance of 2.875(2) Å. The Na(2) atoms are coordinated by the three tris(2−thienyl)methanolato ligands and a tetrahydrofuran molecule. The (C_4H_3S)$_3$CO−Na−O(C_4H_3S)$_3$ angles are between 88.79(8) and 95.45(8)°.

The overall molecular structure of **13** is quite comparable with those obtained for [Na(μ_3−Ombp)(DME)]$_4$, [25] and [Na(OC_6H_4Me−4)(dme)]$_4$.[26] However in contrast to **13**, in these compounds each metal centre is ligated to a solvent molecule. In our case, (see above) only two sodium atoms are surrounded by tetrahydrofuran and intramolecular bonding is also observed: it is in accordance with [Na$_4$(salphen)$_2$(dme)$_2$] and [Na$_4$(salen)$_2$(dme)$_2$],[27] in which only two of alkali metal are bonded to the Schiff base, whereas the other two complete their coordination sphere with the oxygen atom of a dme donor. The Na−OC(C_4H_5S)$_3$ bond distances lie in the range found for [Na(OC_6H_4Me−4)(dme)]$_4$ [2.314(0) Å][26] and [Na(μ_3−Ombp)(DME)]$_4$ [2.33 Å].[25] The (C_4H_3S)$_3$CO−Na−O(C_4H_3S)$_3$ angles are more obtuse and Na−OC(C_4H_3S)$_3$−Na angles more acute than those for [Na(μ_3−Ombp)(DME)]$_4$ [88.4°].[25] These variations of the angles can be explained by the steric difference of the ligands and solvent ligated to the sodium atoms.

4.3 Reactivity of HO−C($C_{14}H_{11}S_2$) (**3**) towards Alkali Metal Hydrides

4.3.1 Reactivity of HO−C($C_{14}H_{11}S_2$) (**3**) towards KH

After consumption of all the KH, concentration of the pure solution afforded colourless crystals of $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (**21**), which were grown at 5°C. Unfortunately, the yield was quite low with 33 %.

The ^{1}H−NMR spectrum recorded in thf/C_6D_6 at room temperature shows four aromatic signals. The multiplets at 7.5, 6.7 and 6.5 ppm, which each integrate for 8H, are assigned to the protons of the thienyl units (5−H, 4−H and 3−H, respectively). Another multiplet at 6.9 ppm, integrating for 20H corresponds to the protons of the phenyl groups.

*4.3.1.1 Crystal Structure Determination of $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (**21**)*

Colourless crystals of $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (**21**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group C2/c in a monoclinic crystal system. The position of each atom was anisotropically refined. The R–value is 12.24 % (this high value is due to the poor quality of the crystals). In Table 2.10 are reported the crystal data and the structure refinement for the compound and in Table 2.11 and Table 2.12 are reported some selected bond lengths and angles of interest.

Nevertheless, in the asymmetric unit of complex **21** there are two crystallographically independent molecules (A and B) having very close geometry (see Table 2.12). Hereinafter we will refer to the molecule A only.

Identification code	sh2608	
Empirical formula	$C_{72}H_{68}K_4O_7S_8$	
Formula weight	1458.14	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.774(2) Å	α = 90°.
	b = 24.210(2) Å	β = 91.55(1)°.
	c = 49.109(3) Å	γ = 90°.
Volume	29444(3) Å^3	

Z	16
Density (calculated)	1.316 Mg/m^3
Absorption coefficient	0.519 mm^{-1}
F(000)	12160
Crystal size	0.55 x 0.37 x 0.22 mm^3
Theta range for data collection	1.18 to 26.49°.
Index ranges	–30<=h<=30, –25<=k<=30, –55<=l<=61
Reflections collected	123598
Independent reflections	30203 [R(int) = 0.0765]
Completeness to theta = 26.49°	99.1 %
Absorption correction	Multiscan
Max. and min. transmission	0.8943 and 0.7633
Refinement method	Full–matrix–block least–squares on F^2
Data / restraints / parameters	30203 / 4 / 1671
Goodness–of–fit on F^2	2.076
Final R indices [I>2sigma(I)]	R1 = 0.1224, wR2 = 0.3011
R indices (all data)	R1 = 0.2232, wR2 = 0.3291
Largest diff. peak and hole	1.207 and –1.201 e.Å^{-3}

Table 2.10. Crystal data and structure refinement for $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (21).

K(1)−O(1)	2.688(5)	K(3)−O(11)	2.809(7)
K(1)−O(2)	2.654(5)	K(4)−O(2)	2.811(5)
K(1)−O(4)	2.714(5)	K(4)−O(3)	2.766(4)
K(1)−O(9)	2.867(9)	K(4)−O(4)	2.726(5)
K(2)−O(1)	2.692(5)	K(1)••••K(2)	3.832(2)
K(2)−O(2)	2.746(5)	K(1)••••K(3)	3.748(2)
K(2)−O(3)	2.673(5)	K(1)••••K(4)	3.771(2)
K(2)−O(10)	2.773(6)	K(2)••••K(4)	3.785(2)
K(3)−O(1)	2.676(5)	K(2)••••K(3)	3.798(2)
K(3)−O(3)	2.775(5)	K(3)••••K(4)	3.756(2)
K(3)−O(4)	2.726(5)		
K(3)−O(1)−K(1)	88.6(1)	O(3)−K(2)−O(10)	119.5(2)
K(3)−O(1)−K(2)	90.1(2)	O(1)−K(3)−O(3)	89.8(2)
K(2)−O(2)−K(4)	85.9(1)	O(1)−K(3)−O(4)	92.1(1)
K(4)−O(3)−K(3)	85.3(1)	O(1)−K(3)−O(11)	126.3(2)
K(1)−O(4)−K(3)	87.1(1)	O(3)−K(3)−O(11)	123.8(2)
O(1)−K(1)−O(9)	132.0(2)	O(4)−K(4)−O(2)	90.6(1)
O(1)−K(1)−O(4)	92.1(2)	O(3)−K(4)−O(2)	91.2(1)
O(2)−K(1)−O(4)	94.3(2)	C(44)−O(4)−K(1)	121.8(4)
O(4)−K(1)−O(9)	125.9(2)	C(1)−O(1)−K(2)	122.1(4)
O(1)−K(2)−O(2)	88.2(1)	C(1)−O(1)−K(3)	128.9(4)
O(1)−K(2)−O(10)	129.8(2)	C(14)−O(3)−K(4)	117.7(4)
O(3)−K(2)−O(1)	91.7(2)	C(29)−O(2)−K(4)	110.8(4)

Table 2.11. Selected bond lengths [Å] and angles [°] for $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (21) (molecule A).

K(5)−O(5)	2.761(6)	K(7)−O(13)	2.732(6)
K(5)−O(6)	2.740(5)	K(8)−O(6)	2.704(5)
K(5)−O(8)	2.750(5)	K(8)−O(7)	2.738(7)
K(6)−O(5)	2.668(6)	K(8)−O(8)	2.752(5)
K(6)−O(6)	2.702(5)	K(8)−O(14)	3.02(1)
K(6)−O(7)	2.740(7)	K(5)••••K(8)	3.717(9)
K(6)−O(12)	2.99(1)	K(6)••••K(7)	3.850(3)
K(7)−O(5)	2.770(6)	K(6)••••K(8)	3.859(3)
K(7)−O(7)	2.687(5)	K(7)••••K(8)	3.774(3)
K(7)−O(8)	2.668(5)		
K(5)−O(5)−K(7)	86.0(2)	O(5)−K(6)−O(12)	115.7(2)
K(5)−O(8)−K(8)	85.0(1)	O(6)−K(6)−O(7)	89.5(2)
K(6)−O(6)−K(5)	86.2(2)	O(6)−K(6)−O(12)	117.8(2)
K(7)−O(7)−K(8)	88.2(2)	O(7)−K(6)−O(12)	138.3(2)
K(7)−O(8)−K(5)	88.2(2)	O(8)−K(7)−O(13)	120.4(2)
K(8)−O(7)−K(6)	89.6(2)	O(7)−K(7)−O(13)	126.5(2)
O(6)−K(5)−O(5)	92.3(2)	C(102)−O(8)−K(5)	111.0(4)
O(6)−K(5)−O(8)	94.1(1)	C(117)−O(7)−K(6)	128.0(5)
O(5)−K(6)−O(7)	90.2(2)	C(117)−O(7)−K(7)	127.0(4)
O(5)−K(6)−O(6)	95.2(2)		

Table 2.12. Selected bond lengths [Å] and angles [°] for $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (21) (molecule B).

4.3.1.1.1 Discussion of the Molecular Structure of $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (21)

A single crystal X−ray analysis of $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (**21**) was carried out for unequivocal identification of the structure as shown in Figure 2.8.

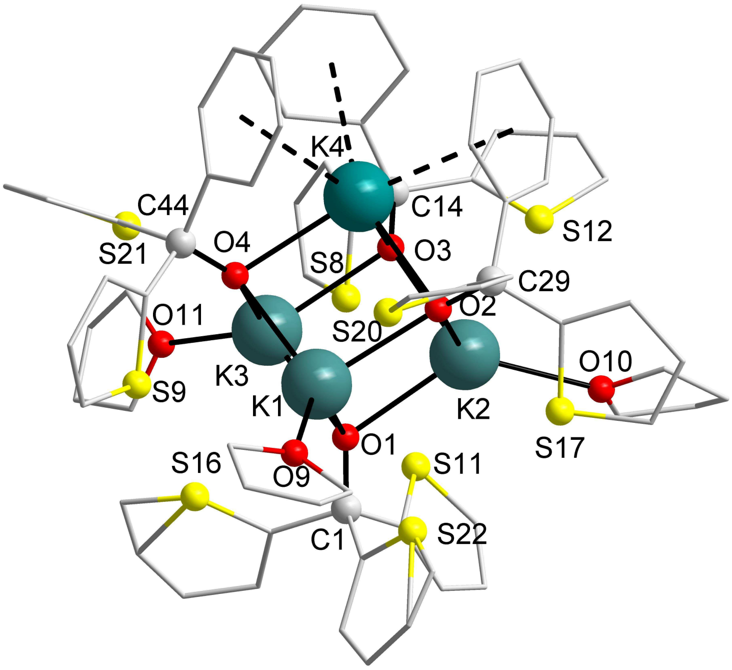


Figure 2.8. Molecular structure of [KOC($C_{14}H_{11}S_2$)]$_4$(thf)$_3$ (21). The sulphur atoms S are found in two split–positions [S(16) and S(22)].

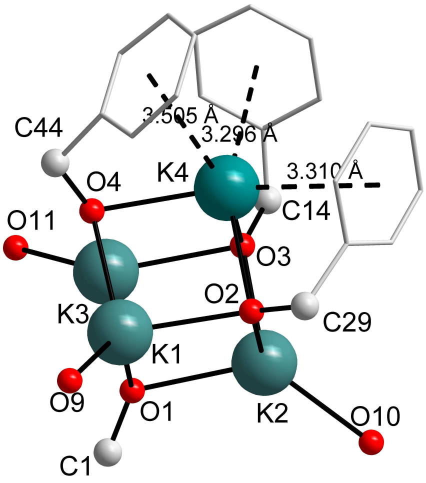


Figure 2.9. Environment around the potassium atoms.

The structure of **21** reveals a tetrameric potassium alcoholate with a distorted cubane configuration since bond lengths are not exactly identical and angle values are around 90°. Each potassium atom is surrounded by three carbinolato ligands and contrarily to {[KOC(C_4H_3S)$_3$]$_4$(thf)$_2$} • thf (**12**) three alkali metals [K(1), K(2) and K(3)] are ligated to a tetrahydrofuran (Figure 2.9). The coordination sphere around K(4) is trigonal pyramidal and those around K(1), K(2) and K(3) tetrahedral. The possible addition of a fourth tetrahydrofuran molecule at K(4) was prevented by three phenyl groups building a shell around the open side of the potassium atom (Figure 2.9). The K–OC($C_{14}H_{11}S_2$) and K–O(thf) distances averaging 2.719(5) Å and 2.816(9) Å, respectively, are longer than those found for **12**.

4.3.2 Reactivity of HO−C($C_{14}H_{11}S_2$) (**3**) towards NaH

After filtration from unreacted sodium hydride and concentration of the thf solution, a light−brown solid precipitated. Unfortunately, no isolation of this compound in form of single crystals has been possible.

The ^{1}H−NMR spectrum of this product in thf/C_6D_6 recorded at room temperature shows three signals. The first at 7.6 ppm, a doublet of doublet integrating for 8H, could be attributed to the 5−H of the thienyl groups. The second at 7.0 ppm, which integrates for 28 H, corresponds to the protons of the phenyl groups and to the 4−H of the thienyl units. The 3−H protons of the thienyl groups (8H) are present at 6.7 ppm.

Therefore, it can be concluded that NaH and HO−C($C_{14}H_{11}S_2$) (**3**) react in the same manner as KH and HO−C($C_{14}H_{11}S_2$) (**3**), or MH (M = Na, K) with HO−(C_4H_3S)$_3$ (**2**) giving rise to [NaOC($C_{14}H_{11}S_2$)]$_4$(thf)$_2$ (**22**).

Moreover, this composition is confirmed by the elemental analysis. The found carbon and hydrogen values of 60.61 and 4.39 % match well with the calculated values of 61.81 and 4.54 %. Therefore we propose a tetranuclear motif for [NaOC($C_{14}H_{11}S_2$)]$_4$(thf)$_2$ (**22**) as depicted in Figure 2.10. This compound was obtained in 32 % yield.

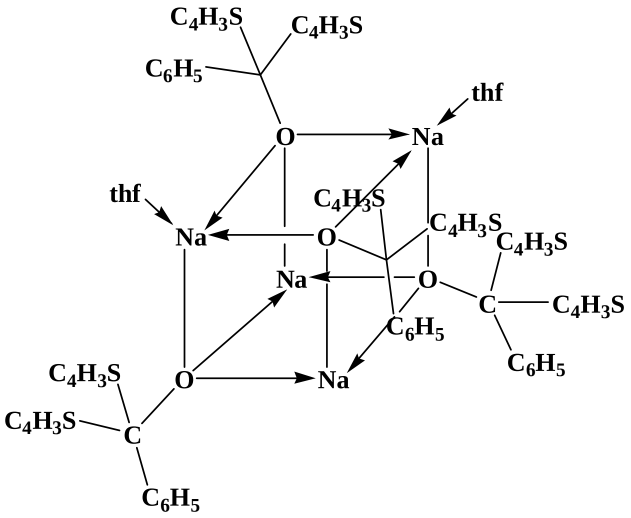


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Figure 2.10. Representation of [NaOC($C_{14}H_{11}S_2$)]$_4$(thf)$_2$ (22).

4.4 Reactivity of HO−C($C_{16}H_{13}S$) (4) towards KH

After consumption of all the KH, concentration of the pure solution afforded colourless crystals of {[KOC($C_{16}H_{13}S$)]$_4$(thf)$_3$} • ½ thf (25), which were grown at 5°C. Unfortunately, the yield was quite low with 34 %.

The ^{1}H−NMR spectrum of this product recorded at room temperature in thf/C_6D_6, reveals four signals in the integration ratio 12:32:4:4. The signals of 5−H, 4−H and 3−H protons of the thienyl units are observed at 7.3, 6.7 and 6.4 ppm, respectively. The peaks at 7.3 and 6.9 ppm are attributed to the protons of the phenyl groups.

4.4.1 Crystal Structure Determination of {[KOC($C_{16}H_{13}S$)]$_4$(thf)$_3$} • ½ thf (25)

Colourless crystals of {[KOC($C_{16}H_{13}S$)]$_4$(thf)$_3$} • ½ thf (25) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)3 in a cubic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 6.26 %. In Table 2.13 are reported the crystal data and the structure refinement for the compound and in Table

2.14 are reported some selected bond lengths and angles of interest. In the asymmetric unit of alcoholate **25** there are two crystallographically independent molecules (A and B) having very close geometries (see Table 2.15). Herein, we will only refer to the molecule A.

Identification code	sh2565	
Empirical formula	$C_{82}H_{78}K_4O_7S_3 \bullet 0.5\ C_4H_8O$	
Formula weight	1464.08	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	P2(1)3	
Unit cell dimensions	a = 24.494(2) Å	α= 90°.
Volume	14695.9(6) Å^3	
Z	8	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.384 mm^{-1}	
F(000)	6160	
Crystal size	0.5 x 0.2 x 0.09 mm^3	
Theta range for data collection	1.18 to 28.26°.	
Index ranges	−26<=h<=32, −32<=k<=32, −32<=l<=29	
Reflections collected	83983	
Independent reflections	12157 [R(int) = 0.1092]	
Completeness to theta = 28.26°	100.0 %	
Absorption correction	None	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	12157 / 0 / 589	
Goodness−of−fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1497	
R indices (all data)	R1 = 0.1109, wR2 = 0.1784	
Absolute structure parameter	0.03(5)	
Largest diff. peak and hole	1.010 and −0.516 e.Å^{-3}	

Table 2.13. Crystal data and structure refinement for {[KOC($C_{16}H_{13}S$)]$_4$(thf)$_3$} • ½ thf (25).

K(1)–O(1)	2.789(3)	K(2)–O(5)	2.765(4)
K(2)–O(1)	2.625(3)	O(2)–C(18)	1.390(9)
K(2)–O(2)	2.696(3)	K(2)••••K(2)	3.754(2)
K(2)–O(1)–K(1)	88.50(9)	O(2)–K(2)–O(5)	113.9(1)
K(2)–O(1)–K(2)	88.3(1)	O(5)–K(2)–O(1)	137.9(1)
O(1)–K(1)–O(1)	91.95(9)	C(1)–O(1)–K(1)	113.4(2)
O(1)–K(2)–O(1)	94.8(1)	C(1)–O(1)–K(2)	146.0(2)
O(1)–K(2)–O(2)	94.37(9)	C(18)–O(2)–K(2)	126.45(8)
O(1)–K(2)–O(5)	115.9(1)		

Table 2.14. Selected bond lengths [Å] and angles [°] for {[KOC($C_{16}H_{13}S$)]$_4$(thf)$_3$} • ½ thf (25) (molecule A).

K(3)–O(3)	2.790(3)	K(4)–O(6)	2.742(4)
K(4)–O(3)	2.702(3)	O(4)–C(46)	1.400(8)
K(4)–O(4)	2.667(3)	K(4)••••K(4)	3.734(2)
K(4)–O(3)–K(3)	86.67(9)	O(3)–K(4)–O(6)	124.3(1)
K(4)–O(4)–K(4)	88.9(1)	O(4)–K(4)–O(6)	117.9(1)
O(3)–K(3)–O(3)	91.35(9)	C(29)–O(3)–K(3)	115.6(2)
O(3)–K(4)–O(6)	126.7(1)	C(29)–O(3)–K(4)	119.0(2)
O(3)–K(4)–O(4)	124.3(1)	C(46)–O(4)–K(4)	126.07(8)

Table 2.15. Selected bond lengths [Å] and angles [°] for $\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (25) (molecule B).

4.4.1.1 Discussion of the Molecular Structure of $\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (25)

A single crystal X−ray analysis of $\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (**25**) was carried out: the structure as shown in Figure 2.11.

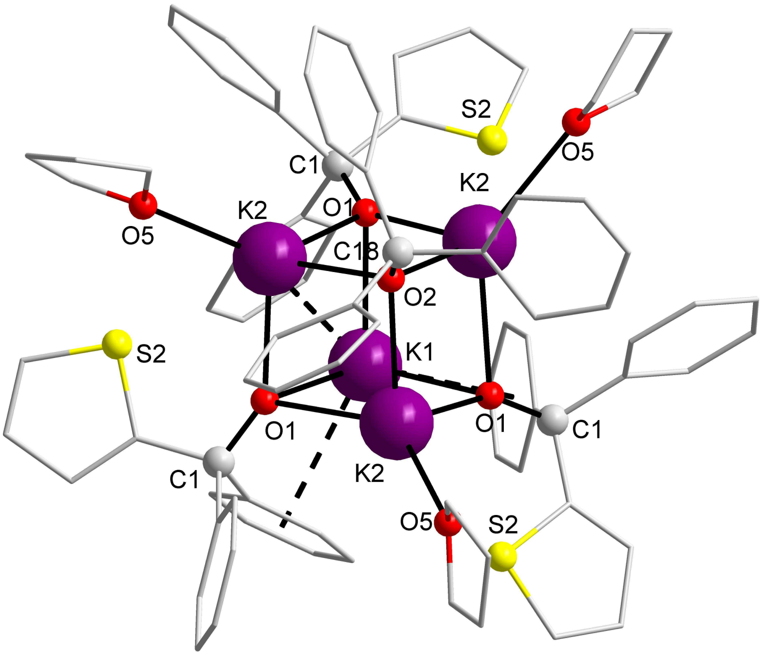


Figure 2.11. Molecular structure of $\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (25). Hydrogen atoms and the tetrahydrofuran lattice molecule are omitted for more clarity.

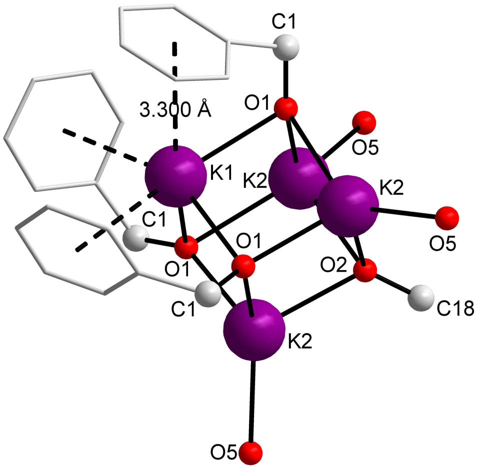


Figure 2.12. Environment around the potassium atoms.

The molecular structure reveals again a tetrameric potassium alcoholate with a cubane–like K_4O_4 core (Figure 2.12). In contrast to {[KOC(C_4H_3S)$_3$]$_4$(thf)$_2$} • thf (**<u>12</u>**), three potassium metals are coordinated with three diphenyl(2–thienyl)methanolato ligands and a tetrahydrofuran molecule as **<u>21</u>**. The coordination sphere around K(1) is trigonal pyramidal (same reasons as above, see Figure 2.12) and those around K(2) tetrahedral. The molecule is situated on a C_3 axis [K(1)–O(2)]. The K–OC($C_{16}H_{13}S$) distances averaging 2.703(3) Å are longer than those observed for **<u>12</u>**, but in accordance with those found for **<u>21</u>**. The K(2)–O(thf) bond lengths of 2.765(4) Å are longer than these observed for **<u>12</u>** and shorter than these found for **<u>21</u>**. The ($C_{16}H_{13}S$)CO–K(1)–OC($C_{16}H_{13}S$) and ($C_{16}H_{13}S$)CO–K(2)–OC($C_{16}H_{13}S$) angles of 91.95(9)° and 94.37(9)°, respectively, are more obtuse than these found for **<u>12</u>** and in the range with those obtained for **<u>21</u>**.

4.5 Reactivity of HO−C($C_{17}H_{15}S$) (<u>5</u>) towards Alkali Metal Hydrides

4.5.1 Reactivity of HO−C($C_{17}H_{15}S$) (<u>5</u>) towards KH

The pure solution was concentrated and placed at 5°C. Few days later, colourless crystals of [KOC($C_{17}H_{15}S$)]$_4$(thf)$_2$ (**<u>31</u>**) were isolated in 34% yield. The ^{1}H–NMR spectrum recorded in thf/C_6D_6 at room temperature exhibits five signals. The protons of the two phenyl groups are at 7.3 and 7.0 ppm integrating in a 16:24 ratio. At 6.4 and 6.2 ppm, the signals which each integrating for 4H, correspond to the 4–H and 3–H of the thienyl groups, respectively. At 2.2 ppm, a singlet attributed to the protons of the methyl groups is present.

*4.5.1.1 Crystal Structure Determination of [KOC($C_{17}H_{15}S$)]$_4$(thf)$_2$ (**31**)*

Colourless crystals of [KOC($C_{17}H_{15}S$)]$_4$(thf)$_2$ (**31**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group C2/c in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 11.07 % (this value is due to the poor quality of the crystals). In Table 2.16 are reported the crystal data and the structure refinement for the compound and in Table 2.17 are reported some selected bond lengths and angles of interest.

Identification code	sh2656	
Empirical formula	$C_{80}H_{76}K_4O_6S_4$	
Formula weight	1418.05	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.647(1) Å	α = 90°.
	b = 14.219(1) Å	β = 94.11(1)°.
	c = 42.900(2) Å	γ = 90°.
Volume	14388(1) Å^3	
Z	8	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.416 mm^{-1}	
F(000)	5952	
Crystal size	0.42 x 0.40 x 0.29 mm^3	
Theta range for data collection	1.67 to 26.44°.	
Index ranges	–27<=h<=29, –17<=k<=17, –53<=l<=53	
Reflections collected	117135	
Independent reflections	14786 [R(int) = 0.0406]	
Completeness to theta = 26.44°	99.7 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8880 and 0.8432	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	14786 / 13 / 874	
Goodness–of–fit on F^2	1.228	
Final R indices [I>2sigma(I)]	R1 = 0.1107, wR2 = 0.2368	
R indices (all data)	R1 = 0.1201, wR2 = 0.2415	

Largest diff. peak and hole	1.386 and –1.718 e.Å^{-3}

Table 2.16. Crystal data and structure refinement for $[KOC(C_{17}H_{15}S)]_4(thf)_2$ (31).

K(1)–O(1)	2.826(4)	K(4)–O(6)	2.752(5)
K(1)–O(2)	2.709(4)	K(4)–O(4)	2.723(4)
K(1)–O(4)	2.633(4)	K(4)–O(3)	2.631(5)
K(2)–O(1)	2.601(4)	K(4)–O(2)	2.733(4)
K(2)–O(3)	2.613(4)	K(1)••••K(3)	3.710(6)
K(2)–O(4)	2.598(4)	K(1)••••K(2)	3.755(7)
K(2)–O(5)	2.623(6)	K(1)••••K(4)	3.609(5)
K(3)–O(1)	2.689(4)	K(2)••••K(3)	3.567(4)
K(3)–O(2)	2.833(4)	K(2)••••K(4)	3.743(3)
K(3)–O(3)	2.626(5)	K(3)••••K(4)	3.943(8)
K(1)–O(2)–K(4)	83.1(1)	O(3)–K(2)–O(5)	119.7(2)
K(1)–O(4)–K(4)	84.7(1)	O(4)–K(2)–O(1)	92.1(1)
K(2)–O(4)–K(1)	91.8(2)	O(4)–K(2)–O(3)	91.3(1)
K(2)–O(3)–K(4)	91.1(1)	O(4)–K(2)–O(5)	114.5(2)
K(2)–O(1)–K(1)	87.5(1)	O(1)–K(3)–O(2)	95.9(1)
K(2)–O(1)–K(3)	84.8(1)	O(3)–K(3)–O(1)	93.4(1)
K(2)–O(3)–K(3)	85.8(1)	O(3)–K(3)–O(2)	84.6(1)
K(3)–O(1)–K(1)	84.5(1)	O(2)–K(4)–O(6)	137.1(1)
K(4)–O(2)–K(3)	90.2(1)	O(3)–K(4)–O(2)	86.6(1)
O(2)–K(1)–O(1)	95.6(1)	O(3)–K(4)–O(4)	88.2(1)
O(4)–K(1)–O(2)	97.2(1)	O(3)–K(4)–O(6)	126.4(1)
O(1)–K(2)–O(5)	133.4(2)	O(4)–K(4)–O(2)	94.6(1)
O(1)–K(2)–O(3)	95.7(1)	O(4)–K(4)–O(6)	111.2(2)

Table 2.17. Selected bond lengths [Å] and angles [°] for $[KOC(C_{17}H_{15}S)]_4(thf)_2$ (31).

4.5.1.1.1 Discussion of the Molecular Structure of $[KOC(C_{17}H_{15}S)]_4(thf)_2$ (31)

A single crystal X−ray analysis of $[KOC(C_{17}H_{15}S)]_4(thf)_2$ (**31**) was carried out for unequivocal identification of the structure as shown in Figure 2.13.

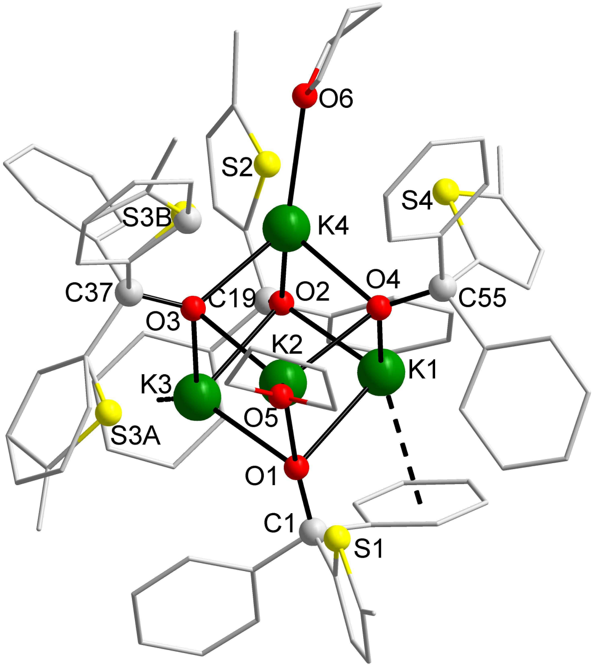


Figure 2.13. Molecular structure of [KOC($C_{17}H_{15}S$)]$_4$(thf)$_2$ (<u>31</u>). Hydrogen atoms are omitted for more clarity. The sulphur atom S(3) is found in two split positions [S(3A) and S(3B)].

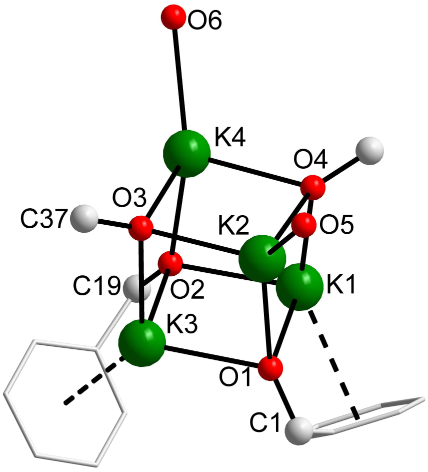


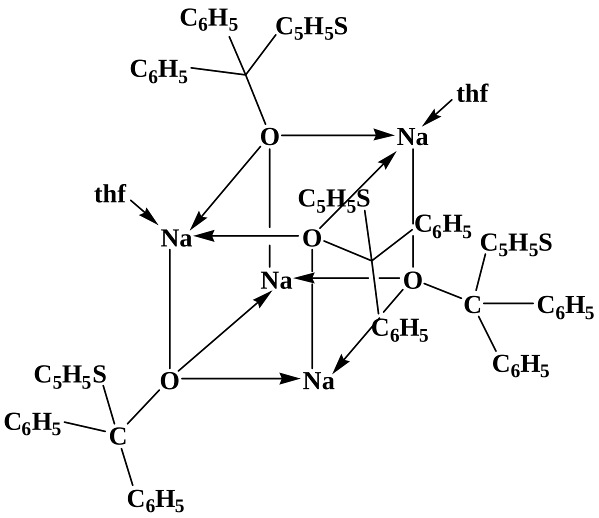
Figure 2.14. Environment around the potassium atoms.

The molecular structure shows again a tetramer in a distorted cubane configuration. Each potassium atom is surrounded by three diphenyl(5–methyl–2–thienyl)methanolato ligands (Figure 2.14). Two of the four alkali metals are also coordinated with a tetrahydrofuran. The geometry detected around K(1) and K(3) is trigonal pyramidal (same reasons as above, see Figure 2.14), whereas those around K(2) and K(4) is distorted tetrahedral. The distances between the potassium and the oxygen of the alcoholates ligands and the K–O(thf) bond lengths average 2.681(5) Å and 2.668(6) Å, respectively, are in good agreement with those obtained for $\{[KOC(C_4H_3S)_3]_4(thf)_2\} \cdot thf$ (**12**). The $(C_{17}H_{15}S)CO–K–OC(C_{17}H_{15}S)$ and $K–OC(C_{17}H_{15}S)–K$ angle values are in the range of 84.6(1) to 97.2(1)° and to 83.1(1) from 91.8(2)°, respectively. These distances and angle values indicate that this heterocuban compounds is not regular, probably due to the difference of steric hindrance between the potassium atoms with and without coordinated tetrahydrofuran molecule.

4.5.2 Reactivity of HO−C($C_{17}H_{15}S$) (**5**) towards NaH

The pure solution was concentrated and placed at 5°C. A white solid precipitated. Unfortunately, no crystals could be obtained. The ^1H–NMR spectrum recorded in thf/C_6D_6 at room temperature of this product is similar with this obtained for $[KOC(C_{17}H_{15}S)]_4(thf)_2$ (**31**). It consists in five signals in the ratio 16:24:4:4:12. At 7.3 and 7.0 ppm, the peaks are attributed to the protons of the phenyl groups. The other signals at 6.4, 6.2 and 2.2 ppm correspond to the 4–H, 3–H and to the methylenic protons of the thienyl groups, respectively.

Therefore, we conclude that NaH and HO–C($C_{17}H_{15}S$) (**5**) reacts in the same manner than KH with HO–C($C_{17}H_{15}S$) (**5**), to form the compound $[NaOC(C_{17}H_{15}S)]_4(thf)_2$ (**32**). Furthermore, the elemental analysis of the white solid confirms the suggested formula. Indeed, 71.00 % of carbon and 5.59 % of hydrogen is in good accordance with the calculated values: 71.00 % and 5.62 %, respectively. Therefore, we tentatively suggest a tetranuclear composition for $[NaOC(C_{17}H_{15}S)]_4(thf)_2$ (**32**) as depicted in Figure 2.15. The compound was obtained in only 14% yield.



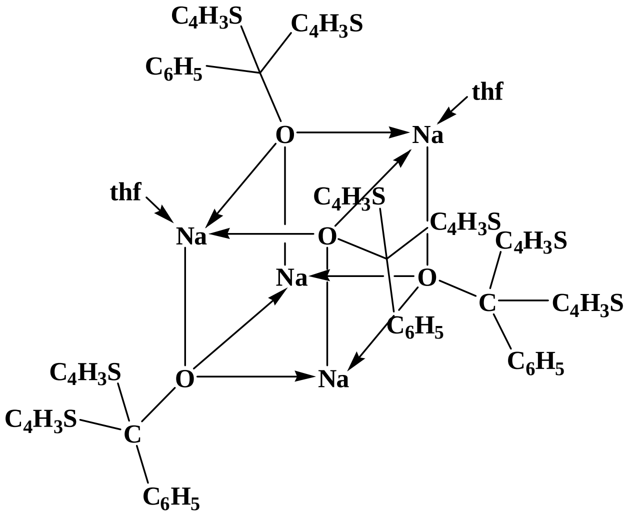
32

Figure 2.15. Representation of $[NaOC(C_{17}H_{15}S)]_4(thf)_2$ (32).

4.6 Reactivity of HO−C($C_{14}H_{11}S_2$) (7) towards NaH

The unreacted NaH was filtered off. The solution was concentrated and placed at 5°C. Colourless crystals were grown few days later, but their poor quality inhibits the determination of the crystal structure. The ^{1}H–NMR spectrum recorded in thf/C_6D_6 at room temperature consists in four signals. The first at 7.2 ppm, integrating for 16H corresponds to the protons of the phenyl groups and the 5–H of the thienyl units. The other phenylic protons are situated at 7.0 ppm (12H). The 4–H (8H) and 2–H (8H) protons of the thienyl moieties are present at 6.8 and 6.2 ppm, respectively.

Based on the ^{1}H–NMR data, and by the analogy with the other sodium and potassium structures (see above) we conclude unambiguously that the compound $[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (**37**) (Figure 2.16) was obtained (in a yield of 22 %).



37

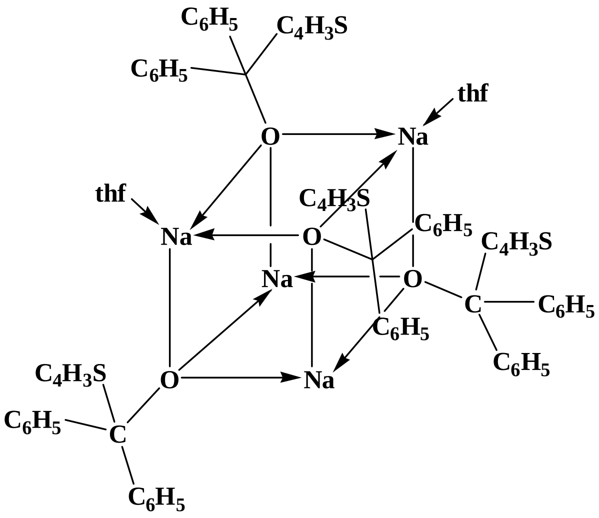
Figure 2.16. Representation of $[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (37).

4.7 Reactivity of HO−C($C_{16}H_{13}S$) (8) towards NaH

The unreacted NaH was filtered off. The solution was concentrated and placed at 5°C. A white solid precipitated, but no X−ray suitable crystals of this compound were obtained.

The ^{1}H–NMR spectrum recorded at room temperature in thf/C_6D_6 shows the characteristic signals of the protons of the thienyl units at 7.3, 6.9 and 6.2 ppm (5–H, 4–H, and 2–H, respectively) and the peaks due to the phenyl protons are present at 7.3 and 7.0. The integration ratio is 12:24:4:4.

By analogy with the other sodium compounds (see above) and in accordance with the ^{1}H–NMR spectrum, which doesn't reveal impurities or the presence of the star–shaped carbinol precursor, the product is identified as $[NaOC(C_{16}H_{13}S)]_4(thf)_2$ (**41**). Furthermore, the elemental analysis confirms the formula. Indeed, 71.03 % of carbon and 5.09 % of hydrogen found are in good accordance with the values calculated: 70.37 and 5.24 %, respectively. These findings indicate that tetranuclear $[NaOC(C_{16}H_{13}S)]_4(thf)_2$ (**41**) (Figure 2.17) was obtained in the yield of 31%.



41

Figure 2.17. Representation of $[NaOC(C_{16}H_{13}S)]_4(thf)_2$ (41).

4.8 Conclusion

Four new potassium **12**, **21**, **25** and **31** and one sodium **13** alcoholates have been isolated as single crystals. Their molecular structures show tetrameric alkali metal alcoholates with a distorted cubane like M_4O_4 core. Each alkali metal is surrounded by three carbinolato ligands and three (for **21** and **25**) or two (for **12**, **13** and **31**) metals have ligated with a tetrahydrofuran molecule. The vast similarity in molecular symmetry was not as clearly reflected in the crystallographic data seen in Table 2.18. The main phenomenon found by the crystal structure determination of these different thienyl-carbinolates was the enormous disorder tendency of the thienyl and/or phenyl rings. The energy difference for an alternative packing position seems here extremely low. The partial resemblance or multiplicity of the unit cell dimensions indicates more tendencies in packing disorder then the relationship of the molecular structure.

Compounds	Crystal System	Space Group	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
12	Orthorhombic	Pccn	14.246(1)	16.743(1)	27.707(1)	90	90	90
13	Monoclinic	C2/c	23.189(2)	13.343(1)	22.976(1)	90	119.97(1)	90
21	Monoclinic	C2/c	24.774(2)	24.210(2)	49.109(3)	90	91.55(1)	90
25	Cubic	P2(1)3	24.494(2)	24.494(2)	24.494(2)	90	90	90
31	Monoclinic	C2/c	23.647(1)	14.219(1)	42.900(2)	90	94.11(1)	90

Table 2.18. Crystal system, space groups and unit cell dimensions of the alkali metal alcoholates.

Four sodium alcoholates have been isolated as solid: the ^{1}H–NMR spectra, elemental analysis and by analogy with the previous results, have identified as **22**, **32**, **37** and **41**. The reactions of NaH with the organic ligands **4** and **6**, or KH with **6**–**8**, in tetrahydrofuran, did not lead to the isolation of the desired molecules despite the gas development observed.

5 Synthesis, NMR Studies and Crystal Structure Determination of Tin(II) Methoxides bearing Thienyl Substituents

5.1 Tin Chemistry

The coordination chemistry of tin(II) compounds (SnR_2), also named stannylene, has received much attention in the context of transition metal−stannylene complexes. Actually, stannylenes use two electrons of their p electrons in covalent bonding and their other two electrons constitute a lone pair that can be used to form an adduct with a Lewis acid. There are also low–lying empty p and d orbitals, which, when used in the hybridation of the orbitals of tin, create empty orbitals suitable for complex formation. There are several hybridization geometries[28] available for stannylene as seen in Figure 2.18. Of these, the second, third, and fourth are most important, with the third, being most prevalent for tin–metal complexes. The first and fifth structures are uncommon for tin in transition metal chemistry. Tin's low–lying empty orbitals are of suitable symmetry and orientation for π bonding, and tin(II) compounds are typically excellent π acceptor.

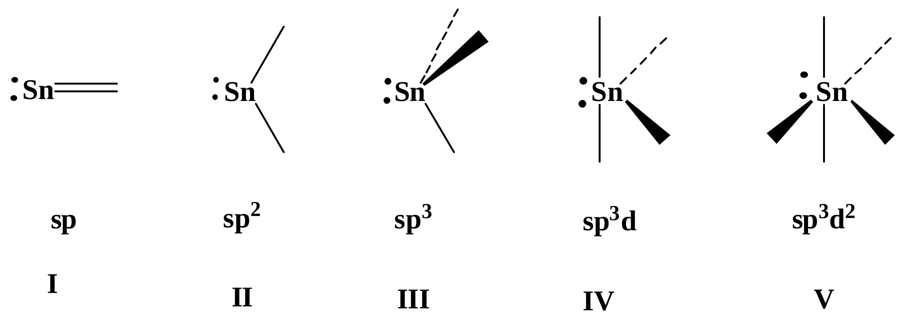


Figure 2.18. Hybridisation geometry for stannylenes.

Stannylenes can form stable adducts both with hard Lewis bases (amines and ethers), hard Lewis acids[29, 30, 31] (boron halides) and soft Lewis acids (transition metals).[28, 32, 33]

Their uncommon electronic features render the bivalent group 14 metallic elements very interesting in the field of coordination chemistry. In 1957, Hieber published an iron–tin complex.[34] Since 1971, the tin chemistry began ostensibly with the works of Marks.[35] The known transition complexes displaying a group 14 metallic element in the oxidation state +2 as ligand can be described in Figure 2.19. These different arrangements summarize roughly the main properties of a bivalent group 14 metal ligand: a neutral fragment behaving as a Lewis acid towards base adducts and behaving as Lewis base through its lone pair towards transition metals.

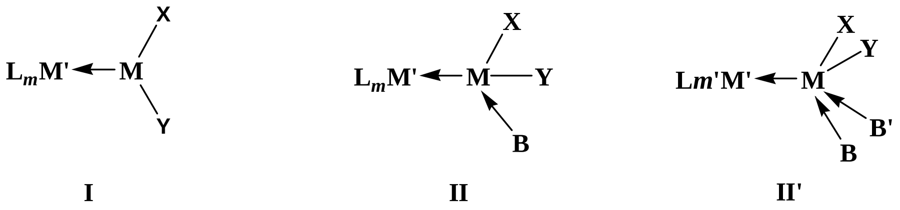


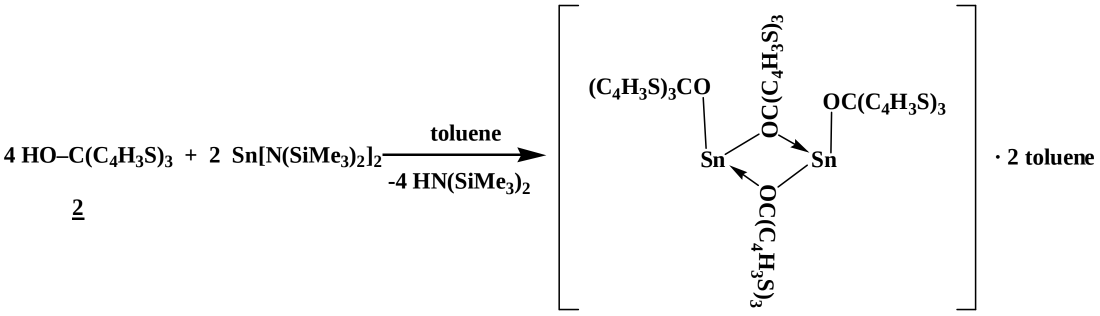
Figure 2.19. Different structures of simple (I) and base–stabilised complexes (II and II') where M stands for a group 14 metal, M' stands for a transition metal, L_m represents a set of ligands, B and B' stand for a neutral Lewis base molecule such as thf or pyridine.

There are few literature reports of compounds containing lanthanides–tin bonds. For example, Schuman and co–workers have prepared tin–lanthanides complexes;[36, 37] nevertheless, these complexes could not be isolated in a pure state because of experimental difficulties. Furthermore, these types of products are very water and oxygen sensitive and not thermodynamically stable.[38] As explained in Chapter 1, lanthanides in the oxidation state +3 have a high charge density and are a few polarisable due to the low spatial extension of their *f* orbitals: they could be considered as hard acid according to the Pearson classification. Therefore, it appeared interesting to form tin–lanthanides alkoxides using tin methoxides bearing thienyl substituents.

5.2 Synthesis, NMR and Crystal Structure Investigations of New Tin(II) Alkoxides Containing Tris(2–thienyl)methoxido Ligands

5.2.1 Reactivity of HO–C(C_4H_3S)$_3$ (1) towards Tin(II) Silyl Amide in Toluene

The compound {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (**14a**) was prepared by the reaction between two equivalents of HO−C(C_4H_3S)$_3$ (2) and one equivalent of Sn[N(SiMe$_3$)$_2$]$_2$, for two days at room temperature (Equation 2.20). After concentration of the solvent, the tin(II) alkoxide **14a** was isolated in form of colourless crystals in the yield of 36 %.



14a

Equation 2.20. Route leading to the desired tin(II) alkoxide.

5.2.1.1 NMR Studies on {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (14a)

The H,H−COSY NMR spectrum of dimeric {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (**14a**), recorded at room temperature in CDCl$_3$, shows two sets of three signals of the thienyl groups. According the spectrum, two compounds are present (Figure 2.20). An equilibrium in solution between the dimeric {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (**14a**) and the monomeric species Sn[OC(C_4H_3S)$_3$]$_2$ (Equation 2.21) is present in a 85:15 ratio. The detection of a mononuclear product is in agreement with literature reports on other Sn(II) alkoxides bearing bulky ligands, which exists exclusively as monomers.[39, 40]

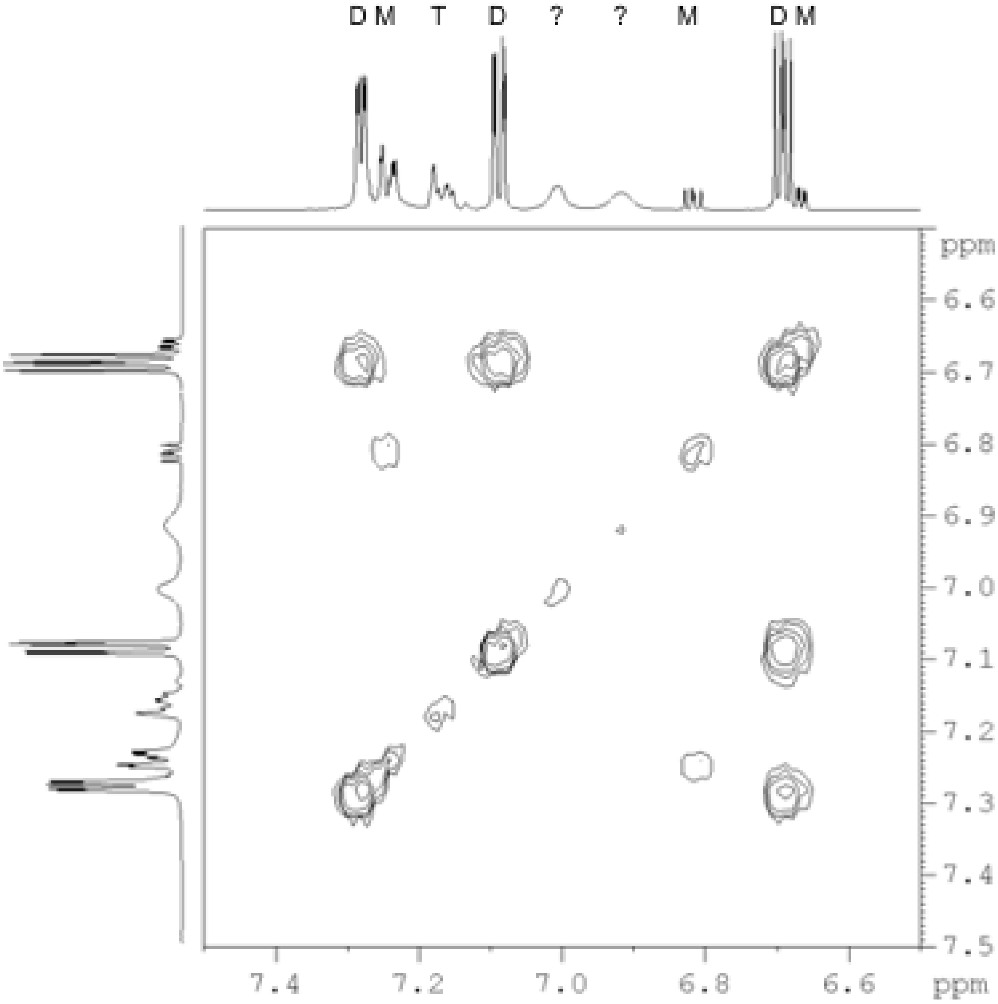


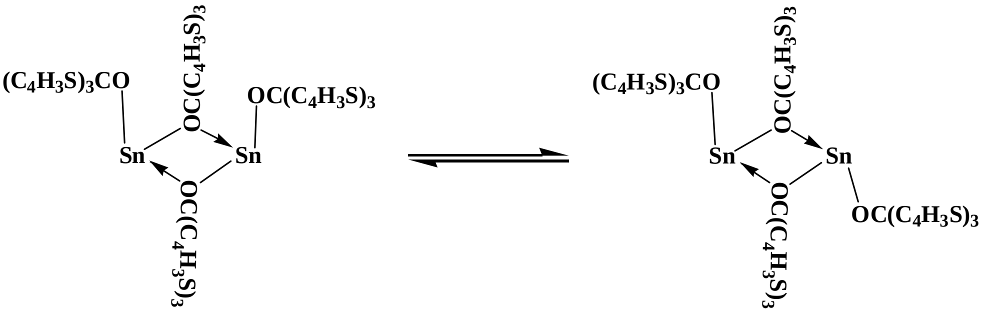
Figure 2.20. H,H–COSY spectrum of 14a in $CDCl_3$ at room temperature. M stands for the monomer, D for the dimer, T for the toluene molecule and ? for an unknown species.

14a

Equation 2.21. Equilibrium between the monomer and the dimer.

The ^{1}H−NMR spectrum of **14a** displays three doublets of doublets (δ = 7.3, 7.1, 6.7 ppm), attributed to the protons of the thienyl groups present in the dimer $\{Sn[OC(C_4H_3S)_3]_2\}_2 \cdot 2$ toluene (**14a**) and the signals due to the toluene molecule in the lattice. The three other doublets of doublets at 7.2, 6.8 and 6.6 ppm correspond to the protons of the thienyl groups in the mononuclear $Sn[OC(C_4H_3S)_3]_2$ compound. As can be seen in the spectrum of Figure 2.20, two broad signals at 7.0 and 6.9 ppm are present. They are attributed to an unknown species, probably due to a partial decomposition of the highly light, water and oxygen sensible tin alkoxide **14a**.

An equilibrium between the *cis* and *trans* arrangement of the terminal alkoxides is possible (Equation 2.22). Unfortunately, no ^{1}H−NMR experiment at variable temperature has been possible because of the thermal instability of the compound.



14a

Equation 2.22. The *cis* and *trans* arrangement of the terminal alkoxides in the dimeric compound.

The ^{119}Sn–NMR data for solution of **14a** display resonance signals at –244.5 ppm and –236.5 ppm for the monomer and the dimer respectively, in the expected range of chemical shift for this type of tin(II) alkoxides.[41]

5.2.1.2 Crystal Structure Determination of $\{Sn[OC(C_4H_3S)_3]_2\}_2 \cdot 2$ toluene (14a)

Colourless crystals of $\{Sn[OC(C_4H_3S)_3]_2\}_2 \cdot 2$ toluene (**14a**) were obtained from a concentrated toluene solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/n in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 5.91 %. In Table 2.19 are reported the crystal data and the structure refinement for the compound and in Table 2.20 are reported some selected bond lengths and angles of interest.

Identification code	sh2438	
Empirical formula	C66 H52 O4 S12 Sn2	
Formula weight	1531.18	
Temperature	148(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.848(2) Å	α= 90°.
	b = 23.425(3) Å	β= 100.27(1)°.
	c = 21.625(3) Å	γ = 90°.
Volume	6404(1) Å^3	
Z	4	
Density (calculated)	1.588 Mg/m^3	
Absorption coefficient	1.220 mm^{-1}	
F(000)	3088	
Crystal size	0.15 x 0.36 x 0.52 mm^3	
Theta range for data collection	1.29 to 34.90°.	
Index ranges	–20<=h<=20, –37<=k<=30, –34<=l<=34	
Reflections collected	146369	
Independent reflections	27903 [R(int) = 0.0343]	
Completeness to theta = 34.90°	99.7 %	
Absorption correction	Multi scan	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	27903 / 37 / 715	
Goodness–of–fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1599	
R indices (all data)	R1 = 0.0757, wR2 = 0.1737	
Largest diff. peak and hole	5.241 and –2.285 e.Å^{-3}	

Table 2.19. Crystal data and structure refinement for $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (14a).

Sn(1)−O(1)	2.182(2)	O(1)−C(1)	1.446(4)
Sn(1)−O(2)	2.233(2)	O(2)−C(14)	1.443(4)
Sn(2)−O(4)	2.062(2)	O(3)−C(27)	1.416(4)
Sn(2)−O(1)	2.243(2)	O(4)−C(40)	1.409(4)
Sn(2)−O(2)	2.194(2)	Sn(1)••••Sn(2)	3.589(8)
Sn(1)−O(3)	2.053(2)		
O(1)−Sn(1)−O(2)	71.65(9)	Sn(2)−O(2)−Sn(1)	108.4(1)
O(3)−Sn(1)−O(1)	85.44(9)	C(1)−O(1)−Sn(1)	121.3(2)
O(3)−Sn(1)−O(2)	93.8(1)	C(14)−O(2)−Sn(1)	125.6(1)
O(2)−Sn(2)−O(1)	71.22(9)	C(40)−O(4)−Sn(2)	123.1(2)
O(4)−Sn(2)−O(1)	93.6(1)	C(1)−O(1)−Sn(2)	121.3(2)
O(4)−Sn(2)−O(2)	88.7(1)	C(14)−O(2)−Sn(2)	122.0(2)
Sn(1)−O(1)−Sn(2)	108.4(1)	C(27)−O(3)−Sn(1)	123.1(2)
Sn(1)−Sn(2)−O(3)	88.89(3)	Sn(2)−Sn(1)−O(4)	87.01(1)

Table 2.20. Selected bond lengths [Å] and angles [°] for $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (<u>14a</u>).

5.2.1.2.1 Discussion of the Molecular Structure of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (<u>14a</u>)

A single crystal X−ray analysis of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (**<u>14a</u>**) was carried out for unequivocal identification of the structure as shown in Figure 2.21.

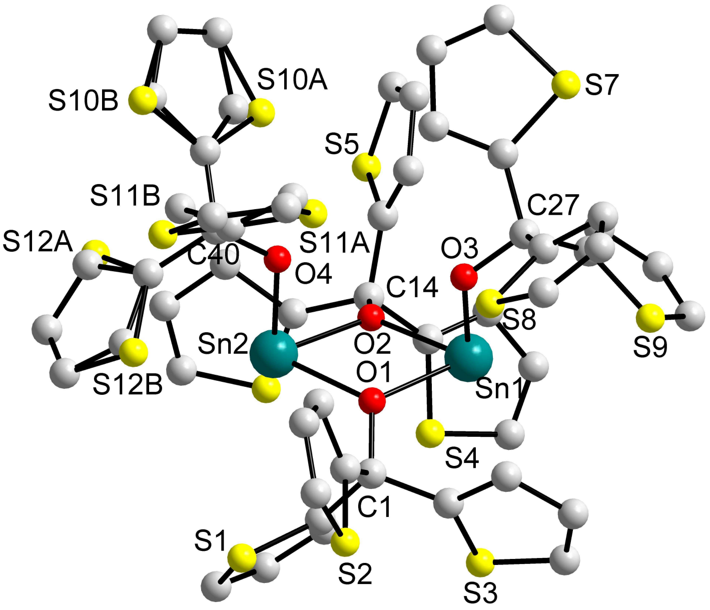


Figure 2.21. Molecular structure of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (<u>14a</u>). Toluene lattice molecules and hydrogen atoms are omitted for more clarity. The sulphur atoms S(10), S(11) and S(12) are found in two split–positions [S(10A) and S(10B), S(11A) and S(11B), S(12A) and S(12B)].

The core of **14a** consists of a nearly planar four−membered ring, which is asymmetric since the Sn(1)−O(1), Sn(1)−O(2), Sn(2)−O(1) and Sn(2)−O(2) bonds are not identical [2.182(2), 2.233(2), 2.243(2), and 2.194(2) Å, respectively]. Each metal centre is coordinated by three (2−thienyl)methoxido ligands: one terminal and two bridging. In contrast to other dimeric alkoxides, the terminal $-OR_3$ ligands are *cis*−arranged (Figure 2.22). For example, in $[Sn(OBu^t)_2]_2$ or $[Sn(O{-}2,6{-}Ph_2C_6H_3)_2]_2$ a *trans*−arrangement of the terminal alkoxides was structurally established.[42 43, 44] In our case, this phenomenon may be explained by the packing effect due to the steric hindrance of the thienyl ligands in the crystalline solid. By this arrangement the free side of both tin atoms is equally covered with three thienyl planes. The $Sn{-}O{-}C(C_4H_3S)_3$ angles of the terminal ligands are found at 123.1(2)°, and the $Sn{-}O{-}C(C_4H_3S)_3$ angles of the bridging ligand average 122.6(2)°.

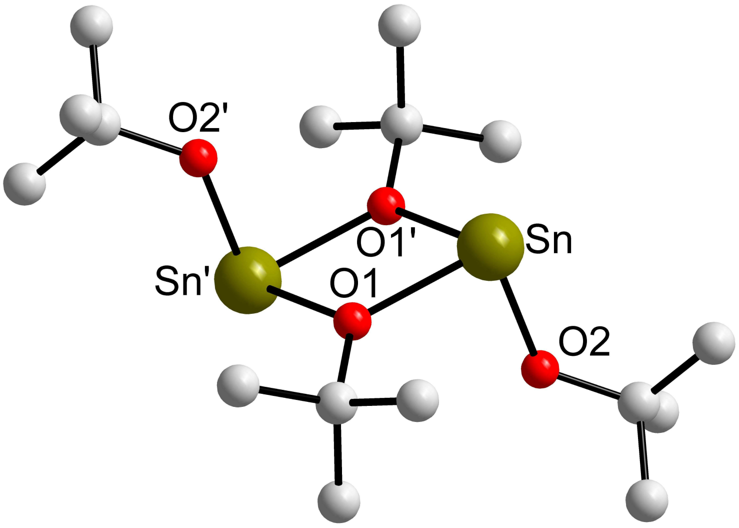


Figure 2.22. Molecular structure of $[Sn(OBu^t)_2]_2$.

As seen in Table 2.21, the $Sn{-}OC(C_4H_3S)_3$ bridging bond distances are in the same range of those found for $[Sn(OBu^t)_2]_2$.[42, 43] The non−bonding Sn(1)····Sn(2) distance is longerthan the one found for $[Sn(OBu^t)_2]_2$.[42, 43] The Sn(1)−O(1)−Sn(2) and Sn(2)−O(2)−Sn(1) angles are slightly more obtuse than those for $[Sn(OBu^t)_2]_2$.[42, 43]

$\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (14a)		**$[Sn(OBu^t)_2]_2$**	
Sn(1)−O(1)	2.182(2)	Sn−O(1)	2.128(4)
Sn(1)−O(2)	2.233(2)		
Sn(2)−O(1)	2.243(2)		
Sn(2)−O(2)	2.194(2)		
Sn(1)−O(3)	2.053(2)	Sn−O(2)	2.009(4)
Sn(2)−O(4)	2.062(2)		
Sn(1)••••Sn(2)	3.589(8)	Sn••••Sn’	3.446(1)
Sn(2)−O(1)−Sn(1)	108.4(1)	Sn−O(1)−Sn	106.8(3)
Sn(2)−O(2)−Sn(1)	108.4(1)	Sn−O(1’)−Sn’	106.8(3)

Table 2.21. Comparative bond lengths [Å] and angle values [°] obtained for $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (14a) and $[Sn(OBu^t)_2]_2$.[42]

Presumably due to packing effect, the Sn−O bonds of the terminal *cis*–oriented Sn−O−C$(C_4H_3S)_3$−ligands are almost in an eclipsed situation with a deviation of 11.5(1)° from the ideal position (Figure. 2.23).

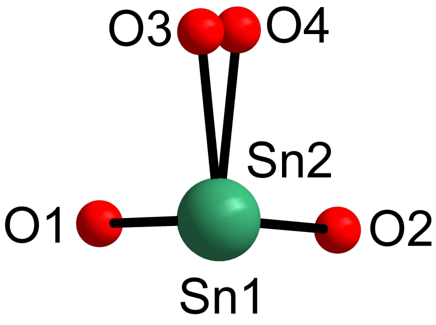


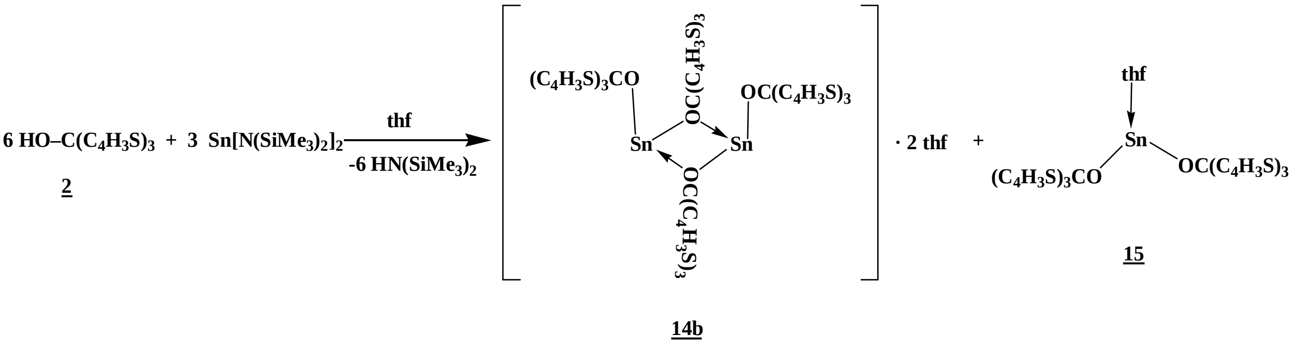
Figure. 2.23. Projection of the four membered−ring along the Sn••••Sn axis in 14a showing the “eclipsed” orientation of Sn(1)−O(3) and Sn(2)−O(4).

5.2.1.3 Conclusion

This reaction leads, in solid state, to a dimeric product. Nevertheless, the NMR spectra indicate the co−presence of a monomeric stannylene species in solution. The product is very moisture and light sensitive either as solid or in solution. Nevertheless, it appeared be tempting to perform the same reaction in a donor solvent to study possible Lewis acid−Lewis base interactions between the oxygen atoms of the alkoxyligand and the divalent tin centres. Therefore, the same reaction was conducted in tetrahydrofuran instead of toluene.

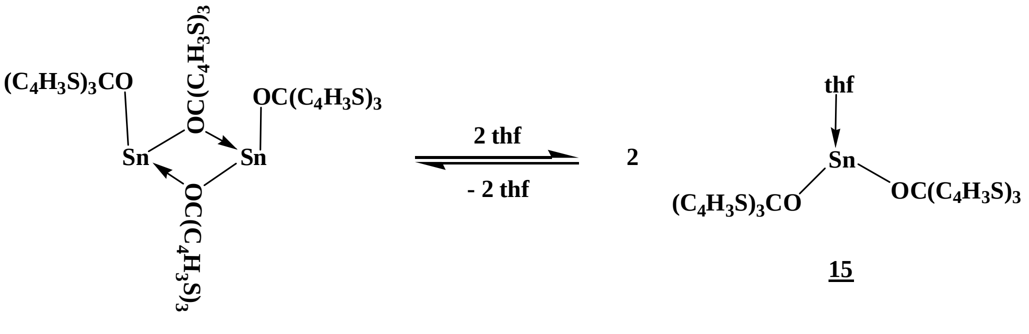
5.2.2 Reactivity of HO–C(C_4H_3S)$_3$ (2) towards Tin(II) Silyl Amide in Tetrahydrofuran

The reaction of six equivalents of tris(2–thienyl)methanol with three equivalents of tin(II) silyl amide, for two days at room temperature, led to the formation of two products: a dinuclear {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 thf (**14b**) and a mononuclear Sn[OC(C_4H_3S)$_3$]$_2$(thf) (**15**) compound (Equation. 2.23) and were separated by sorting out different crystals due to their crystal shape.



Equation 2.23. Route leading to the tin(II) alkoxides.

The two thf molecules of compound **14b** are not bonds to tin and serve only as fillers in the crystal lattice. Probably, the two different compounds **14b** and **15** result from a dynamic equilibrium between the monomeric species in which tin is coordinated by two alkoxide ligands together with the thf donor molecule and the dimeric compound which results from Lewis acid base interactions between the oxygen atoms of the alkoxy ligand and the low−coordinated divalent tin centres (Equation 2.24).



14b

Equation 2.24. Equilibrium between the monomer and the dimer.

5.2.2.1 NMR Studies of {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 thf (14b) and a Mononuclear Sn[OC(C_4H_3S)$_3$]$_2$(thf) (15)

In the ^{1}H–NMR spectrum of a solution of the dimer (**14b**) / monomer (**15**) in $CDCl_3$, at room temperature, two sets of three signals of the thienyl groups show up with each of the three protons displaying the characteristic pattern of doublets of doublets. Surprisingly, this spectrum is identical with the ^{1}H–NMR spectrum of {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (**14a**), which has no additional base like thf and which means that in solution there is an equilibrium between the dimer {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ (• 2 thf) (**14b**) and the mononuclear Sn[OC(C_4H_3S)$_3$]$_2$ (• thf) (**15**) compound in a 65:35 ratio (Figure 2.24).

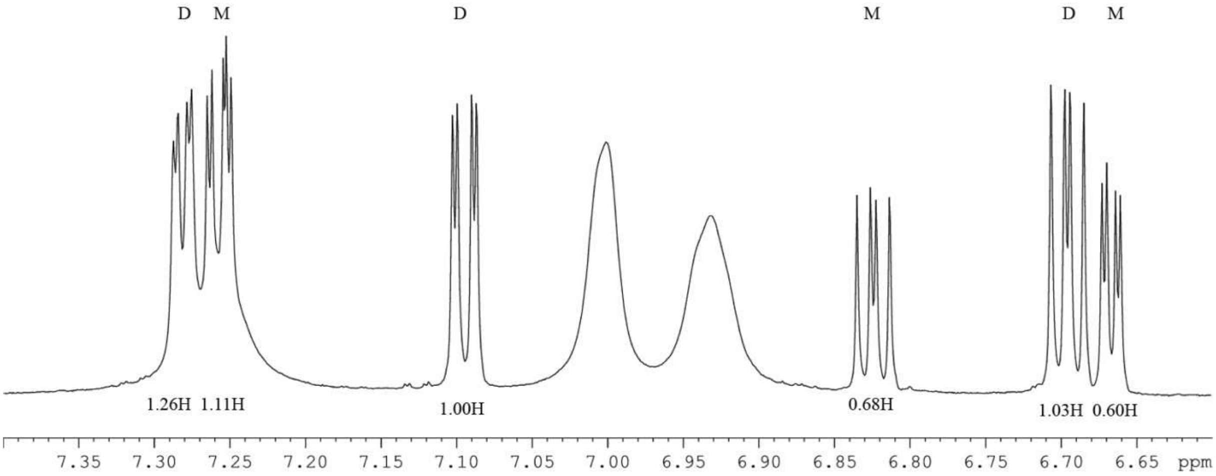


Figure 2.24. ^{1}H–NMR recorded in $CDCl_3$ at room temperature. D stands for dimer and M for monomer.

Analysis of the coupling constants and the H,H–COSY off diagonal signals reveals correlation of the signal sets, which either belong to the monomer or the dimer compound (Figure 2.25).

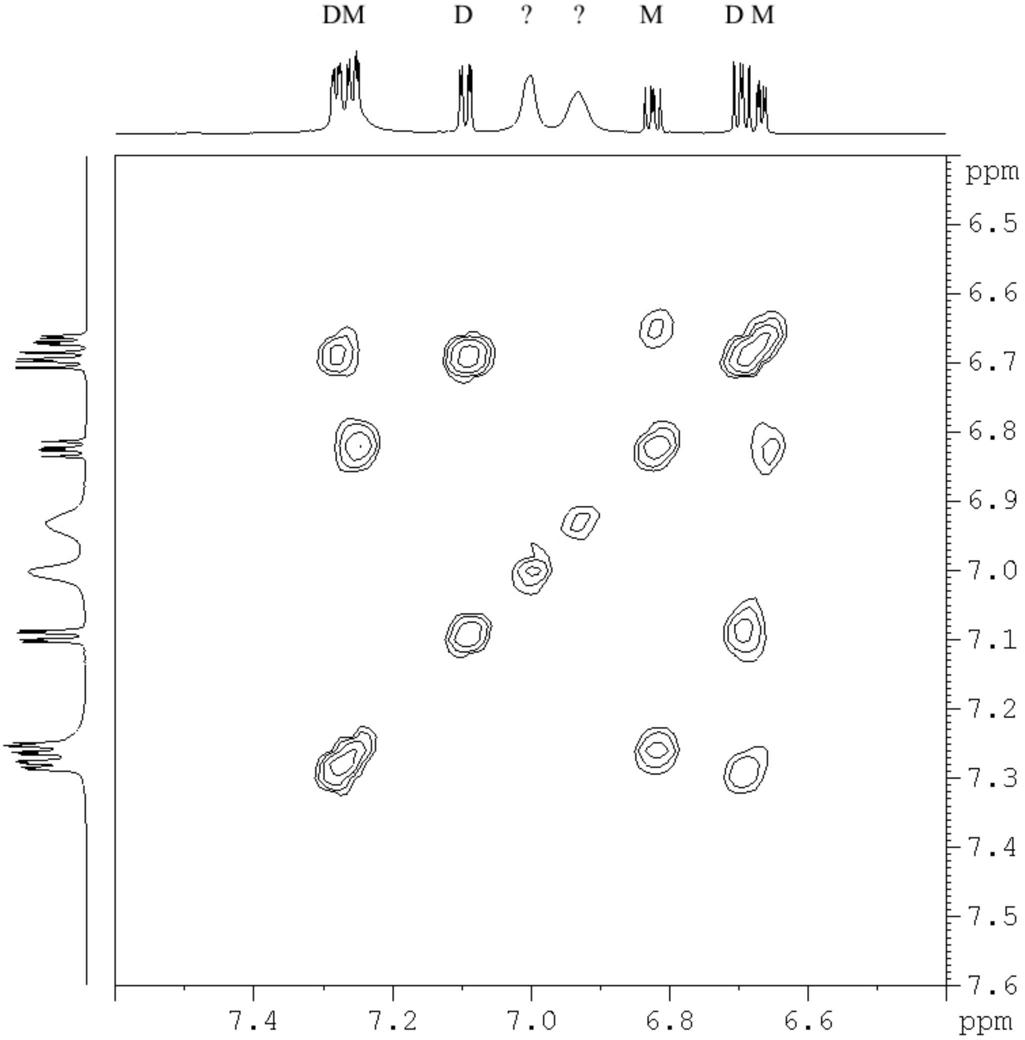


Figure 2.25. H,H–COSY spectrum in $CDCl_3$ at room temperature of the monomer and dimer product. M stands for the monomer, D for the dimer and ? for an unknown product.

In the ^{13}C–NMR spectrum of **14b** and **15**, a ^{13}C^{119}Sn coupling of 64.4 Hz (Figure 2.26) between the quaternary carbon and the tin centre is observed which is typical for a $^{2}J(^{13}C^{119}Sn)$ and which sustains our description of **14b** and **15** as an alcoholate derivative.[45]

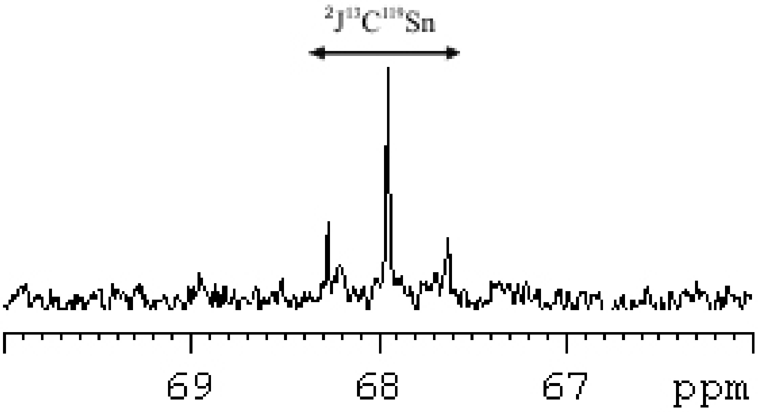


Figure 2.26. ^{13}C NMR of spectrum showing the ^{13}C^{119}Sn coupling to the quaternary carbon recorded at room temperature in $CDCl_3$.

The ^{119}Sn−NMR data spectra, in $CDCl_3$, shows two peaks at −236.5 and −244.5 ppm attributed to the tin on the dimer and on the monomer, respectively. Again, these values are identical with those observed for **14a**.

*5.2.2.2 Crystal Structure Determination of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (**14b**)*

Colourless crystals of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (**14b**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/c in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 5.00 %. In Table 2.22 are reported the crystal data and the structure refinement for the compound and in Table 2.23 are reported some selected bond lengths and angles of interest.

Identification code	sh2349	
Empirical formula	$C_{60}H_{52}O_6S_{12}Sn_2$	
Formula weight	1491.12	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.043(4) Å	α= 90°.
	b = 17.317(4) Å	β= 110.90(3)°.

	c = 23.051(5) Å	γ = 90°.
Volume	6728(2) $Å^3$	
Z	4	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	1.161 mm^{-1}	
F(000)	3008	
Crystal size	0.6 x 0.44 x 0.3 mm^3	
Theta range for data collection	1.89 to 24.10°.	
Index ranges	–20<=h<=20, –19<=k<=19, –26<=l<=26	
Reflections collected	41568	
Independent reflections	10449 [R(int) = 0.0409]	
Completeness to theta = 24.10°	97.8 %	
Absorption correction	None	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	10449 / 16 / 707	
Goodness–of–fit on F^2	1.764	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1753	
R indices (all data)	R1 = 0.0583, wR2 = 0.1808	
Largest diff. peak and hole	1.887 and –1.114 e.$Å^{-3}$	

Table 2.22. Crystal data and structure refinement for $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (14b).

Sn(1)−O(1)	2.209(4)	O(1)−C(1)	1.462(6)
Sn(1)−O(2)	2.217(4)	O(2)−C(14)	1.444(6)
Sn(1)−O(4)	2.062(4)	O(3)−C(27)	1.407(7)
Sn(2)−O(1)	2.241(4)	O(4)−C(40)	1.425(7)
Sn(2)−O(2)	2.223(4)	Sn(1)••••Sn(2)	3.572(2)
Sn(2)−O(3)	2.059(4)		
O(1)−Sn(1)−O(2)	72.9(1)	Sn(1)−O(2)−Sn(2)	107.2(2)
O(4)−Sn(1)−O(1)	89.5(2)	C(1)−O(1)−Sn(1)	121.9(3)
O(4)−Sn(1)−O(2)	91.4(2)	C(14)−O(2)−Sn(1)	128.2(3)
O(2)−Sn(2)−O(1)	72.2(1)	C(40)−O(4)−Sn(1)	122.8(3)
0(3)−Sn(2)−O(1)	93.8(2)	C(1)−O(1)−Sn(2)	121.8(3)
O(3)−Sn(2)−O(2)	85.9(2)	C(14)−O(2)−Sn(2)	124.0(3)
Sn(1)−O(1)−Sn(2)	106.8(2)	C(27)−O(3)−Sn(2)	124.4(4)
Sn(1)−Sn(2)−O(3)	85.6(1)	Sn(2)−Sn(1)−O(4)	86.2(1)

Table 2.23. Selected bond lengths [Å] and angles [°] for $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (14b).

*5.2.2.2.1 Discussion of the Molecular Structure of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (**14b**)*

A single crystal X−ray analysis of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (**14b**) was carried out for unequivocal identification of the structure as shown in Figure 2.27.

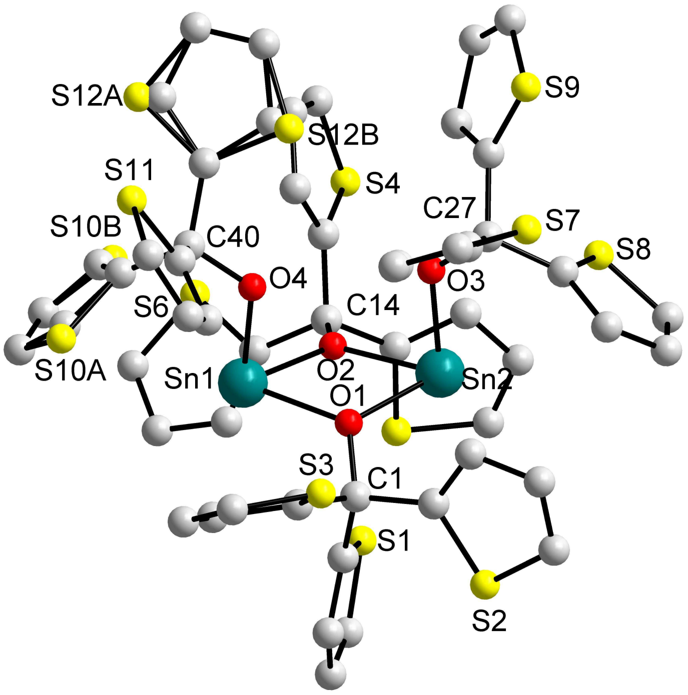


Figure 2.27. Molecular structure of {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 thf (14b). Tetrahydrofuran lattice molecules and hydrogen atoms are omitted for more clarity. The sulphur atoms S(10) and S(12) are found in two split–positions [S(10A) and S(10B), S(12A) and S(12B)].

The molecular structure of **14b** consists of a nearly planar four−membered ring quite similar to those observed for {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (**14a**). Two molecules of tetrahydrofuran are present in the crystal lattice. The two terminal alkoxide groups are again in a *cis*−arrangement which can be explained by the packing effect due to the bulky ligands in the crystal solid. Despite the presence of tetrahydrofuran molecules instead of toluene molecules, only minor variations of the bond length or angles are found between {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (**14a**) and {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 thf (**14b**) (Table 2.24). As found in **14a**, an eclipsed arrangement of the two terminal groups is noticeable with a deviation from the ideal value of 8.3(1)°.

	{Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (<u>14a</u>)	**{Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 thf (<u>14b</u>)**
Sn(1)−O(1)	2.182(2)	2.209(4)
Sn(1)−O(2)	2.233(2)	2.217(4)
Sn(2)−O(1)	2.243(2)	2.241(4)
Sn(2)−O(2)	2.194(2)	2.223(4)
Sn(1)−O(4/3)	2.053(2)	2.062(4)
Sn(2)−O(3/4)	2.062(3)	2.059(4)
Sn(1)••••Sn(2)	3.589(8)	3.572(2)
Sn(1)−O(1)−Sn(2)	108.4(1)	106.8(2)
Sn(2)−O(2)−Sn(1)	108.4(1)	107.2(2)
C(1)−O(1)−Sn(2)	121.3(2)	121.9(3)
C(14)−O(2)−Sn(1)	125.6(2)	128.2(3)

Table 2.24. Comparative bond lengths [Å] and angle values [°] obtained for Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 toluene (<u>14a</u>) and {Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 thf (<u>14b</u>).

The angles between the plane defined by Sn(1)−O(1)−Sn(2)−O(2) and the lines Sn(1)−O(4) or Sn(2)−O(2) are 86.2(9)° and 85.5(8)°, respectively (Figure 2.28).

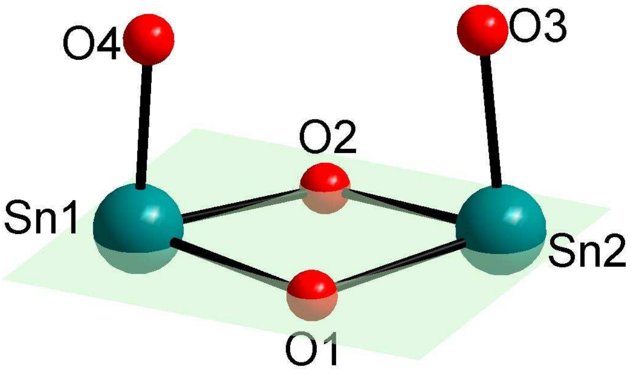


Figure 2.28. Environment around the metal centres.

5.2.2.3 Crystal Structure Determination of Sn[OC(C_4H_3S)$_3$]$_2$(thf) (<u>15</u>)

Colourless crystals of Sn[OC(C_4H_3S)$_3$]$_2$(thf) (<u>15</u>) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group Pnma in an orthorhombic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 6.37 %. In Table 2.25 are reported the crystal data and the structure refinement for the compound and in Table 2.26 are reported some selected bond lengths and angles of interest.

Identification code	sh2400	
Empirical formula	$C_{30}H_{26}O_3S_6Sn$	
Formula weight	745.56	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 13.941(1) Å	α= 90°.
	b = 23.572(2) Å	β= 90°.
	c = 9.220(1) Å	γ = 90°.
Volume	3029.7(4) Å^3	
Z	4	
Density (calculated)	1.635 Mg/m^3	
Absorption coefficient	1.289 mm^{-1}	
F(000)	1504	
Crystal size	0.17 x 0.38 x 0.76 mm^3	
Theta range for data collection	1.73 to 41.46°.	
Index ranges	−25<=h<=24, −43<=k<=43, −16<=l<=16	
Reflections collected	136807	
Independent reflections	10184 [R(int) = 0.0400]	
Completeness to theta = 41.46°	97.8 %	
Absorption correction	Multi scan	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	10184 / 0 / 196	
Goodness−of−fit on F^2	1.249	
Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.1488	
R indices (all data)	R1 = 0.0785, wR2 = 0.1566	
Largest diff. peak and hole	2.838 and −5.639 e.Å^{-3}	

Table 2.25. Crystal data and structure refinement for $Sn[OC(C_4H_3S)_3]_2$(thf) (15).

Sn−O(1)	2.036(2)	O(1)−Sn−O(1)	81.5(1)
Sn−O(2)	2.261(4)	O(1)−Sn−O(2)	86.16(9)
O(1)−C(1)	1.406(3)	C(1)−O(1)−Sn	128.6(2)

Table 2.26. Selected bond lengths [Å] and angles [°] for $Sn[OC(C_4H_3S)_3]_2$(thf) (15).

5.2.2.3.1 Discussion of the Molecular Structure of $Sn[OC(C_4H_3S)_3]_2$(thf) (15)

A single crystal X−ray analysis of $Sn[OC(C_4H_3S)_3]_2$(thf) (**15**) was carried out for unequivocal identification of the structure as shown in Figure 2.29.

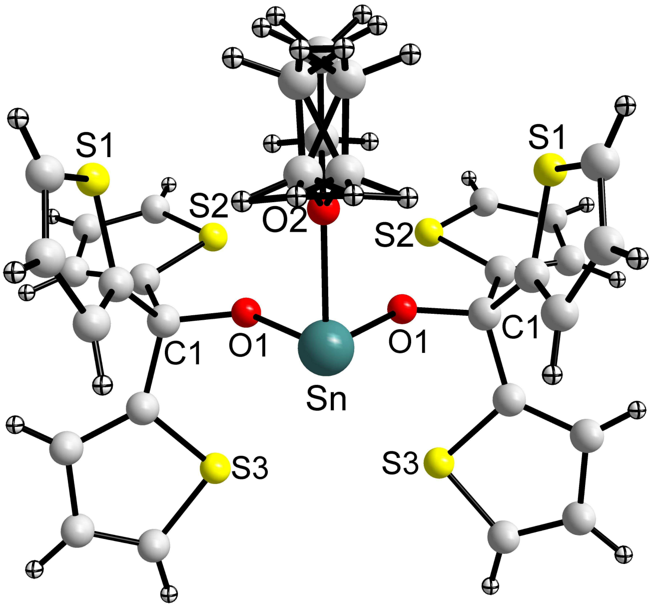


Figure 2.29. Molecular structure of Sn[OC(C_4H_3S)$_3$]$_2$(thf) (<u>15</u>). The carbon and hydrogen atoms of the tetrahydrofuran molecule are found in two split–positions.

The base−stabilized monomeric thf−adduct (**<u>15</u>**) is situated on a mirror plane of the lattice and shows a trigonal pyramidal structure in its local metalloid coordination sphere. The three ligands that define the pyramidal triangle consist of the two ligands O(1) and the thf molecule O(2) (Figure 2.30). The molecule possesses a C_S point symmetry with the thf molecule in a split position. The angles O−Sn−O range from 81.5(1)° for O(1)−Sn−O(1) and 86.16(9)° for O(1)−Sn−O(2) and are in agreement with a p^3 bonding type situation on tin with the lone pair formally occupying an s orbital. The (C_4H_3S)$_3$CO−Sn−OC(C_4H_3S)$_3$ angles are more acute than these found for Sn[OCH(CF_3)$_2$]$_2$($HNMe_2$) [90.1(2)°],[44] Sn(OC_6H_2Me−4−Bu^t_2−2,6)$_2$ [88.8(2)°][39] or Sn($OC_{14}H_{21}$)$_2$ [88.8(1)°].[40] The (C_4H_3S)$_3$C−O(1)−Sn angle is 128.6(2)° (see above for comparison). The Sn−OC(C_4H_3S)$_3$ distances of 2.036(2) Å are similar than those obtained for Sn[OCH(CF_3)$_2$]$_2$($HNMe_2$) [2.084(4) Å],[44] for example. The Sn−O(2) bond length is found at 2.261(4) Å which compares well with distances of W(CO)$_6$[$SnCl_2$(thf)] [2.223(6) Å][46] but is shorter than those in SnBrCl(thf)$_2$ by 0.17−0.23 Å.[47]

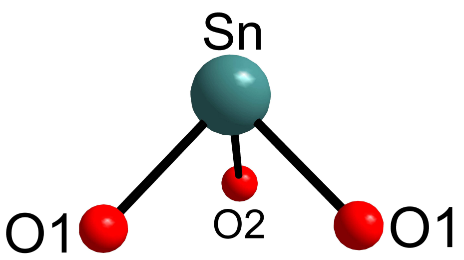


Figure 2.30. Environment around Sn[OC(C_4H_3S)$_3$]$_2$(thf) (<u>15</u>).

5.2.2.4 Conclusion

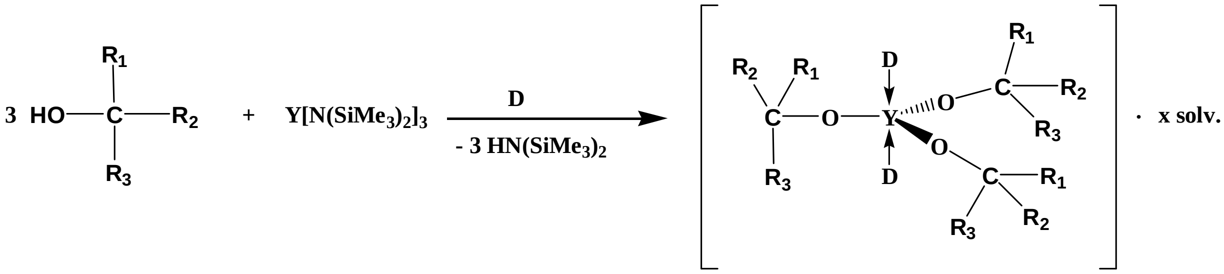
The reaction, in tetrahydrofuran, led to the formation of a mononuclear and a dinuclear products. But, these compounds are very sensitive and unstable towards light, moisture, and temperature, as solution or as solid.

<u>Part 2 Synthesis and Crystal Structure Determination of New Rare Earth Methoxides Containing Thienyl Substituents</u>

1 <u>Synthesis and Crystal Structure Determination of Yttrium Methoxides Containing Thienyl Substituents</u>

1.1 General Synthesis

The yttrium alkoxides containing tetrahydrofuran adducts were synthesized by the reaction between one equivalent of silyl amide {Y[N($SiMe_3$)$_2$]$_3$} and three equivalents of the carbinol in tetrahydrofuran for two days at room temperature. To compare the variation of the molecular structures with the solvent ligated to the yttrium metal, the pyridine adducts were prepared in an analogous manner by using a toluene/pyridine solvent mixture in the ratio (9:1) instead of tetrahydrofuran (Equation 2.25). The compounds were isolated as crystals or as solids.



Equation 2.25. General route leading to the yttrium alkoxides. x = 0, ½ or 1, solv. = toluene, D = thf or py. R_1, R_2 and R_3 stand for the thienyl or/and phenyl groups.

1.2 Reactivity of HO–C($C_8H_5S_2$)$_3$(<u>1</u>) towards Yttrium Silyl Amide in Tetrahydrofuran

After completion of the reaction, the solvent was evaporated and the green solid was re–dissolved in toluene. Unfortunately, only a few green crystals of the yttrium dithienylmethoxide Y[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_2$ (**<u>9</u>**) have been obtained in a very low yield (2 %). This unsatisfying result may be explained by the important steric hindrance of the ligand system **<u>1</u>** bearing three dithienyl groups and/or the difficulty to isolate the product. The ^{1}H–NMR spectrum of **<u>9</u>** in benzene solution shows the characteristic signals of the protons of the dithienyl units between 6.6 to 6.9 ppm and the methylene protons of the ligated tetrahydrofuran molecules at 1.4 and 3.6 ppm. Note that no product could be isolated when conducting the reaction in pyridine.

1.2.1 Crystal Structure Determination of Y[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_2$ (<u>9</u>)

Green crystals of Y[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_2$ (**<u>9</u>**) were obtained from a concentrated toluene solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/*n* in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 5.33 %. In Table 2.27 are reported the crystal and the structure refinement data for **<u>9</u>** and in Table 2.28 are reported some selected bond lengths and angles.

Identification code	sh2375	
Empirical formula	$C_{83}H_{62}O_5S_{18}Y$	
Formula weight	1805.32	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.525(2) Å	α= 90°.
	b = 15.182(2) Å	β= 97.48(1)°.
	c = 41.606(5) Å	γ = 90°.
Volume	7844(2) $Å^3$	
Z	4	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	1.276 mm^{-1}	
F(000)	3708	
Crystal size	0.3 x 0.5 x 0.65 mm^3	
Theta range for data collection	0.99 to 29.79°.	
Index ranges	–17<=h<=12, –21<=k<=21, –56<=l<=57	
Reflections collected	104589	
Independent reflections	22216 [R(int) = 0.0785]	
Completeness to theta = 29.79°	98.9 %	
Absorption correction	Semi–empirical from equivalents	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	22216 / 32 / 994	
Goodness–of–fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0533, wR2 = 0.1207	
R indices (all data)	R1 = 0.1014, wR2 = 0.1436	
Largest diff. peak and hole	1.392 and –1.073 e.$Å^{-3}$	

Table 2.27. Crystal data and structure refinement for $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (9).

Y–O(1)	2.075(2)	O(1)–Y–O(2)	120.25(9)
Y–O(2)	2.106(3)	O(1)–Y–O(3)	110.1(1)
Y–O(3)	2.086(2)	O(3)–Y–O(2)	128.64(9)
Y–O(4)	2.348(2)	O(1)–Y–O(5)	91.93(9)
Y–O(5)	2.356(2)	O(1)–Y–O(4)	89.98(9)
O(1)–C(1)	1.390(4)	O(2)–Y–O(4)	87.46(9)
O(2)–C(27)	1.400(4)	O(3)–Y–O(5)	90.65(9)
O(3)–C(52)	1.397(4)	C(1)–O(1)–Y	173.9(2)
		C(27)–O(2)–Y	161.4(2)
		C(52)–O(3)–Y	168.4(2)
		O(4)–Y–O(5)	174.28(9)

Table 2.28. Selected bond lengths [Å] and angles [°] for $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (9).

1.2.1.1 Discussion of the Molecular Structure of $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (9)

A single crystal X−ray analysis of $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**9**) was carried out for unequivocal identification of the structure as shown in Figure 2.31.

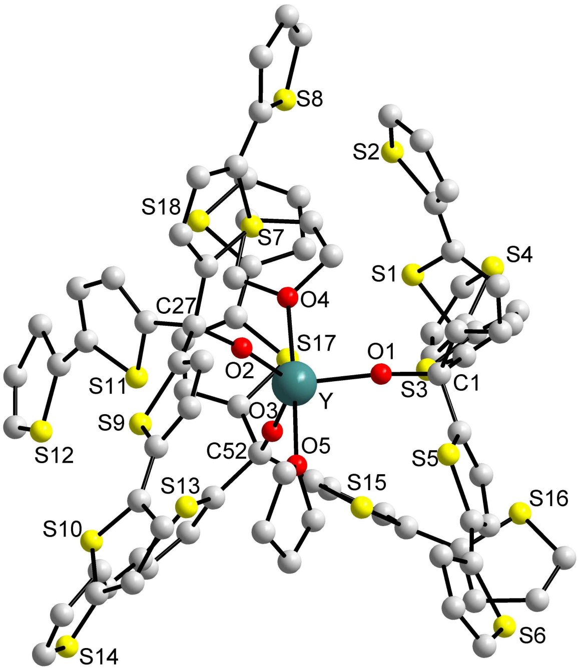


Figure 2.31. Molecular structure of Y[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_2$ (9). Hydrogen atoms are omitted for clarity.

In contrast to many literature–known yttrium alkoxides, which are dimeric[48] or are coordinated by three solvent molecules,[49] this alkoxide is mononuclear and the metal centre is ligated by only two solvent molecules. The molecular structure exhibits distorted trigonal–bipyramidal geometry around the yttrium centre with three equatorial alkoxides and two axial molecules of tetrahydrofuran. The sum of the [($C_8H_5S_2$)$_3$C]O–Y–O[C($C_8H_5S_2$)$_3$] angles is 359.99(9)° and the O(thf)–Y–O[C($C_8H_5S_2$)$_3$] angles are between 87.46(9)° and 91.93(9)°. The bond lengths of the Y–O[C($C_8H_5S_2$)$_3$] and Y–O(thf) are in the range of 2.075(2)–2.106(3) Å and 2.348(2)–2.356(2) Å, respectively.

1.3 Reactivity of HO–C(C_4H_3S)$_3$ (2) towards Yttrium Silyl Amide

1.3.1 Reaction in Tetrahydrofuran

After evaporation of the solvent, the light–brown solids were re–dissolved in toluene to obtain colourless single crystals of the yttrium thienylmethoxides Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (**16a**) and {Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$} • toluene (**16b**) (yields: 23 % for **16a** and 37 % for **16b**).

The ^{1}H–NMR spectra of **16a** and **16b** recorded in C_6D_6 display three broad signals in the integral ratio 9:9:9 attributed to the protons of the thienyl units (δ = 7.1, 6.9 and 6.7 ppm) and two signals due to the methylene protons of the ligated tetrahydrofuran molecules (δ = 3.7 and 1.4 ppm). The broadening of the signals could be due to a dynamic phenomenon of the organic ligands. For **16b**, the signals of the toluene lattice molecule (δ = 7.0 and 2.5 ppm) are also present.

1.3.2 Reaction in Pyridine

After concentration of the solution, the pyridine adducts $Y[OC(C_4H_3S)_3]_3(py)_2$ (**17a**) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (**17b**) were isolated as light–brown crystals in yields of 10 and 61 %, respectively. The ^{1}H–NMR spectra of $Y[OC(C_4H_3S)_3]_3(py)_2$ (**17a**) and$\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (**17b**) consist of three well resolved doublets of doublets in the integral ratio 9:9:9 (δ= 6.9, 6.8 and 6.6 ppm) and signals of the protons of pyridine (δ= 8.4, 6.9 and 6.6 ppm). In addition, the spectrum of **17b** displays the methyl protons of the toluene lattice molecule at δ= 7.0 and 2.1 ppm. No dynamic phenomenon is noted in these cases.

1.3.3 Crystal Structure Determination of $Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a) and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (16b)

Colourless crystals of $Y[OC(C_4H_3S)_3]_3(thf)_2$ (**16a**) and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (**16b**) were obtained from a concentrated toluene solution placed at 5°C. Appropriate crystals were isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/c for **16a** and P2(1) for **16b** in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–values are 7.42 and 5.35 %, respectively. In Tables 2.29 and 2.30 are reported the crystal and the structure refinement data for **16a,b** and in Table 2.31 are reported some selected bond lengths and angles.

Identification code	sh2359
Empirical formula	$C_{47}H_{43}O_5S_9Y$

Formula weight	1065.26	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.889(4) Å	α= 90°.
	b = 14.421(3) Å	β= 94.75(3)°.
	c = 16.190(3) Å	γ = 90°.
Volume	4860(2) Å^3	
Z	4	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	1.631 mm^{-1}	
F(000)	2192	
Crystal size	0.25 x 0.4 x 0.55 mm^3	
Theta range for data collection	1.89 to 24.11°.	
Index ranges	–23<=h<=22, –16<=k<=16, –18<=l<=18	
Reflections collected	28041	
Independent reflections	7593 [R(int) = 0.0738]	
Completeness to theta = 24.11°	98.2 %	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7593 / 0 / 559	
Goodness–of–fit on F^2	1.972	
Final R indices [I>2sigma(I)]	R1 = 0.0742, wR2 = 0.2067	
R indices (all data)	R1 = 0.0876, wR2 = 0.2130	
Largest diff. peak and hole	1.981 and –1.057 e.Å^{-3}	

Table 2.29. Crystal data and structure refinement for $Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a).

Identification code	sh2443	
Empirical formula	$C_{54}H_{51}O_5S_9Y$	
Formula weight	1157.40	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.724(1) Å	α= 90°.
	b = 15.930(1) Å	β= 114.40(1)°.
	c = 14.327(1) Å	γ = 90°.
Volume	2644.6(3) Å^3	
Z	2	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	1.505 mm^{-1}	
F(000)	1196	
Crystal size	0.3 x 0.5 x 0.65 mm^3	
Theta range for data collection	1.56 to 36.80°.	
Index ranges	–20<=h<=21, –25<=k<=26, –24<=l<=21	
Reflections collected	63311	
Independent reflections	23073 [R(int) = 0.0342]	
Completeness to theta = 36.80°	99.0 %	
Absorption correction	Semi–empirical from equivalents	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	23073 / 9 / 629	

Goodness–of–fit on F^2	1.440
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1460
R indices (all data)	R1 = 0.0676, wR2 = 0.1489
Absolute structure parameter	–0.002(3)
Largest diff. peak and hole	3.226 and –1.747 e.Å^{-3}

Table 2.30. Crystal data and structure refinement for $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (16b).

	$Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a)	$\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (16b)
Y–O(1)	2.091(4)	2.111(2)
Y–O(2)	2.083(4)	2.062(2)
Y–O(3)	2.111(3)	2.082(2)
Y–O(4)	2.386(4)	2.348(2)
Y–O(5)	2.404(4)	2.349(2)
O(1)–C(1)	1.339(7)	1.386(3)
O(2)–C(14)	1.394(7)	1.382(3)
O(3)–C(27)	1.409(7)	1.409(3)
O(2)–Y–O(1)	121.2(2)	118.75(8)
O(1)–Y–O(3)	115.0(2)	127.17(8)
O(2)–Y–O(3)	123.5(2)	113.85(9)
O(1)–Y–O(5)	87.3(2)	83.55(8)
O(1)–Y–O(4)	90.4(2)	89.97(8)
O(2)–Y–O(4)	92.4(2)	97.33(8)
O(3)–Y–O(5)	90.1(2)	86.48(8)
C(1)–O(1)–Y	166.8(4)	152.6(2)
C(14)–O(2)–Y	174.3(4)	178.5(2)
C(27)–O(3)–Y	153.6(4)	159.2(2)
O(4)–Y–O(5)	177.7(2)	166.50(7)

Table 2.31. Selected bond lengths [Å] and angles [°] for $Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a) and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (16b).

1.3.3.1 Discussion of the Molecular Structure of $Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a) and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (16b)

Single crystal X−ray analyses of $Y[OC(C_4H_3S)_3]_3(thf)_2$ (**16a**) and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (**16b**) were carried out for unequivocal identification of the structure and are shown in Figures 2.32 and 2.33.

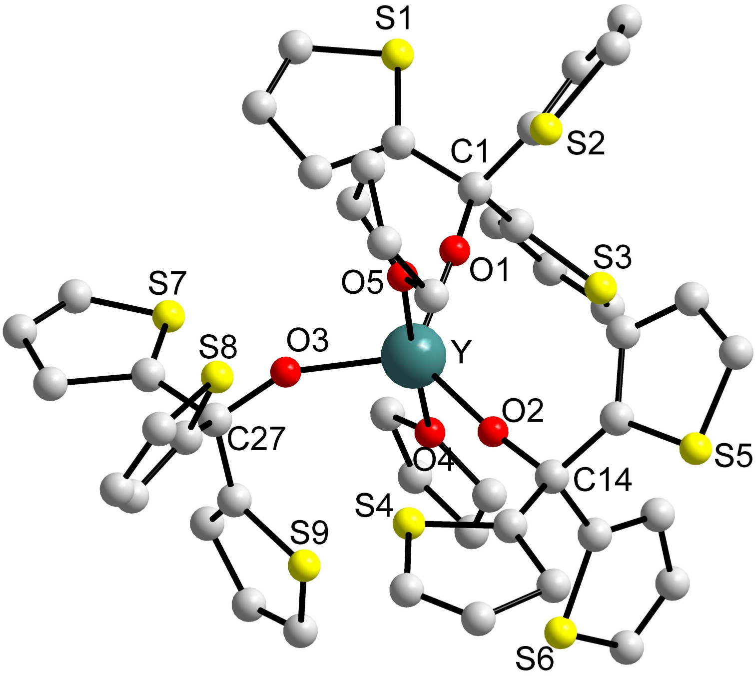


Figure 2.32. Molecular structure of Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (<u>16a</u>).

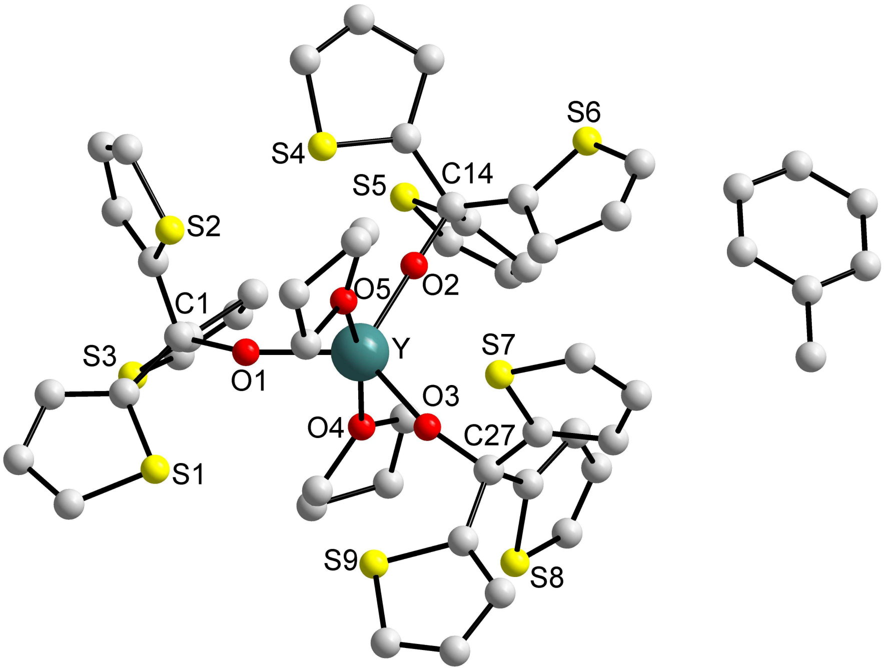


Figure 2.33. Molecular structure of {Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$} • toluene (<u>16b</u>). Hydrogen atoms are omitted for clarity.

Despite the fact that the ligand –OC(C_4H_3S)$_3$ is sterically less demanding than –OC($C_8H_5S_2$)$_3$, the molecular structures of compounds Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (**16a**) and {Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$} • toluene (**16b**) exhibit again exclusively mononuclear units with a five–coordinated yttrium centre in distorted trigonal–bipyramidal geometry: three alkoxide ligands in equatorial positions and two tetrahydrofuran in axial positions are found. Due to package effects, a toluene molecule can be included in the structure lattice, giving rise to the crystal structure of solvated **16b**. For Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (**16a**), the angles involving the pairs of –O[C(C_4H_3S)$_3$] ligands are in the range from 115.0(2)° to 123.5(2)° and the O(thf)–Y–O[C(C_4H_3S)$_3$] angles vary from 87.3(2)° to 92.4(2)°. The Y–O[C(C_4H_3S)$_3$] bond lengths are between 2.091(4) Å and 2.111(3) Å, which is in good agreement with the distances found for related tris(2,6–dimethylphenoxide)yttrium complexes.[48, 50] The Y–O(thf) bond distances [2.386(4) Å and 2.404(4) Å] correspond to those observed in similar yttrium tert–butoxide complexes (2.41 Å).[48, 51] These different distances are in agreement with these observed for Y[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_2$ **(9)**. The mean O–C(C_4H_3S)$_3$ distances of 1.381(3) Å are shorter than the value determined for the carbinol ligand **2** **[**1.440(4) Å]; this shortening is due to the additional charges on the oxygen atoms (charge δ^-) of the thienylmethoxides and the metal centre (δ^+ charge). No important alterations of the geometry of **16b** were observed compared to **16a** (see Table 2.30).

1.3.4 Crystal Structure Determination of Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$ (17a) and {Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$} • toluene (17b)

Light–brown single crystals Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$ (**17a**) and {Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$} • toluene (**17b**) were obtained from a concentrated solution of a 90% toluene/10% pyridine solvent mixture placed at 5°C. Appropriate crystals were isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/c for **17a** and P2(1) for **17b** in a monoclinic crystal system. The position of each atom was anisotropically refined. The R–values are 4.97 and 4.29 %, respectively. In Tables 2.32 and 2.33 are reported the crystal and the structure refinement data of **17a,b** and in Table 2.34 are reported some selected bond lengths and angles of interest.

Identification code	sh2344
Empirical formula	$C_{49}H_{37}N_2O_3S_9Y$
Formula weight	1079.26

Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.802(4) Å	α= 90°.
	b = 14.573(3) Å	β= 93.55(3)°.
	c = 16.041(3) Å	γ = 90°.
Volume	4854(2) Å^3	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	1.633 mm^{-1}	
F(000)	2208	
Crystal size	0.35 x 0.45 x 0.6 mm^3	
Theta range for data collection	1.89 to 24.13°.	
Index ranges	–23<=h<=23, –15<=k<=16, –18<=l<=18	
Reflections collected	30211	
Independent reflections	7590 [R(int) = 0.0517]	
Completeness to theta = 24.13°	98.0 %	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7590 / 48 / 620	
Goodness–of–fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1291	
R indices (all data)	R1 = 0.0620, wR2 = 0.1352	
Largest diff. peak and hole	1.813 and –1.397 e.Å^{-3}	

Table 2.32. Crystal data and structure refinement for $Y[OC(C_4H_3S)_3]_3(py)_2$ (17a).

Identification code	sh2437	
Empirical formula	$C_{56}H_{45}N_2O_3S_9Y$	
Formula weight	1171.39	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.449(1) Å	α= 90°.
	b = 16.232(1) Å	β= 112.31(1)°.
	c = 14.186(1) Å	γ = 90°.
Volume	2651.9(3) Å^3	
Z	2	
Density (calculated)	1.467 Mg/m^3	
Absorption coefficient	1.501 mm^{-1}	
F(000)	1204	
Crystal size	0.2 x 0.4 x 0.55 mm^3	
Theta range for data collection	1.77 to 29.05°.	
Index ranges	–16<=h<=16, –22<=k<=21, –19<=l<=15	
Reflections collected	24074	
Independent reflections	11138 [R(int) = 0.0427]	
Completeness to theta = 29.05°	85.9 %	
Absorption correction	Multi scan	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	11138 / 9 / 647	
Goodness–of–fit on F^2	0.999	

Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.0971
R indices (all data)	R1 = 0.0564, wR2 = 0.1000
Absolute structure parameter	0.001(4)
Largest diff. peak and hole	1.130 and –0.897 e.Å^{-3}

Table 2.33. Crystal data and structure refinement for $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (17b).

	$Y[OC(C_4H_3S)_3]_3(py)_2$ (17a)	$\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (17b)
Y–O(1)	2.109(3)	2.092(2)
Y–O(2)	2.100(3)	2.067(3)
Y–O(3)	2.107(3)	2.098(3)
Y–N(2)	2.520(3)	2.471(3)
Y–N(1)	2.493(3)	2.481(3)
O(1)–C(1)	1.399(5)	1.392(4)
O(2)–C(14)	1.394(5)	1.413(4)
O(3)–C(27)	1.406(5)	1.405(4)
O(2)–Y–O(1)	123.8(1)	122.3(1)
O(3)–Y–O(1)	115.1(1)	122.1(1)
O(2)–Y–O(3)	120.9(1)	115.6(1)
N(2)–Y–O(1)	87.1(1)	91.9(1)
O(1)–Y–N(1)	91.7(1)	85.1(1)
O(2)–Y–N(1)	94.0(1)	95.3(1)
O(3)–Y–N(2)	91.0(1)	86.6(1)
C(1)–O(1)–Y	164.0(3)	161.6(3)
C(14)–O(2)–Y	172.7(3)	172.4(2)
C(27)–O(3)–Y	154.5(2)	149.1(2)
N(1)–Y–N(2)	178.7(1)	169.3(1)

Table 2.34. Selected bond lengths [Å] and angles [°] for $Y[OC(C_4H_3S)_3]_3(py)_2$ (17a) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (17b).

1.3.4.1 Discussion of the Molecular Structure of $Y[OC(C_4H_3S)_3]_3(py)_2$ (17a) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (17b)

Single crystal X−ray analyses of $Y[OC(C_4H_3S)_3]_3(py)_2$ (**17a**) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (**17b**) were carried out for unequivocal identification of the structure which are depicted in Figure 2.34 and Figure 2.35.

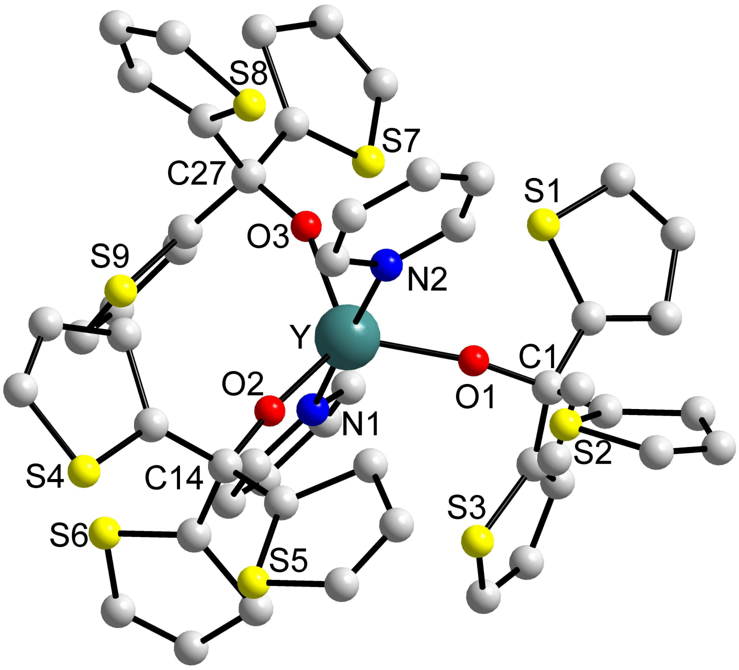


Figure 2.34. Molecular structure of $Y[OC(C_4H_3S)_3]_3(py)_2$ (17a).

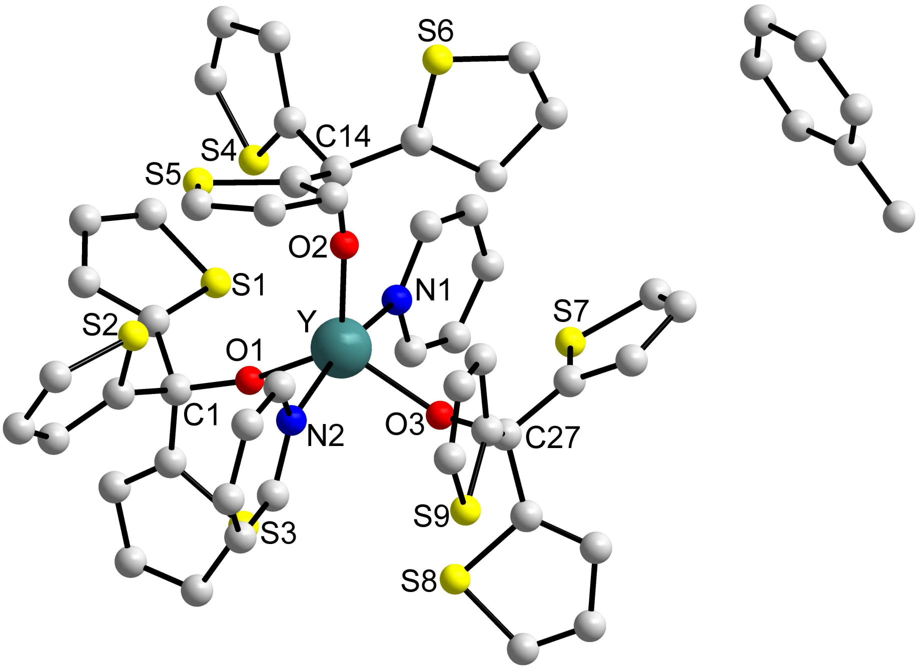


Figure 2.35. Molecular structure of $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (17b).

As can be seen in Figures 2.35 and 2.36, their trigonal–bipyramidal geometries are similar to those observed for compounds **16a** and **16b**, with an axial arrangement of the two pyridine ligands. For $Y[OC(C_4H_3S)_3]_3(py)_2$ (**17a**), the $[(C_4H_3S)_3C]O–Y–N$ angles are between 87.1(1)° and 94.0(1)° and the sum of the $[(C_4H_3S)_3C]O–Y–O[C(C_3H_4S)_3]$ angles is 359.8(1)°. Despite the presence of pyridine instead of tetrahydrofuran, no significant variations of the $[(C_4H_3S)_3C]O–Y–O[C(C_4H_3S)_3]$ and $[(C_4H_3S)_3]C]–O–Y$ angles or $Y–O[C(C_4H_3S)_3]$ bond distances are observed. The Y–N distances are in the range of 2.493(3)–2.520(3) Å. Again, the mean $O–C(C_4H_3S)_3$ lengths of 1.400(1) Å are shorter than the value obtained for the starting compound **2**. In the second solid state structure **17b**, one molecule of toluene is included: only some minor variations of the angles are observed (see Table 2.34).

1.4 Reactivity of HO–C($C_{16}H_{13}S$) (4) towards Yttrium Silyl Amide

1.4.1 Reaction in Tetrahydrofuran

After evaporation of the solvent, the white solid was re–dissolved in toluene to obtain colourless single crystals at 5°C of the yttrium alkoxide $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene **(26)** in a yield of 55 %. The ^{1}H–NMR spectrum of **26** recorded in $CDCl_3$ shows a multiplet at 7.3 ppm, which integrates for 33 protons of the phenyl and thienyl units (5–H), a multiplet and a doublet (δ = 6.9 and 6.7 ppm) due to the 4–H and 3–H of the thienyl groups, respectively. The signal of the protons of the tetrahydrofuran (δ = 1.8 and 3.7 ppm) and the lattice toluene molecule (δ = 2.3 and 7.1 ppm) are also present.

1.4.2 Reaction in Pyridine

After evaporation of the solution, the white solid was re–dissolved in toluene colourless single crystals at 5°C of the pyridine adduct $\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (**27**) in a yield of 42 %. The ^{1}H–NMR spectrum of **27** recorded in $CDCl_3$ displays a multiplet at 7.2 ppm integrating for 33 protons of the aryl and the 5–H of the thienyl groups. Two broad signals at 6.8 and 6.6 ppm in the integral ratio 3:3 are attributed to the 4–H and 3–H protons of the thienyl units, respectively. Four signals due to the methylene protons of the ligated tetrahydrofuran molecules (δ = 3.7 and 1.4 ppm) and the protons of the lattice toluene molecule (δ = 2.3 and 7.1 ppm) are also present. The broadening of the signals could be due to a dynamic phenomenon of the organic ligands.

1.4.3 Crystal Structure Determination of {Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (<u>26</u>)

Colourless crystals {Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (**<u>26</u>**) were obtained from a concentrated toluene solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/c in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 14.96 %. This high value is due to the poor quality of the measured crystal. In Table 2.35 are reported the crystal and the structure refinement data for **<u>26</u>** and in Table 2.36 are reported some selected bond lengths and angles.

Identification code	sh2579	
Empirical formula	$C_{66}H_{63}O_5S_3Y$	
Formula weight	1121.25	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.678(2) Å	α= 90°.
	b = 13.760(2) Å	β= 94.50(1)°.
	c = 27.649(3) Å	γ = 90°.
Volume	5567(1) Å^3	
Z	4	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	1.211 mm^{-1}	
F(000)	2344	
Crystal size	0.56 x 0.4 x 0.23 mm^3	
Theta range for data collection	1.39 to 26.78°.	
Index ranges	–18<=h<=18, –17<=k<=17, –29<=l<=35	
Reflections collected	56064	
Independent reflections	11862 [R(int) = 0.1223]	
Completeness to theta = 26.78°	99.7 %	
Absorption correction	Multiscan	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	11862 / 0 / 633	
Goodness–of–fit on F^2	2.530	
Final R indices [I>2sigma(I)]	R1 = 0.1496, wR2 = 0.3516	
R indices (all data)	R1 = 0.2070, wR2 = 0.3647	
Largest diff. peak and hole	1.829 and –2.047 e.Å^{-3}	

Table 2.35. Crystal data and structure refinement for {Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (<u>26</u>).

Y–O(1)	2.110(6)	O(2)–Y–O(1)	122.3(3)
Y–O(2)	2.051(6)	O(3)–Y–O(1)	123.0(3)
Y–O(3)	2.102(6)	O(2)–Y–O(3)	114.6(3)
Y–O(4)	2.336(6)	O(1)–Y–O(5)	86.6(2)
Y–O(5)	2.326(6)	O(1)–Y–O(4)	86.4(2)
O(1)–C(1)	1.38(1)	O(2)–Y–O(4)	98.3(3)
O(2)–C(18)	1.45(1)	O(3)–Y–O(5)	86.8(2)
O(3)–C(35)	1.38(1)	O(5)–Y–O(4)	168.2(2)
		C(1)–O(1)–Y	170.2(7)
		C(18)–O(2)–Y	168.8(6)
		C(35)–O(3)–Y	151.3(6)

Table 2.36. Selected bond lengths [Å] and angles [°] for $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (26).

1.4.3.1 Discussion of the Molecular Structure of $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (26)

A single crystal X−ray analysis of $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (**26**) was carried out for unequivocal identification of the structure, which is depicted in Figure 2.36.

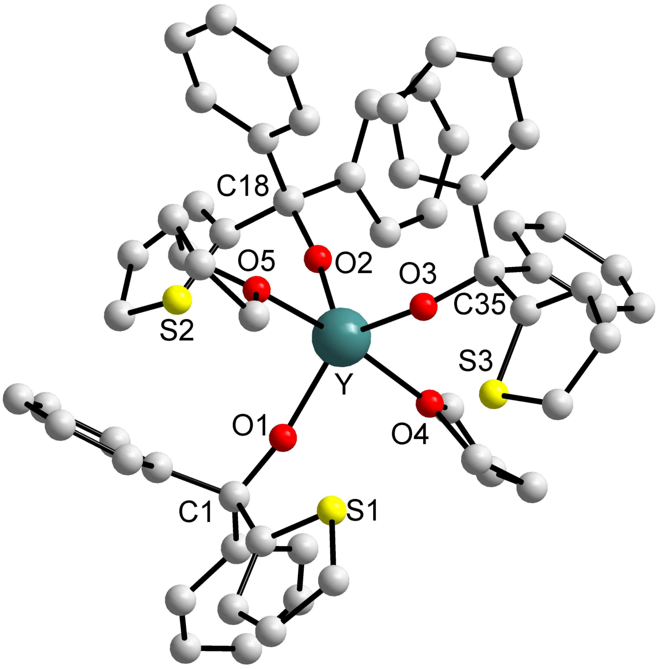


Figure 2.36. Molecular structure of $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (26). The toluene lattice molecule is omitted for more clarity.

The molecular structure exhibits a five–coordinated yttrium in a distorted trigonal–bipyramidal coordination sphere: three alkoxide ligands in equatorial positions and two tetrahydrofuran molecules in axial positions are found. Due to the packing effect, a toluene molecule is included in the structure lattice. The Y–O bond lengths of the diphenyl(2−thienyl)methoxido ligands range from 2.051(6) Å to 2.110(6) Å which is in good agreement with similar distances observed for $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**9**), $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ (**16a**), and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (**17b**), $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ (**17a**) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (**17b**). The Y–O bond lengths of the coordinated tetrahydrofuran molecules [2.326(6) Å and 2.336(6)Å] are equal to the ones found for $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (**16b**) [2.349(2) and 2.348(2) Å]. The three methoxide oxygen atoms around yttrium centre are coplanar with ∑ O–Y–O = 359.9(3)° (Figure 2.37), this value is comparable with those in $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**9**) [359.99(9)°], $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$(**16a**) [359.7(2)°], and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (**16b**) [359.77(9)°]. The O(4)–Y–O(5) angle of 168.2(2)° slightly more obtuse than this found for $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (**16b**) [166.50(7)°]. The angle between the planes {O(5)YO(4)} and {O(3)YO(1)O(2)} amounts to 89.26(8)° (Figure 2.37). The O(thf)–Y–OC(C_4H_3S) angles vary from 86.6(2) to 98.3(3)°.

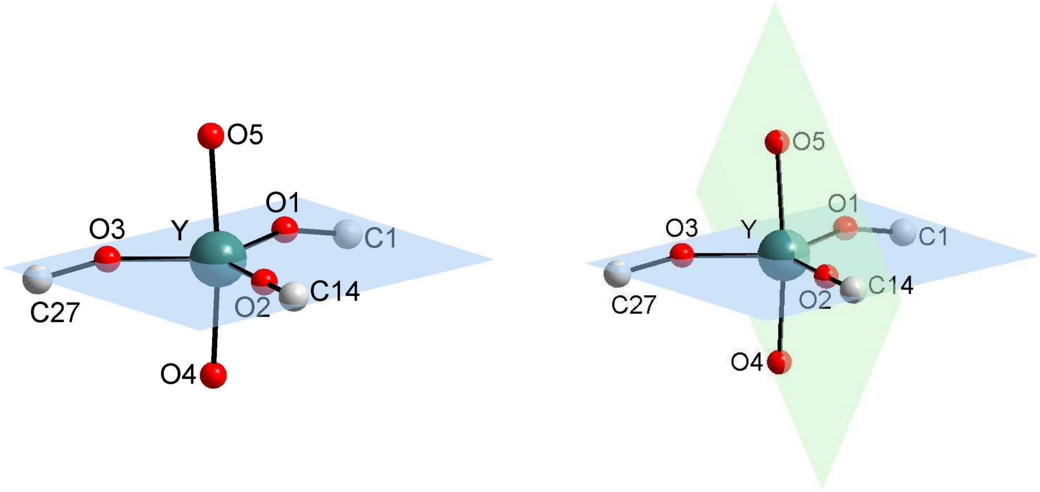


Figure 2.37. Environments around the yttrium centre of compound 26.

1.4.4 Crystal Structure Determination of $\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (27)

Colourless crystals of $\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (**27**) were obtained in toluene at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P−1 in a triclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 8.65 %. In Table 2.37 are reported the crystal and the structure refinement data for **27** and in Table 2.38 are reported some selected bond lengths and angles.

Identification code	sh2620	
Empirical formula	$C_{68}H_{57}N_2O_3S_3Y$	
Formula weight	1135.25	
Temperature	146(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P–1	
Unit cell dimensions	a = 12.676(1) Å	α= 97.75(1)°.
	b = 14.042(1) Å	β= 95.19(1)°
	c = 18.164(1) Å	γ = 116.59(1)°.
Volume	2823(2) $Å^3$	
Z	2	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	1.194 mm^{-1}	
F(000)	1180	
Crystal size	0.52 x 0.33 x 0.12 mm^3	
Theta range for data collection	1.15 to 29.05°.	
Index ranges	–17<=h<=17, –19<=k<=19, –24<=l<=24	
Reflections collected	64544	
Independent reflections	14865 [R(int) = 0.0383]	
Completeness to theta = 29.05°	98.5 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8739 and 0.5751	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	14865 / 1 / 673	
Goodness–of–fit on F^2	2.401	
Final R indices [I>2sigma(I)]	R1 = 0.0865, wR2 = 0.2458	
R indices (all data)	R1 = 0.1098, wR2 = 0.2536	
Largest diff. peak and hole	2.440 and –1.952 e.$Å^{-3}$	

Table 2.37. Crystal data and structure refinement for $\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (27).

Y–O(1)	2.084(2)	O(1)–Y–O(2)	121.4(1)
Y–O(2)	2.090(3)	O(3)–Y–O(1)	113.8(1)
Y–O(3)	2.083(3)	O(3)–Y–O(2)	124.8(1)
Y–N(2)	2.509(4)	O(1)–Y–N(2)	88.8(1)
Y–N(1)	2.474(4)	O(1)–Y–N(1)	91.1(1)
O(1)–C(1)	1.397(5)	O(2)–Y–N(1)	86.3(1)
O(2)–C(18)	1.404(5)	O(3)–Y–N(2)	93.3(1)
O(3)–C(36)	1.399(5)	N(1)–Y–N(2)	175.0(1)
		C(1)–O(1)–Y	164.9(3)
		C(18)–O(2)–Y	176.4(3)
		C(36)–O(3)–Y	173.5(3)

Table 2.38. Selected bond lengths [Å] and angles [°] for {$Y[OC(C_{16}H_{13}S)]_3(py)_2$} • toluene (27).

1.4.4.1 Discussion of the Molecular Structure of {$Y[OC(C_{16}H_{13}S)]_3(py)_2$} • toluene (27)

A single crystal X−ray analysis of {$Y[OC(C_{16}H_{13}S)]_3(py)_2$} • toluene (**27**) was carried out for unequivocal identification of the structure which is depicted in Figure 2.38.

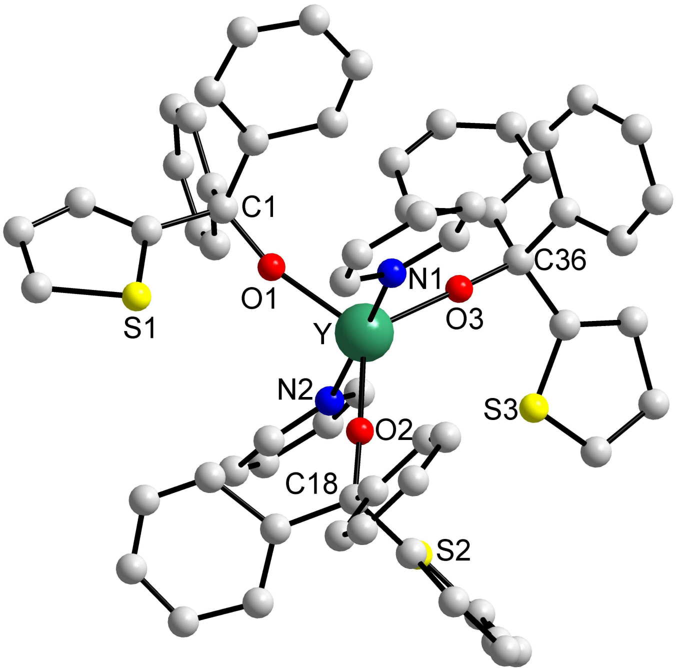


Figure 2.38. Molecular structure of {$Y[OC(C_{16}H_{13}S)]_3(py)_2$} • toluene (27). Hydrogen atoms and the lattice toluene molecule are omitted for clarity.

The X–ray structure mononuclear five–coordinated {$Y[OC(C_{16}H_{13}S)]_3(py)_2$} • toluene (**27**) reveals a distorted trigonal–bipyramidal coordination sphere around the yttrium centre: three alkoxide ligands in equatorial positions and two pyridine molecules in axial positions are found. This geometry is similar to these obtained for the other yttrium compounds (see above). Due to the packing effect, a toluene molecule is included in the structure lattice. The angles involving the pair of $–OC(C_{16}H_{13}S)$ ligands are in the range of 113.8(1)° to 124.8(1)° and their sum is to 360.0(1)° which is in good agreement with these found for $Y[OC(C_4H_3S)_3]_3(py)_2$ (**17a**) [359.8(1)°] and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (**17b**) [360.0(1)°]. The $N–Y–OC(C_{16}H_{13}S)$ angles vary from 86.3(1) to 93.3(1)°. The $Y–OC(C_{16}H_{13}S)$ bond lengths average 2.085(3) Å and correspond the those observed in the similar yttrium alkoxides (see above). The Y–N bond lengths of the coordinated pyridine molecules [2.474(4) and 2.509(4) Å] are equal to the ones found for $Y[OC(C_4H_3S)_3]_3(py)_2$ (**17a**) [2.493(3) and 2.520(3) Å] and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (**17b**) [2.471(3) and 2.481(3) Å]. Despite the presence of pyridine instead of coordinated tetrahydrofuran molecules as in $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (**26**), no significant variations of the $(C_{16}H_{13}S)CO–Y–OC(C_{16}H_{13}S)$ and $(C_{16}H_{13}S)C–O–Y$ angles or $Y–OC(C_{16}H_{13}S)$ bond distances are observed.

1.5 Reactivity of HO–C($C_{17}H_{15}S$) (5) towards Yttrium Silyl Amide

1.5.1 Reaction in Tetrahydrofuran

After the evaporation of the solvent, the white solid was re–dissolved in toluene to obtain colourless crystals of $\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (**33**) in yield of 11 %. This poor yield can be explained by the difficulty to isolate the product as single crystals. The ^1H–NMR spectrum of **33** recorded in $CDCl_3$ shows two multiplets at 7.3 and 7.4 ppm attributed to the protons of the phenyl groups and two doublets at 6.6 and 6.4 which each integrates for 3H, corresponding to the 4–H and 3–H of the thienyl units. Moreover, at 2.7 ppm, a singlet of the $–CH_3$ functions is present. The remaining signals are due to the tetrahydrofuran and the lattice toluene molecules.

1.5.2 Reaction in Pyridine

After the evaporation of the solvent, the white solid was re–dissolved in toluene to obtain colourless crystals of $\{Y[OC(C_{17}H_{15}S)]_3(py)_2\}$ • toluene (**34**) in a yield of 61 %. The unresolved ^{1}H–NMR spectrum of **34** recorded in $CDCl_3$ displays the typical aromatic signals of the phenyl and thienyl groups from 6.4 to 7.6 ppm. At 2.9 ppm, a singlet integrating for 9H is attributed to the $–CH_3$ functions. The signals of the pyridine and toluene are also observed.

1.5.3 Crystal Structure Determination of $\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (33)

Colourless crystals $\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (**33**) were obtained in toluene at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/c in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 11.10 %. This high value is due to the poor quality of the measured crystal. In Table 2.39 are reported the crystal and the structure refinement data for **33** and in Table 2.40 are reported some selected bond lengths and angles.

Identification code	sh2667	
Empirical formula	$C_{69}H_{69}O_5S_3Y$	
Formula weight	1163.33	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.687(4) Å	α = 90°.
	b = 14.686(3) Å	β = 93.56(3)°.
	c = 28.052(6) Å	γ = 90°.
Volume	7684(3) $Å^3$	
Z	4	
Density (calculated)	1.006 Mg/m^3	
Absorption coefficient	0.880 mm^{-1}	
F(000)	2440	
Crystal size	0.61 x 0.46 x 0.32 mm^3	
Theta range for data collection	2.33 to 28.32°.	
Index ranges	–24<=h<=24, –19<=k<=19, –36<=l<=37	
Reflections collected	68245	
Independent reflections	18377 [R(int) = 0.1499]	
Completeness to theta = 28.32°	95.9 %	

Absorption correction	None
Max. and min. transmission	0.7661 and 0.6160
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	18377 / 2 / 703
Goodness–of–fit on F^2	1.546
Final R indices [I>2sigma(I)]	R1 = 0.1110, wR2 = 0.2847
R indices (all data)	R1 = 0.2374, wR2 = 0.3113
Largest diff. peak and hole	1.070 and –0.656 e.Å^{-3}

Table 2.39. Crystal data and structure refinement for $\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (33).

Y–O(1)	2.098(5)	O(1)–Y–O(2)	124.8(2)
Y–O(2)	2.082(6)	O(3)–Y–O(1)	118.5(2)
Y–O(3)	2.075(6)	O(3)–Y–O(2)	116.4(2)
Y–O(4)	2.376(5)	O(1)–Y–O(5)	90.0(2)
Y–O(5)	2.352(5)	O(1)–Y–O(4)	85.7(2)
O(1)–C(1)	1.407(9)	O(2)–Y–O(4)	85.8(2)
O(2)–C(19)	1.43(1)	O(3)–Y–O(5)	97.7(2)
O(3)–C(37)	1.41(1)	O(5)–Y–O(4)	168.8(2)
		C(1)–O(1)–Y	161.6(5)
		C(19)–O(2)–Y	162.2(5)
		C(37)–O(3)–Y	175.7(6)

Table 2.40. Selected bond lengths [Å] and angles [°] for $\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (33).

1.5.3.1 Discussion of the Molecular Structure of $\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (33)

A single crystal X–ray analysis of $\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (**33**) was carried out for unequivocal identification of the structure which is depicted in Figure 2.39.

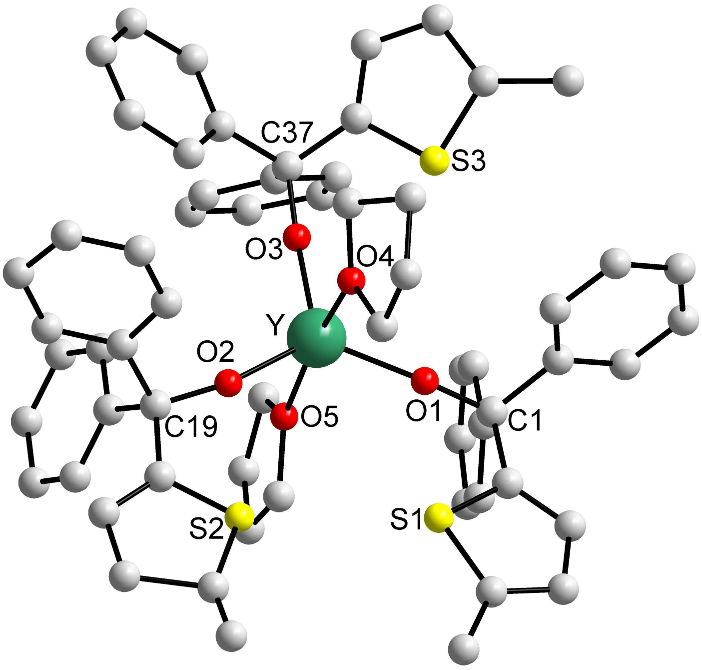


Figure 2.39. Molecular structure of {Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (33). Hydrogen atoms and the lattice toluene molecule are omitted for clarity.

The molecular structure reveals a mononuclear unit with a five−coordinated yttrium in distorted trigonal–bipyramidal geometry. The metal centre is surrounded by three diphenyl(5–methyl–2–thienyl)methoxido ligands in equatorial positions and two tetrahydrofuran molecules in axial positions. This geometry is similar to these obtained for the other yttrium compounds (see above). Due to the package effect, a toluene molecule is included in the structure lattice. The angles between the pairs of –OC($C_{17}H_{15}S$) are in the range of 116.4(2) to 124.8(2)°, their sum is 359.7(2)° showing that the three methoxide oxygen atoms around the yttrium centre have a planar array. The O(thf)–Y–OC($C_{17}H_{15}S$) are from 85.7(2) to 97.7(2)°. The Y–OC($C_{17}H_{15}S$) and Y–O(thf) average 2.085(6) and 2.364(5) Å. In comparison with {Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (**26**), where the thienyl unit of the organic ligand is not functionalized with a methyl group, only insignificant variations of bond lengths are noticed (Table 2.41). Due to the presence of the methyl substituents at the 2−position of the thienyl ligands, which increase the steric hindrance, the variations of the metric values of the angles are somewhat more pronounced.

	{Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (33)	{Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (26)
Y–O(1)	2.098(5)	2.110(6)
Y–O(2)	2.082(6)	2.051(6)
Y–O(3)	2.075(6)	2.102(6)
Y–O(4)	2.376(5)	2.336(6)
Y–O(5)	2.352(5)	2.326(6)
O(1)–Y–O(2)	124.8(2)	122.3(3)
O(3)–Y–O(1)	118.5(2)	123.0(3)
O(3)–Y–O(2)	116.4(2)	114.6(3)
O(1)–Y–O(5)	90.0(2)	86.6(2)
O(1)–Y–O(4)	85.7(2)	86.4(2)
O(2)–Y–O(4)	85.8(2)	98.3(3)
O(3)–Y–O(5)	97.7(2)	86.8(2)
O(5)–Y–O(4)	168.8(2)	168.2(2)

Table 2.41. Selected bond lengths [Å] and angles [°] for {Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (26) and {Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (33).

1.5.4 Crystal Structure Determination of {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34)

Colourless crystals {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (**34**) were obtained in toluene at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P–1 in a triclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 7.79 %. In Table 2.42 are reported the crystal and the structure refinement data for **34**. Table 2.43 presents some selected bond lengths and angles of interest.

Identification code	sh2703	
Empirical formula	$C_{71}H_{63}N_2O_3S_3Y$	
Formula weight	1177.32	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P–1	
Unit cell dimensions	a = 12.627(1) Å	α = 97.84(1)°.
	b = 14.478(2) Å	β = 95.21(1)°.
	c = 18.270(2) Å	γ = 113.65(1)°.
Volume	2991.5(5) Å^3	
Z	2	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	1.129 mm^{-1}	
F(000)	1228	
Crystal size	0.77 x 0.28 x 0.27 mm^3	
Theta range for data collection	1.14 to 27.93°.	

Index ranges	–16<=h<=15, –18<=k<=19, –23<=l<=21
Reflections collected	50050
Independent reflections	13931 [R(int) = 0.0363]
Completeness to theta = 27.93°	97.2 %
Absorption correction	Multiscan
Max. and min. transmission	0.7533 and 0.4760
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	13931 / 0 / 682
Goodness–of–fit on F^2	2.086
Final R indices [I>2sigma(I)]	R1 = 0.0779, wR2 = 0.2188
R indices (all data)	R1 = 0.1038, wR2 = 0.2267
Largest diff. peak and hole	1.607 and –1.728 e.Å^{-3}

Table 2.42. Crystal data and structure refinement for {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34).

Y–O(1)	2.086(3)	O(2)–Y–O(1)	120.2(1)
Y–O(2)	2.080(3)	O(3)–Y–O(1)	117.7(1)
Y–O(3)	2.083(3)	O(2)–Y–O(3)	122.1(1)
Y–N(1)	2.492(4)	O(1)–Y–N(2)	88.1(1)
Y–N(2)	2.515(4)	O(1)–Y–N(1)	90.7(1)
O(1)–C(1)	1.399(5)	O(2)–Y–N(1)	88.2(1)
O(2)–C(19)	1.384(5)	O(3)–Y–N(2)	92.1(1)
O(3)–C(37)	1.403(5)	N(1)–Y–N(2)	174.4(1)
		C(1)–O(1)–Y	160.3(3)
		C(19)–O(2)–Y	173.0(3)
		C(37)–O(3)–Y	177.5(3)

Table 2.43. Selected bond lengths [Å] and angles [°] for {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34).

1.5.4.1 Discussion of the Molecular Structure of {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34)

A single crystal X–ray analysis of {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (**34**) was carried out for unequivocal identification of the structure, which is depicted in Figure 2.40.

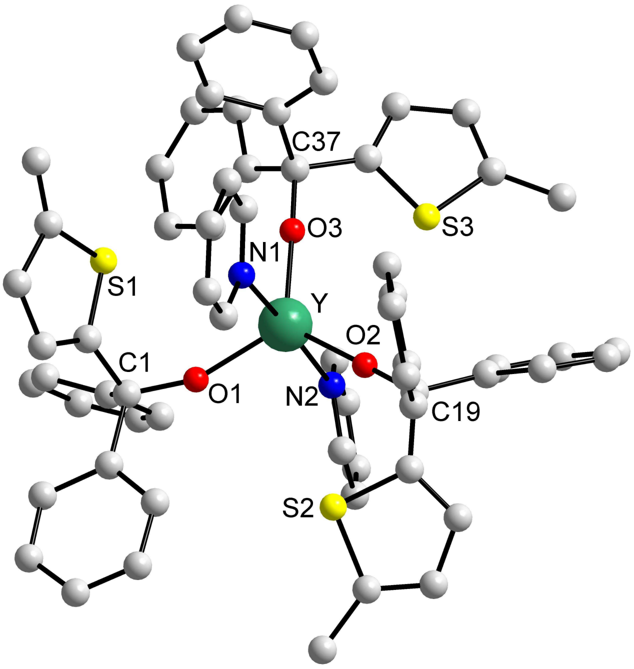


Figure 2.40. Molecular structure of {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34). Hydrogen atoms and the lattice toluene molecule are omitted for clarity.

The molecular structure exhibits a mononuclear compound. The geometry around the yttrium metal centre is distorted trigonal–bipyramidal with three diphenyl(5–methyl–2–thienyl)methoxido ligands in equatorial positions and two pyridine molecules in axial positions. Due to the packing effect, a toluene molecule is included in the structure lattice. The sum of the ($C_{17}H_{15}S$)CO–Y–OC($C_{17}H_{15}S$) angles is 360.0(1)° and the N–Y–OC($C_{17}H_{15}S$) angles are between 88.1(1) and 92.1(1)°. The bond lengths of the Y–OC($C_{17}H_{15}S$) and Y–N are in the range of 2.080(3)–2.086(3) Å and 2.492(4)–2.515(4) Å, respectively. Despite the presence of pyridine instead of coordinated tetrahydrofuran molecules as in {Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (**33**), no significant variations of the ($C_{17}H_{15}S$)CO–Y–OC($C_{17}H_{15}S$) angles or Y–OC($C_{17}H_{15}S$) bond distances are observed (Table 2.44).

	{Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34)	**{Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (33)**
Y–O(1)	2.086(3)	2.098(5)
Y–O(2)	2.080(3)	2.082(6)
Y–O(3)	2.083(3)	2.075(6)
O(1)–C(1)	1.399(5)	1.407(9)
O(2)–C(19)	1.384(5)	1.43(1)
O(3)–C(37)	1.403(5)	1.41(1)
O(2)–Y–O(1)	120.2(1)	124.8(2)
O(3)–Y–O(1)	117.7(1)	118.5(2)
O(2)–Y–O(3)	122.14(1)	116.4(2)
C(1)–O(1)–Y	160.3(3)	161.6(5)
C(19)–O(2)–Y	173.0(3)	162.2(5)
C(37)–O(3)–Y	177.5(3)	175.7(6)

Table 2.44. Selected bond lengths [Å] and angles [°] for {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34) and {Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (33).

In comparison with {Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$} • toluene (**27**), whose thienyl unit of the organic ligand is not functionalized with a methyl group, only some insignificant variations of the bond lengths are observed (Table 2.45). However, the angles are somewhat more affected due to the presence of methyl groups, which increase the steric hindrance exerted by the organic ligands.

	{Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34)	**{Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$} • toluene (27)**
Y–O(1)	2.086(3)	2.084(2)
Y–O(2)	2.080(3)	2.090(3)
Y–O(3)	2.083(3)	2.083(3)
Y–N(1)	2.492(4)	2.509(4)
Y–N(2)	2.515(4)	2.474(4)
O(2)–Y–O(1)	120.2(1)	121.4(1)
O(3)–Y–O(1)	117.7(1)	113.8(1)
O(2)–Y–O(3)	122.1(1)	124.8(1)
O(1)–Y–N(2)	88.1(1)	88.8(1)
O(1)–Y–N(1)	90.7(1)	91.1(1)
O(2)–Y–N(1)	88.2(1)	86.3(1)
O(3)–Y–N(2)	92.1(1)	93.3(1)
N(1)–Y–N(2)	174.4(1)	175.0(1)

Table 2.45. Selected bond lengths [Å] and angles [°] for {Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (35) and {Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$} • toluene (27).

1.6 Reactivity of HO–C($C_{14}H_{11}S_2$) (<u>7</u>) towards Yttrium Silyl Amide

1.6.1 Reaction in Tetrahydrofuran

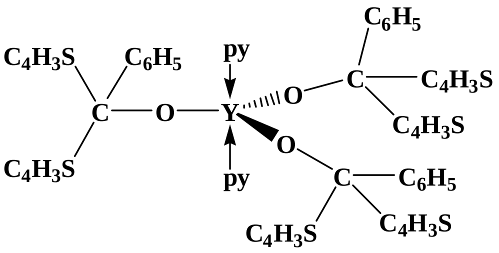
After evaporation of the solvent, the white solid was re–dissolved in toluene to obtain colourless single crystals at 5°C of the yttrium alkoxide $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (<u>**38**</u>) in a yield of 40 %. The ^{1}H–NMR spectrum recorded in $CDCl_3$, at room temperature, displays unresolved signals. The signals of the phenyl groups are situated at 7.3 and 7.1 ppm. The other aromatic signals at 6.9, 7.1 and 6.8 ppm correspond to the 5–H, 4–H and 2–H of the thienyl units, respectively.

1.6.2 Reaction in Pyridine

After concentration of the solution, a white solid precipitated. Unfortunately, no crystals could be obtained. The H,H–COSY spectrum of this solid dissolved in $CDCl_3$ shows five unresolved signals. The first at 7.2 ppm integrating for 21H is attributed to the protons of the phenyl groups and to the 5–H protons of the thienyl units. This signal has a correlation with that at 6.9 ppm, which integrates for 12H corresponding so to the 4–H and 2–H of the thienyl groups. The three other signals at 8.4, 7.6 and 7.2 ppm are due to the protons of the pyridine adducts. The broadening of the signals could be due to a dynamic phenomenon of the organic ligands.

Therefore, it is quite plausible that $Y[N(SiMe_3)_2]_3$ and HO–C($C_{14}H_{11}S_2$) (<u>7</u>) react in the same manner as $Y[N(SiMe_3)_2]_3$ with <u>**7**</u> in tetrahydrofuran as solvent leading to $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (<u>**38**</u>), or with <u>**2**</u> and <u>**4**</u> to form $Y[OC(C_{14}H_{11}S_2)](py)_2$ (<u>**39**</u>). Three –OC($C_{14}H_{11}S_2$) groups are ligated to the yttrium metal centre. Like in the other yttrium compounds $Y[OC(C_4H_3S)_3]_3(py)_2$ (<u>**17a**</u>) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (<u>**17b**</u>) and $\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (<u>**27**</u>), probably two pyridine molecules are also axially coordinated to the metal centre. Moreover, this composition is confirmed by the results of elemental analyses. All experimental values match well with the calculated ones: 63.51 % for the carbon (value calculated: 62.26 %), 4.15 % for the hydrogen (value calculated: 4.06 %) and 3.15 % for the nitrogen (value calculated: 2.64 %).

Therefore we conclude that $Y[OC(C_{14}H_{11}S_2)](py)_2$ (<u>**39**</u>) (Figure 2.41) is formed with a yield of 70 %.



39

Figure 2.41. $Y[OC(C_{14}H_{11}S_2)](py)_2$ (39)

1.6.3 Crystal Structure Determination of $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (38)

Colourless crystals $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (**38**) were obtained in toluene at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P2(1)/n in a monoclinic crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 7.37 %. In Table 2.46 are reported the crystal and the structure refinement data for **38**.Table 2.47 presents some selected bond lengths and angles of interest.

Identification code	sh2737	
Empirical formula	$C_{53}H_{49}O_5S_6Y$ x 0.5 C_7H_8	
Formula weight	1093.26	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.598(3) Å	α = 90°.
	b = 16.935(3) Å	β = 102.22(3)°.
	c = 23.892(5) Å	γ = 90°.
Volume	5377(1) $Å^3$	
Z	4	
Absorption coefficient	1.364 mm^{-1}	
F(000)	2268	
Crystal size	0.40 x 0.35 x 0.23 mm^3	
Theta range for data collection	2.39 to 28.19°.	
Index ranges	–17<=h<=17, –22<=k<=22, –31<=l<=31	
Reflections collected	55056	
Independent reflections	12833 [R(int) = 0.1099]	
Completeness to theta = 28.19°	97.1 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.7444 and 0.6114	
Refinement method	Full–matrix least–squares on F^2	

Data / restraints / parameters	12833 / 0 / 578
Goodness–of–fit on F^2	1.138
Final R indices [I>2sigma(I)]	R1 = 0.0737, wR2 = 0.1701
R indices (all data)	R1 = 0.1420, wR2 = 0.1894
Largest diff. peak and hole	1.086 and –0.771 e.Å^{-3}

Table 2.46. Crystal data and structure refinement for $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (38).

Y–O(1)	2.083(3)	O(1)–Y–O(2)	123.1(1)
Y–O(2)	2.112(3)	O(3)–Y–O(1)	119.0(1)
Y–O(3)	2.070(3)	O(3)–Y–O(2)	117.6(1)
Y–O(4)	2.414(3)	O(1)–Y–O(5)	89.3(1)
Y–O(5)	2.364(3)	O(1)–Y–O(4)	85.1(1)
O(1)–C(1)	1.398(6)	O(2)–Y–O(4)	88.9(1)
O(2)–C(16)	1.414(6)	O(3)–Y–O(5)	96.5(1)
O(3)–C(31)	1.406(5)	O(5)–Y–O(4)	172.6(1)
		C(1)–O(1)–Y	172.7(3)
		C(16)–O(2)–Y	158.3(3)
		C(31)–O(3)–Y	173.1(3)

Table 2.47. Selected bond lengths [Å] and angles [°] for $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (38).

1.6.3.1 Discussion of the Molecular Structure of $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (38)

A single crystal X–ray analysis of $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (**38**) was carried out for unequivocal identification of the structure depicted in Figure 2.42. Unfortunately, the differentiation between the thienyl and phenyl groups is difficult. This may be attributed to the fact that the crystallization process has taken place with a distorted arrangement of the thienyl and phenyl groups.

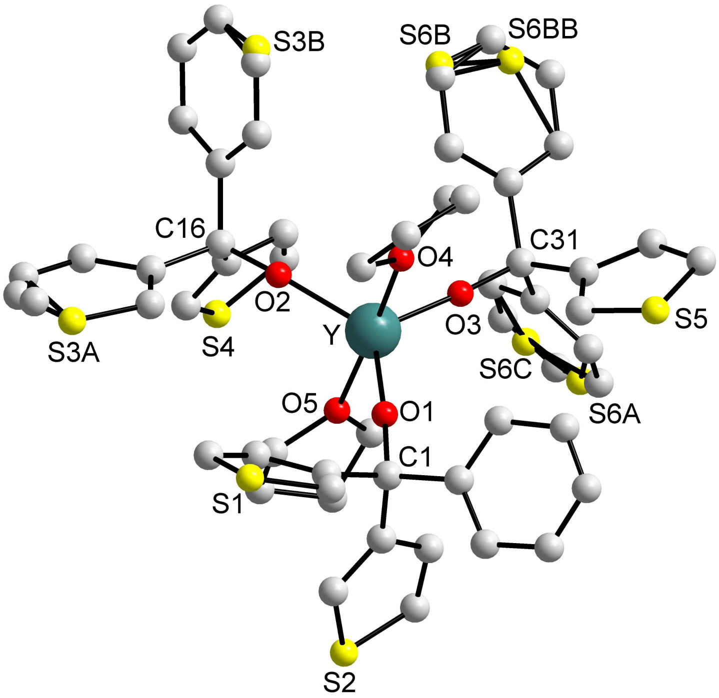


Figure 2.42. Molecular structure of {Y[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_2$} • ½ toluene (<u>38</u>). Toluene lattice molecule and hydrogen atoms are omitted for more clarity. The sulphur atom S(3) are found in two split–positions [S(3A) and S(3B)] and the thienyl and phenyl groups are found in two split–positions [S(6A), S(6B), S(6BB) and S(6C)].

The molecular structure exhibits a five–coordinated yttrium in a distorted trigonal–bipyramidal coordination sphere: three carbinolato ligands are found in equatorial positions and two tetrahydrofuran molecules in axial positions. Due to the packing effect, a toluene molecule is included in the structure lattice. The Y–O bond lengths of the phenylbis(3–thienyl)methoxido ligands range from 2.070(3) to 2.112(3) Å which is in good agreement with similar distances found for the other yttrium alkoxides (see above). The Y–O bond length of the tetrahydrofuran molecules [2.414(3) and 2.364(3) Å] are slightly longer than those found for {Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$} • toluene (**<u>16b</u>**) [2.349(2) and 2.348(2) Å] and{Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (**<u>26</u>**) [2.326(6) and 2.336(6) Å]. The three methoxido oxygen atoms around the yttrium centre are coplanar with ∑ O–Y–O = 359.7(1)° and the O(5)–Y–O(4) angle value is 172.6(1)°.

1.7 Reactivity of HO–C($C_{16}H_{13}S$) (**8**) towards Yttrium Silyl Amide in Pyridine

After concentration of the solution, a white solid precipitated. Unfortunately, no crystals could be obtained. The H,H–COSY spectrum of this solid recorded in $CDCl_3$ shows five broad signals. The first at 7.2 ppm integrating for 33H is attributed to the protons of the phenyl groups and to the 5–H protons of the thienyl units. This signal has a correlation with this at 6.9 ppm which integrates for 6H corresponding so to the 4–H and 2–H of the thienyl groups. The three other signals at 8.4, 7.6 and 7.2 ppm are due to the protons of the pyridine adducts. The broadening of the signals could be due to a dynamic phenomenon of the organic ligands.
Therefore we suggest that $Y[N(SiMe_3)_2]_3$ and HO–C($C_{16}H_{13}S$) (**8**) react in the same way as $Y[N(SiMe_3)_2]_3$ with **2** and **4** to form $Y[OC(C_{16}H_{13}S_2)](py)_2$ (**42**). Three –OC($C_{16}H_{13}S$) groups are ligated to the yttrium metal centre. In analogy with the other yttrium compounds $Y[OC(C_4H_3S)_3]_3(py)_2$ (**17a**), $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (**17b**), $\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (**27**) and $\{Y[OC(C_{17}H_{15}S)]_3(py)_2\}$ • toluene (**34**), the two pyridine molecules occupy probably the two axial positions. Moreover, this composition is confirmed by the results of elemental analyses. All experimental values match well with the calculated ones: 70.88 % for the carbon (value calculated: 70.25 %) and 5.19 % for the hydrogen (value calculated: 4.70 %). Therefore we propose a mononuclear five−coordinated structure for $Y[OC(C_{16}H_{13}S)](py)_2$ (**42**) as illustrated in Figure 2.43. This compound was obtained in a yield of 75 %.

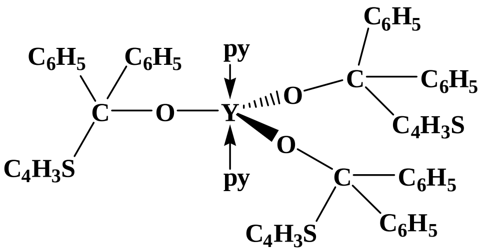


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Figure 2.43. $Y[OC(C_{16}H_{13}S)](py)_2$ (42)

1.8 Conclusion

Single−crystal X−ray diffraction studies have performed on five new yttrium alkoxides ligated with tetrahydrofuran (**9**, **16a–b**, **26**, **33** and **38**), and on the three pyridine adducts **17a–b**, **27** and **34**. The determination of their molecular structure confirms the mononuclear nature of these novel compounds. For each product, a trigonal bipyramidal geometry has been observed around the yttrium metal centre: they are surrounded by three methoxido ligands in equatorial positions and two solvent molecules occupying the axial positions. Due to packing effects, a toluene molecule can be included in the structure lattice, except of **16** and **17**, which can be found with or without toluene. In Table 2.48, their crystal systems, space groups and unit cell dimensions are reported for comparison. The strong similarity of **16a** / **17a** and **16b** / **17b** shows the minor influence of the axial coordinated donors, whereas solvent incorporation gives a tremendous change in solid state packing from an acentric to a centrosymmetric arrangement. This is also true for the examples **26** , **27** and **33**, **34**. The additional methyl group at the thienyl-ring has no influence **27**, **34** as the quantity of toluene (2 molecules) is constant. This is also the reason for the conspicuous difference of the a-axis at **26** (one toluene) and **33** (three toluene). Only major changes of the Y−compound (e.g. **9**) have an effect of the unit cell dimensions. This quality is supported by the massive ring disorder behaviour of the ligands recognised for all crystallised products.

Compounds	**Crystal System**	**Space Group**	**Z**	**a [Å]**	**b [Å]**	**c [Å]**	**α [°]**	**β [°]**	**γ [°]**
9	Monoclinic	P2(1)/n	4	12.525(2)	15.182(2)	41.606(5)	90	97.48(1)	90
16a	Monoclinic	P2(1)/c	4	20.889(4)	14.421(3)	16.190(3)	90	94.75(3)	90
16b	Monoclinic	P2(1)	2	12.724(1)	15.930(1)	14.327(1)	90	114.40(1)	90
17a	Monoclinic	P2(1)/c	4	20.802(4)	14.573(3)	16.041(3)	90	93.55(3)	90
17b	Monoclinic	P2(1)	2	12.449(1)	16.232(1)	14.186(1)	90	112.31(1)	90
26	Monoclinic	P2(1)/c	4	14.678(2)	13.760(2)	27.649(1)	90	94.49(6)	90
27	Triclinic	P–1	2	12.676(1)	14.042(1)	18.164(1)	97.75(1)	95.19(1)	116.59(1)
33	Monoclinic	P2(1)/c	4	18.687(4)	14.686(3	28.052(6)	90	93.56(3)	90
34	Triclinic	P–1	2	12.627(1)	14.478(2)	18.270(2)	97.84(1)	95.21(1)	113.65(1)
38	Monoclinic	P2(1)/n	4	13.598(3)	16.935(3)	23.892(5)	90	102.22(3)	90

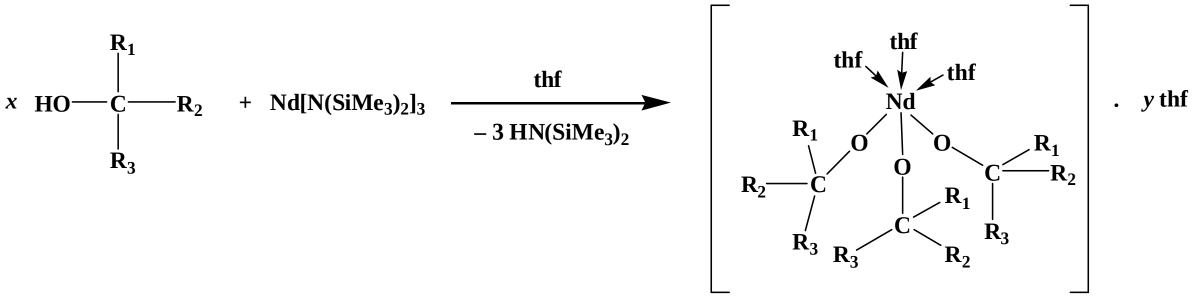
Table 2.48. Crystal system, space groups and unit cell dimensions of the yttrium alkoxides.

Two products have been isolated as solid: they have been identified as $Y[OC(C_{14}H_{11}S_2)](py)_2$ (**39**) and $Y[OC(C_{16}H_{13}S)](py)_2$ (**42**) in accordance with their ^{1}H–NMR spectra, elemental analyses and by analogy with the previous structural results. The reactions between the other carbinols **3** and **6** and the yttrium silyl amide, either in tetrahydrofuran or pyridine as solvent, did not allow an isolation of the molecules as single crystals or as solids. Moreover, the same reaction with the carbinol **8** in tetrahydrofuran, or **1** in pyridine, did not form the desired compounds. We cannot exclude that in these reactions the desired yttrium alkoxides were formed; an unambiguous characterisation of the resulting compounds was however hampered by their reluctance to crystallize. Mass spectra studies should give an answer to this open question.

2 Synthesis and Crystal Structure Determination of Neodymium Methoxides Containing Thienyl Substituents

2.1 General Synthesis

The neodymium alkoxides were synthesized by the reaction between the silyl amide {Nd[N(SiMe$_3$)$_2$]$_3$} and the carbinol in tetrahydrofuran for two days at room temperature (Equation 2.26). The compounds could be isolated in crystalline form or as solid.



Equation 2.26. General route leading to the neodymium alkoxides.

2.2 Reactivity of HO–C(C$_8$H$_5$S$_2$)$_3$(1) towards Neodymium Silyl Amide

The neodymium alkoxide was synthesized by the reaction between one equivalent of the silyl amide {Nd[N(SiMe$_3$)$_2$]$_3$} and three equivalents of the carbinol in tetrahydrofuran for two days at room temperature. The dark green solution was concentrated and placed at 5°C. Few days later, green crystals of {Nd[OC(C$_8$H$_5$S$_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**10**) were obtained in a yield of 50 %. The variable–temperature ^{1}H–NMR spectra of this compound, recorded in CDCl$_3$ exhibit only broad peaks in the temperature range between 20−60°C. This is probably due to the paramagnetic character of the neodymium metal centre.[52] At room temperature, the spectrum displays a multiplet for the protons of the dithienyl units centred at 7.1 ppm. Four broad signals at 3.7, 1.8, 1.2 and 0.8 ppm are also present and correspond to the different protons of the tetrahydrofuran molecules, with or without bonding to neodymium.

2.2.1 Crystal Structure Determination of $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf (10)

Green crystals of $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf (**10**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P–1 in a triclinic crystal system. The R–value is 4.77 %. In Table 2.49 are reported the crystal and the structure refinement data for **10**. Table 2.50 presents some selected bond lengths and angles of interest.

Identification code	sh2385
Empirical formula	$C_{103}H_{101}NdO_{10}S_{18}$
Formula weight	2220.16
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P–1
Unit cell dimensions	a = 13.906(1) Å α= 90.94(1)°. b = 17.797(1) Å β= 102.88(1)°. c = 20.701(1) Å γ = 93.13(1)°.
Volume	4986.5(2) $Å^3$
Z	2
Density (calculated)	1.479 Mg/m^3
Absorption coefficient	0.957 mm^{-1}
F(000)	2294
Crystal size	0.3 x 0.6 x 0.7 mm^3
Theta range for data collection	1.01 to 19.61°.
Index ranges	–13<=h<=13, –16<=k<=16, –19<=l<=19
Reflections collected	46816
Independent reflections	8779 [R(int) = 0.0331]
Completeness to theta = 19.61°	99.9 %
Absorption correction	Semi–empirical from equivalents
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	8779 / 50 / 1164
Goodness–of–fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1201
R indices (all data)	R1 = 0.0589, wR2 = 0.1308
Largest diff. peak and hole	1.574 and –0.804 e.$Å^{-3}$

Table 2.49. Crystal data and structure refinement for $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf (10).

Nd–O(1)	2.173(5)	O(1)–Nd–O(3)	98.3(2)
Nd–O(2)	2.203(5)	O(1)–Nd–O(2)	102.0(2)
Nd–O(3)	2.202(5)	O(3)–Nd–O(2)	102.0(2)
Nd–O(4)	2.563(5)	O(3)–Nd–O(6)	87.6(2)
Nd–O(5)	2.558(5)	O(2)–Nd–O(5)	89.1(2)
Nd–O(6)	2.550(5)	O(5)–Nd–O(4)	85.4(2)
O(1)–C(1)	1.380(9)	O(6)–Nd–O(4)	71.6(2)
O(2)–C(26)	1.401(9)	O(6)–Nd–O(5)	73.2(2)
		C(1)–O(1)–Nd	176.1(5)
		C(26)–O(2)–Nd	174.9(4)
		C(51)–O(3)–Nd	161.1(4)

Table 2.50. Selected bond lengths [Å] and angles [°] for {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (10).

2.2.1.1 Discussion of the Molecular Structure of {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (10)

A single crystal X−ray analysis of {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**10**) was carried out for unequivocal identification of the structure, which is shown in Figure 2.44.

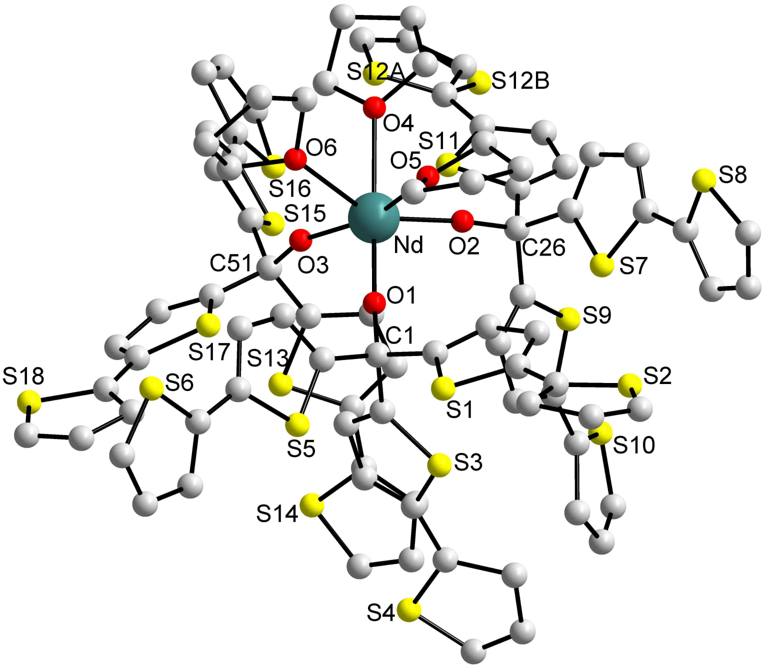


Figure 2.44. Molecular structure of {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (10). The four tetrahydrofuran lattice molecules are omitted for more clarity.

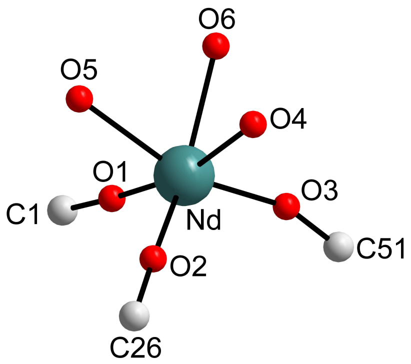


Figure 2.45. Environment around the neodymium metal centre of the compound 10.

The structure determination reveals the mononuclear nature of **10** with an approximately octahedral geometry around the neodymium atom: this metal centre is surrounded by three (2,2’−bithienyl–5–yl)methoxido ligands and three tetrahydrofuran molecules in a facial arrangement (Figure 2.45). Four additional molecules of tetrahydrofuran are situated in the crystal with no interaction with the molecule. Obviously, the neodymium(III) is wrapped up by the ligands, which leads to a quite low coordination number. Moreover, the bulky ligands and their high electronic density prevent to the formation of polymer. The overall structure of **10** is similar to that of $Sm(O–2,6–i–Pr_2C_6H_3)_3(thf)_3$ [53] and of $Sm(O–2,4,6–Me_3C_6H_2)_3(thf)_3$.[54] The $[(C_8H_5S_2)_3C]O–Nd–O[C(C_8H_5S_2)_3]$ angles, which average 100.8(2)°, are more acute than those for $Sm(O–2,4,6–Me_3C_6H_2)_3(thf)_3$ [103.39(13)°].[54] But, the O(thf)–Nd–O(thf) bond angles [76.7(2)°] are in accordance with those found for $Sm(O–2,4,6–Me_3C_6H_2)_3(thf)_3$ [77.5(1)°].[54] The $Nd–O[C(C_8H_5S_2)_3]$ distances [2.193(5) Å] are in good agreement with those obtained for $Nd_2(O–2,6–i–Pr_2C_6H_3)_6$ [2.211(8) Å][13, 52] a dinuclear compound possessing bridging alkoxide ligands. The Nd–O(thf) bond lengths [2.557(5) Å] are shorter than those found for $[Nd_3(\mu_3–OtBu)_2(\mu_2–OtBu)_3(OtBu)_4(thf)_2]$ [2.661(4) Å].[10] The $O–C(C_8H_5S_2)_3$ distances, which average 1.392(2) Å, are similar with these observed for $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**9**) [1.390(9) Å], and are shorter than the value obtained for the alcohol **1** [1.440(8) Å]: this shortening is due to the additional charge on the oxygen (δ^-) of the dithienylmethoxides and the metal centre (δ^+). The $(C_8H_5S_2)_3C–O–Nd$ angles are included between 161.1(4)° and 176.1(5)° are also in the range of those found for $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**9**) [161.4(2)° to 174.2(8)°].

2.3 Reactivity of $HO{-}C(C_4H_3S)_3$ (2) towards Neodymium Silyl Amide

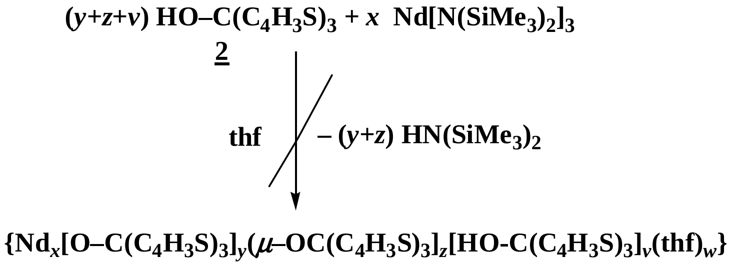
The compound $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**) was synthesized by the reaction between one equivalent of the silyl amide $\{Nd[N(SiMe_3)_2]_3\}$ and three equivalents of the carbinol in tetrahydrofuran for two days at room temperature. The reaction mixture was placed at 5°C, and blue crystals of $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**) were grown few days later, in a yield of 15 %. The variable–temperature ^1H−NMR spectra of $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**) recorded in $CDCl_3$ exhibits only broad peaks in the range of 20°C to 60°C: this is again probably due to the paramagnetic character of the neodymium metal centre. At room temperature, the spectrum shows a broad signal at 7.5 ppm assigned to the protons of the thienyl ligands and three further broad resonances at 3.4, 2.7 and 0.8 ppm. These latter signals reveal the presence of methylene protons of tetrahydrofuran entities, either coordinated or not coordinated to the metal centre. Electronic ionisation (EI) and fast atom bombardment (FAB) mass spectrometric techniques have been used to characterise this compound. This technique is appropriate for metal−containing inorganic compounds. Two quite intense peaks are observed at *m/z* = 960 and 1180, corresponding to $[M{-}CH_3{-}(thf)_3{-}thf]^+$ and $[M{-}thf]^{\bullet+}$, respectively.

With the aim of synthesizing a heteroleptic mixed amide–alkoxide compound (Equation 2.27), $Nd[N(SiMe_3)_2]_3$ was treated with ligand **2** in a 1:1 ratio at ambient temperature in tetrahydrofuran as solvent. However, we succeeded only in isolating the octahedrally coordinated neodymium thf–adduct $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**) in form of moisture–sensitive blue crystals, albeit in low yield (16 %). Surprisingly, decrease the metal–to–ligand ratio to 1:1 did not improve the yield.

$$\underset{\underline{\mathbf{2}}}{\mathbf{HO{-}C(C_4H_3S)_3}} + \mathbf{Nd[N(SiMe_3)_2]_3} \;\cancel{\xrightarrow[-\,\mathbf{HN(SiMe_3)_2}]{\mathbf{thf}}}\; \mathbf{Nd[OC(C_4H_3S)_3][N(SiMe_3)_2]_2(thf)_x}$$

Equation 2.27. Tentative route to form a heteroleptic mixed–alkoxide compound.

With the objective to synthesize a polynuclear product (Equation 2.28), $Nd[N(SiMe_3)_2]_3$ was reacted with an excess of the carbinol **2** (6 equivalents), in tetrahydrofuran during two days. Unfortunately, only the $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**) product was obtained. Nevertheless, the yield was significantly optimized to 73 %. This finding clearly demonstrates the strong influence of the ligand concentration on the overall yield, which is important in shifting the equilibrium to the thienylmethoxide side.



$$(y+z+v)\ \mathrm{HO{-}C(C_4H_3S)_3} + x\ \mathrm{Nd[N(SiMe_3)_2]_3}\ \xrightarrow[\text{thf}]{-\,(y+z)\ \mathrm{HN(SiMe_3)_2}}\ \{\mathrm{Nd}_x[\mathrm{O{-}C(C_4H_3S)_3}]_y(\mu\mathrm{{-}OC(C_4H_3S)_3})_z[\mathrm{HO{-}C(C_4H_3S)_3}]_v(\mathrm{thf})_w\}$$

Equation 2.28. Route to form a polynuclear compound.

2.3.1 Crystal Structure Determination of $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**)

Blue crystals of $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**) were obtained from a tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group R3 in a rhombohedral crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 4.46 %. In Table 2.51 are reported the crystal and the structure refinement data for **18**. Table 2.52 are presents some selected bond lengths and angles of interest.

Identification code	sh2390	
Empirical formula	$C_{55}H_{59}NdO_7S_9$	
Formula weight	1264.80	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R3	
Unit cell dimensions	a = b = 13.969(1) Å	α = β= 90°.
	c = 24.631(1) Å	γ = 120°.
Volume	4162.3(3) $Å^3$	
Z	3	
Density (calculated)	1.514 Mg/m^3	
Absorption coefficient	1.325 mm^{-1}	
F(000)	1947	
Crystal size	0.3 x 0.5 x 0.55 mm^3	
Theta range for data collection	1.88 to 45.44°.	
Index ranges	–22<=h<=27, –28<=k<=27, –49<=l<=39	

Reflections collected	102475
Independent reflections	14318 [R(int) = 0.0292]
Completeness to theta = 45.44°	100.0 %
Absorption correction	Semi–empirical from equivalents
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	14318 / 1 / 212
Goodness–of–fit on F^2	1.491
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1203
R indices (all data)	R1 = 0.0446, wR2 = 0.1204
Absolute structure parameter	0.009(8)
Largest diff. peak and hole	5.174 and –3.235 e.Å^{-3}

Table 2.51 Crystal data and structure refinement for {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (18).

Nd–O(1)	2.186(1)	O(1)–Nd–O(1)	100.81(6)
Nd–O(2)	2.620(2)	O(1)–Nd–O(2)	92.82(6)
O(1)–C(1)	1.389(2)	O(2)–Nd–O(2)	73.55(6)
		C(1)–O(1)–Nd	169.9(1)

Table 2.52. Selected bond lengths [Å] and angles [°] for {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (18).

2.3.1.1 Discussion of the Molecular Structure of {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (18)

A single crystal X−ray analysis of {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**18**) was carried out for unequivocal identification of the structure depicted in Figure 2.46.

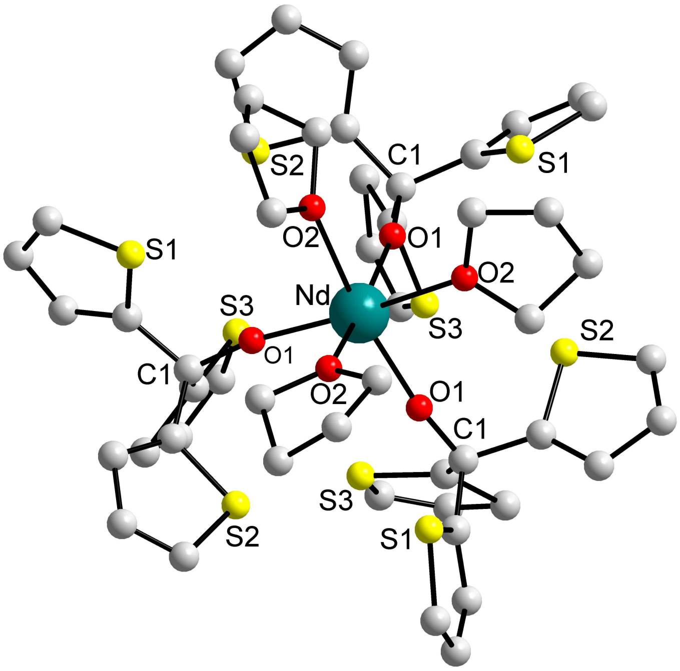


Figure 2.46. Molecular structure of {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (18). Tetrahydrofuran lattice molecule and hydrogen atoms are omitted for more clarity.

The crystal structure exhibits exclusively mononuclear units with a six–coordinated neodymium atom in an octahedral geometry around the metal: three organic ligands and three tetrahydrofuran molecules. The molecule is situated on a threefold axis in the crystal. The facial coordination geometry around the metal is similar to that in {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**10**). One additional molecule of tetrahydrofuran is in the lattice with no apparent interaction with the central molecule. Evidently, neodymium(III) is also wrapped up by the ligand, leading to a quite low coordination number. The Nd–OC(C_4H_3S)$_3$ bond lengths [2.186(1) Å] correspond to these observed for {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**10**) [2.173(5) to 2.203(5) Å]. Nevertheless, the Nd–O(thf) lengths [2.620(2) Å] are longer [2.550(5) to 2.563(5) Å]. The O–C(C_4H_3S)$_3$ distances [1.389(2) Å] are also longer than the value obtained for alcohol **2**. In comparison with compound {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**10**), the angles O(thf)–Nd–OC(C_4H_3S)$_3$ [92.82(6)°] are less acute, the O(thf)–Nd–O(thf) angles are 73.55(6)°, and the [(C_4H_3S)$_3$]CO–Nd–OC[(C_4H_3S)$_3$] and (C_4H_3S)$_3$C–O–Nd angles are 100.81(6)° and 169.9(1)°, respectively. These variations of angles compared to those in {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**10**) could be rationalized by the weaker steric repulsion exerted by the ligand in {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**18**).

2.4 Reactivity of HO–C($C_{14}H_{11}S_2$) (**3**) towards Neodymium Silyl Amide

The neodymium alkoxide was synthesized by the reaction between one equivalent of the silyl amide {Nd[N($SiMe_3$)$_2$]$_3$} and three equivalents of the carbinol **3** in tetrahydrofuran for two days at room temperature. The blue solution was concentrated and placed at 5°C. Few days later, blue crystals of {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (**23**) were obtained in a yield of 60 %. The ^{1}H–NMR spectrum of **23** recorded in $CDCl_3$ exhibits only broad peaks, probably due to the paramagnetic character of the neodymium metal centre. At 7.3 ppm, the broad signal, which integrates for 21H, is attributed to the protons of the phenyl groups and the 5–H of the thienyl units. Another aromatic signal, at 6.9 ppm, integrating for 12H, corresponds to the 4–H and 3–H of the thienyl groups. In accordance with the compounds **10** and **18**, the spectrum displays four broad signals at 3.7, 1.8, 1.2 and 0.8 ppm due to the different protons of the tetrahydrofuran molecules, with or without bonding to neodymium.

2.4.1 Crystal Structure Determination of {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (23)

Blue crystals of {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (**23**) were obtained from a tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group R3 in a rhombohedral crystal system. The R–value is 5.15 %. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. In Table 2.53 are reported the crystal and the structure refinement data for **23**. Table 2.54 are presents some selected bond lengths and angles of interest.

Identification code	sh2595	
Empirical formula	$C_{61}H_{65}NdO_7S_6$	
Formula weight	1246.73	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R3	
Unit cell dimensions	a = b = 14.135(1) Å	α = β = 90°.
	c = 24.897(2) Å	γ = 120°.
Volume	4307.8(3) Å^3	
Z	3	

Density (calculated)	1.442 Mg/m^3
Absorption coefficient	1.174 mm^{-1}
F(000)	1929
Crystal size	0.44 x 0.3 x 0.25 mm^3
Theta range for data collection	1.85 to 28.31°.
Index ranges	–18<=h<=18, –18<=k<=18, –33<=l<=33
Reflections collected	33002
Independent reflections	4775 [R(int) = 0.0378]
Completeness to theta = 28.31°	99.9 %
Absorption correction	Multiscan
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	4775 / 9 / 210
Goodness–of–fit on F^2	1.720
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1372
R indices (all data)	R1 = 0.0515, wR2 = 0.1372
Absolute structure parameter	–0.04(2)
Largest diff. peak and hole	2.182 and –1.327 e.Å^{-3}

Table 2.53. Crystal data and structure refinement for {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (23).

Nd–O(1)	2.184(4)	O(1)–Nd–O(1)	100.0(2)
Nd–O(2)	2.635(4)	O(1)–Nd–O(2)	93.2(2)
O(1)–C(1)	1.388(6)	O(2)–Nd–O(2)	73.6(2)
		C(1)–O(1)–Nd	168.9(4)

Table 2.54. Selected bond lengths [Å] and angles [°] for {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (23).

2.4.1.1 Discussion of the Molecular Structure of {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (23)

A single crystal X−ray analysis of {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (**23**) was carried out for unequivocal identification of the structure depicted in Figure 2.47.

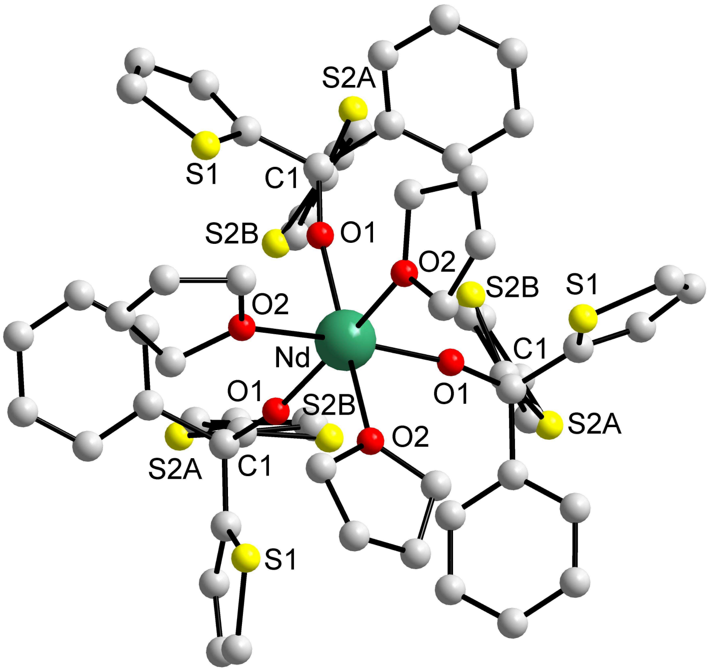


Figure 2.47. Molecular structure of {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (<u>23</u>). Tetrahydrofuran lattice molecule and hydrogen atoms are omitted for more clarity. The sulphur atoms S(2) are found in two split–positions [S(2A) and S(2B)].

The crystal structure of <u>**23**</u> displays mononuclear units. The coordination sphere around the neodymium atom is octahedral: it includes three phenylbis(2−thienyl)methoxido ligands and three tetrahydrofuran molecules. The molecule is situated on a threefold axis in the crystal. One additional molecule of tetrahydrofuran is in the lattice with no interaction with the central molecule. Evidently, neodymium(III) is also wrapped up by the ligand, leading to a quite low coordination number. The Nd–OC($C_{14}H_{11}S_2$), and Nd–O(thf) distances are 2.184(4) and 2.635(4) Å, respectively. These distances are very similar to those found in the neodymium analogue {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (<u>**18**</u>). The ($C_{14}H_{11}S_2$)CO–Nd–OC($C_{14}H_{11}S_2$), ($C_{14}H_{11}S_2$)O–Nd–O(thf) and O(thf)–Nd–O(thf) bond angles [100.0(2), 93.2(2) and 73.6(2)°, respectively] are in the range of those observed for {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (<u>**18**</u>). The C(1)–O(1)–Nd angles amount to 168.9(4)°.

2.5 Reactivity of HO–C($C_{16}H_{13}S$) (**4**) towards Neodymium Silyl Amide

{Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**28**) was synthesized by the reaction between one equivalent of silyl amide {Nd[N(SiMe$_3$)$_2$]$_3$} and three equivalents of diphenyl(2–thienyl)methanol (**4**) in tetrahydrofuran during two days at room temperature. The solution was concentrated and placed at 5°C. Few days later, blue crystals of the neodymium alkoxides were obtained in the yield of 34%. As noticed for the other neodymium alkoxides (see above), the ^{1}H–NMR spectrum of **28**, displays broad signals at room temperature in $CDCl_3$. Three aromatic signals at 7.3, 6.9 and 6.7 ppm are present. The first one, which integrates for 33H, corresponds to the 5–H of the thienyl units and to the protons of the six phenyl groups. The second and the third ones, integrating for 3H, are attributed to the 4–H and 3–H of the thienyl groups, respectively. The remaining other signals at 3.6, 1.7, 1.2 and 0.8 ppm are assigned to the different protons of the tetrahydrofuran molecules ligated or not to the metal centre.

2.5.1 Crystal Structure Determination of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**28**)

Blue crystals of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**28**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P31c in a trigonal crystal system. The R–value is 5.95 %. In Table 2.55 are reported the crystal and the structure refinement data for **28**. Table 2.56 are presents some selected bond lengths and angles of interest.

Identification code	sh2591	
Empirical formula	$C_{64}H_{86}NdO_7S_3$	
Formula weight	1207.75	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = b = 14.602(1) Å	α = β= 90°.
	c = 15.893(1) Å	γ = 120°.
Volume	2934.9(3) Å^3	
Z	2	
Density (calculated)	1.367 Mg/m^3	
Absorption coefficient	1.044 mm^{-1}	
F(000)	1268	

Crystal size	0.31 x 0.28 x 0.18 mm^3
Theta range for data collection	1.61 to 27.18°.
Index ranges	–18<=h<=18, –18<=k<=18, –20<=l<=20
Reflections collected	59099
Independent reflections	4365 [R(int) = 0.0546]
Completeness to theta = 27.18°	100.0 %
Absorption correction	Multiscan
Max. and min. transmission	0.8377 and 0.7387
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	4365 / 1 / 174
Goodness–of–fit on F^2	2.049
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1646
R indices (all data)	R1 = 0.0636, wR2 = 0.1687
Absolute structure parameter	0.03(4)
Largest diff. peak and hole	1.012 and –0.755 e.Å^{-3}

Table 2.55. Crystal data and structure refinement for {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (28).

Nd–O(1)	2.178(4)	O(1)–Nd–O(1)	102.1(2)
Nd–O(2)	2.595(6)	O(1)–Nd–O(2)	90.4(2)
O(1)–C(1)	1.397(7)	O(2)–Nd–O(2)	76.9(2)
		C(1)–O(1)–Nd	173.9(4)

Table 2.56. Selected bond lengths [Å] and angles [°] for {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (28).

2.5.1.1 Discussion of the Molecular Structure of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (28)

A single−crystal X−ray analysis of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**28**) was carried out for unequivocal identification of the structure illustrated in Figure 2.48. Unfortunately, the differentiation between the thienyl and phenyl groups is difficult. This may be attributed to the fact that the crystallization process has taken place with a disordered arrangement of the thienyl and phenyl groups.

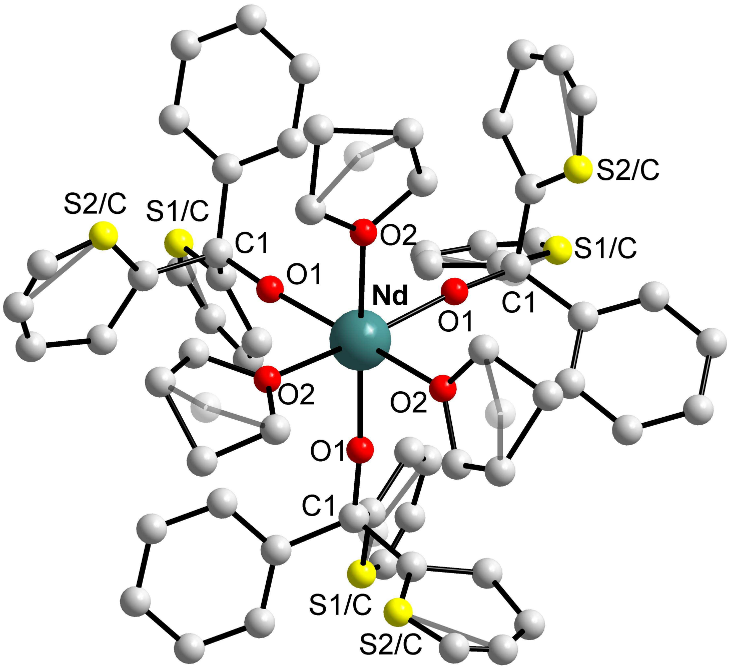
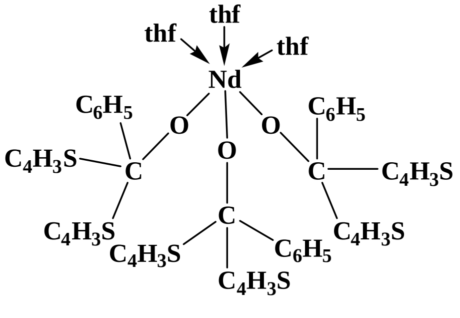


Figure 2.48. Molecular structure of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (28). Tetrahydrofuran lattice molecule is omitted for more clarity. The thienyl and phenyl units are found in two split–positions [S(1) and S(2)].

The facial coordination sphere around the metal centre is similar to that of the other neodymium methoxides containing thienyl functions. The neodymium is surrounded by three diphenyl(2–thienyl)methoxido ligands and three facially arranged tetrahydrofuran molecules. A tetrahydrofuran lattice molecule is also present in the crystal without any apparent interaction with the central molecule. Once again, neodymium(III) is wrapped up by the ligand. Moreover, the neodymium molecule is situated on a threefold axis in the crystal. The Nd–OC($C_{16}H_{13}S$) bond lengths are [2.178(4) Å] are in the range of those determined for {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**18**) [2.186(1) Å] and {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (**23**) [2.184(4) Å]. The Nd–O(thf) distances [2.595(6) Å] are shorter than these found for {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**18**) [2.620(2) Å] and {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (**23**) [2.635(4) Å]. In comparison with {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**18**) and {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (**23**), the angles O(thf)–Nd–C($C_{16}H_{13}S$) [90.4(2)°], O(thf)–Nd–O(thf) [76.9(2)°] are more acute. This widening of the Nd−O angles could be explained by the variations of steric hindrance exerted by ligands, which possess in this case only one thienyl unit, and two phenyl groups.

2.6 Reactivity of HO–C($C_{14}H_{11}S_2$) (7) towards Neodymium Silyl Amide

Three equivalents of phenylbis(3−thienyl)methanol **7** were reacted with one equivalent of the neodymium silyl amide in tetrahydrofuran for two days at room temperature. The blue solution was concentrated and placed at 5°C. Some weeks later, a blue solid precipitated. It was filtered and washed with thf. Unfortunately, no single crystals of this product could be grown. The H,H–COSY spectrum, recorded at 298 K in $CDCl_3$, displays five broad signals. This broadening is probably due to the paramagnetic character of the neodymium(III). The first aromatic signal, at 7.2 ppm, integrating for 21H, is attributed to the protons of the phenyl groups and the 5–H of the thienyl units. The second aromatic signal, at 6.9 ppm which integrates for 12H, and correlating with this at 7.2 ppm, corresponds to the 2–H and 4–H of the thienyl units. The two other signals at 3.7 and 1.8 ppm, each integrating for 12H, show the presence of tetrahydrofuran molecules. Based on these NMR data, we suppose that the carbinol **7** reacts with the neodymium silyl amide in the same manner as the organic ligands **1** to **4**, providing $Nd[OC(C_{14}H_{11}S_2)]_3(thf)_3$ (**40**). A tentative structural proposal is illustrated in Figure 2.51. Furthermore, the elemental analysis and the neodymium titration support the composition of compound **40**, which was obtained in a yield of 26 %. Indeed, 56.93 % of carbon, 4.80 % of hydrogen and 12.43 % of neodymium found are in good accordance with the calculated values: 58.31, 4.85 and 12.29 %, respectively.



40

Figure 2.49. $Nd[OC(C_{14}H_{11}S_2)]_3(thf)_3$ (**40**).

2.7 Reactivity of HO–C($C_{16}H_{13}S$) (8) towards Neodymium Silyl Amide

The neodymium alkoxide {$Nd[OC(C_{16}H_{13}S)]_3(thf)_3$} • thf (**43**) was synthesized by the reaction between one equivalent of the silyl amide {$Nd[N(SiMe_3)_2]_3$} and three equivalents of the carbinol **8** in tetrahydrofuran during two days at room temperature. The blue solution was concentrated and placed at 5°C. Few days later, blue crystals of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**43**) were grown in a yield of 26 %. The ^{1}H–NMR spectrum of **43**, recorded at 298 K in $CDCl_3$, shows only broad signals probably due to the paramagnetic character of the neodymium(III) metal centre. It reveals, at 6.9 ppm, a signal integrating for 33H assigned to the protons 5–H of the thienyl units and the protons of the phenyl groups. At 6.9 ppm, another broad signal which integrates for 6H, corresponds to the 2–H and 4–H of the thienyl moieties. Three further broad resonances at 3.6, 2.7, 1.7 and 1.2 ppm, indicate the presence of methylene protons of tetrahydrofuran entities coordinated or not to the metal centre.

2.7.1 Crystal Structure Determination of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (43)

Blue crystals of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**43**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P31c in a trigonal crystal system. The R–value is 4.63 %. In Table 2.57 are reported the crystal and the structure refinement data for **43**. Table 2.58 presents some selected bond lengths and angles of interest.

Identification code	sh2698	
Empirical formula	$C_{67}H_{71}NdO_7S_3$	
Formula weight	1228.66	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = b = 14.566(1) Å	α = β = 90°.
	c = 15.933(1) Å	γ = 120°.
Volume	2927.9(2) Å^3	
Z	2	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	1.048 mm^{-1}	
F(000)	1274	
Crystal size	0.49 x 0.43 x 0.20 mm^3	
Theta range for data collection	1.61 to 38.88°.	
Index ranges	–25<=h<=25, –25<=k<=25, –28<=l<=28	
Reflections collected	142021	
Independent reflections	11239 [R(int) = 0.0313]	
Completeness to theta = 38.88°	99.7 %	
Absorption correction	Multiscan	

Max. and min. transmission	0.8178 and 0.6267
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	11239 / 1 / 225
Goodness–of–fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1254
R indices (all data)	R1 = 0.0521, wR2 = 0.1321
Absolute structure parameter	0.01(2)
Largest diff. peak and hole	1.214 and –0.699 e.Å^{-3}

Table 2.57. Crystal data and structure refinement for {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (43).

Nd–O(1)	2.181(2)	O(1)–Nd–O(1)	101.57(7)
Nd–O(2)	2.601(2)	O(1)–Nd–O(2)	91.17(9)
O(1)–C(1)	1.393(3)	O(2)–Nd–O(2)	76.5(1)
		C(1)–O(1)–Nd	174.1(2)

Table 2.58. Selected bond lengths [Å] and angles [°] for {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (43).

2.7.1.1 Discussion of the Molecular Structure of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (43)

A single crystal X−ray analysis of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**43**) was carried out for unequivocal identification of the structure shown in Figure 2.50. Once again, the differentiation between the thienyl and phenyl groups is difficult. This may be attributed to the fact that the crystallization process has taken place with a disordered arrangement of the thienyl and phenyl groups.

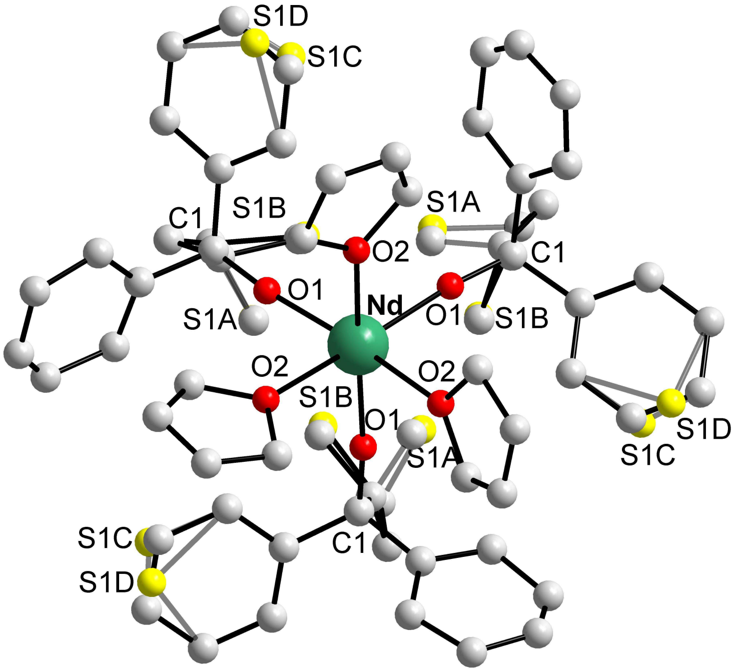


Figure 2.50. Molecular structure of {Nd[OC($C_{16}H_{13}$S)]$_3$(thf)$_3$} • thf (<u>43</u>). Tetrahydrofuran lattice molecule is omitted for more clarity. The thienyl and phenyl units are found in two split–positions [S(1A), S(1B), S(1C) and S(1D)].

The crystal structure reveals, again, a mononuclear compound with an approximately octahedral geometry around the neodymium metal centre. The lanthanide is surrounded by three diphenyl(3−thienyl)methoxido ligands and by three tetrahydrofuran molecules in a facial arrangement. A solvent molecule is also present in the crystal cell with no interaction with the molecule. Once again, the neodymium(III) is wrapped up by the ligand leading to a quite low coordination number. Most probably, the bulkiness of the ligands and their high electronic density prevent the formation of a polynuclear product. The molecule is situated in a threefold axis in the crystal. The Nd–OC($C_{16}H_{13}$S) and Nd–O(thf) bond lengths are 2.1808(18) and 2.601(2)Å, respectively. The ($C_{16}H_{13}$S)CO–Nd–OC($C_{16}H_{13}$S), ($C_{16}H_{13}$S)CO–Nd–O(thf) and O(thf)–Nd–O(thf) angles values of 101.57(7), 91.17(9) and 76.5(1)° are in the range of these found for the other neodymium alkoxides containing thienyl substituent(s) (see above).

In comparison with this Nd[OC($C_{16}H_{13}$S)](thf)$_3$} • thf (<u>28</u>) analogue (Table 2.59), which has diphenyl(2−thienyl)methoxido ligands instead of diphenyl(3−thienyl)methoxide ligands, no significant variations of bond lengths and angles values are observed.

	Nd[OC($C_{16}H_{13}S$)](thf)$_3$} • thf (43)	**Nd[OC($C_{16}H_{13}S$)](thf)$_3$} • thf (28)**
Nd–O(1)	2.181(2)	2.178(4)
Nd–O(2)	2.601(2)	2.595(6)
O(1)–C(1)	1.393(3)	1.397(7)
O(1)–Nd–O(1)	101.57(7)	102.2(2)
O(1)–Nd–O(2)	91.17(9)	90.4(2)
O(2)–Nd–O(2)	76.5(1)	76.9(2)
C(1)–O(1)–Nd	174.1(2)	173.9(4)

Table 2.59. Comparison of selected bond lengths [Å] and angle [°] for {Nd[OC($C_{16}H_{13}S$)](thf)$_3$} • thf (43) and for {Nd[OC($C_{16}H_{13}S$)](thf)$_3$} • thf (28).

2.8 Conclusion

Five new neodymium alkoxides have been obtained as single crystals: **10**, **18**, **23**, **28** and **43**. Their crystal structures contain exclusively mononuclear compounds. For each product, an octahedral geometry has been observed around the neodymium metal centre: they are surrounded by three methoxido ligands and three tetrahydrofuran molecules in a facial arrangement. These molecules are situated on a threefold axis in the crystal cell excepted of for **10**. As can be seen in the Table 2.60, the neodymium alkoxides crystallise in three different crystal systems: triclinic for **10**, rhombohedral for **18** and **23**, and trigonal for **28** and **43**. The difference between **10** and the others neodymium analogues might be due to the more important steric hindrance of the organic ligands and the co–crystallisation of four tetrahydrofuran molecules per compounds leading to a different packing.

Compounds	**Crystal System**	**Space Group**	**Z**	**a [Å]**	**b [Å]**	**c [Å]**	**α [°]**	**β [°]**	**γ [°]**
10	Triclinic	P–1	2	13.906(1)	17.797(1)	20.701(1)	90.94(1)	102.88(1)	93.13(1)
18	Rhombohedral	R3	3	13.969(1)	13.969(1)	24.631(1)	90	90	120
23	Rhombohedral	R3	3	14.135(1)	14.135(1)	24.897(2)	90	90	120
28	Trigonal	P31c	2	14.602(1)	14.602(1)	15.893(1)	90	90	120
43	Trigonal	P31c	2	14.566(1)	14.566(1)	15.933(1)	90	90	120

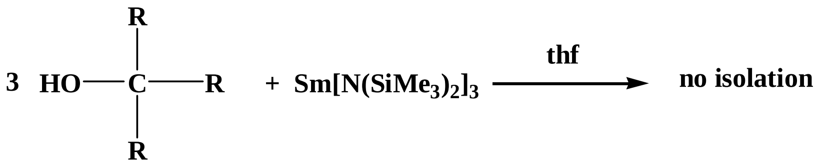
Table 2.60. Crystal system, space groups and unit cell dimensions of the neodymium alkoxides.

One product has been isolated as a blue solid: based on the ^{1}H–NMR spectrum and by analogy with the previous results, it has been identified as $\mathrm{Nd[OC(C_{14}H_{11}S_2)](thf)_3\} \bullet thf}$ (**40**). The reactions between the carbinols **5** and **6** and the neodymium silyl amide did not allow an isolation of the molecules as single crystals or as solids. We cannot rule out that these reactions didn't form the desired neodymium alkoxides; we suppose that it is essentially a problem of crystallization.

3 Synthesis and Crystal Structure Determination of Samarium(III) Methoxides Containing Thienyl Substituents

3.1 Reactivity of HO–C($C_8H_5S_2$)$_3$ (1) and HO–C(C_4H_3S)$_3$ (2) towards Samarium Silyl Amide

To study the influence of the *4f* −metals on the geometry of the molecules, the synthesis of new samarium alkoxides containing thienyl−substituents have been performed. According to the previous results obtained with yttrium and neodymium, the reaction between three equivalents of the carbinols HO–C($C_8H_5S_2$)$_3$ (**1**) or HO–C(C_4H_3S)$_3$ (**2**) and one equivalent of $\mathrm{Sm[N(SiMe_3)_2]_3}$ have been conducted at room temperature with a reaction time of two days (Equation 2.29).



$$3\ \mathrm{HO{-}}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}\mathrm{{-}R} + \mathrm{Sm[N(SiMe_3)_2]_3} \xrightarrow{\mathrm{thf}} \text{no isolation}$$

1, **2**

Equation 2.29. Route studied to lead samarium alkoxides.

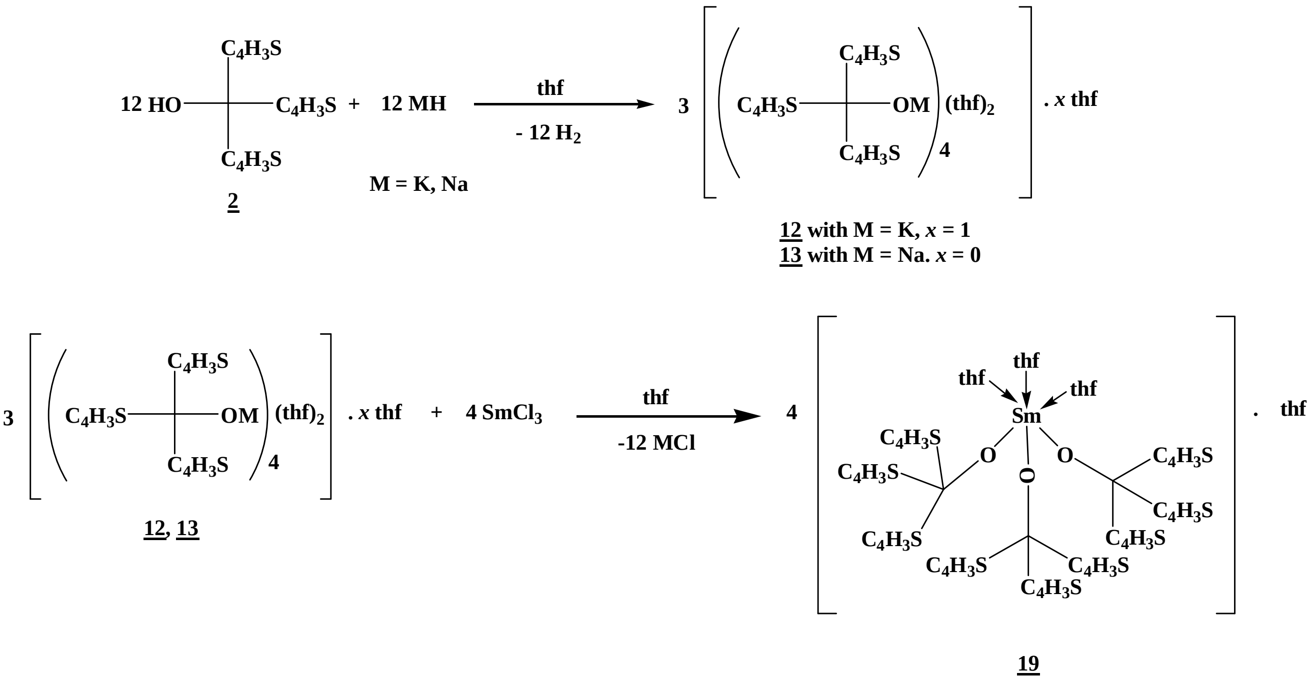
During the reaction of **1** with the silyl amide, a colour change of the mixture from colourless to green, then dark green has been observed. Nevertheless, no isolation of the product as crystals or solids has been obtained. Also in the reaction of **2** with the silyl amide, an isolation of the metal alkoxide failed. Since this route did not allow the isolation of the desired products, we therefore have chosen another alternative synthetic strategy: the salt metathesis reaction.

3.2 Synthesis and Crystal Structure Determination of Samarium(III) Methoxides Containing Thienyl Groups via Salt Metathesis Reactions

As explained above, this synthesis involves two steps. The first step consists in the formation of the corresponding sodium or potassium alcoholates and their subsequent *in situ* reaction with $SmCl_3$.

3.2.1 Synthesis of Samarium(III) Alkoxides with HO–$C(C_4H_3S)_3$ (2) as Star–Shaped Ligand

The star–shaped alcohol **2** reacts with NaH or KH in tetrahydrofuran at room temperature overnight to form the salts$\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf (**12**) or $[NaOC(C_4H_3S)_3]_4(thf)_2$ (**13**), respectively. Their solution was added to a suspension of samarium chloride, the mixture was stirred at room temperature for three days (Equation 2.30). Then, the sodium or potassium chloride was filtered, the pale yellow solution was concentrated and placed at 5°C, and few days later, light−brown crystals of $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**19**) were obtained in a yield of 24 % and 13 %, respectively. The low yields are due to the difficulty to separate KCl.



Equation 2.30. Salt metathesis reaction leading to the samarium alkoxide $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (19).

The ^{1}H–NMR spectrum of **<u>19</u>**, recorded at room temperature in $CDCl_3$, displays broad signals, probably due to the paramagnetic character of the samarium(III). A broad aromatic signal at 7.2 ppm, which integrates for 27H, is attributed to the protons of the thienyl units. The other signals at 3.4, 1.7, 1.2 and 0.9 ppm are assigned to the different protons of the tetrahydrofuran molecules ligated or not to the metal centre.

3.2.1.1 Crystal Structure Determination of $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (19)

Brown−light crystals of $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**<u>19</u>**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group R3 in a rhombohedral crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 4.82 %. In Table 2.61 are reported the crystal and the structure refinement data for **<u>19</u>**. Table 2.62 presents some selected bond lengths and angles of interest.

Identification code	sh2557	
Empirical formula	$C_{55}H_{59}O_7S_9Sm$	
Formula weight	1270.91	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R3	
Unit cell dimensions	a = b = 13.940(1) Å	$\alpha = \beta = 90°$.
	c = 24.700(4) Å	$\gamma = 120°$.
Volume	4156.8(8) Å^3	
Z	3	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	1.450 mm^{-1}	
F(000)	1953	
Crystal size	0.3 x 0.44 x 0.5 mm^3	
Theta range for data collection	1.88 to 34.27°.	
Index ranges	–20<=h<=22, –21<=k<=21, –17<=l<=39	
Reflections collected	26806	
Independent reflections	5629 [R(int) = 0.0350]	
Completeness to theta = 34.27°	99.9 %	
Absorption correction	Multiscan	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	5629 / 1 / 216	
Goodness–of–fit on F^2	1.433	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1311	
R indices (all data)	R1 = 0.0488, wR2 = 0.1318	

Absolute structure parameter	0.02(1)
Largest diff. peak and hole	2.826 and –1.752 e.Å^{-3}

Table 2.61. Crystal data and structure refinement for {Sm[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (19).

Sm–O(1)	2.156(3)	O(1)–Sm–O(1)	101.1(1)
Sm–O(2)	2.594(3)	O(1)–Sm–O(2)	92.5(1)
O(1)–C(1)	1.391(5)	O(2)–Sm–O(2)	73.7(1)
		C(1)–O(1)–Sm	170.53(6)

Table 2.62. Selected bond lengths [Å] and angles [°] for {Sm[OC($C_4H_3S_3$)]$_3$(thf)$_3$} • thf (19).

3.2.1.1.1 Discussion of the Molecular Structure of {Sm[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (19)

A single−crystal X−ray diffraction study of {Sm[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**19**) was carried out for unequivocal identification of the structure which is shown in Figure 2.51.

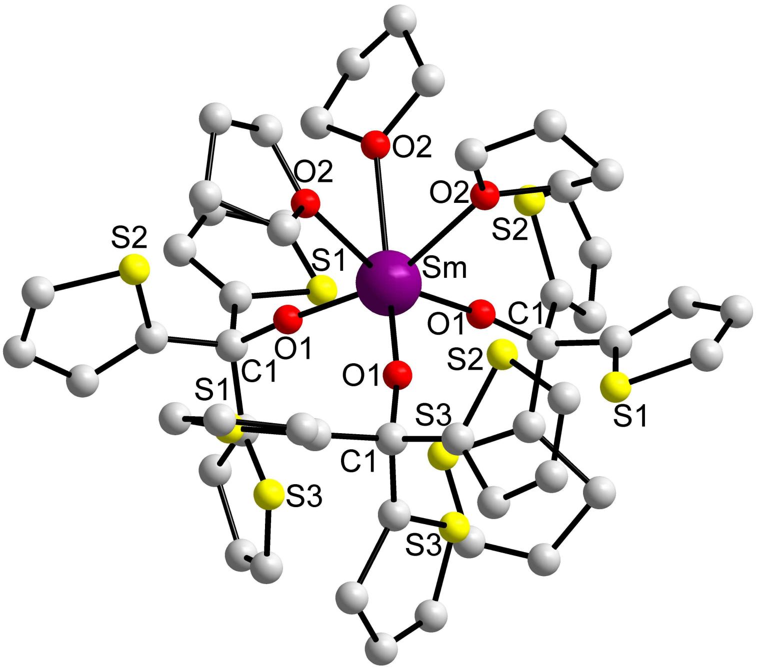
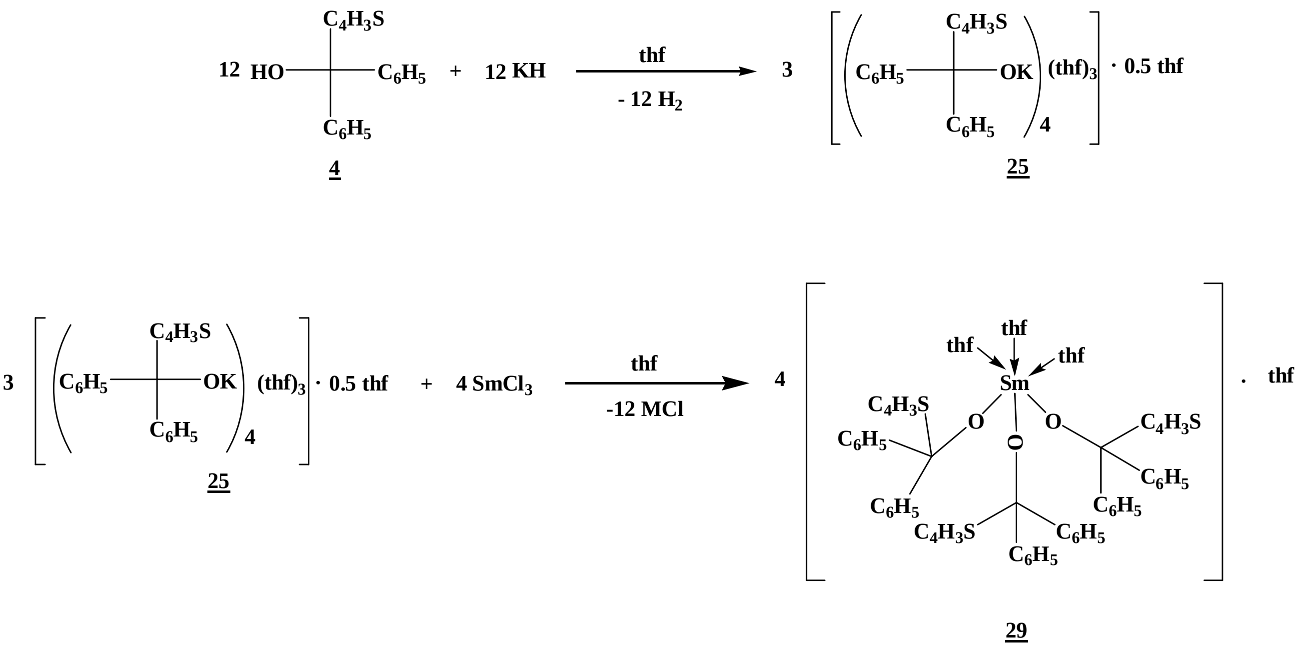


Figure 2.51. Molecular structure of {Sm[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (19). The tetrahydrofuran lattice molecule and hydrogen atoms are omitted for more clarity.

The crystal structure exhibits a six–coordinate mononuclear complex with three (2–thienyl)methoxido ligands and three tetrahydrofuran molecules around the samarium atom, in a facial arrangement. An additional thf molecule is situated in the crystal with no interaction with the molecule. As observed for the neodymium alkoxides (see above), the samarium(III) is wrapped up by the ligands. The molecule is situated on a threefold axis in the crystal. The overall structure of $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**<u>19</u>**) is similar to that in $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**<u>18</u>**), $Sm(O–2,4,6–Me_3C_6H_2)(thf)_3$[54] or $Sm(O–2,6–i–Pr_2C_6H_3)_3(thf)_3$.[53] The geometry about the samarium centre is distorted octahedral, as evidence the $(C_4H_3S)_3CO–Sm–OC(C_4H_3S)_3$ [101.11(2)°] and the O(thf)–Sm–O(thf) angles [73.7(1)°], which are more acute than these found for $Sm(O–2,6–i–Pr_2C_6H_3)_3(thf)_3$ [102.29(6)° and 79.3(1)°, respectively][53] or $Sm(O–2,4,6–Me_3C_6H_2)_3(thf)_3$ [103.4(1) and 77.5(1)°, respectively]:[54] these differences could be explained by the steric hindrance exerted by the ligand. Nevertheless, they are in good accordance with those observed for $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**<u>18</u>**) [100.81(6) and 73.55(6)°, respectively]. The Sm–O–$C(C_4H_3S)_3$ angles of 170.3(6)° are also similar to those in $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**<u>18</u>**) [169.9(1)°] and, in $Sm(O–2,4,6–Me_3C_6H_2)_3(thf)_3$ [170.0(3)°].[54] The Sm–$OC(C_4H_3S)_3$ distances of 2.156(3) Å are similar to those in $Sm(O–2,4,6–Me_3C_6H_2)_3(thf)_3$ [2.160(0) Å] ,[54] $Sm(O–2,6–i–Pr_2C_6H_3)_3(thf)_3$ [2.158(2) Å][53] and $[Sm(OC_6H_2Bu^t_2–2,6–Me–4)_3(thf)]$ • thf [2.152(7) Å].[55] The Sm–O(thf) distances are 2.594(3) Å which are in the range with those observed for $Sm(O–2,6–i–Pr_2C_6H_3)_3(thf)_3$ [2.542(2) Å].[53] These distances are also in accordance with those found for the compound $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**<u>18</u>**). The O(1)–C(1) distances [1.391(5) Å] are similar in $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**<u>18</u>**) [1.389(2) Å] and are shorter than the value obtained for the alcohol **<u>2</u>** [1.440(4) Å]: this shortening is due to the additional charge on the oxygen (δ^-) of the thienylmethoxides and the metal centre (δ^+).

3.2.2 Synthesis of Sm(III) Alkoxides with HO–$C(C_{16}H_{13}S)$ (<u>4</u>) as Star–Shaped Ligand

The star–shaped molecule **<u>4</u>** reacts with KH in tetrahydrofuran at room temperature overnight to form the salt $\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (**<u>25</u>**). This solution was added to a suspension of $SmCl_3$, the mixture was stirred at room temperature for three days (Equation 2.31). Then, the potassium chloride was filtered, the pale yellow solution was concentrated and placed at 5°C. A few days later, white crystals of $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (**<u>29</u>**) were obtained with a low yield of only 13 %.



Equation 2.31. Salt metathesis reaction leading to the samarium alkoxide {Sm[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (29).

The ^{1}H–NMR spectrum of **29**, recorded at room temperature in $CDCl_3$ displays five signals. The first, at 7.3 ppm, is a multiplet, which integrates for 33 H attributed to the protons of the phenyl groups and the 5–H of the thienyl groups. The two other aromatic signals, doublet of doublets at 6.9 and 6.7 ppm (each integrating for 3H), correspond to the 4–H and 3–H of the thienyl groups, respectively. The methylene protons of tetrahydrofuran are present at 3.7 and 1.8 ppm.

3.2.2.1 Crystal Structure Determination of {Sm[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (29)

White crystals of {Sm[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**29**) were obtained from a concentrated tetrahydrofuran solution placed at 5°C. An appropriate crystal was isolated and anchored at a cryo−loop. From the determination and the refinement of the unit cell dimensions arose the space group P31c in a trigonal crystal system. The position of each atom, except the hydrogen atoms, was anisotropically refined. Hydrogen atoms were refined as rigid groups with the attached carbon atoms in ideal positions. The R–value is 4.90 %. In Table 2.63 are reported the crystal and the structure refinement data for **29**. Table 2.64 lists some selected bond lengths and angles of interest.

Identification code	sh2605	
Empirical formula	$C_{67}H_{71}O_7S_3Sm$	
Formula weight	1234.77	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = b = 14.568(1) Å	α = β = 90°.
	c = 15.780(1) Å	γ = 120°.
Volume	2900.4(3) Å^3	
Z	2	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	1.175 mm^{-1}	
F(000)	1278	
Crystal size	0.50 x 0.37 x 0.06 mm^3	
Theta range for data collection	1.61 to 26.41°.	
Index ranges	–18<=h<=17, –17<=k<=18, –19<=l<=19	
Reflections collected	16454	
Independent reflections	3955 [R(int) = 0.0397]	
Completeness to theta = 26.41°	100.0 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.9328 and 0.5895	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	3955 / 1 / 209	
Goodness–of–fit on F^2	1.375	
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1275	
R indices (all data)	R1 = 0.0560, wR2 = 0.1318	
Absolute structure parameter	–0.06(3)	
Largest diff. peak and hole	0.916 and –0.416 e.Å^{-3}	

Table 2.63. Crystal data and structure refinement for $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (29).

Sm–O(1)	2.160(4)	O(1)–Sm–O(1)	102.3(2)
Sm–O(2)	2.552(5)	O(1)–Sm–O(2)	90.8(2)
O(1)–C(1)	1.395(8)	O(2)–Sm–O(2)	76.9(2)
		C(1)–O(1)–Sm	173.3(5)

Table 2.64. Selected bond lengths [Å] and angles [°] for $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (29).

3.2.2.1.1 Discussion of the Molecular Structure of $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (29)

A single crystal X−ray analysis of $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (**29**) was carried out for unequivocal identification of the structure as shown in Figure 2.52. Unfortunately, the differentiation between the thienyl and phenyl groups is difficult. This may be attributed to the fact that the crystallization process has taken place with a disordered arrangement of the thienyl and phenyl groups.

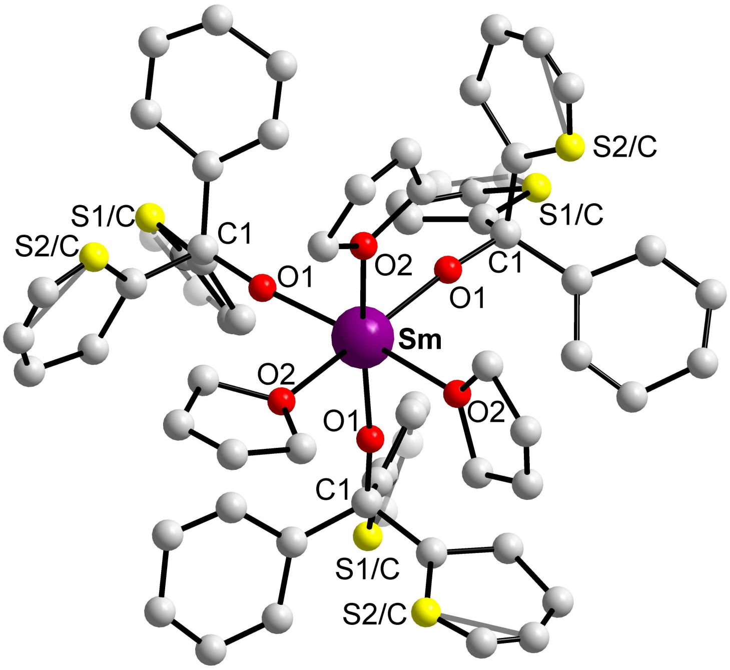


Figure 2.52. Molecular structure of {Sm[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (29). The tetrahydrofuran lattice molecule and hydrogen atoms are omitted for more clarity. Thienyl and phenyls group are found in different positions [S(1) and S(2)].

The facial coordination sphere around the metal centre is similar to that of {Sm[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**19**). The samarium(III) is surrounded by three diphenyl(2–thienyl)methoxido ligands and three tetrahydrofuran molecules, a tetrahydrofuran lattice molecule is also present in the crystal without interaction with the central molecule. Again, here, samarium(III) is wrapped up by the ligand. Moreover, it is situated on a threefold axis in the crystal. The Sm–OC($C_{16}H_{13}S$) and Sm–O(thf) bond lengths are 2.160(4) and 2.552(5) Å. The ($C_{16}H_{13}S$)CO–Sm–OC($C_{16}H_{13}S$), ($C_{16}H_{13}S$)CO–Sm–O(thf) and O(thf)–Sm–O(thf) angles values are 102.3(2), 90.8(2) and 76.9(2)°, respectively. In comparison with its neodymium analogue {Nd[OC($C_{16}H_{13}S$)]$_3$ (thf)$_3$} • thf **(28)** and the {Sm[OC(C_4H_3S)$_3$]$_3$ (thf)$_3$} • thf (**19**) alkoxide (Table 2.65), the M–O bond lengths and the O(1)–Sm–O(1) angles are in the same range. However, some minor variations of the O(1)–M–O(2), O(2)–M–O(2) and C(1)–O(1)–M angles are observed.

	$\{Sm[OC(C_4H_3S)_3]_3$ $(thf)_3\}$ • thf (19)	**$\{Nd[OC(C_{16}H_{13}S)]_3$ $(thf)_3\}$ • thf (28)**	**$\{Sm[OC(C_{16}H_{13}S)]_3$ $(thf)_3\}$ • thf (29)**
M–O(1)	2.156(3)	2.178(4)	2.160(4)
M–O(2)	2.594(3)	2.595(6)	2.552(5)
O(1)–C(1)	1.391(5)	1.397(7)	1.395(8)
O(1)–M–O(1)	101.1(1)	102.2(2)	102.3(2)
O(1)–M–O(2)	92.5(1)	90.4(2)	90.8(2)
O(2)–M–O(2)	73.7(1)	76.9(2)	76.9(2)
C(1)–O(1)–M	170.53(6)	173.9(4)	173.3(5)

Table 2.65. Comparative bond lengths [Å] and angles [°] for $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (19), $\{Nd[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (28) and $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (29).

3.3 Conclusion

Only two structures of mononuclear samarium(III) methoxides containing thienyl substituents were obtained: $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**19**) and $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (**29**). Using the star−shaped molecules **3** and **5** to **8** as reagents, no well−characterized complexes have been isolated. This failure is probably due to the difficulty of filtered off NaCl or KCl and the high moisture sensitive of the products. The molecular structures reveal only mononuclear compounds. The samarium metal centre is surrounded by three carbinolato ligands and three tetrahydrofuran molecules. Note that a further tetrahydrofuran molecule is also present in the cell but with no interaction with the molecule. As presented in the Table 2.66, the samarium alkoxide **19** and this neodymium analogue **18** are isostructural. The same observation has been made for **28** and **29**.

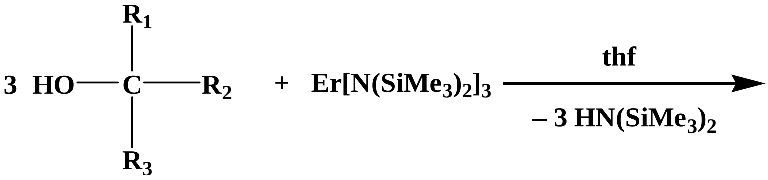
Compounds	Crystal System	Space Group	Z	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
18	Rhombohedral	R3	3	13.969(1)	13.969(1)	24.631(1)	90	90	120
19	Rhombohedral	R3	3	13.940(1)	13.940(1)	24.700(4)	90	90	120
28	Trigonal	P31c	2	14.602(1)	14.602(1)	15.893(1)	90	90	120
29	Trigonal	P31c	2	14.568(1)	14.568(1)	15.780(1)	90	90	120

Table 2.66. Crystal system, space groups and unit cell dimensions of the samarium alkoxides and their neodymium analogues.

4 Synthesis and Crystal Structure Determination of Erbium Methoxides Containing Thienyl Substituents

4.1 General Synthesis

The erbium alkoxides were synthesized by the reaction between one equivalent of the silyl amide {$Er[N(SiMe_3)_2]_3$} and three equivalents of the carbinol in tetrahydrofuran for two days at room temperature (Equation 2.32). All novel compounds could be isolated as crystals.



$$3\ HO-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{C}}-R_2 \quad + \quad Er[N(SiMe_3)_2]_3 \xrightarrow[-\ 3\ HN(SiMe_3)_2]{thf}$$

Equation 2.32. General route leading to the erbium alkoxides.

4.2 Reactivity of $HO–C(C_8H_5S_2)_3$ (**1**) towards Erbium Silyl Amide

The brown solution was concentrated and placed at 5°C. Few days later, brown crystals of $Er[OC(C_8H_5S_2)]_3(thf)$ (**11**) were grown in a yield of 15 %. The variable–temperature ^1H–NMR spectra in the range of 20°C to 60°C in chloroform show only broad peaks probably due to the paramagnetic character of the erbium metal centre. At room temperature, a multiplet at 7.1 ppm integrating for 45H could be assigned to the protons of the bithienyl units. At 3.7, 1.9 and 1.2 ppm, three broad signals, corresponding to the methylene protons of the tetrahydrofuran molecule, are present.

Furthermore, electronic ionisation (EI) and fast atom bombardment (FAB) mass spectrometric techniques have been used allowing the analysis of compound $Er[OC(C_8H_5S_2)]_3(thf)$ (**11**). Two more intense peaks observed at *m/z* = 166 and 523, correspond to $[M–[OC(C_8H_5S_2)_3]_3–thf]^+$ and $[M–Er–[OC(C_8H_5S_2)]_2–thf]^+$, respectively.

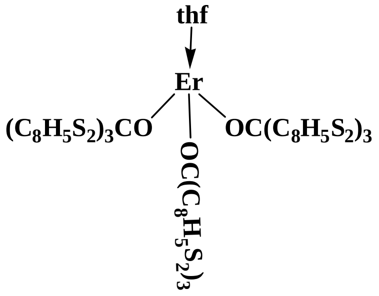
4.2.1 Crystal Structure Determination of $Er[OC(C_8H_5S_2)_3]_3(thf)$ (**11**)

Brown crystals of **11** were obtained from a concentrated tetrahydrofuran solution placed at 5°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system. The unit cell dimensions are given in Table 2.67.

a [Å]	**b [Å]**	**c [Å]**	**α [°]**	**β [°]**	**γ [°]**
16.25(1)	16.31(1)	45.87(2)	90	90.17(2)	90

Table 2.67. Unit cell dimensions of compound 11.

Unfortunately, the X–ray structure determination for this erbium alkoxide could not be refined in a satisfying manner because of the poor quality of the crystal. Nevertheless, the data allow us to conclude unambiguously that the coordination sphere around the erbium atom is tetrahedral, consisting of three (2,2'−bithienyl–5–yl)methoxido ligands and one tetrahydrofuran molecule coordinating to the metal centre (Figure 2.53). This overall structure could be compared with that of the tetrahedral compound {tris(2,6–di–*tert*–butyl–4–methylphenolato–*O*)(thf)–erbium} • toluene,[56] and it is also similar to that of the tetrahedral compound Sm(O–2,6–*tert*–$Bu_2C_6H_3)_3$(thf).[57]



11

Figure 2.53. Schematic representation of Er[OC($C_8H_5S_2$)]$_3$(thf) (11).

The ^{1}H–NMR spectra and EI mass spectroscopic data are in good accordance with the proposed structure.

4.3 Reactivity of HO–C(C_4H_3S)$_3$ (2) towards Erbium Silyl Amide

The red solution was concentrated, and placed at 5°C. Few days later, pink crystals of Er[OC(C_4H_3S)]$_3$(thf)$_3$ (**20**) were obtained in a yield of 14 %. The variable–temperature ^{1}H–NMR spectra in the range of 20°C to 60°C in chloroform show only broad peaks probably due to the paramagnetic character of the erbium metal centre. At room temperature, a multiplet at 7.0 ppm integrating for 27H is assigned to the protons of the thienyl units. At 3.5, 1.2 and 0.9

ppm, three broad signals, corresponding to the methylene protons of the tetrahydrofuran molecule, are present.

Furthermore, electronic ionisation (EI) and fast atom bombardment (FAB) mass spectrometric techniques have been used allowing analyse of compound $Er[OC(C_4H_3S)_3]_3(thf)_3$ (**20**).Two more intense peaks observed at *m/z* = 166 and 277, correspond to $[M–[OC(C_4H_3S)]_3–(thf)_3]^+$ and $[M–Er–[OC(C_4H_3S)_3]_2–thf]^+$, respectively.

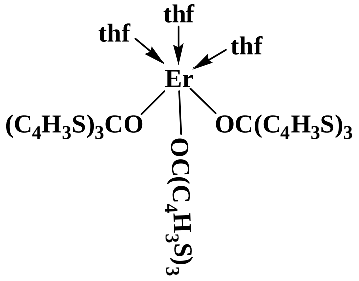
4.3.1 Crystal Structure Determination of $Er[OC(C_4H_3S)_3]_3(thf)_3$ (20)

Pink crystals were obtained from a concentrated tetrahydrofuran solution placed at 5°C. From the determination and the refinement of the unit cell dimensions arose a trigonal crystal system. The unit cell dimensions are given in Table 2.68.

a = b[Å]	**c [Å]**	**α = β [°]**	**γ [°]**
13.91(3)	25.6(2)	90	120

Table 2.68. Unit cell dimensions of compound 20.

As $Er[OC(C_8H_5S_2)]_3(thf)$ (**11**), the X–ray structure determination could not be refined in a satisfying manner because of the poor quality of the crystals. Nevertheless, the data allow to conclude unambiguously that the coordination sphere around the erbium metal centre is octahedral: it includes three tris(2–thienyl)methoxido ligands and three tetrahydrofuran molecules (Figure 2.54). This octahedral geometry is in good agreement with that found in $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**18**) (see above).



20

Figure 2.54. Schematic representation of $Er[OC(C_4H_3S)_3]_3(thf)_3$ (20).

The ^{1}H–NMR spectra and EI mass spectrometric techniques are in good accordance with the structure proposed.

4.4 Reactivity of HO–C($C_{14}H_{11}S_2$) (<u>3</u>) towards Erbium Silyl Amide

The pink solution was concentrated and placed at 5°C. Few days later, pink crystals of Er[OC($C_{14}H_{11}S_2$)]$_3$(thf) (**<u>24</u>**) were grown in a yield of 15 %. The ^{1}H–NMR spectrum, recorded in $CDCl_3$ at room temperature, shows unresolved signals (Figure 2.55), probably due to the paramagnetic character of the erbium centre. The signal at 7.3 ppm integrating for 21H could be assigned to the protons of the phenyl groups and the 5–H protons of the thienyls units. At 6.9 ppm, a peak which integrates for 12H, is assigned to the 3–H and 4–H protons of the thienyls groups. Two other signals at 3.1 and 1.2 ppm in the 4:4 ratio, indicate the presence of a tetrahydrofuran molecule.

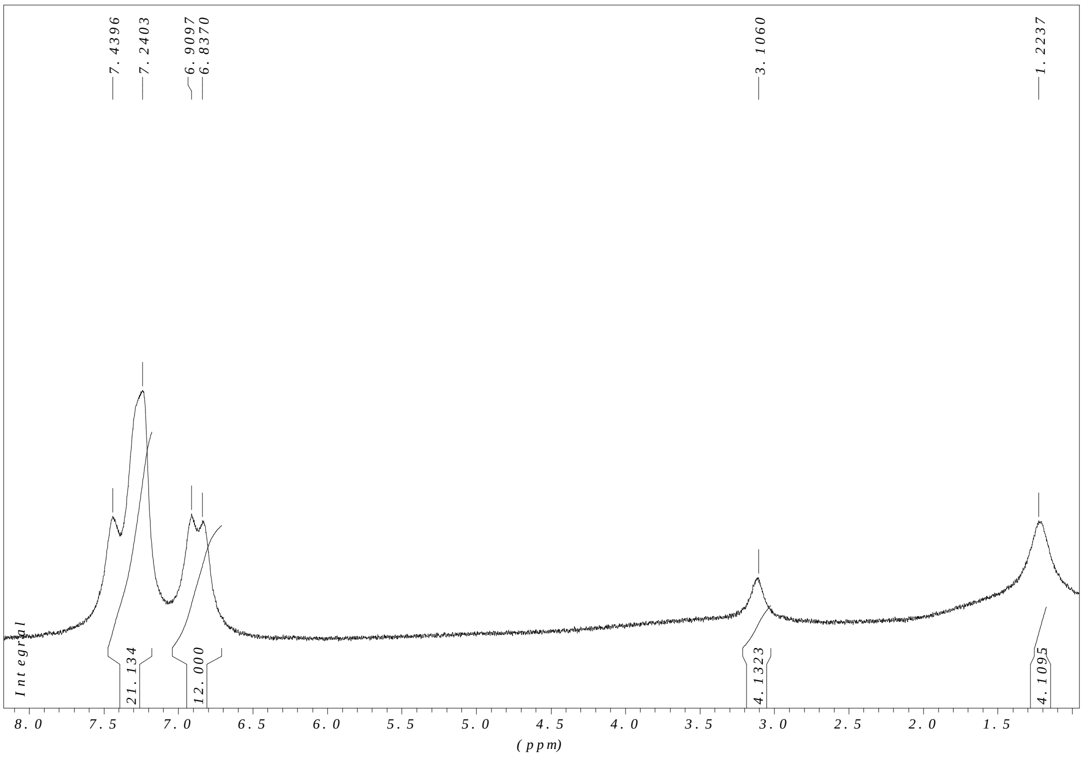


Figure 2.55. ^{1}H–NMR spectrum in $CDCl_3$ of Er[OC($C_{14}H_{11}S_2$)]$_3$(thf) (<u>24</u>).

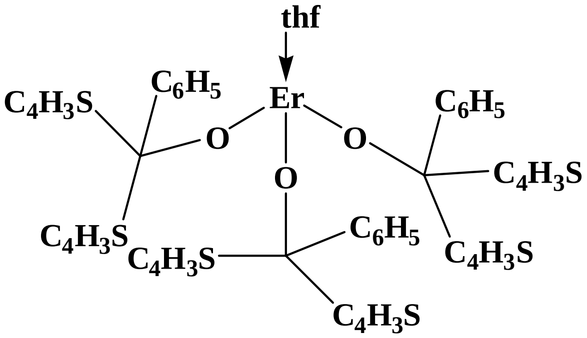
4.4.1 Crystal Structure Determination of Er[OC($C_{14}H_{11}S_2$)]$_3$(thf) (24)

Pink crystals were obtained from a concentrated tetrahydrofuran solution placed at 5°C. From the determination and the refinement of the unit cell dimensions arose a trigonal crystal system. The unit cell dimensions are given in Table 2.69.

a = b [Å]	c [Å]	α = β [°]	γ [°]
14.229(3)	26.397(1)	90	120

Table 2.69. Unit cell dimensions of compound 24.

As the other erbium alkoxides (see above), the X–ray structure determination could not be refined in a satisfying manner because of the poor quality of the crystals. Nevertheless, the data allow to conclude unambiguously that the coordination sphere around the erbium metal centre is tetrahedral: it includes three phenylbis(2–thienyl)methoxido ligands and, according with the NMR studies, one tetrahydrofuran molecule (Figure 2.56). This tetrahedral geometry is in good agreement with that found in Er[OC($C_8H_5S_2$)]$_3$(thf) (**11**) (see above).



24

Figure 2.56. Schematic representation of Er[OC($C_{14}H_{11}S_2$)]$_3$(thf) (24).

4.5 Reactivity of 4−6 towards Erbium Silyl Amide

4.5.1 Reactivity of 6 towards Erbium Silyl Amide

The pink solution was concentrated and placed at 5°C. Few days later, pink crystals of $Er[OC(C_{17}H_{15}S)]_3[HOC(C_{17}H_{15}S)]$ (**36**) were grown in a yield of only 7 %. The ^{1}H–NMR spectrum, recorded at room temperature in $CDCl_3$, shows four broad signals. The aromatic signal, at 7.2 ppm, integrates for 48H is attributed to the protons of the thienyl and phenyl groups. Unfortunately, the broadening inhibits the differentiation between the carbinol and the carbonilato ligands present in the molecule. At 3.6 ppm, the proton of the alcohol function is observed. The two additional singlets at 2.1 and 1.8 ppm are assigned to the methyl groups attached at the beta position of the thienyl substituents.

4.5.1.1 Crystal Structure Determination of $Er[OC(C_{17}H_{15}S)]_3$ $[HOC(C_{17}H_{15}S)]$ (36)

Pink crystals were obtained from a concentrated tetrahydrofuran solution placed at 5°C. From the determination and the refinement of the unit cell dimensions arose a trigonal crystal system. The unit cell dimensions are given in Table 2.70.

a = b [Å]	**c [Å]**	**α = β [°]**	**γ [°]**
14.329(1)	26.68(1)	90	120

Table 2.70. Unit cell dimensions of compound 36.

Unfortunately, the X–ray structure determination, again, could not be refined in a satisfying manner because of the unfavoured direction of the methoxido ligands. Therefore no differentiation between the thienyl and phenyl groups has been possible. Nevertheless, the data allow us to conclude unambiguously that the coordination sphere around the erbium metal centre is tetrahedral. It is surrounded by three diphenyl(4−methyl−2−thienyl)methoxido ligands, and a diphenyl(4−methyl−2−thienyl)methanol ligand is also coordinated to the metal via this oxygen atom (Figure 2.57).

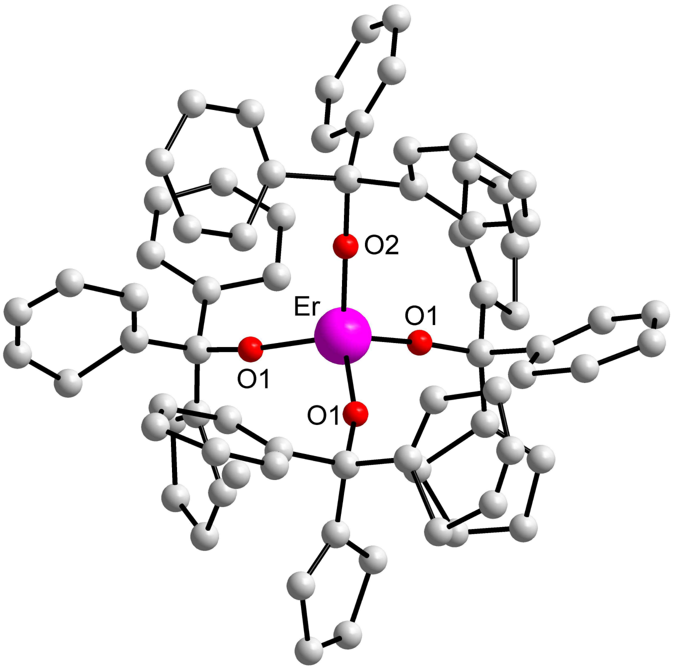


Figure 2.57. Geometry around the erbium metal centre of Er[OC($C_{17}H_{15}S$)]$_3$[HOC($C_{17}H_{15}S$)] (36).

4.5.2 Reactivity of 4 and 5 towards Erbium Silyl Amide

The reaction of **4** with the silyl amide led to the precipitation of pink solid which is filtered, and re–dissolved in tetrahydrofuran by heating in reflux. The solution was placed at 5°C and pink crystals were grown. Unfortunately, due to their poor quality, no crystallographic measurement has been possible.

The ^{1}H–NMR spectrum of the compound, recorded at room temperature in $CDCl_3$, shows only two broad peaks (Figure 2.58). This broadening could be explained by the presence of the paramagnetic erbium metal centre (see above). The first signal, at 7.2 ppm is aromatic, integrating for 52H and corresponds to the protons of the phenyl and thienyl groups. Unfortunately, the broadening inhibits the possible determination of the presence of a carbinol coordinated to metal centre. Nevertheless, at 3.0 ppm, a broad signal is present and could be attributed to the proton of the alcohol function.

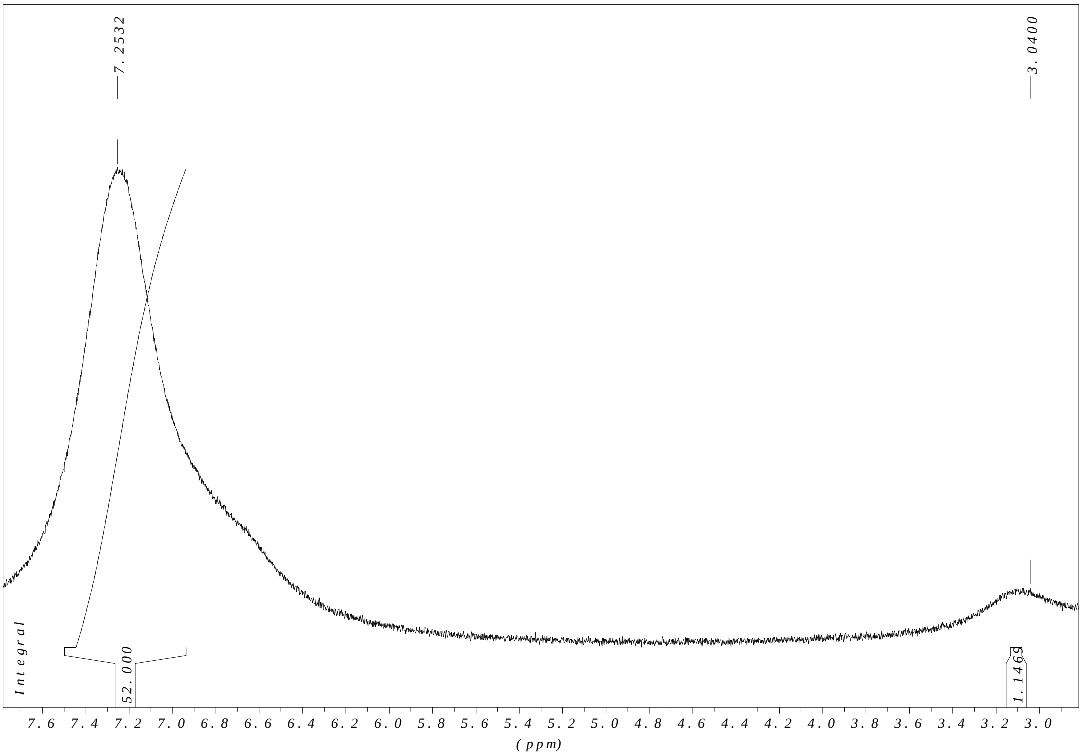


Figure 2.58. ^{1}H–NMR spectrum in $CDCl_3$ of the crystal obtained by the reaction of 4 with the erbium silyl amide.

Therefore, we suggest that $Er[N(SiMe_3)_2]_3$ and $HO–C(C_{16}H_{13}S)$ (**4**) react in the same way as $Er[N(SiMe_3)_2]_3$ with **6** to form $Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$ (**30**) in the yield of 7 % (Figure 2.59).

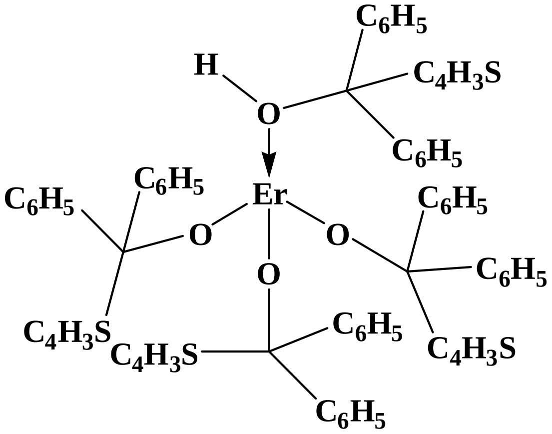
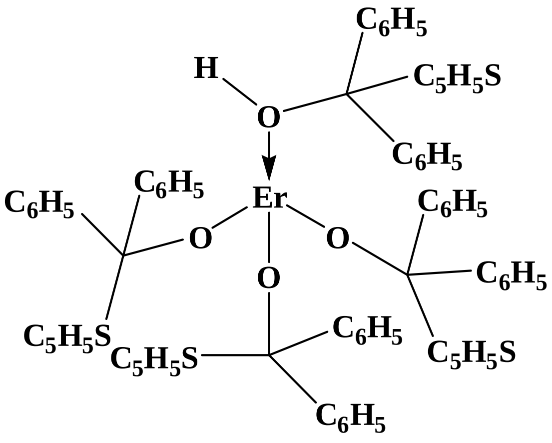


Figure 2.59. Schematic representation of 30.

During the reaction of **5** with the silyl amide, a colour change of the mixture from light–pink to brown has been observed. The solution obtained was concentrated and placed at 5°C. Few days later, brown crystals were grown. Unfortunately, due to their poor quality, no crystallographic measurement has been possible.

The ^{1}H–NMR spectrum, recorded at room temperature in $CDCl_3$, shows broad signals. The aromatic signal, at 7.2 ppm, integrates for 40H and is attributed to the protons of the phenyl groups. The other aromatic signal at 6.5 ppm, integrating for 8H is assigned to the protons of the thienyl units. At 3.7 ppm, a broad signal is present indicating an alcohol function. The two further signals, at 2.8 and 2.4 ppm are assigned to the methylic function present in the alpha position of the thienyl groups showing that two different types of ligands are presents. Note that, this spectrum is in agreement with than the one of $Er[OC(C_{17}H_{15}S)]_3[HOC(C_{17}H_{15}S)]$ (**36**), in which the methylic function is in the 4–position of the thienyl units.

By analogy with the compounds **30**, and **36** (see above) and in accordance with the ^{1}H–NMR spectrum, the product is identified as $Er[OC(C_{17}H_{15}S)]_3[HOC(C_{17}H_{15}S)]$ (**35)** (yield of 10 %) (Figure 2.60).



35

Figure 2.60 Schematic representation of $Er[OC(C_{17}H_{15}S)]_3[HOC(C_{17}H_{15}S)]$ (35).

4.6 Reactivity of HO–$C(C_{16}H_{13}S)$ (8) towards Erbium Silyl Amide

A pink precipitated was obtained. It was filtered off, and re–dissolved in tetrahydrofuran by heating to reflux. The obtained pink solution was placed at 5°C and pink crystals of $Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$ (**44**) were isolated (3 %). The ^{1}H–NMR spectrum, recorded at room temperature in $CDCl_3$, shows only two broad peaks. This broadening could be explained by the presence of the paramagnetic erbium metal centre (see above). The first signal, at 7.2 ppm is aromatic. It integrates for 52H and corresponds to the protons of the phenyl and thienyl groups. Unfortunately, the broadening excludes the differentiation between the carbinol and the carbonilato ligands present in the molecule. At 2.8 ppm, the proton of the alcohol function is observed.

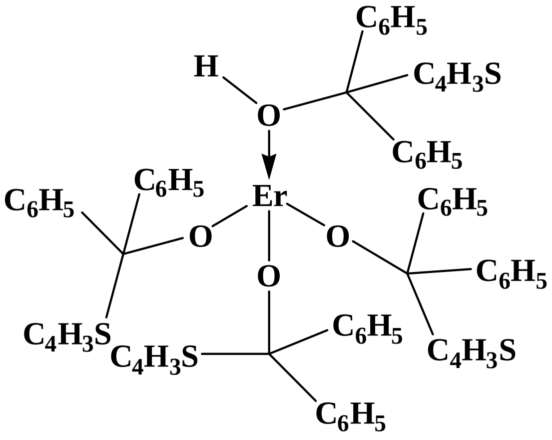
4.6.1 Crystal Structure Determination of $Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$ (<u>44</u>)

Pink crystals were obtained from a concentrated tetrahydrofuran solution placed at 5°C. From the determination and the refinement of the unit cell dimensions arose a trigonal crystal system. The unit cell dimensions are given in Table 2.71.

a = b [Å]	**c [Å]**	**α = β [°]**	**γ [°]**
14.132(1)	26.49(2)	90	120

Table 2.71. Unit cell dimensions of compound <u>24</u>.

As the other erbium alkoxides (see above), the X–ray structure determination could not be refined in a satisfying manner because of the poor quality of the crystals. Nevertheless, the data allow to conclude unambiguously that the coordination sphere around the erbium metal centre is tetrahedral: it includes three diphenyl(3–thienyl)methoxido ligands and, according with the NMR studies, one diphenyl(3–thienyl)methanol molecule (Figure 2.61). This result is in agreement with the structure proposed for $Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$ (**<u>30</u>**) which contains three diphenyl(2–thienyl)methoxido ligands and one diphenyl(2–thienyl)methanol molecule.



44

Figure 2.61. Schematic representation of Er[OC($C_{16}H_{13}S$)]$_3$[HOC($C_{16}H_{13}S$)] (44).

4.7 Conclusion

Seven new erbium alkoxides have been obtained as single crystals: **11**, **20**, **24**, **30**, **35**, **36** and **44**. Unfortunately, the X–ray structure determinations could not be refined in satisfying manner because of the poor quality of the crystals. Nevertheless, the preliminary data allows us to conclude the coordination sphere around the metal centre. Indeed, an octahedral geometry was found for Er[OC(C_4H_3S)$_3$]$_3$(thf)$_3$ (**20**) which the metal centre is surrounded by three carbinolato ligands and three tetrahydrofuran molecules. A tetrahedral geometry was found for Er[OC($C_8H_5S_2$)]$_3$(thf) (**11**) and Er[OC($C_{14}H_{11}S_2$)]$_3$(thf) (**24**), in these case only one tetrahydrofuran molecule instead of three is coordinated to the metal centre. The other compounds, Er[OC($C_{16}H_{13}S$)]$_3$[HOC($C_{16}H_{13}S$)] (**30**), Er[OC($C_{17}H_{15}S$)]$_3$[HOC($C_{17}H_{15}S$)] (**35**), Er[OC($C_{17}H_{15}S$)]$_3$[HOC($C_{17}H_{15}S$)] (**36**) and Er[OC($C_{16}H_{13}S$)]$_3$[HOC($C_{16}H_{13}S$)] (**44**) exhibit again a tetrahedral geometry, nevertheless, in these cases the erbium metal centre is surrounded by three carbinolato ligands and ligated by the carbinol via the oxygen atoms. All these results were confirmed by NMR studies. The reactions between the other carbinols **7** and **9** and the erbium silyl amide did not lead to an isolation of the molecules as single crystals or as solids. We cannot rule out that these reactions didn't form the desired erbium alkoxides; we suppose that it is essentially a problem of crystallization.

Part 4 Conclusion

In this chapter, we have presented the synthesis and crystal structure investigations of numerous novel rare earth methoxides containing thienyl substituents. After some generalities about alkoxides and about their different ways of synthesis, the organic ligands used, functionalized by a tertiary alcohol function, were introduced. They have been synthesized by varying the number of thienyl and phenyl groups. Two new star–shaped molecules (Table 2.72) in which the heterocycle is functionalized by a methyl group in this 4 or 5 position have been obtained.

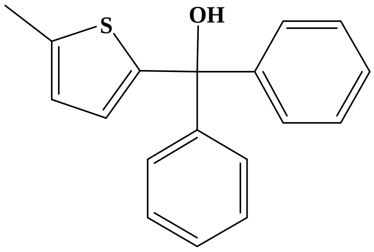
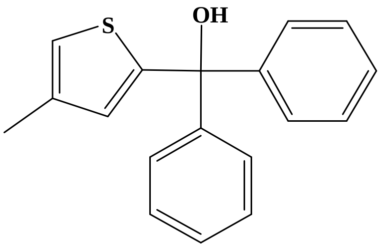
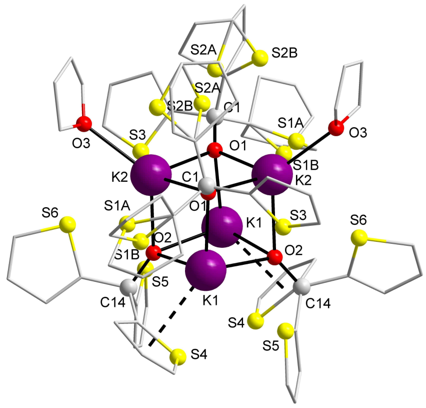
	
HO–C($C_{17}H_{15}S$) (**5**)	HO–C($C_{17}H_{15}S$) (**6**)

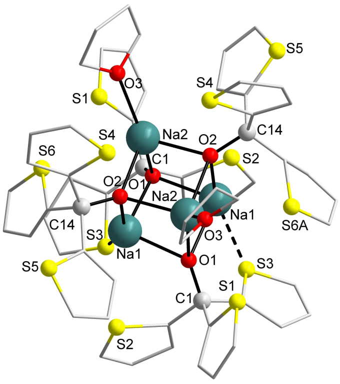
Table 2.72. The new organic ligands used.

Thanks to these systematic variations of the carbinols, their structural impact and steric effects on the molecular geometry of the new rare earth thienyl–substituted methoxides has been evaluated.

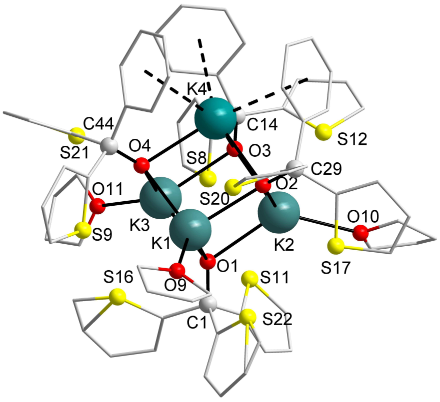
Two several synthetic pathways leading to alkoxides have been investigated such as the salt metathesis reactions between MCl_3 and carbinolates and the reactions between $M[N(SiMe_3)_2]_3$ and acidic carbinols. The first method requires the formation of the alkali metal alcoholates. The latter have been obtained by deprotonation of the carbinol with potassium or sodium hydride. The products have been isolated as single crystals or as solid. The molecular structures have shown the presence of tetrameric alkali metal alcoholates with a distorted cubane−like M_4O_4 core. Each alkali metal is surrounded by three carbinolato ligands and two or three alkali ions are additionally ligated with a tetrahydrofuran molecule (Table 2.73).



$\{[KOC(C_4H_3S)_3]_4(thf)_2\} \cdot thf$ (**<u>12</u>**)



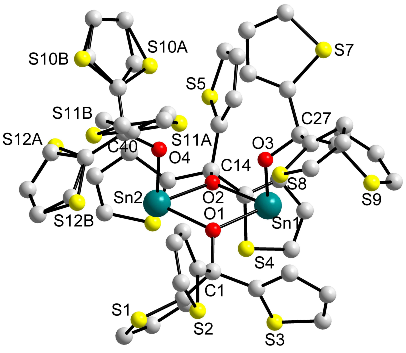
$[NaOC(C_4H_3S)_3]_4(thf)_2$ (**<u>13</u>**)



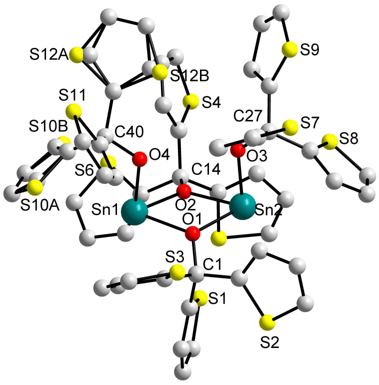
$[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (**<u>21</u>**)

Table 2.73. Examples of molecular structures of new alkali metal alcoholates. The tetrahydrofuran lattice molecule of <u>12</u> is omitted for more clarity.

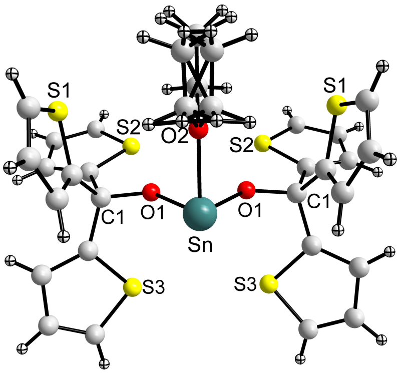
With the aim to prepare heterometallic alkoxides containing lanthanide–main group metal bonds, we have decided to work with tin(II). The reactions between $Sn[N(SiMe_3)_2]_2$ and acidic carbinol **<u>2</u>** in toluene led to the formation of a dimeric compound **<u>14a</u>** (Table 2.74). The same reaction performed in tetrahydrofuran instead of toluene has produced a dimeric **<u>14b</u>** and a monomeric **<u>15</u>** products (Table 2.74). Nevertheless, their high instabilities inhibit their reactivity studies towards rare earths.



$\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (**14a**)



$\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (**14b**)



$Sn[OC(C_4H_3S)_3]_2(thf)$ (**15**)

Table 2.74. Molecular structures of new tin(II) alkoxides. The toluene and the tetrahydrofuran lattice molecules of 14a and 14b, respectively, are omitted for more clarity.

The new rare earth alkoxides of yttrium, neodymium and erbium were synthesized by reactions between $Ln[N(SiMe_3)_2]_3$ (Ln = Y, Nd and Er) and acidic carbinols. The molecular structures have shown only mononuclear compounds. Indeed, the bulky ligand used and their high electronic density prevent the formation of polymeric products. For all the yttrium alkoxides, the coordination sphere around the metal centre is distorted trigonal–bipyramidal: the rare earth is surrounded by three carbinolato ligands in equatorial positions and two tetrahydrofuran or pyridine in axial positions (Table 2.75). The molecular structures of the neodymium compounds have revealed octahedral geometry around the metal centre: it is ligated by three methoxido ligands and three tetrahydrofuran molecules in a facial arrangement (Table 2.75). Note that, the change of the organic ligands used did not lead to a different geometry around the yttrium or neodymium metal centre: only some variations of angles and bond lengths have been noticed.

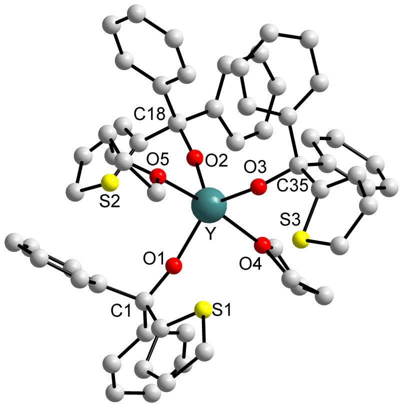
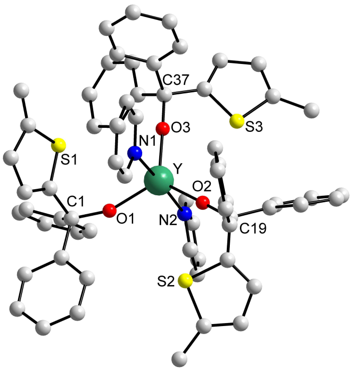
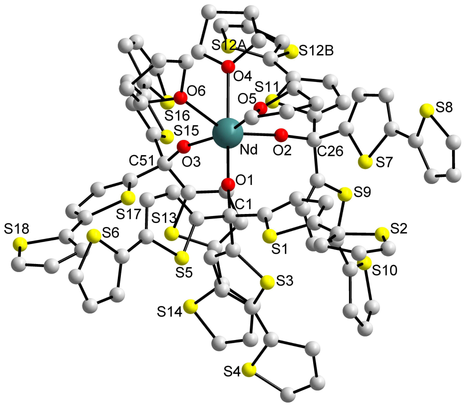
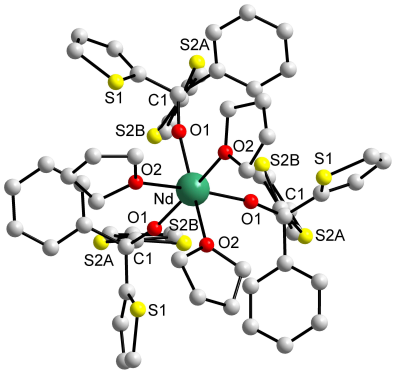
 {Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (**26**)	 {Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (**34**)
 {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**10**)	 {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (**23**)

Table 2.75. Examples of molecular structures of new yttrium and neodymium alkoxides. The toluene lattice molecule of 26 and 34, and the tetrahydrofuran lattice molecule(s) of 10 and 23, are omitted for more clarity.

The samarium alkoxides **19** and **29** were not obtained by the previous route but by the salt metathesis reactions between the potassium **12** and **25** or/and sodium **13** alcoholates and the samarium chloride. Their structural characterisation revealed that they are also mononuclear like their neodymium analogues. Only compounds with an octahedral geometry around the samarium atom have been observed. The octahedron is built up by three carbinolato ligands and three facially arranged tetrahydrofuran molecules (Table 2.76).

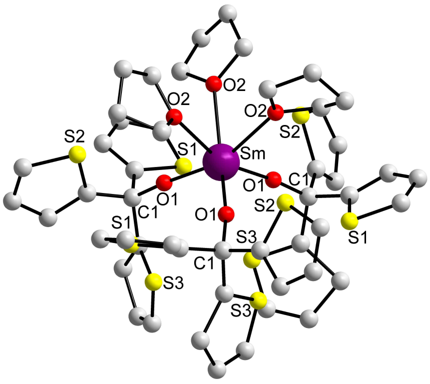
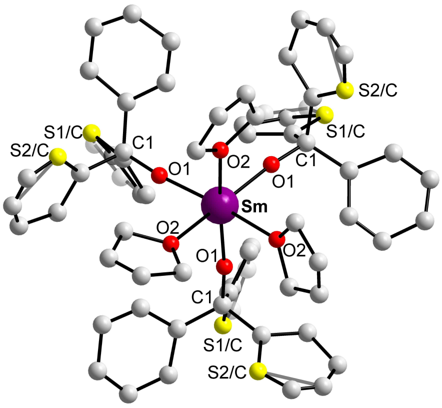
 $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**19**)	 $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (**29**)

Table 2.76. Molecular structure of the new samarium alkoxides. The tetrahydrofuran lattice molecule of each compounds is omitted for more clarity.

Unfortunately, the X–ray structure determinations of the new erbium alkoxides have not been refined in satisfying manner because of the poor quality of the crystals. Nevertheless, the preliminary data allows us to conclude that three different coordination spheres around the metal centre have been obtained (Table 2.77): an octahedral (in which the metal centre is surrounded by three carbinolato ligands and three tetrahydrofuran molecules), and two tetrahedrals (only one instead of three tetrahydrofuran molecule is coordinated to the erbium centre. Alternatively, the metal it is surrounded by three carbinolato ligands and ligated by a carbinol via the oxygen atoms).

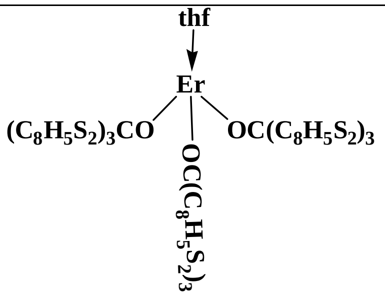
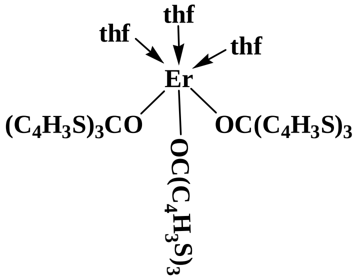
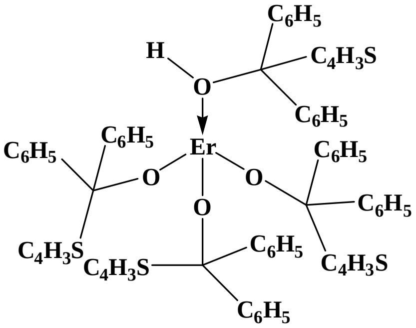
<table>
<tr>
<td>
$Er[OC(C_8H_5S_2)]_3(thf)$ (**11**)</td>
<td>
$Er[OC(C_4H_3S)_3]_3(thf)_3$ (**20**)</td>
</tr>
<tr>
<td colspan="2">
$Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$ (**44**)</td>
</tr>
</table>

Table 2.77. The different coordination spheres found around the erbium metal centre.

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Chapter 3 Electrochemical Studies of Metal Methoxides Containing Thienyl Substituents

Part 1 Introduction

The number of research articles concerning the electrochemistry of organic thiophene derivatives is nowadays extremely large (for example, see the reference[1]). In contrast, the redox properties of alkali metal or rare earth derivatives containing thienyl substituents have been barely investigated.[2] In this chapter, we will study the effect of the metal on the electrochemical properties of the compounds. For each organic star–shaped compound **1**–**8**, the redox properties will be investigated in different solvents (acetonitrile and dichloromethane, excepted for **1**) and at different scan rates (100 and 500 mV.s^{-1}). The electrochemical oxidation of the thienyl units will be analyzed. Moreover, the formation of polymeric films will be investigated, and the films obtained characterized. After the studies of the organic ligands, the oxidation of the metal derivatives will be presented. Thus, we can compare the different behaviours during the oxidation process, and study the redox properties of the metal centres and their influence on electrochemical properties of the ligands.

Unfortunately, for some new products, these investigations have not been performed due to the low yield of their synthesis (**9**, **24**, **30**, **35** and **44**) or their high instabilities (**14a**, **14b** and **15**).

Part 2 Organic Ligands

1 Electrochemical Properties of 1–4

1.1 Organic ligand HO−C($C_8H_5S_2$)$_3$ (1)

The values of the peak potentials of HO–C($C_8H_5S_2$)$_3$ (**1**) obtained in dichloromethane are listed in Table 3.1.

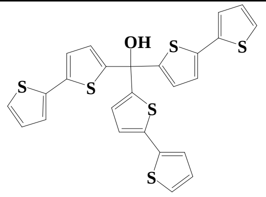
	100 mV.s^{-1}		**500 mV.s^{-1}**	
	E_{pa} [V]	**E_{pc} [V]**	**E_{pa} [V]**	**E_{pc} [V]**
 **1**	0.92, 1.68	0.38, −0.25	0.97, 2.02	0.56, −0.39

Table 3.1. Values of peak potentials [V, vs. Ag/AgClO$_4$] of HO–C($C_8H_5S_2$)$_3$ (1) in dichloromethane (10^{-3} M) deducted from CV measurements on a platinum electrode (diameter 1 mm).

The voltammogram at 100 mV.s^{-1} (or at 500 mV.s^{-1}) between –1.50 and 2.50 V vs. Ag/AgClO$_4$ (Figure 3.1) exhibits two oxidation waves at 0.92 and 1.68 V (or 0.97 and 2.02 V). The first peak potential is attributed to the oxidation of the dithienyl units forming the radical cation **$1^{\bullet+}$**; the second could be assigned to the oxidation of the radical cation leading to the dication **1^{2+}** (Scheme 3.1) or to the oxidation of the oligomers formed during the polymerization process.[3]

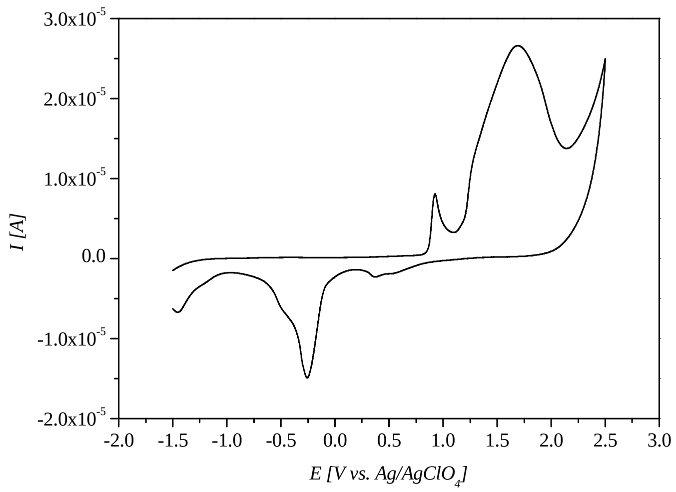
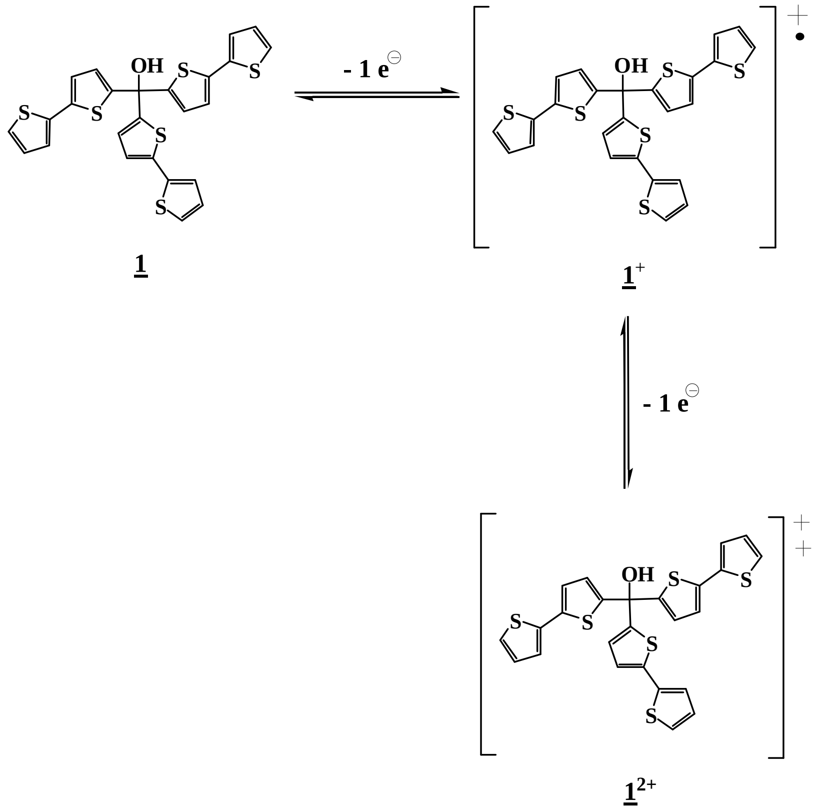
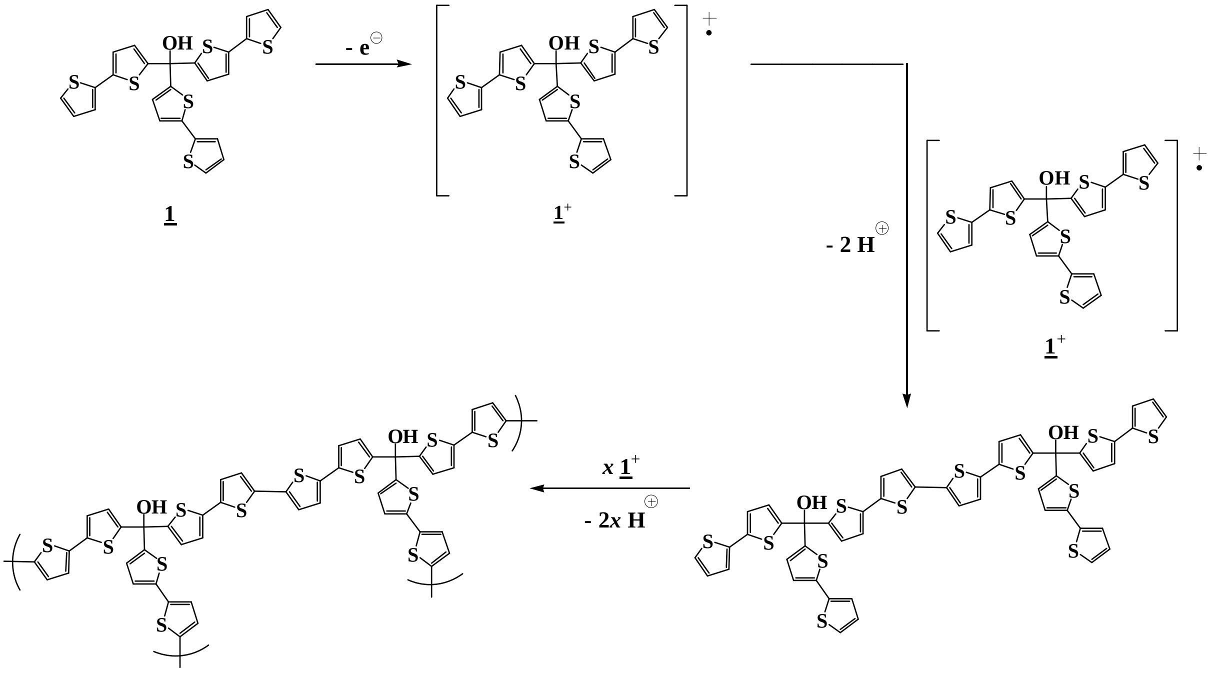


Figure 3.1. Cyclic voltammogram recorded on a platinum electrode (diameter 1 mm) in a dichloromethane solution containing 1 (10^{-3} M) and $[NBu_4][PF_6]$ (0.1 M), vs. $Ag/AgClO_4$, scan rate 100 $mV.s^{-1}$.

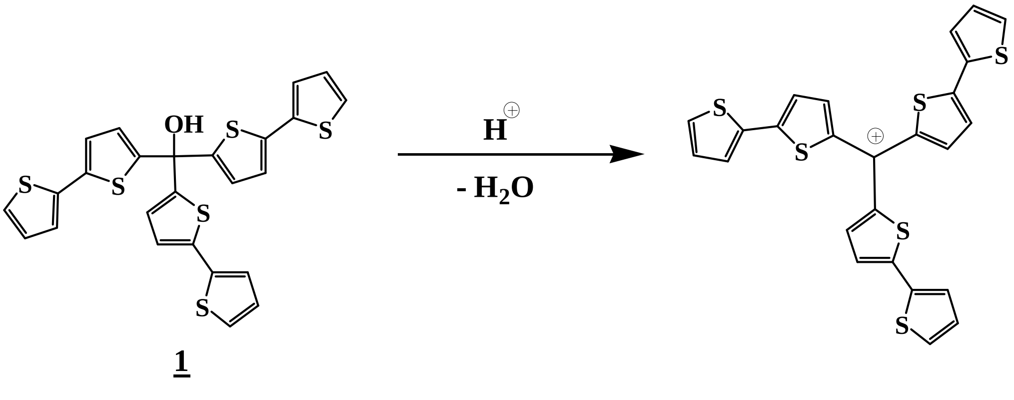


Scheme 3.1. Formation of the radical cation and of the dication.

The two reduction waves at 0.38 and –0.25 V (or 0.56 and –0.39 V) correspond to the reduction of the dimer, or oligomers, and the reduction of the carbocation. Indeed, during the oxidation process and the formation of the polymeric film (Scheme 3.2), some H^+ are liberating and could easily react with the carbinol to form a stable carbocation (Scheme 3.3). The electrochemical studies of **1** are in agreement with those obtained in previous experiments.[1a, 1b]



Scheme 3.2. Polymerization mechanism of HO–C($C_8H_5S_2$)$_3$ (1).



Scheme 3.3. Formation of carbocation stemming from HO–C($C_8H_5S_2$)$_3$ (1).

1.2 Organic ligands 2–4

The values of peak potentials of **2**, **3** and **4** obtained in dichloromethane or in acetonitrile are listed in Table 3.2.

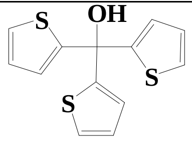
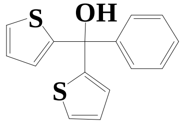
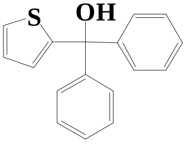
	Acetonitrile				Dichloromethane			
	100 mV.s^{-1}		500 mV.s^{-1}		100 mV.s^{-1}		500 mV.s^{-1}	
	E_{pa}	E_{pc}	E_{pa}	E_{pc}	E_{pa}	E_{pc}	E_{pa}	E_{pc}
 **2**	1.54	–0.12	1.59	–0.14	1.48	–0.20	1.50	–0.21
 **3**	1.50	–0.16	1.53	–0.19	1.43, 1.63	–0.19	1.66	–0.22
 **4**	1.55	–0.11	1.61	–0.13	1.64	–0.22	1.72	–0.17

Table 3.2. Values of peak potentials [V, vs. Ag/AgClO$_4$] of 2–4 in acetonitrile or in dichloromethane (10^{-3} M) deducted from CV measurements on a platinum electrode (diameter 1 mm).

In acetonitrile, the voltammograms of **2**–**4** between –0.50 and +2.00 V vs. Ag/AgClO$_4$ on a platinum electrode at 100 mV.s^{-1} or at 500 mV.s^{-1} lead to two irreversible signals (for example see Figure 3.2). The first wave is assigned to the oxidation of the thienyl units. These values are in agreement with those obtained for compounds containing thienyls units, for example 3,4–propylenedisulfanythiophene.[1e] The second waves correspond to the reduction of the carbocation. Indeed, during the oxidation of the thienyl units, some H$^+$ are formed and can deprotonated the carbinols leading to a stable carbocation.

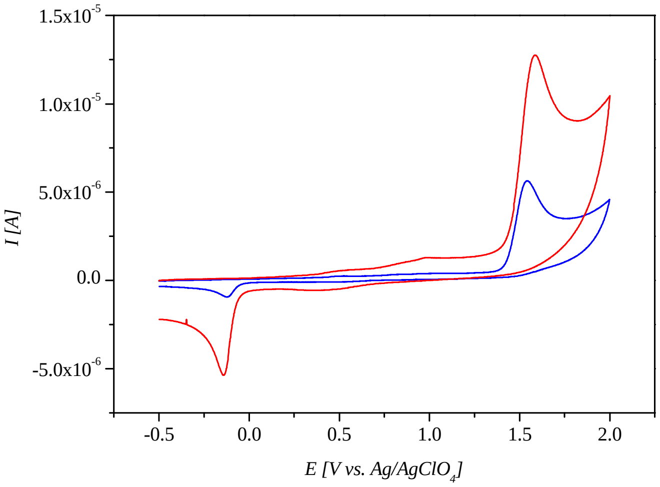


Figure 3.2. Cyclic voltammograms recorded on a platinum electrode (diameter 1 mm) in an acetonitrile solution containing 2 (10^{-3} M) and $[NBu_4][PF_6]$ (0.1 M), vs. Ag/$AgClO_4$, scan rate 100 mV.s^{-1} (blue line) and 500 mV.s^{-1} (red line).

As can be seen in Figure 3.3, in acetonitrile, for the compound **2**, the reduction wave of the carbocation appears from 70 mV.s^{-1}. Therefore, the lifetime of this species is about to 37 seconds.

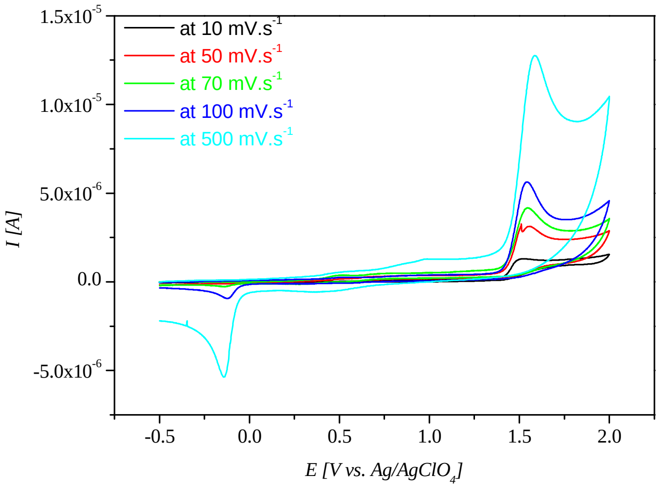


Figure 3.3. Cyclic voltammograms recorded on a platinum electrode (diameter 1 mm) in an acetonitrile solution containing 2 (10^{-3} M) and $[NBu_4][PF_6]$ (0.1 M), vs. Ag/$AgClO_4$, at different scan rates.

In dichloromethane, at 100 or 500 mV.s^{-1}, two irreversible waves are also obtained for **2** and **4** assigned to the oxidation of the thienyl moieties and the reduction of the carbocation. Compared with the results obtained in acetonitrile, only unimportant variations of the peak potential values are found. This change is certainly due to the formation of different solvated species.

Note that for **3** (Figure 3.4), at 100 mV.s^{-1}, the voltammogram depicts two oxidation waves: the first at 1.43 V is attributed to the oxidation of the thienyl units forming the radical cation; the second at 1.63 V is due to the oxidation of the radical cation leading to the dication (Scheme 3.4). The reduction peak of the carbocation at –0.19 V is also present. At 500 mV.s^{-1}, only a broad oxidation wave at 1.66 V is observed: this broadening can be due to the oxidation of the thienyl units following by the oxidation of the radical cation to the dication.

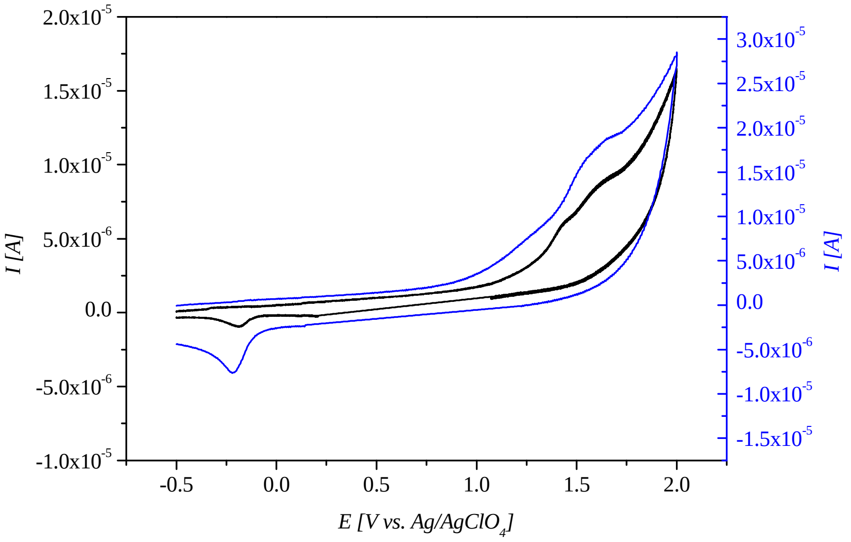
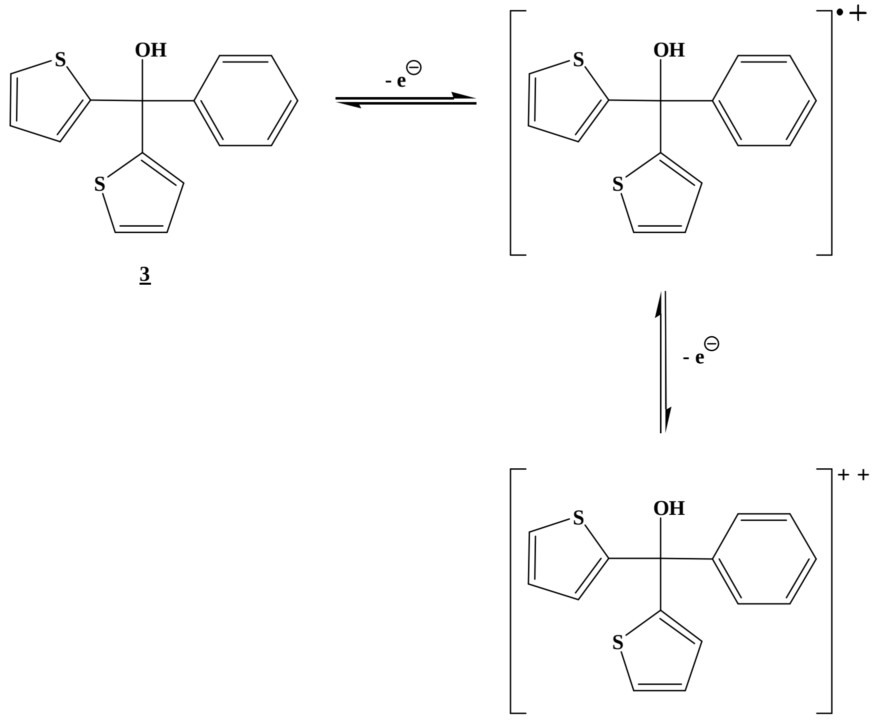


Figure 3.4. Cyclic voltammograms recorded on a platinum electrode (diameter 1 mm) in an dichloromethane solution containing 3 (10^{-3} M) and [NBu$_4$][PF$_6$] (0.1 M), vs. Ag/AgClO$_4$, scan rate 100 mV.s^{-1} (black line) and at 500 mV.s^{-1} (blue line).



Scheme 3.4. Formation of the radical cation and of the dication.

Contrarily to **1**, either in acetonitrile or in dichloromethane, by repetitive CVs of **2**–**4**, no formation of polymeric films is evidenced. This failure may be explained by the high reactivity of the cation radicals generated, which can react with a molecule of solvent or undergo nucleophilic attack. These results are in good agreement with observations performed on other molecules with an unsubstituted α–position on pyrroles[4] or thiophenes.[5]

In comparison with **1**, the oxidation peak potentials of **2**–**4** are shifted towards higher values due to the decrease of the electronic density of the compounds, thus leading to a more difficult oxidation process of the heterocycles. Note that, compared with **2**, the substitution of a thiophene unit by a phenyl group does not lead to a significant variation of the oxidation value. Therefore it can be concluded that the electronic effects of the phenyl or thiophene groups in this type of compounds are quite similar.

2 Electrochemical Properties of 5 and 6

The values for the peak potentials of **5** and **6** obtained in acetonitrile or in dichloromethane are listed in Table 3.3.

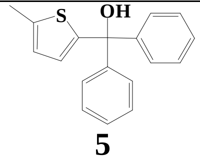
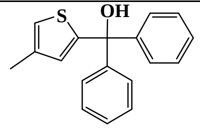
	Acetonitrile				Dichloromethane			
	100 mV.s^{-1}		500 mV.s^{-1}		100 mV.s^{-1}		500 mV.s^{-1}	
	E_{pa}	E_{pc}	E_{pa}	E_{pc}	E_{pa}	E_{pc}	E_{pa}	E_{pc}
 **5**	1.39	–	1.40	–0.24	1.39	–0.31	1.42, 1.64	–0.29
 **6**	1.43	–	1.48	–0.17	1.42, 1.65	–0.18	1.51, 1.68	–0.19

Table 3.3. Values of peak potentials [V, vs. Ag/AgClO$_4$] of 5 and 6 in acetonitrile or in dichloromethane (10^{-3} M) deducted from CV measurements on a platinum electrode (diameter 1 mm).

The voltammograms of **5** and **6** display in the range between –0.5 and 2 V (100 mV.s^{-1} in MeCN) only the irreversible waves due to the oxidation of the thienyl unit. At this scan rate, the lifetime of the carbocation is not long enough to be reduced; nevertheless, the voltammogram, at 500 mV.s^{-1}, reveals this reduction. In the voltammogram of **5** in dichloromethane at 100 mV.s^{-1}, the occurrence of two irreversible signals is noticed. The first one is attributed to the oxidation of the thienyl unit and the second one to the reduction of the carbocation forming during oxidation process. At 500 mV.s^{-1}, a second oxidation wave is present and corresponds to the oxidation of the radical cation leading to the dication. Indeed, the presence of methyl group on the thiophene unit stabilizes the radical cation formed during the oxidation process. At 100 mV.s^{-1}, the lifetime of the generated radical cation is not important enough to be oxidized, in contrast to the case of **6**.

Noteworthy is the finding that no formation of polymeric films has been observed during the oxidation of **2**–**4**.

In comparison with HO–C($C_{16}H_{13}S$) (**4**), the oxidation peak potentials measured in acetonitrile or in dichloromethane are shifted towards lower values (1.55 V for **4**, 1.39 V for **5** and 1.44 V for **6** in acetonitrile at 100 mV.s^{-1}, for example): the introduction of a electronic donor (methyl group) facilitates the oxidation process manifested by a decrease of potentials.

3 Electrochemical Properties of 7 and 8

The values of peak potentials of **7** and **8** obtained in acetonitrile or in dichloromethane are listed in Table 3.4. No studies at the scan rate of 500 mV.s^{-1} have been done due to the difficulty to obtain workable voltammograms.

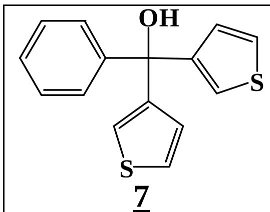
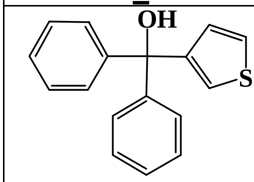
	Acetonitrile		Dichloromethane	
	E_{pa}	**E_{pc}**	**E_{pa}**	**E_{pc}**
 **7**	1.62	–	1.59	–0.11
 **8**	1.77	–	1.61	–0.06

Table 3.4. Values of peak potentials [V, vs. Ag/AgClO$_4$] of 7 and 8 in acetonitrile or in dichloromethane (2 × 10^{-3} M) deducted from CV measurements on a platinum electrode (diameter 1 mm) at 100 mV.s^{-1}.

The voltammograms of **7** and **8** in acetonitrile, at 100 mV.s^{-1}, depict only the irreversible wave due to the oxidation of the thienyl groups, at 1.62 V and 1.77 V, respectively. No reduction of the carbocation is observed, contrarily to the voltammograms recorded in dichloromethane (for example see Figure 3.5). No formation of a polymeric film is noticed when **7** and **8** are oxidized, in accordance with the previous results (see above).

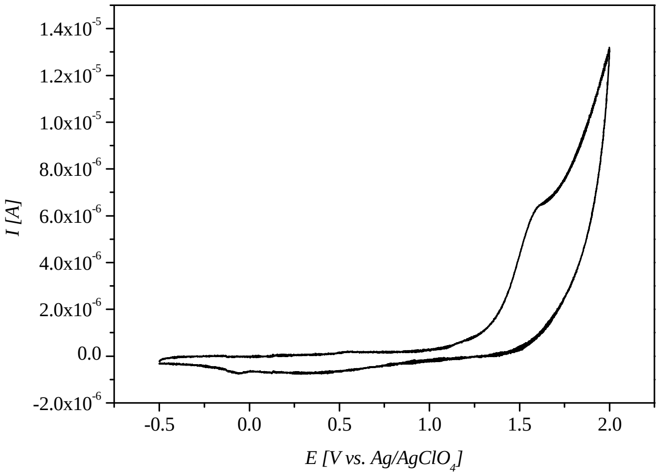


Figure 3.5. Cyclic voltammogram recorded on a platinum electrode (diameter 1 mm) in a dichloromethane solution containing HO–C($C_{16}H_{13}S$) (8) (2 × 10^{-3} M) and [NBu_4][PF_6] (0.1 M), vs. Ag/$AgClO_4$, scan rate 100 mV.s^{-1}.

Compared with their analogues HO–C($C_{14}H_{11}S_2$) (**3**) and HO–C($C_{16}H_{13}S$) (**4**), the oxidation peak potentials of **7** and **8** are shifted to higher values. This is probably due to the fact that, contrarily to **3** and **4**, the two alpha positions of the thienyl units are unsubstituted.

Part 3 Alkali Metal Alcoholates (K, Na)

The general representation of the alkali metal alcoholates studied is given in Figure 3.6.

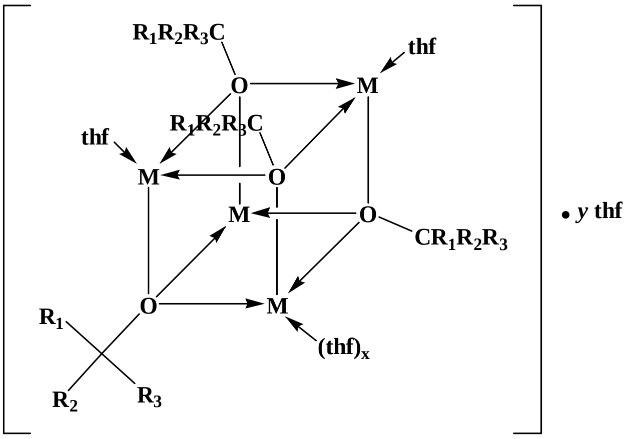


Figure 3.6. Alkali metal alcoholates studied. M = K, Na. R_1, R_2 and R_3 stand for the thiophene or the phenyl groups.

The values of peak potentials of carbinols and these alkali metal derivatives obtained in acetonitrile are listed in Table 3.5.

	100 mV.s^{-1}		500 mV.s^{-1}	
	E_{pa}	E_{pc}	E_{pa}	E_{pc}
$HO–C(C_4H_3S)_3$ (2)	1.54	–0.12	1.59	–0.14
$\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf (12)	1.53	–	1.53	–0.17
$[NaOC(C_4H_3S)_3]_4(thf)_2$ (13)	1.47	–0.13	1.53	–0.17
$HO–C(C_{14}H_{11}S_2)$ (3)	1.50	–0.16	1.53	–0.19
$[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (21)	1.41	–0.18	1.52	–0.20
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (22)	1.42	–	1.49	–0.18
$HO–C(C_{16}H_{13}S)$ (4)	1.55	–0.11	1.61	–0.13
$\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (25)	1.50	–0.14	1.59	–0.16
$HO–C(C_{17}H_{15}S)$ (5)	1.39	–	1.40	–0.24
$[KOC(C_{17}H_{15}S)]_4(thf)_2$ (31)	1.30	–	1.34	–0.28
$[NaOC(C_{17}H_{15}S)]_4(thf)_2$ (32)	1.29	–0.27	1.33	–0.28
$HO–C(C_{14}H_{11}S_2)$ (7)	1.62	–		
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (37)	1.67	–0.21		
$HO–C(C_{16}H_{13}S)$ (8)	1.77	–		
$[NaOC(C_{16}H_{13}S)]_4(thf)_2$ (41)	1.76	–0.17		

Table 3.5. Values peak potentials [V, vs. Ag/AgClO$_4$] of the carbinols and these alkali metal derivatives, in acetonitrile (10^{-3} M or 2 × 10^{-3} for 7, 37, 8 and 41) deduced from CV measurements on a platinum electrode (diameter 1 mm). No studies at 500 mV.s^{-1} for 7, 8, 37 and 41 have been made due to the difficulty to obtain a workable voltammogram at this scan rate.

The voltammograms at 100 mV.s^{-1} (for example see Figure 3.7), except for the compounds **12**, **22** and **31**, show two irreversible waves due to the oxidation of the thiophene moieties and to the reduction of the carbocation. At this scan rate, the voltammograms of **12**, **22** and **31** depict one irreversible oxidation wave due to oxidation of the thienyl units. For these products, the lifetime of the carbocation formed during the oxidation is not long enough to be reduced. At 500 mV.s^{-1}, the voltammograms of **12**, **22** and **31** reveal the reduction of this carbocation. No polymeric film is obtained during the oxidation process: this result matches with the findings obtained for the respective ligands.

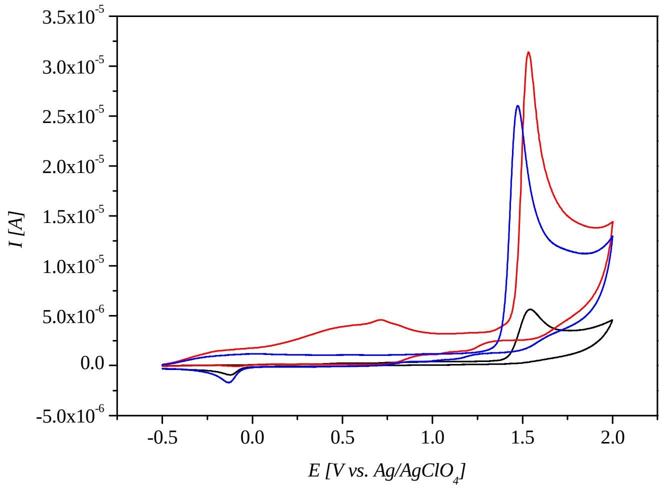


Figure 3.7. Cyclic voltammograms recorded on a platinum electrode (diameter 1 mm) in an acetonitrile solution containing HO–C(C_4H_3S)$_3$ (2) (black line), {[KOC(C_4H_3S)$_3$]$_4$(thf)$_2$} • thf (12) (red line) and [NaOC(C_4H_3S)$_3$]$_4$(thf)$_2$ (13) (blue line) (10^{-3} M) and [NBu_4][PF_6] (0.1 M), vs. Ag/$AgClO_4$, scan rate 100 mV.s^{-1}. Note that for 12, another oxidation wave at 0.7 V is present, probably due to an impurity in solution.

In comparison with the corresponding carbinol, the oxidation peak potentials are shifted towards lower values (from 0.01 to 0.10 V), probably due to the presence of the alkali metal which increase the electronic density of the thiophene moieties leading to an easier oxidation of this species. Nevertheless, this observation has not been made for the sodium alcoholate **37**: in this case the oxidation peak potential is shifted towards an incomprehensible higher value (1.62 V for **7** and 1.67 V for **37**).

Part 4 Yttrium and Neodymium Alkoxides

The general representation of the yttrium and neodymium alkoxides studies is given in Figure 3.8.

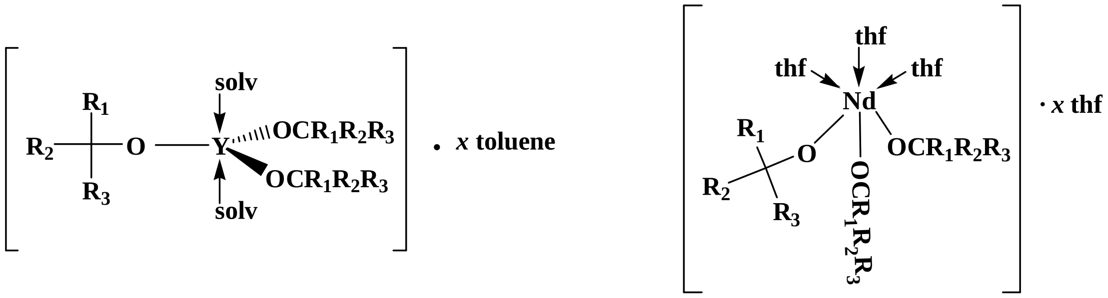


Figure 3.8. Yttrium and neodymium alkoxides studied. R_1, R_2 and R_3 stand for the thiophene or the phenyl groups.

The values of peak potentials of carbinols and these yttrium and neodymium alkoxides obtained in dichloromethane are listed in Table 3.6.

	100 mV.s^{-1}		500 mV.s^{-1}	
	E_{pa}	E_{pc}	E_{pa}	E_{pc}
$HO–C(C_8H_5S_2)_3$ (1)	0.92, 1.68	0.38, −0.25	0.97, 2.02	0.56, −0.39
$\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf (10)	0.95, 1.41	0.95, –0.42	1.13, 1.55	0.89, –0.46
$HO–C(C_4H_3S)_3$ (2)	1.48	–0.20	1.50	–0.21
$Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a)	1.49	–	1.57	–0.24
$Y[OC(C_4H_3S)_3]_3(py)_2$ (17a)	1.59	–	1.61	–
$\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (18)	1.53	–	1.59	–0.27
$HO–C(C_{14}H_{11}S_2)$ (3)	1.43, 1.63	–0.19	1.66	–0.22
$\{Nd[OC(C_{14}H_{11}S_2)]_3(thf)_3\}$ • thf (23)	1.53	–0.19	1.77	–0.26
$HO–C(C_{16}H_{13}S)$ (4)	1.64	–0.22	1.72	–0.17
$\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (26)	1.69	–0.10		
$\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (27)	1.69	–0.21		
$\{Nd[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (28)	1.66	–0.10	1.79	–0.21
$HO–C(C_{17}H_{15}S)$ (5)	1.39	–0.31	1.42, 1.63	–0.29
$\{Y[OC(C_{17}H_{15}S)]_3(thf)_2\}$ • toluene (33)	1.41	–0.32	1.46	–0.38
$\{Y[OC(C_{17}H_{15}S)]_3(py)_2\}$ • toluene (34)	1.55	–	1.81	–0.28
$HO–C(C_{14}H_{11}S_2)$ (7)	1.59	–0.11		
$\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (38)	1.76	–0.28		
$Y[OC(C_{14}H_{11}S_2)]_3(py)_2$ (39)	1.71	–		
$Nd[OC(C_{14}H_{11}S_2)]_3(thf)_3$ (40)	1.69	–		
$HO–C(C_{16}H_{13}S)$ (8)	1.61	–0.06		
$Y[OC(C_{16}H_{13}S)]_3(py)_2$ (42)	1.81	–		
$\{Nd[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (43)	1.81	–		

Table 3.6. Values peak potentials [V, vs. $Ag/AgClO_4$] of the carbinols and these yttrium and neodymium alkoxides, in dichloromethane (10^{-3} M or 2 × 10^{-3} for 7, 40, 8, 42 and 43) deduced from CV measurements on a platinum electrode (diameter 1 mm). Note that no studies at 500 mV.s^{-1} for 7, 8, 26, 27, 38, 39, 40, 42 and 43 have been performed due to the difficulty to obtain a workable CV at this scan rate.

1 Neodymium Alkoxide 10 Obtained with the Organic Ligand 1

The voltammogram of **10** at 100 mV.s^{-1}, exhibits two oxidation waves assigned to the bithienyl units (formation of the radical cation and dication or oligomers) and two reduction waves attributed, respectively, to the reduction of dication or of the oligomers and to the reduction of the carbocation. The same observations have been made at 500 mV.s^{-1}. No oxidation or reduction waves due to the metal centre have been observed. The oxidation peak of the monomer is shifted towards higher potentials, compared with **1** due to the presence of the metal centre, which lowers the electronic density of the thiophene units.

When the potential is cycled, at 500 mV.s^{-1} for example, the deposition of a material on the electrode is observed (Figure 3.9). From the second cycle, a new oxidation wave at 0.40 V is present due to the oxidation of an unknown product formed during the cycling.

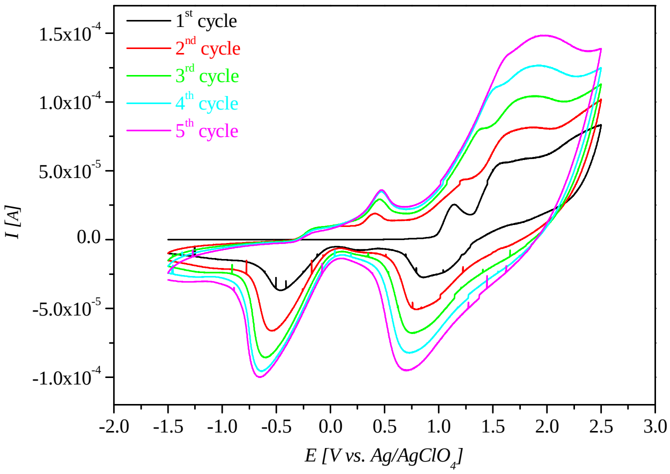


Figure 3.9. Repetitive cyclic voltammograms recorded on a platinum electrode in a dichloromethane solution containing <u>10</u> (10^{-3} M) and $[NBu_4][PF_6]$ (0.1 M), vs. $Ag/AgClO_4$, scan rate 500 mV.s^{-1}.

The resulting thin film obtained after five cycles is characterized by an electrochemical experiment in a solution containing only the solvent and the supporting electrolyte, without monomers. It displays an electroactive character analogous to polythiophene with a broad reversible peak at an average potential of 1.23 V and a reduction wave at −0.70 V assigned to the carbocation (Figure 3.10). This result is in good agreement with those obtained previously for the organic precursor **<u>1</u>**.[1a] Moreover an oxidation wave at 0.13 V is observed corresponding to an unknown compound formed during the deposition.

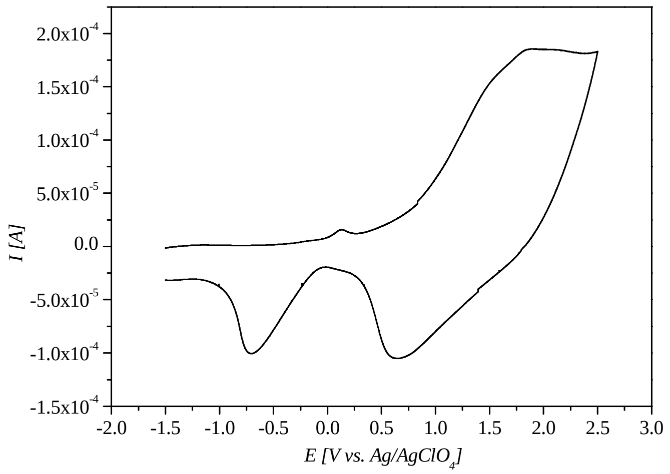


Figure 3.10. Cyclic voltammogram of poly (10), prepared by 5 oxidation–reductions on a platinum electrode (diameter 1 mm) at 500 mV.s^{-1}, in dichloromethane [NBu$_4$][PF$_6$] (0.1 M), vs. Ag/AgClO$_4$, scan rate 500 mV.s^{-1}.

2 Neodymium and Yttrium Alkoxides Obtained with the Organic Ligands 2–8

At 100 mV.s^{-1} (for example, see Figure 3.11), the voltammograms displays two irreversible waves (except for **16a**, **17a**, **18**, **34**, **39**, **42** and **43**): the first peak potential is attributed to the oxidation of the thiophene units, and the second to the reduction of the carbocation. For the redox chemistry of **16a**, **17a**, **18**, **34**, **39**, **42** and **43**, the voltammograms reveal only, an irreversible peak assigned to the oxidation of the thienyl units. At 500 mV.s^{-1}, they occur in addition (except for **17a**), a reduction wave due to reduction of the carbocation. At this scan rate, the lifetime of the carbocation formed is long enough to be reduced during the experiment.

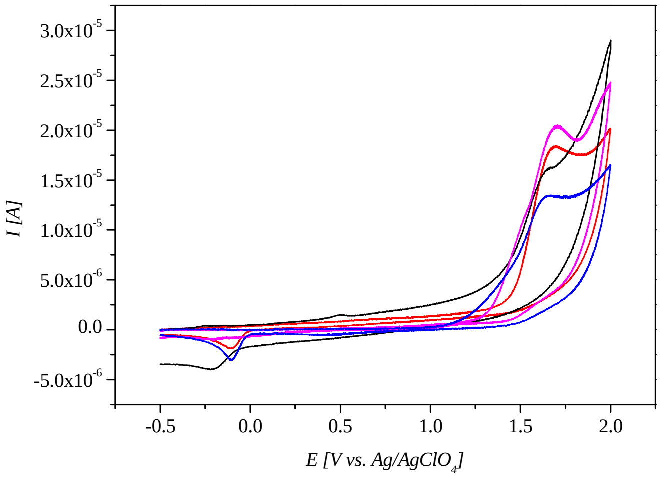


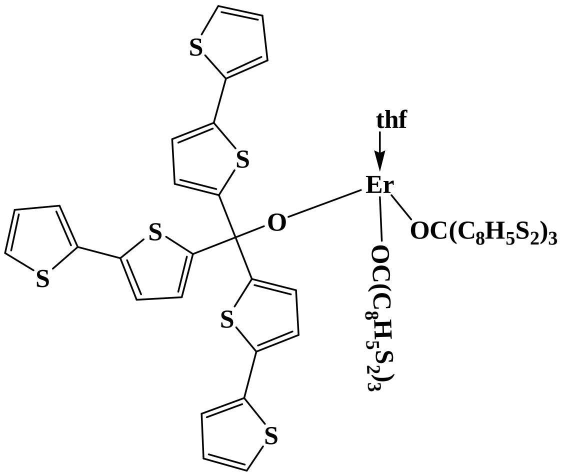
Figure 3.11. Cyclic voltammograms recorded on a platinum electrode (diameter 1 mm) in a dichloromethane solution containing HO–C($C_{16}H_{13}S$) (4) (black line), {Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (26) (red line), {Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$} • toluene (27) (magenta line) and {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (28) (blue line), (10^{-3} M) and [NBu_4][PF_6] (0.1 M), vs. Ag/$AgClO_4$, scan rate 100 mV.s^{-1}.

Note that the voltammograms of **23**, **33** and **34** show only one irreversible oxidation wave assigned to the formation of the radical cation. No oxidation of this specie to form the dication is visible contrarily to the carbinols **3** and **5**. These radical cations are not enough stable to be oxidized. No oxidation or reduction waves implying the metal centre have been observed.

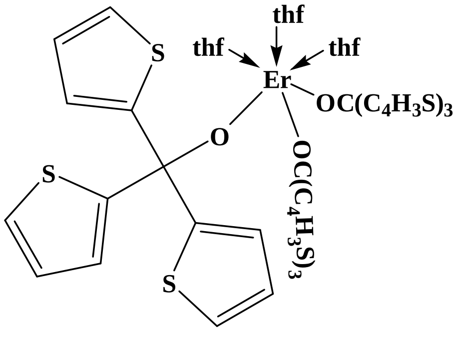
Contrarily to the alkali metal alcoholates, here, for all the metal alkoxides, the oxidation peaks are shifted towards higher potentials compared with oxidation potential of the corresponding carbinol. It might be caused by the presence of the yttrium or neodymium metal, which lowers the electronic density of the thiophene moieties. Repetitive CVs have not generated deposition of polymeric films, in accordance with their carbinols.

Part 5 Erbium Alkoxides

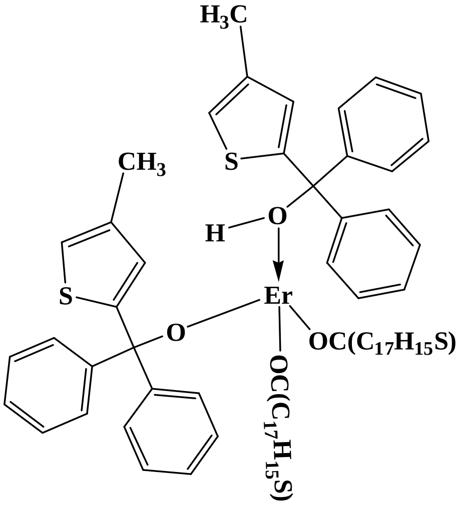
In this section, only some selected erbium alkoxides will be treated because of the low reactions yield and the pronounced high moisture sensitivity of these compounds. The metal alkoxides studies are represented in Figure 3.12.



11



20



36

Figure 3.12. Erbium alkoxides studied.

The values for the peak potentials of the carbinols and these erbium alkoxides obtained in dichloromethane are listed in Table 3.7.

	100 mV.s^{-1}		**500 mV.s^{-1}**	
	E$_{pa}$	**E$_{pc}$**	**E$_{pa}$**	**E$_{pc}$**
HO–C($C_8H_5S_2$)$_3$ (<u>1</u>)	0.92, 1.68	0.38, −0.25	0.97, 2.02	0.56, −0.39
Er[OC($C_8H_5S_2$)$_3$]$_3$(thf) (<u>11</u>)	0.81, 1.19	0.64, –0.66	0.79, 1.22	0.66, –0.64
HO–C(C_4H_3S)$_3$ (<u>2</u>)	1.48	–0.20	1.50	–0.21
Er[OC(C_4H_3S)$_3$]$_3$(thf)$_3$ (<u>20</u>)	1.39	–0.32	1.44	–0.37
HO–C($C_{17}H_{15}S$) (<u>6</u>)	1.42, 1.65	–0.18	1.51, 1.68	–0.19
Er[OC($C_{17}H_{15}S$)]$_3$[HOC($C_{17}H_{15}S$)] (<u>36</u>)	1.46	–0.22	1.55	–0.28

Table 3.7. Values peak potentials [V, vs. Ag/AgClO$_4$] of the carbinols and erbium alkoxides, in dichloromethane (10^{-3} M) deduced from CV measurements on a platinum electrode (diameter 1 mm).

1 <u>Erbium Alkoxide 11 Obtained with the Organic Ligand 1</u>

The voltammogram of **<u>11</u>** displays at 500 mV.s^{-1} (or at 100 mV.s^{-1}), two oxidation waves at 0.79 and 1.22 V (or 0.81 and 1.19 V) corresponding to the oxidations of the dithienyl units (formation of the radical cation and dication or oligomers) and two reduction waves at 0.66 and –0.64 V (or 0.64 and –0.66 V) due to the reduction of the dication or of the oligomers and the carbocation, respectively. No oxidation or reduction waves due to the metal centre have been obtained. In comparison with **<u>1</u>**, the oxidation potentials (radical cation) of **<u>11</u>** are shifted to lower values, contrarily to **<u>10</u>**. This phenomenon may be explained by the increase of the electronic density of the thiophene moieties due to the erbium metal centre.

Either at 100 mV.s^{-1} or at 500 mV.s^{-1}, a polymeric film is deposited on the platinum electrode during the oxidation process (Figure 3.13). Beginning from the second cycle, a new oxidation wave at −0.41 V is present due to the oxidation of an unknown species formed during the cycling.

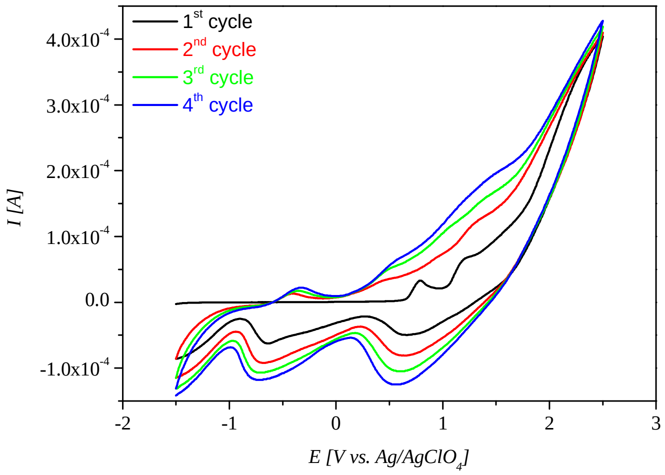


Figure 3.13. Repetitive cyclic voltammograms recorded on a platinum electrode in a dichloromethane solution containing <u>11</u> (10^{-3} M) and $[NBu_4][PF_6]$ (0.1 M), vs. $Ag/AgClO_4$, scan rate 500 $mV.s^{-1}$.

The resulting thin film obtained after four oxidation–reduction cycles at 500 $mV.s^{-1}$ is characterized by an electrochemical experiment in a solution containing only the solvent and the supporting electrolyte (without monomers) (Figure 3.14). It displays, as its neodymium analogue, an electroactive character with a broad reversible peak at an average potential of 1.02 V and a reduction wave at –0.64 V assigned to the carbocation. Moreover, an oxidation wave at −0.12 V is observed corresponding to an unknown compound formed during the deposition.

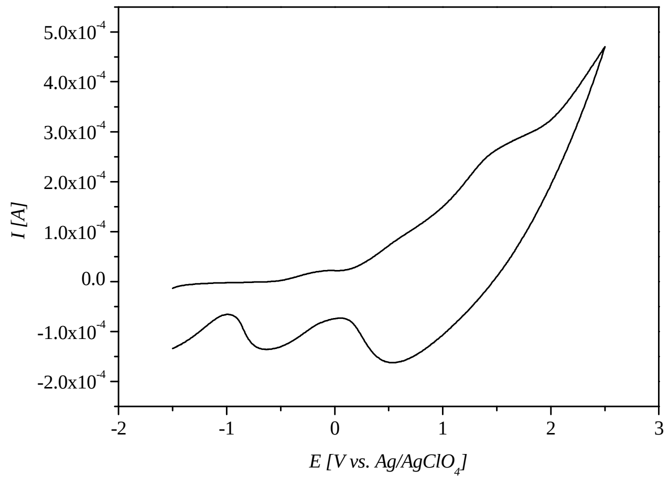


Figure 3.14. Cyclic voltammogram of poly (11), prepared by 4 oxidation–reductions on a platinum electrode (diameter 1 mm) at 500 mV.s^{-1}, in dichloromethane [NBu$_4$][PF$_6$] (0.1 M), vs. Ag/AgClO$_4$, scan rate 500 mV.s^{-1}.

2 Erbium Alkoxides Obtained with the Organic Ligand 2 and 6

The voltammograms of **20** and **36** at 100 mV.s^{-1} or at 500 mV.s^{-1} show an irreversible oxidation wave attributed to the oxidation of the thienyls and a reduction peak due to the carbocation. For **36**, contrarily to **6**, no oxidation of the radical cation generated during the oxidation process is visible, probably due to the low stability of this specie. Moreover, in the voltammogram of **36** no differentiation of the oxidation of the carbinol and the oxidation of the alkoxides ligated to the erbium centre is possible (Figure 3.15).

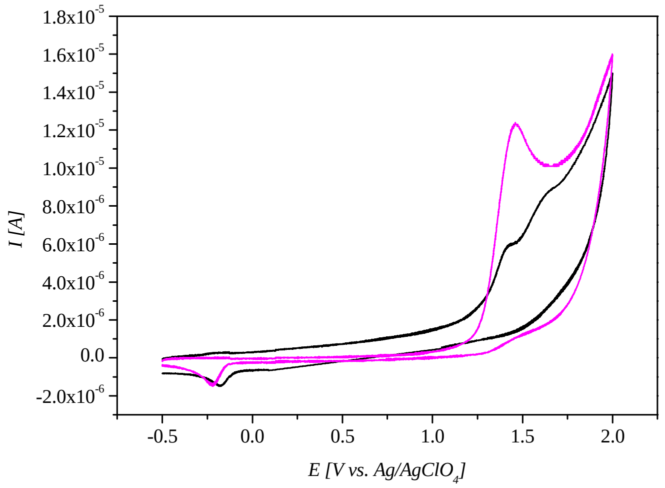


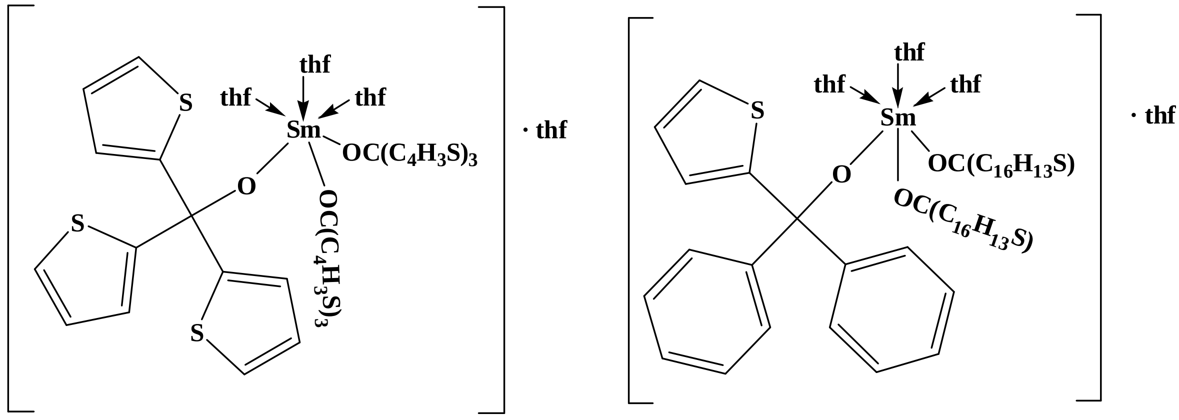
Figure 3.15. Cyclic voltammograms recorded on a platinum electrode in a dichloromethane solution containing HO–C($C_{16}H_{13}S$) (6) (black line) and Er[OC($C_{17}H_{15}S$)]$_3$[HOC($C_{17}H_{15}S$)] (36) (pink line) (10^{-3} M) and [NBu_4][PF_6] (0.1 M), vs. Ag/$AgClO_4$, scan rate 100 mV.s^{-1}.

Contrarily to the neodymium alkoxide **18**, the oxidation peak is shifted to lower potentials than this obtained for **2**: this result is in accordance with this observed for **11**. Nevertheless, in comparison with **6**, a shift towards higher peak potential for **36** is noticed: in this case, the erbium metal centre decreases the electronic density of the thiophene moieties.

For these erbium alkoxides, no reduction or the oxidation of the metal centre is evidenced and no polymeric films are obtained in accordance with the star–shaped molecules **2** and **6**, respectively.

Part 6 Samarium Alkoxides

The study includes the samarium alkoxides {Sm[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (**19**) and {Sm[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**29**) represented in Figure 3.16.



19 **29**

Figure 3.16. Samarium alkoxides studied.

The values of peak potentials of carbinols and these samarium alkoxides obtained in dichloromethane are listed in Table 3.8.

	E_{pa}
HO–C(C_4H_3S)$_3$ (2)	1.48
{Sm[OC(C_4H_3S)$_3$]$_3$(thf)$_3$} • thf (19)	1.62
HO–C(C_4H_3S)$_3$ (4)	1.64
{Sm[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (29)	1.56

Table 3.8. Values peak potentials [V, vs. Ag/AgClO$_4$] of the carbinols and samarium alkoxides, in dichloromethane (3. 15 ×10^{-3} M for 19 and 3.32 ×10^{-3} M for 29) deduced from CV measurements (0 → –1.5 → 1.5 →0 V) on a platinum electrode (diameter 1 mm) at 100 mV.s^{-1}.

By cycling at 100 mV.s^{-1}, no reduction of samarium(III) to samarium(II) is visible at about –0.8 V.[6] The samarium metal centre is wrapped up by the electron–rich organic ligands which inhibit the reduction process and stabilize the metal centre. Only the irreversible waves at 1.62 V for **19** and at 1.56 V for **29** (Figure 3.17) due to the oxidation of the thienyl moieties are present.

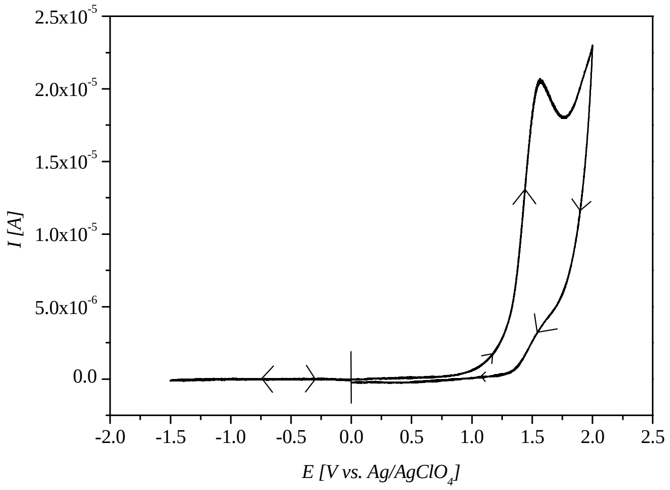


Figure 3.17. Cyclic voltammogram recorded on a platinum electrode in a dichloromethane solution containing <u>29</u> (3.32 × 10^{-3} M) and $[NBu_4][PF_6]$ (0.1 M), vs. $Ag/AgClO_4$, scan rate 100 $mV.s^{-1}$, between 0→ –1.5 → 2 and 0 V.

In comparison with the carbinol **<u>2</u>** and **<u>4</u>**, the oxidation peak of the thiophene units is shifted towards higher values for **<u>19</u>**, whereas for **<u>29</u>**, a shift towards lower values is observed. In agreement with the star–shaped molecules **<u>2</u>** and **<u>4</u>**, no formation of polymeric films is observed during the oxidation process.

Part 7 Conclusion

In this chapter, we have studied and compared the electrochemical behaviours of the organic star−shaped molecules and their corresponding metal derivatives.

The cyclic voltammograms are dominated by the oxidation wave of the thiophene groups. In addition, reduction waves could be obtained due to the reduction of a carbocation.[1b] Indeed, the protons liberated during the oxidation process can protonate these compounds. Subsequent elimination of a H_2O molecule generates then this species with a stabilized tertiary sp^2–hybridized carbon atom.

Contrarily to the other compounds, the cycling of potentials of $HO–C(C_8H_5S_2)_3$ (**<u>1</u>**), $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}$ • 4 thf (**<u>10</u>**) and $Er[OC(C_8H_5S_2)_3]_3(thf)$ (**<u>11</u>**) lead to the formation of polymeric film. These results are in accordance with the alcohol containing dithienyl–substituents.[1c, 5a, 7] The functionalization of the thienyl groups at the α or β−position by a methyl substituent (**5** and **6**) stabilizes the radical cations generated during the oxidation leading to the dications.[3] The oxidation of the dication is also observed for the organic ligand **3**.

We have also demonstrated that the introduction of yttrium or neodymium metals increases the oxidation peak of the thienyl units. These lanthanide ions decrease the electronic density of the heterocycles, which are therefore more difficult to oxidize.

No reduction or oxidation of the yttrium, neodymium or erbium metal centres has been noticed. Surprisingly, even no reduction of samarium(III) to samarium (II) has been encountered for the compounds **19** and **29**. This finding is rationalized by the fact that the samarium metal centre is wrapped up by the electron–rich organic ligands, thus inhibiting the reduction process.

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Chapter 4 Luminescence Studies of Metal Methoxides Containing Thienyl Substituents

Part 1 Introduction

Interest in the photophysical properties of lanthanide ion complexes has grown considerably since J. M. Lehn[1] proposed that such complexes could be seen as light conversion molecular devices (LCMDs). He coined the term "antenna effect" to denote the absorption, energy−transfer, emission sequence involving distinct absorbing (the ligand) and emitting (the lanthanide ion) components, thus overcoming the very small intrinsic absorption coefficients of the lanthanide ions. The design of efficient lanthanide complexes has become an important research goal, being pursued by several groups,[2] working with many different classes of ligands (e.g cryptands,[3] podands,[4] calixarenes,[5] macrocyclic ligands,[6] β−diketones,[7] carboxylic acid derivatives,[8] terphenyl ligands,[9] ect …). Most of the investigated complexes emit red or green light (Eu^{3+} and Tb^{3+} luminescence, respectively), but there are also complexes of different Ln^{3+} ions that luminesce in other spectral regions: near−IR (Yb^{3+}, Nd^{3+}, Er^{3+})[10], orange (Sm^{3+})[11], yellow (Dy^{3+})[5], blue (Tm^{3+})[12] or near−UV (Ce^{3+}, Gd^{3+}).[3, 13]

Recently, emission from rare earth compounds containing thienyl substituents as chromophores has been reported.[14] In our case, the compounds used are assumed to be very suitable for efficient luminescent materials due to the lack of high phonon groups like OH or NH in the ligands, which would lead to some quenching processes.[15]

First of all, the absorption and luminescence behavior of the carbinols will be presented. Then, the alkali metal alcoholates and yttrium compounds will be investigated to get some informations about the position of the electronic excited states of the bonded ligands in relation to the free ones, since K^+, Na^+ and Y^{3+} possess no excited f−states. To finish, the photophysical properties of the neodymium and samarium alkoxides will be studied and the efficiency of the energy transfer from the excited states of the ligand to the excited states of the lanthanide ion will be compared.

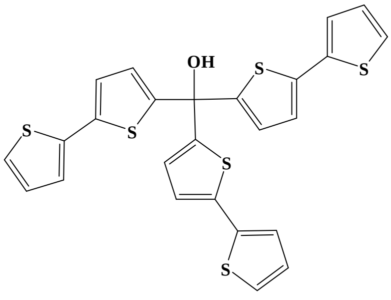
Unfortunately, photophysical investigations of tin(II) alkoxides **14a−b** and **15** could not be performed due to their high instability (see chapter 2). The luminescence spectra of the compounds $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (**26**) and $\{Y[OC(C_{16}H_{13}S)]_3(py)_2\}$ • toluene (**27**) and the erbium alkoxides have not be workable probably due to the decomposition of the solids during the measurements.

Part 2 Organic Ligands

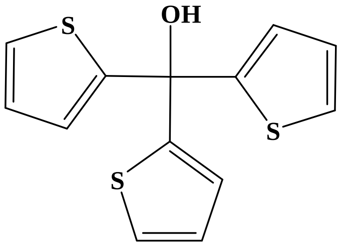
1 Organic Ligands 1 and 2

1.1 UV−Visible Absorption Spectra

The normalized UV−Vis absorption spectra of **1** and **2** (Figure 4.1) measured in dichloromethane at room temperature (Figure 4.2) show an intense absorption band at 236 and 238 nm, respectively. This band is a feature of thiophene units and is assigned to $\pi \rightarrow \pi^*$ transitions of theses moieties.[16] For **2**, two other less intense absorptions at 267 and 314 nm are also present. They are tentatively attributed to $\pi \rightarrow \pi^*$ transitions due to the different conformations of the thienyl groups.[17]



1



2

Figure 4.1. Organic ligands 1 and 2.

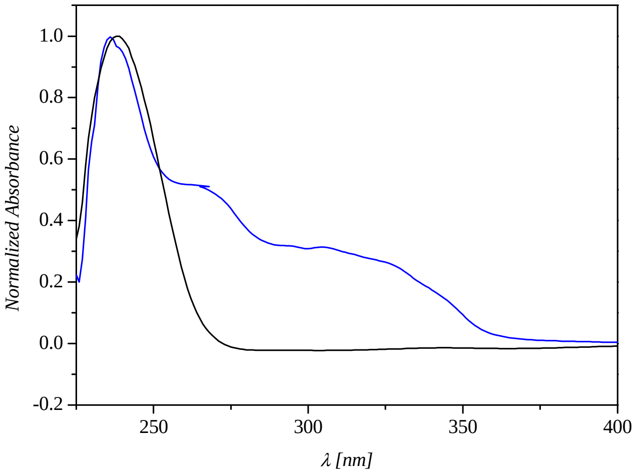


Figure 4.2. Normalized UV−Vis spectra of <u>1</u> (blue line) and <u>2</u> (black line) recorded in dichloromethane at room temperature.

1.2 Luminescence Properties

Solid−state luminescence spectra of the compounds HO−C($C_8H_5S_2$)$_3$ (**<u>1</u>**) and HO−C(C_4H_3S)$_3$ (**<u>2</u>**) are depicted in Figures 4.3 and 4.4. Both carbinols show broad emission bands which can be assigned to $\pi^*\rightarrow\pi$ transitions of the thienyl units. The maxima are located at about 488 and 538 nm (**<u>1</u>**) as well as 430 nm (**<u>2</u>**), respectively. As expected the red shift of the maxima of **<u>1</u>** compared to those of **<u>2</u>** is due to the increasing size of the π system in the latter. The excitation spectrum of **<u>2</u>** has a maximum at 356 nm, while for **<u>1</u>** two different excitation spectra with maxima at about 423 and 464 nm could be detected with emission detection at different energies. This clearly shows that these emission bands not belong to one single thiophenic unit, but must be assigned to two units with different conformations.

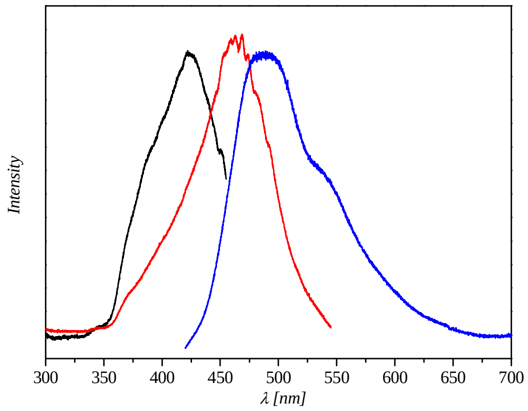


Figure 4.3. Room temperature solid−state luminescence spectra HO−C($C_8H_5S_2$)$_3$ (1). Black line: excitation spectrum, λ_{em} = 470 nm.; red line: excitation spectrum, λ_{em} = 560 nm; blue line: emission spectrum, λ_{ex} = 400 nm.

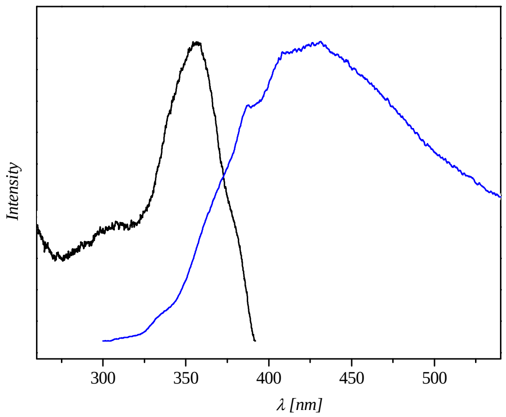


Figure 4.4. Room temperature solid−state luminescence spectra of HO−C(C_4H_3S)$_3$ (2). Black line: excitation spectrum, λ_{em} = 410 nm. Blue line: emission spectrum, λ_{ex} = 280 nm.

2 Organic Ligands 3 and 4

2.1 UV−Visible Absorption Spectra

As noticed for the carbinol **2**, the UV−Vis absorption spectra of **3** and **4** are dominated by a broad band at 237 and 235 nm (Table 4.1), respectively, attributed to the $\pi\rightarrow\pi^*$ transitions of the aromatic moieties. Note that in comparison with **2**, the absorption wavelengths decrease with the number of thiophene units present, probably due to reduction of the conjugation inside the molecule.

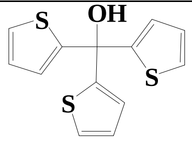
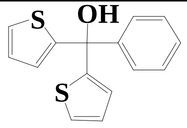
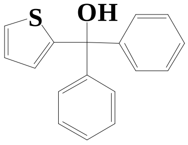
	λ_{abs} [nm]
 **2**	238
 **3**	237
 **4**	235

Table 4.1. Absorption maxima λ_{abs} [nm] of the ligands 2, 3 and 4 recorded at room temperature, dissolved in dichloromethane.

2.2 Luminescence Properties

As can be seen in the Figure 4.5 and Figure 4.6, the emission depends on the excitation wavelengths. Indeed, for **3**, after excitation at 260 nm, the emission observed is at 402 nm attributed to $\pi^* \rightarrow \pi$ transitions of the aromatic units. But, upon an excitation at 340 nm, a new band is present centered at 500 nm: this emission can be assigned to the dimer (excimer[i]) due to a π interaction (π−stacking) between the aromatic groups.[18] For the organic ligand **4**, the same phenomenon is observed.

---

[i] Excimers are dimers in the excited state (the term excimer results from the contraction of "excited dimer"). They are formed by collision between an excited molecule and an identical unexcited molecule:

$^1M^* + {}^1M \leftrightarrow {}^1(MM)^*$

The symbolic representation (MM)* shows that the excitation energy is delocalized over the two moieties

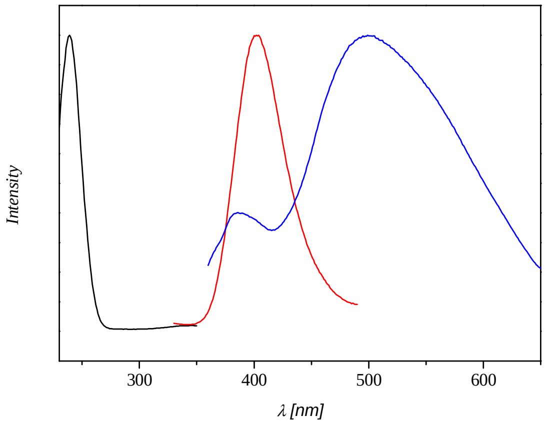


Figure 4.5. Room temperature solid−state luminescence spectra HO−C($C_{14}H_{11}S_2$) (3). Black line: excitation spectrum, λ_{em} = 400 nm.; red line: emission spectrum, λ_{em} = 260 nm; blue line: emission spectrum, λ_{ex} = 340 nm.

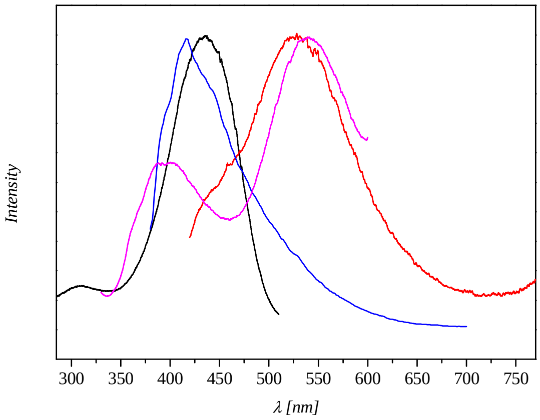


Figure 4.6. Room temperature solid−state luminescence spectra HO−C($C_{16}H_{13}S$) (4). Black line: excitation spectrum, λ_{em} = 510 nm.; red line: emission spectrum, λ_{em} = 400 nm; blue line: emission spectrum, λ_{ex} = 360 nm, magenta line: emission spectrum, λ_{ex} = 310 nm.

In agreement with the UV−Vis spectra, the emission bands are shifted towards lower wavelengths when the number of thiophene groups decreases (430 nm for **2**, 402 nm for **3** and 392 nm for **4**).

3 Organic Ligands 5 and 6

3.1 UV−Visible Absorption Spectra

The UV−Vis absorption spectra normalized of **5** and **6** measured in dichloromethane at room temperature (Table 4.2) show an intense absorption band at 241 and 231 nm, respectively, again assigned to the $\pi \rightarrow \pi^*$ transitions.

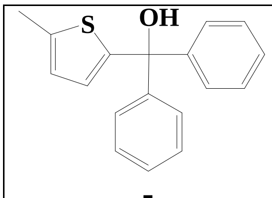
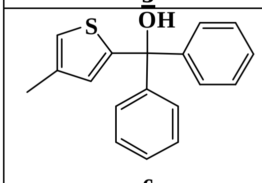
	λ_{abs} **[nm]**
 **5**	241
 **6**	231

Table 4.2. Absorption maxima λ_{abs} [nm] of the ligands 5 and 6 recorded at room temperature, dissolved in dichloromethane.

3.2 Luminescence Properties

The compounds **5** and **6** show a broad emission at 527 and 400 nm, respectively (Table 4.3). They are again attributed to the $\pi^* \rightarrow \pi$ transitions of the aromatic units. Note that for **5**, the emission of the dimer (excimer) is visible at 619 nm.

	λ_{em} **[nm]**
5	527, 619
6	400

Table 4.3. Solid−state emission maxima λ_{em} [nm] of the carbinols 5 and 6, λ_{ex} = 260 nm.

4 Organic Ligands 7 and 8

4.1 UV−Visible Absorption Spectra

The UV−Vis absorption spectra of **7** and **8** measured in dichloromethane at room temperature (Figure 4.7) display broad band at 237 (ε = 15600 $M^{-1}.cm^{-1}$) and 231 nm (ε = 12750 $M^{-1}.cm^{-1}$), respectively, attributed to the $\pi \rightarrow \pi^*$ transitions of the aromatic units. The second maxima at 296 nm (ε = 470 and 2060 $M^{-1}.cm^{-1}$, respectively) can also be assigned to a transition $\pi \rightarrow \pi^*$.

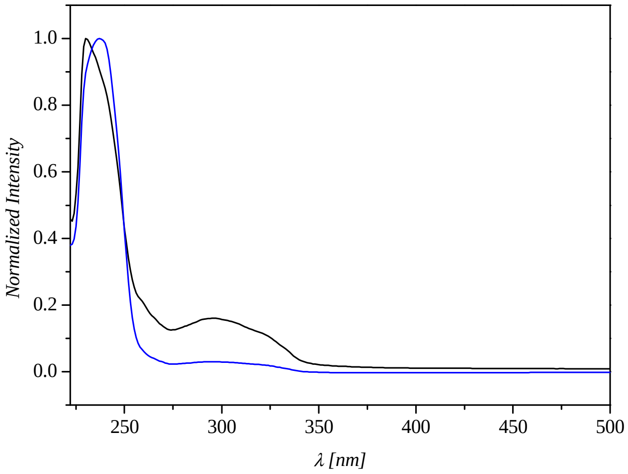


Figure 4.7. Normalized UV−Vis spectra of 7 (blue line) and 8 (black line) recorded in dichloromethane at room temperature.

In agreement with **2**−**4**, the more intense absorption wavelength of **7** and **8** decreases with the number of thiophene units present in the molecule.

4.2 Luminescence Properties

The emission spectra of **7** and **8** are dominated by a broad band at 400 and 398 nm, respectively, due to the $\pi^* \rightarrow \pi$ transitions of the aromatic moieties (Table 4.4).

	λ_{em} [nm]
7	400
8	398

Table 4.4. Solid−state emission maxima λ_{em} [nm] of the carbinols 7 and 8, λ_{ex} = 260 nm.

Compared to the analogues **3** and **4**, no significant variations have been observed.

Part 3 Alkali Metal Alcoholates

The general representation of the alkali metal alcoholates studied is given in Figure 4.8.

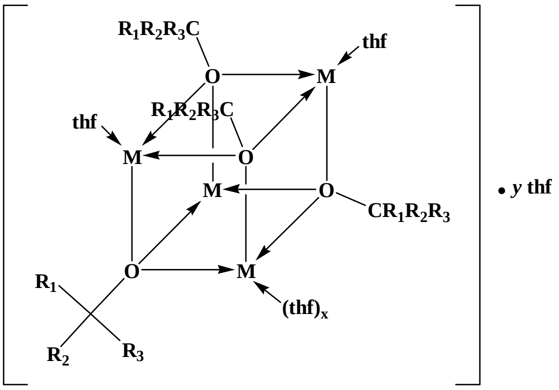


Figure 4.8. Alkali metal alcoholates studied. M = K, Na. R_1, R_2 and R_3 stand for the thiophene or the phenyl groups.

1 UV−Visible Absorption Spectra

The UV−Vis absorption spectra of the alkali metal alcoholates (K, Na) recorded in acetonitrile at room temperature display one single band, assigned to the $\pi \rightarrow \pi^*$ transitions of the aromatic groups (Table 4.5). For **7** and **8**, a second absorption band in the 250−280 nm range is present whereas for the alkali metal alcoholates **37** and **41** no absorption was visible in this region.

	λ_{abs} [nm]
$HO–C(C_4H_3S)_3$ (2)	241
$\{[KOC(C_4H_3S)_3]_4(thf)_2\} \bullet thf$ (12)	238
$[NaOC(C_4H_3S)_3]_4(thf)_2$ (13)	235
$HO–C(C_{14}H_{11}S_2)$ (3)	240
$[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (21)	237
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (22)	237
$HO–C(C_{16}H_{13}S)$ (4)	239
$\{[KOC(C_{16}H_{13}S)]_4(thf)_3\} \bullet \frac{1}{2}\, thf$ (25)	235
$HO–C(C_{17}H_{15}S)$ (5)	241
$[KOC(C_{17}H_{15}S)]_4(thf)_2$ (31)	242
$[NaOC(C_{17}H_{15}S)]_4(thf)_2$ (32)	240
$HO–C(C_{14}H_{11}S_2)$ (7)	240, 269
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (37)	236
$HO–C(C_{16}H_{13}S)$ (8)	239, 265
$[NaOC(C_{16}H_{13}S)]_4(thf)_2$ (41)	235

Table 4.5. Absorption maxima λ_{abs} [nm] of the ligands and alkali metal compounds (K, Na) recorded at room temperature, in acetonitrile.

In comparison with their respective carbinol precursors, a slight blue shift of the $\pi \rightarrow \pi^*$ transitions is evident, apart from the case of salt **31** and **32**.

2 Luminescence Properties

The alkali metal alcoholate solid−state emission spectra consist of broad bands which are attributed to the $\pi^* \rightarrow \pi$ transitions of the aromatic ligands (Table 4.6). In accordance with the UV−Vis absorption spectra, blue shifts of the emission maxima compared to those of the thiophenic alcohols are observed (excepted for **22**, may be due to a different excitation value).

	λ_{ex} [nm]	λ_{em} [nm]
$HO–C(C_4H_3S)_3$ (2)	280	430
$\{[KOC(C_4H_3S)_3]_4(thf)_2\} \bullet thf$ (12)	240	390
$[NaOC(C_4H_3S)_3]_4(thf)_2$ (13)	240	393
$HO–C(C_{14}H_{11}S_2)$ (3)	260	402
$[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (21)	250	396
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (22)	360	408
$HO–C(C_{16}H_{13}S)$ (4)	310	392
$\{[KOC(C_{16}H_{13}S)]_4(thf)_3\} \bullet ½\ thf$ (25)	310	385
$HO–C(C_{17}H_{15}S)$ (5)	360	527
$[KOC(C_{17}H_{15}S)]_4(thf)_2$ (31)	390	486
$[NaOC(C_{17}H_{15}S)]_4(thf)_2$ (32)	340	430
$HO–C(C_{14}H_{11}S_2)$ (7)	260	400
$[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (37)	260	398
$HO–C(C_{16}H_{13}S)$ (8)	260	398
$[NaOC(C_{16}H_{13}S)]_4(thf)_2$ (41)	260	397

Table 4.6. Solid−state emission maxima λ_{em} [nm] of the carbinols and these alkali metal alkoxides (K, Na) upon a λ_{ex} [nm] excitation.

Part 4 Yttrium Alkoxides

The general representation of the yttrium alkoxides studied is given in Figure 4.9.

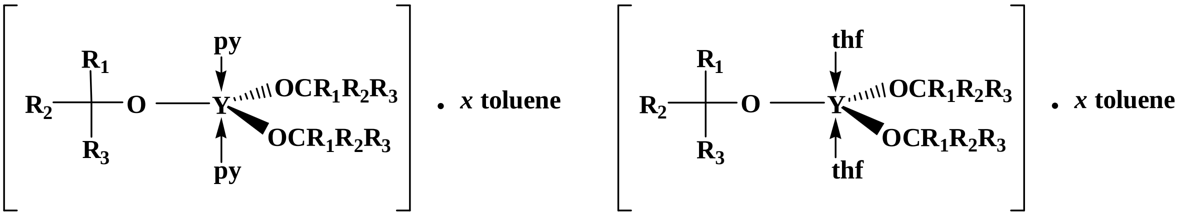


Figure 4.9. Yttrium alkoxides studies. R_1, R_2 and R_3 stand for the thiophene or the phenyl groups.

1 UV−Visible Absorption Spectra

The UV−Vis absorption spectra of the yttrium methoxides containing thiophene derivatives, show, similar as their organic ligands, a broad band assigned to the $\pi\rightarrow\pi^*$ transitions of the aromatic groups (Table 4.7). The absorptions appear at about the same or at more important wavelengths than their corresponding alcohols. This bathochromic effect can be explained by a stabilization of the ligand π^* orbitals shifting their absorptions to lower energy, caused by their coordination on metal centre.[14b, 19] Note that for complexes **38**, **39** and **42**, only one absorption band is visible, contrarily to their respective carbinols.

	λ_{abs} [nm]
HO–C(C_4H_3S)$_3$ (2)	238
Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (16a)	257
Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$ (17a)	250
HO–C($C_{16}H_{13}S$) (4)	235
{Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (26)	236
{Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$} • toluene (27)	235
HO–C($C_{17}H_{15}S$) (5)	241
{Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (33)	241
{Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34)	244
HO–C($C_{14}H_{11}S_2$) (7)	237, 296
{Y[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_2$} • ½ toluene (38)	237
Y[OC($C_{14}H_{11}S_2$)]$_3$(py)$_2$ (39)	245
HO–C($C_{16}H_{13}S$) (8)	231, 296
Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$ (42)	244

Table 4.7. Absorption maxima λ_{abs} [nm] of the ligands and yttrium compounds recorded at room temperature, in dichloromethane.

2 Luminescence Properties

The solid−state emission maxima of the carbinols and their corresponding yttrium alkoxides are given in Table 4.8.

	λ_{ex} [nm]	λ_{em} [nm]
HO–C(C_4H_3S)$_3$ (2)	280	430
Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (16a)	250	394
Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$ (17a)	250	338, 392
HO–C($C_{17}H_{15}S$) (5)	360	527
{Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (33)	260	399
{Y[OC($C_{17}H_{15}S$)]$_3$(py)$_2$} • toluene (34)	260	398
HO–C($C_{14}H_{11}S_2$) (7)	260	400
{Y[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_2$} • ½ toluene (38)	260	398
Y[OC($C_{14}H_{11}S_2$)]$_3$(py)$_2$ (39)	260	399
HO–C($C_{16}H_{13}S$) (8)	260	398
Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$ (42)	260	399

Table 4.8. Solid−state emission maxima λ_{em} [nm] of the carbinols and these yttrium alkoxides upon a λ_{ex} [nm] excitation.

The yttrium alkoxides emission spectra are very similar and consist of broad, nearly Gaussian shaped bands which are attributed to the $\pi^* \rightarrow \pi$ transitions of the aromatic ligands. Nearly identical maxima are obtained. The full width at half maximum (FWHM) of e.g. **17a** is 3900 cm^{-1}. In comparison with **16a**, **17a** also presents an emission band at 338 nm which can be assigned to the pyridine rings (Figure 4.10). Nevertheless, this pyridine band is not detectable in the emission spectra of the other pyridine adducts (for example see Figure 4.11).

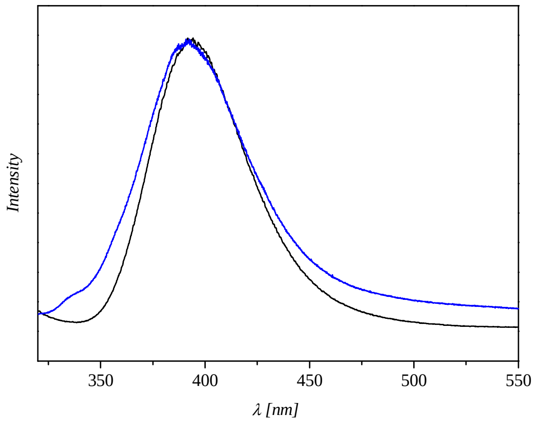


Figure 4.10. Solid−state emission spectra recorded at room temperature of the compounds 16a (black line), 17a (blue line), λ_{ex} = 250 nm.

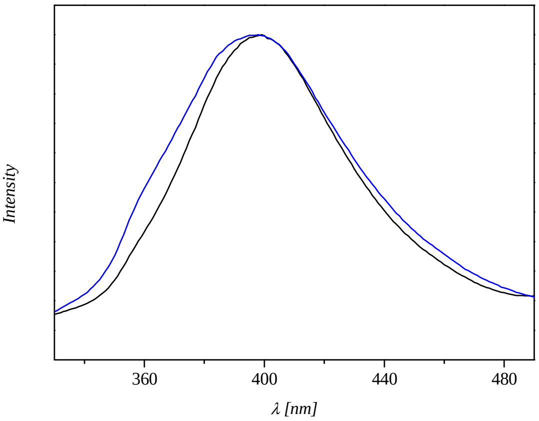


Figure 4.11. Solid−state emission spectra recorded at room temperature of the compounds 33 (black line), 34 (blue line), λ_{ex} = 250 nm.

In contrast to the absorption spectra, a blue shift of the transitions in the emission spectra compared to those of the thiophenic alcohols is observable. This blue shift is probably due to some distortions of these units in the solid−state upon coordination to the yttrium ions.

Part 5 Neodymium Alkoxides

The general representation of the neodymium alkoxides studied is given in Figure 4.12.

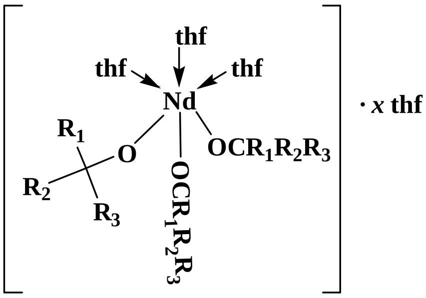


Figure 4.12. Neodymium alkoxides studied. R_1, R_2 and R_3 stand for the thiophene or the phenyl groups.

1 UV−Visible Absorption Spectra

The UV−Vis absorption spectra of the neodymium alkoxides exhibit, as their respective carbinol, the $\pi \rightarrow \pi^*$ transitions of the aromatic groups (Table 4.9). Note that contrarily to the carbinol **8**, the UV−Vis absorption spectrum of the neodymium alkoxide **43** does not display an absorption band in the range between 280−310 nm.

	λ_{abs} [nm]
HO–$C(C_8H_5S_2)_3$ (1)	236, 267, 314
{Nd[$OC(C_8H_5S_2)_3]_3(thf)_3$} • 4 thf (10)	232, 262, 312
HO–$C(C_4H_3S)_3$ (2)	238
{Nd[$OC(C_4H_3S)_3]_3(thf)_3$} • thf (18)	239
HO–$C(C_{14}H_{11}S_2)$ (3)	237
{Nd[$OC(C_{14}H_{11}S_2)]_3(thf)_3$} • thf (23)	237
HO–$C(C_{16}H_{13}S)$ (4)	235
{Nd[$OC(C_{16}H_{13}S)]_3(thf)_3$} • thf (28)	232
HO–$C(C_{14}H_{11}S_2)$ (7)	237, 296
Nd[$OC(C_{14}H_{11}S_2)]_3(thf)_3$ (40)	235, 264
HO–$C(C_{16}H_{13}S)$ (8)	231, 296
{Nd[$OC(C_{16}H_{13}S)]_3(thf)_3$} • thf (43)	229

Table 4.9. Absorption maxima λ_{abs} [nm] of the ligands and neodymium compounds recorded at room temperature, in dichloromethane.

Compared to the carbinol precursors, the absorption wavelengths of these neodymium alkoxides are in the same range or shifted towards lower values. These small blue shifts have been also observed by D’Aléo *et al.*[20] for lanthanide complexes containing push−pull donor−π−conjugated dipicolinic acid ligands. Nevertheless, no RE−transitions (RE = Rare Earth) are visible probably due to the low concentration of the solution (measurements at more important concentration are not possible because of the low solubility of these products). Therefore, for the compounds **10** and **18**, reflection spectra have been investigated.

2 Reflexion Properties of 10 and 18

The solid−state DR (DR = diffuse reflectance) spectra of **10** and **18** recorded at room temperature are shown in Figure 4.13. In the UV region (250−400 nm), all broad absorption bands are observed and can be assigned to electronic transition of the organic ligands. In the region above 400 nm, in this figure, each absorption bands correspond to a characteristic transition two spin−orbit coupling levels of the neodymium ion. Based on the energy level scheme of this ion, these bands can be attributed to the transitions from the ground state $^4I_{9/2}$ to the higher energy levels for the neodymium alkoxides.[21]

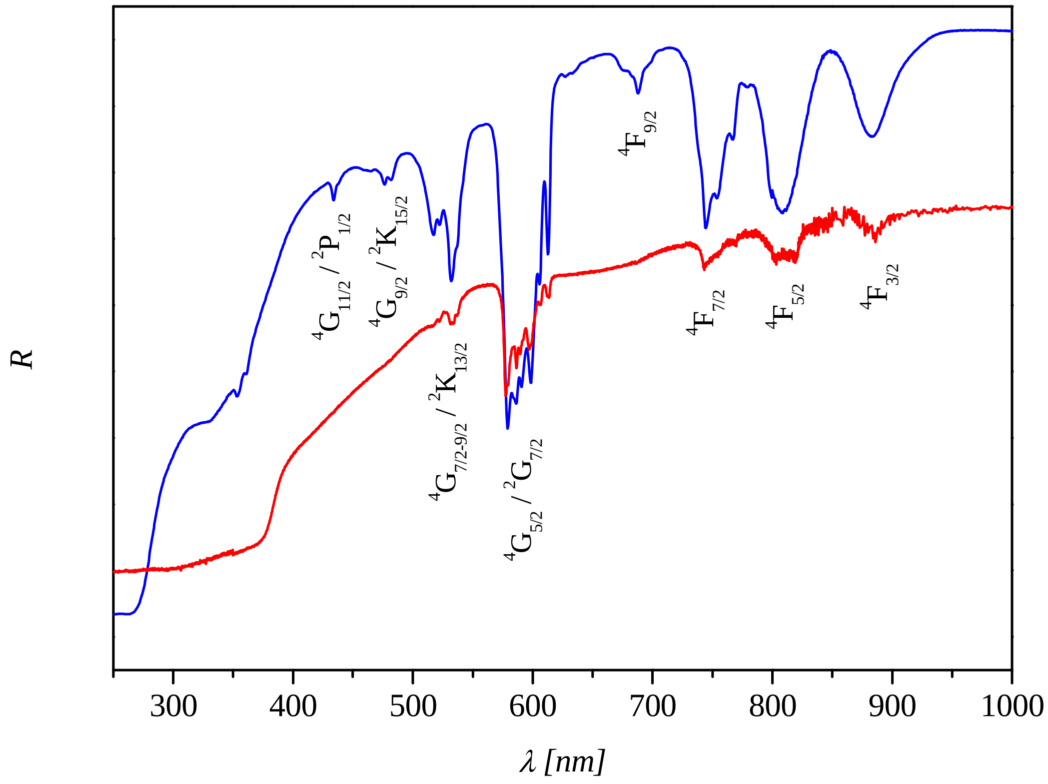


Figure 4.13. DR spectra of 10 (red line) and 18 (blue line).

3 Luminescence Properties

3.1 Neodymium Alkoxides 10 and 18

Room temperature solid−state emission spectra of $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\} \bullet 4\ thf$ (**10**) and $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\} \bullet thf$ (**18**) in the NIR range upon excitation of the ligands (see below) are depicted in Figure 4.14. Typical Nd^{3+} $4f^3 \rightarrow 4f^3$ transitions are detected which can be assigned to emission from the excited $^4F_{3/2}$ state to $^4I_{9/2}$ (around 900 nm), $^4I_{11/2}$ (1070 nm), and $^4I_{13/2}$ (1350 nm) ground states (Figure 4.15).[21b, 22] Due to the pure Nd compounds the bands are relatively broad and no crystal field splitting is resolved. This process is known as the "antenna effect", resulting in an energy transfer from the ligand to the lanthanide centre.[23] No ligand emission bands could be detected in the visible leading to the assumption of relatively efficient energy transfer processes.

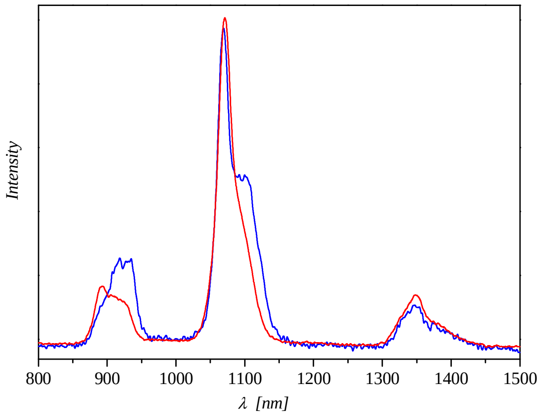


Figure 4.14. NIR solid−state emission spectra at room temperature for compounds 10 (blue line), 18 (red line) λ_{ex} = 373 (10) and 347 nm (18).

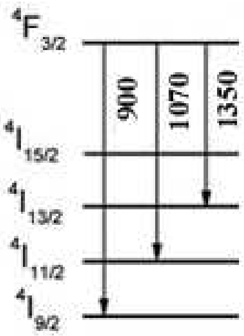


Figure 4.15. Representation and assignment of the emission Nd^{3+} *f−f* transitions (in nm).

Their respective solid−state excitation spectra monitoring the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition (Figure 4.16) consist of bands corresponding to Nd^{3+} *f−f* transitions, as well as broader bands due to the ligand transitions. The maxima and assignements of the former of **18** are listed in Table 4.10. These spectra are similar than those obtained for the reflexion studies. Due to the manifold of excited 4f states in the visible region, some transitions to different states are not resolved, and the bands are relatively broad compared to doped compounds.[24] The ligand bands are located at 373 nm (**10**) and 345 nm (**18**), respectively. For **18** it can be assumed that they are at comparable energy than those of the yttrium compounds (**16a**: emission at 394 nm, see above). Due to the larger *π* system, the maximum for **10** is at lower energy. Because the ligand emission bands will be located at lower energy than the excitation bands there is a good overlap with some *4f* Nd excited states which is the condition of dipole−dipole energy transfer mechanism which can be assumed in the present case.[25]

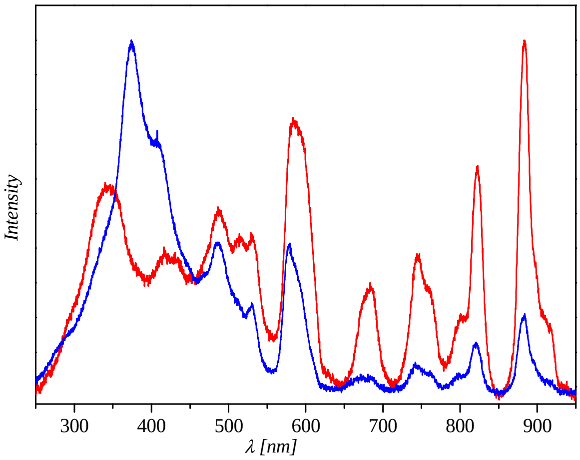


Figure 4.16. Solid−state excitation spectra at room temperature for compounds 10 (blue line) and 18 (red line), λ_{em} = 1070 nm.

Transitions	Wavelengths [nm]
$^4I_{9/2} \rightarrow {}^4F_{3/2}$	884
$^4I_{9/2} \rightarrow {}^4F_{5/2}$	822
$^4I_{9/2} \rightarrow {}^4F_{7/2}$	746
$^4I_{9/2} \rightarrow {}^4F_{9/2}$	682
$^4I_{9/2} \rightarrow {}^4G_{5/2}/{}^2G_{7/2}$	585
$^4I_{9/2} \rightarrow {}^4G_{7/2-9/2}/{}^2K_{13/2}$	530, 512
$^4I_{9/2} \rightarrow {}^4G_{9/2}/{}^2K_{15/2}$	486
$^4I_{9/2} \rightarrow {}^4G_{11/2}/{}^2P_{1/2}$	420

Table 4.10. Maxima and assignments of Nd^{3+} *f−f* transitions of 18.

The existence of an energy transfer is also proofed by the presence of ligand excitation bands while monitoring the Nd emission. Moreover, the differences of the relative intensities of the ligand and Nd excitation bands give further information about the energy transfer efficiency. For **18** the intensity of the Nd *4f* bands is much higher than those of the ligand bands. Therefore, Nd emission intensity is much larger if exciting Nd directly than exciting the ligands, especially because *4f−4f* transitions are forbidden and, thus, rather weak. On the other hand, the absence of ligand emission shows that energy transfer is not inefficient or the ligand emission is fully quenched. Because the latter is not very probable the Nd emission may be rather quenched by some amount after ligand excitation, but not after Nd excitation. The situation is different in the case of **10**, where the excitation ratio I(ligands)/I(Nd) is much higher, showing a much more efficient Nd emission after ligand excitation. This phenomenon is probably due to the location of the ligand bands at lower energy leading to a better overlap with Nd *4f* excited states or a more advantageous arrangement of the ligands around the metal ions. In general, the observation of Nd NIR emission bands after ligand excitation confirms the applicability for the present ligands in this context due to the absence of high energy phonons.[25]

3.2 Neodymium Alkoxides 23 and 28

Solid−state excitation and emission spectra of complexes **23** and **28** are illustrated in Figures 4.17 and 4.18. Electronic *f−f* transitions of a lanthanide ion are only weakly affected by the ligands surrounding the complex. Therefore assignments of the line−like bands arising from *f−f* transitions can be attributed using published data (see above).

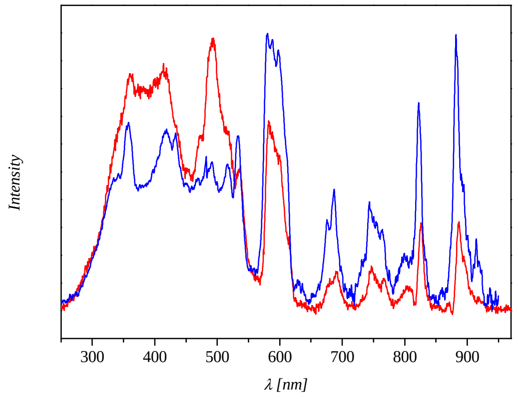


Figure 4. 17. Solid−state excitation spectra at room temperature for compounds 23 (blue line) and 28 (red line), λ_{em} = 1068 (23) and 1080 (28) nm.

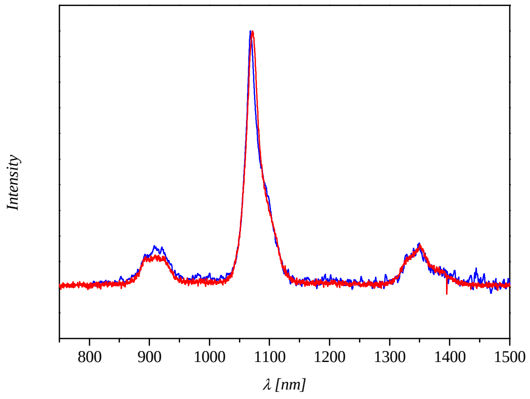


Figure 4.18. NIR solid−state emission spectra at room temperature for compounds 23 (blue line), 28 (red line) λ_{ex} = 373 (23) and 360 nm (28).

The excitation spectra monitoring the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition display broad bands (centred at 373 nm for **23** and 360 nm for **28**) due to the absorption of the ligand (π−π* transitions) superimposed with bands originating from Nd^{3+} transitions.[21d] As in the case of **18**, the excitation bands of the Nd^{3+} ion are more intense than that of the ligands. Therefore, in these examples, Nd emission intensity is much stronger if exciting Nd directly than exciting the ligands. Nevertheless, the characteristic emission stemming from Nd^{3+} upon excitation on the ligand absorption [λ_{ex} = 373 (**23**) and 360 nm (**28**)] clearly suggests that the luminescence of complexes **23** and **28** are achieved by an energy transfer from the ligand excited state to the neodymium excited state, following the schematic representation of the "antenna effect" and in accordance with a dipole−dipole energy transfer mechanism.

The I(ligand)/I(Nd) of the excitation spectra can provide some information about the efficiency of the energy transfer for the different neodymium alkoxides. In this view, it can be classified as following: **18** < **23** < **28** < **10**. This storing can be explained by the location of the ligand bands at a different energy leading to a better overlap to Nd *4f* excited states or a more advantageous arrangement of the ligands to the metal ions.

3.3 Neodymium Alkoxides 40 and 43

The solid−stat excitation spectra of complexes **40** and **43** were obtained by monitoring the characteristic emission of the Nd^{3+} ion at 1065 nm (Figure 4.19). These spectra display bands ranging from 250−290 nm for both compounds assigned to the absorption of the organic ligands. The absorption transitions of the Nd^{3+} ions are also observed. These *f−f* transitions correspond to $^4I_{9/2} \rightarrow {}^4D_{1/2}$ (360 nm), $^4I_{9/2} \rightarrow {}^4G_{11/2} / {}^2P_{1/2}$ (436 nm), $^4I_{9/2} \rightarrow {}^4G_{9/2} / {}^2K_{15/2}$ (482 nm), $^4I_{9/2} \rightarrow {}^4G_{7/2-9/2} / {}^2K_{13/2}$ (518 and 535 nm) and $^4I_{9/2} \rightarrow {}^4G_{5/2} / {}^2G_{7/2}$ (583 nm). The presence of ligand absorption suggests the existence of an energy transfer from the ligand to the neodymium metal centre.

The solid−state emission spectra (Figure 4.20) upon an excitation on the neodymium [588 (**40**) and 360 nm (**43**)] consist of three bands at λ = 900, 1070 and 1350 nm, attributed to the *f−f* transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, respectively. They are in agreement with those of the emission spectra of the other neodymium alkoxides (see above).

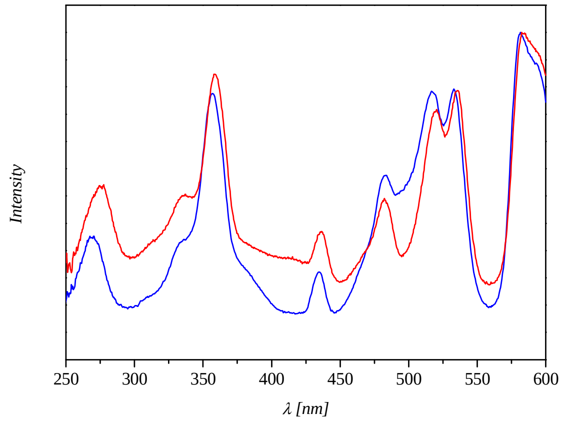


Figure 4.19. Solid−state excitation spectra at room temperature for compounds 40 (blue line) and 43 (red line), λ_{em} = 1065 nm.

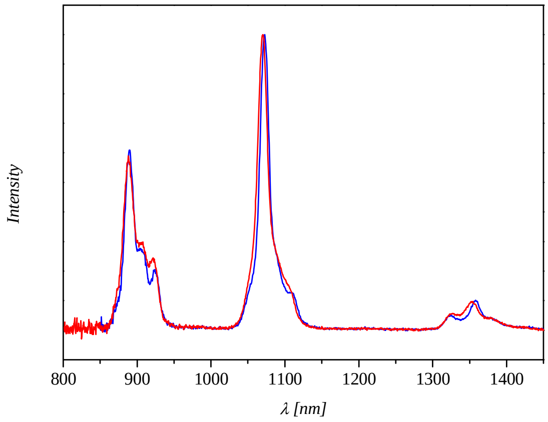
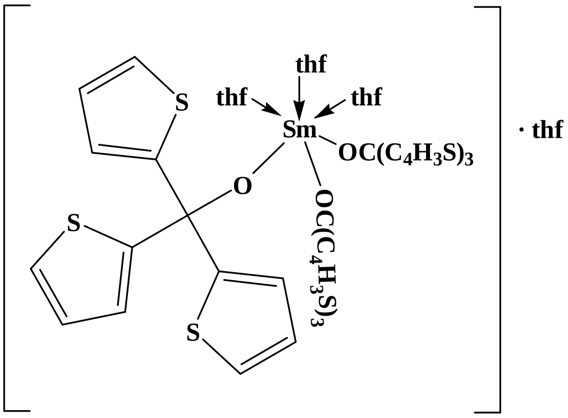


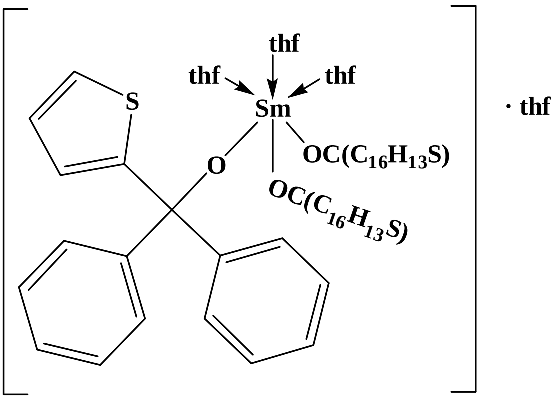
Figure 4.20. NIR solid−state emission spectra at room temperature for compounds 40 (blue line), 43 (red line) λ_{ex} = 588 (23) and 360 nm (28).

Part 6 Samarium Alkoxides

This section will treat the samarium alkoxides $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (**19**) and $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (**29**) represented in Figure 4.21.



19



29

Figure 4.21. Samarium alkoxides studied.

1 UV−Visible Absorption Spectra

The UV−Vis absorption spectra of the samarium methoxides containing thiophene substituents, exhibit, like their corresponding organic ligands, a broad band assigned to the $\pi \rightarrow \pi^*$ transitions of the aromatic groups (Table 4.11). As noticed for their neodymium alkoxide counterparts, their absorptions are found at somewhat lower wavelengths than their respective alcohols.

	λ_{abs} [nm]
HO–$C(C_4H_3S)_3$ (2)	238
$\{Sm[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (19)	236
HO–$C(C_4H_3S)_3$ (4)	235
$\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (29)	233

Table 4.11. Absorption maxima λ_{abs} [nm] of the ligands and samarium compounds recorded at room temperature, solved in dichloromethane.

However, no RE−transitions are visible probably due to the low concentration of the solution (measurements at more important concentration are not possible because of the low solubility of these products).

2 Luminescence Properties

2.1 Luminescence Properties of 19

The solid−state excitation and emission spectra of **19** recorded at room temperature are given in Figures 4.22 and 4.23.

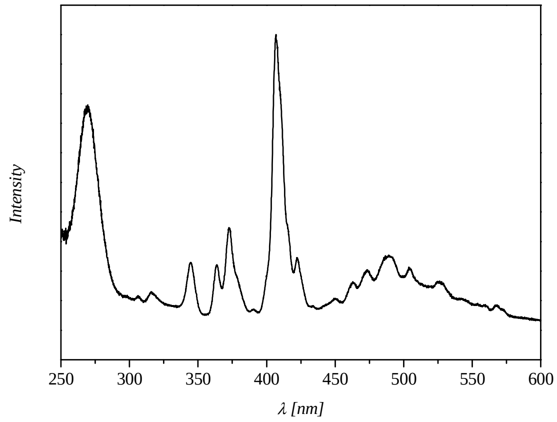


Figure 4.22. Solid−state excitation spectrum at room temperature for compound 19, λ_{em} = 651 nm.

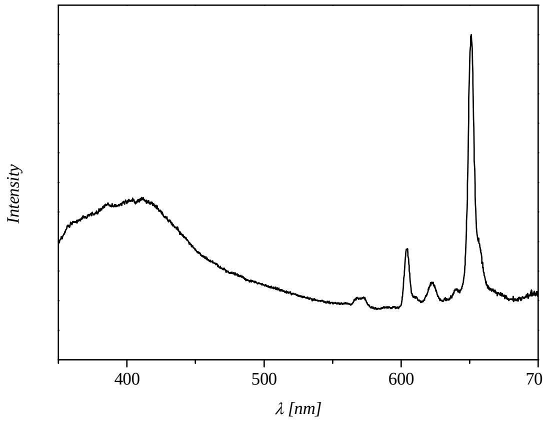


Figure 4.23. Solid−state emission spectrum at room temperature for compound 19, λ_{ex} = 270 nm.

The excitation spectrum of the samarium alkoxide **19** monitoring the $^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ transition reveals a broad band that covers the entire 250−300 nm region with a maximum at 270 nm attributed to the $\pi \rightarrow \pi^*$ transitions of the organic ligands. This observation suggests the existence of an energy transfer from the organic ligands to the metal centre. The spectrum also presents several narrow bands of the Sm^{3+} ion arising from the intraconfigurational transitions from the $^{6}H_{5/2}$ ground state to the following levels: $^{4}H_{9/2}$ (344 nm), $^{4}F_{9/2}$ (363 nm), $^{4}L_{17/2}$ (373 nm), $^{4}F_{7/2}$ (406 nm), $(^{6}P, {}^{4}P)_{5/2}$ (422 nm), $^{4}G_{9/2}$ (450 nm), $^{4}I_{13/2}$ (462 nm), $^{4}I_{11/2}$ (473 nm), $^{4}I_{9/2}$ (488 nm), $^{4}G_{7/2}$ (504 nm), $^{4}F_{3/2}$ (526 nm) and $^{4}G_{5/2}$ (568 nm). These transition values are in agreement with those found for Sm^{3+} doped germinate glasses and glass ceramic (Figure 4.24), and those for samarium complexes.[14c, 26] As **18**, the intensity of the lanthanide *4f* bands is much higher than those of the ligand bands. Therefore, the Sm emission intensity is much larger if exciting Sm directly than exciting the ligands.

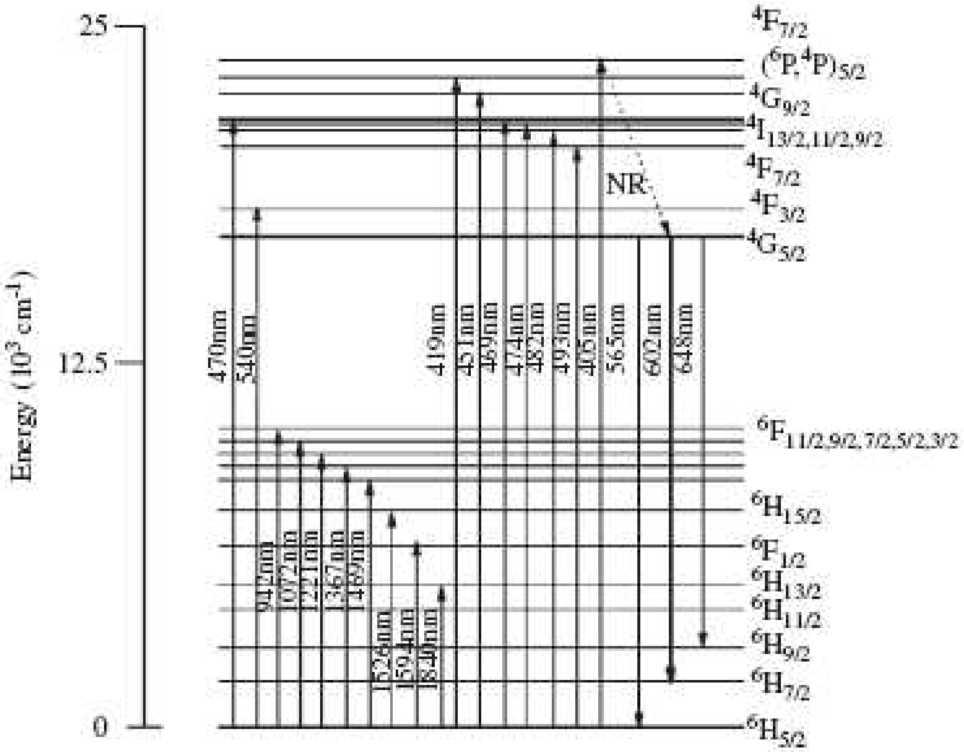


Figure 4.24. Energy levels scheme for absorption, excitation and emission transitions of Sm^{3+} doped germinate glasses and glass ceramics.

The emission spectrum of **19** upon an excitation on the organic ligand (λ_{ex} = 270 nm) displays the typical Sm^{3+} bands at around 570, 604, 650 nm. They are attributed to $4f^5$−$4f^5$ transitions $^4G_{5/2}$ → $^6H_{5/2}$ (zero−zero band: forbidden transition), $^4G_{5/2}$ → $^6H_{7/2}$ (magnetic dipole transition), $^4G_{5/2}$ → $^6H_{9/2}$ (electric dipole transition), respectively.[27] Note that another samarium band at 622 nm is observed, probably also due to the $^4G_{5/2}$ → $^6H_{7/2}$ transition: it might be a result of splitting due to ligand field. In addition to the Sm^{3+} emission, a broad band is assigned to the fluorescence from the organic ligand in the range from 350 to 520 nm. The relative intensity between the broad band and the Sm^{3+} emission lines suggests that the efficiency of the energy transfer ligand−to−metal process (dipole−dipole energy transfer mechanism) is not efficient.

Comparing the luminescence properties with those of the lanthanide compound **18**, one may conclude that the organic ligand to the metal ion energy transfer processes is more efficient in the case of Nd^{3+} than in the case of Sm^{3+}. This finding can be explained based on the more favourable energy mismatch conditions in the case of Nd^{3+}.

2.2 Luminescence Properties of 29

The solid−state excitation and emission spectra of **29** are depicted in Figures 4.25 and 4.26.

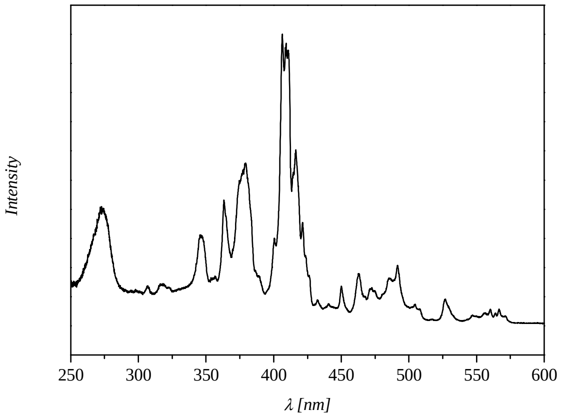


Figure 4.25. Solid−state excitation spectrum at room temperature for compound 29, λ_{em} = 650 nm.

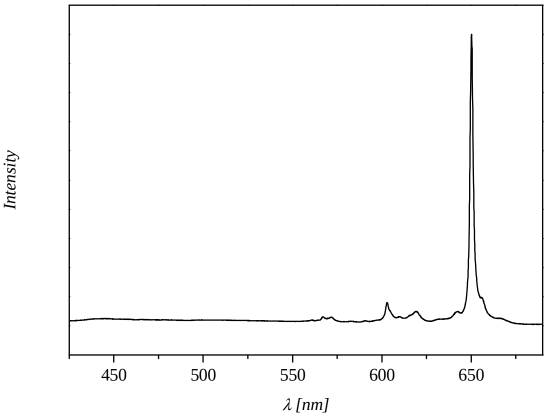


Figure 4.26. Solid−state emission spectrum at room temperature for compound 29, λ_{ex} = 410 nm.

The excitation spectrum of the samarium alkoxide **29** monitoring the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition reveals, as in the case of **19**, a broad band that covers the entire 250−395 nm region with a maximum at 273 nm. This is attributed to the $\pi \rightarrow \pi^*$ transitions of the organic ligands which suggest again the existence of an energy transfer from the organic ligands to the metal centre. In addition, within this spectrum occurs the typical *f*−*f* absorption of the Sm^{3+} ions.

When the $^4F_{7/2}$ level (410 nm) is excited, the emission spectrum of this compound is composed of a series of straight lines assigned to the Sm^{3+} intra−$4f^5$ transitions: $^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2}$. Note that, as **19**, a samarium band at 622 nm is observed, probably also due to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition: it might be a result of splitting due to ligand field.

The I(ligand)/I(Sm) ratio of the excitation spectra can provide some information about the efficiency of the energy transfer for the different samarium alkoxides. In this regard, and contrarily to this found for the neodymium alkoxides, it can be classified as following: **29** < **19**. The reason for this inversion may be the location of the ligand bands at higher energy, leading to a better overlap to Sm *4f* excited states or a more advantageous arrangement of the ligands around the metal ions.

Part 7 Conclusion

This chapter discusses the photophysical properties of the carbinols and their corresponding metal derivatives. The UV−Vis absorption spectra are dominated by the organic ligands ($\pi \rightarrow \pi^*$ transitions of the aromatic groups). Compared to the carbinols, the absorption wavelengths of the alkali metal alcoholates and the neodymium and samarium alkoxides are in the same range or show a weak blue shift. However, the yttrium alkoxides have absorption at the same or at somewhat higher wavelengths than their alcohols. Theses bathochromic effects can be explained by a stabilization of the ligand π^* orbitals shifting their absorptions to lower energy, caused by their coordination of the metal centre. No RE−transitions for the neodymium and samarium alkoxides are visible probably due to the low concentration of the solution (measurements at more important concentration are not possible because of the low solubility of these products). Therefore, for the compounds **10** and **18**, reflection spectra have been investigated. Their DR spectra display the characteristic transition two spin−orbit coupling levels of the neodymium ion and the broad band due to the organic ligands.

The emission spectra of the potassium, sodium and yttrium compounds reveal broad bands attributed to the $\pi^* \rightarrow \pi$ transitions of the aromatic ligands.

Furthermore, the luminescence spectra of the Nd^{3+} and Sm^{3+} alkoxides exhibit an energy transfer from the ligand to the lanthanide centre. However, the presence of the typical lanthanide absorptions in the excitation spectra monitoring the RE transitions demonstrated that the energy transfer is not really efficient.

References

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Chapter 5 Summary and Outlook

The present work focuses on the synthesis, crystal structures, electrochemistry and photophysics of thienyl−substituted methoxides of alkali, tin(II) and trivalent rare earth metals. This choice has been justified for several reasons: i) the electron−rich system of the thiophene units may act as chromophore, ii) the electroactive character of these organic ligands, and iii) the luminescence applications of the rare earths compounds. This work is divided in three parts.

In a first part, investigations concerning the synthesis, NMR and crystal structures of the metal methoxides containing thienyl−substituents have been presented. With the objective to synthesize new rare earths alkoxides, we have chosen to study the reactivity of tertiary alcohols containing thienyl substituents (for example see Figure 5.1) towards lanthanides and to determine their crystal structures.

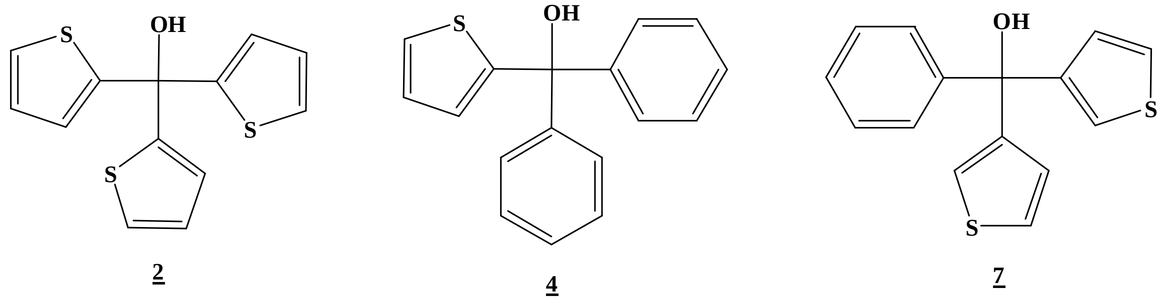


Figure 5.1. Examples of organic ligands used.

The propensities of these carbinols to act as alkoxide ligands via covalent M–O bonding are based on the inherent weak acidity of these compounds, which therefore can be easily deprotonated. To correlate structural and steric effects on the molecular geometry, electrochemical and photophysical properties, a systematic series of rare earth methoxides containing thienyl substituents was prepared. They were synthesized by varying two parameters: i) the nature of the alkoxothiophene ligand, and ii) the nature of metal centre. Two several synthetic pathways leading to alkoxides have been explored: i) the salt metathesis reactions between MCl_3 and carbinolates and ii) the reactions between $M[N(SiMe_3)_2]_3$ and acidic carbinols.

To investigate the salt metathesis reaction, the synthesis and crystal structures of the alkali metal alcoholates were explored. The latter have been prepared by deprotonation of the carbinols in the presence of potassium or sodium hydride. The products have been isolated as single crystals or as solid. The crystal structures revealed the occurrence of tetrameric alkali metal alcoholates with a distorted cubane−like M_4O_4 core. Each alkali metal is surrounded by three carbinolato ligands and two or three metals are ligated with a tetrahydrofuran solvent molecule (for example see Figure 5.2).

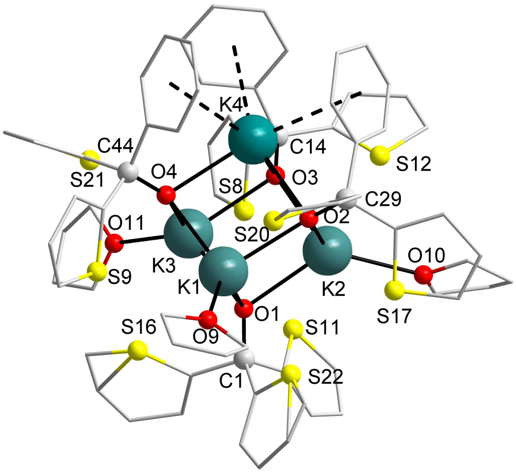
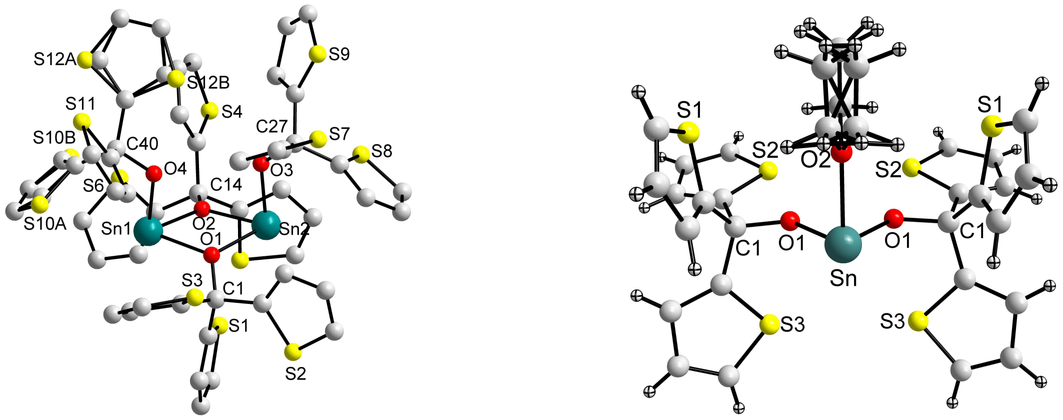


Figure 5.2. Example of a crystal structure of one alkali metal alcoholate: $[KOC(C_{14}H_{11}S_2)]_4(thf)_3$ (<u>21</u>).

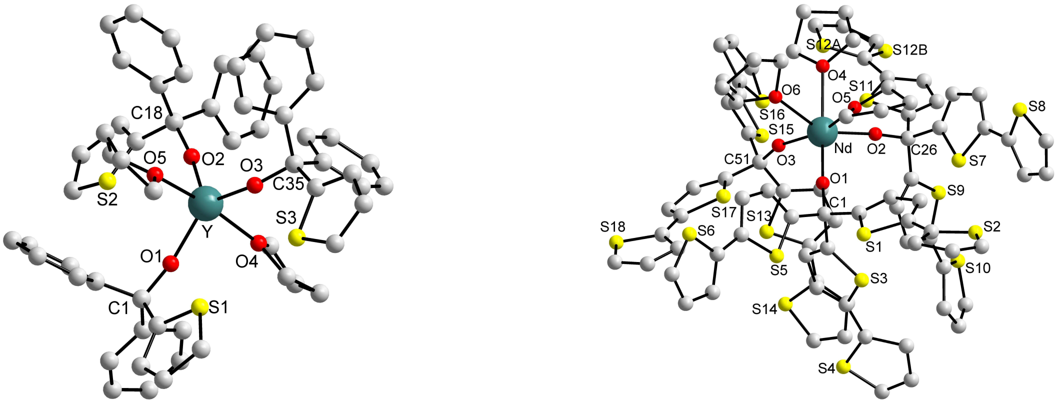
With the aim to built up heterometallic alkoxides containing lanthanide–main group metal bonds, we have attempted to work with tin(II). Although the necessary tin alkoxydes as potential precursors could be obtained by the reaction between $Sn[N(SiMe_3)_2]_2$ and acidic carbinol <u>**2**</u>. These novel tin(II) methoxides containing thienyl−substituents (Figure 5.3) were too moisture, thermal and light sensitive. Therefore we abandoned the idea to explore their reactivity toward lanthanide complexes.



{Sn[OC(C_4H_3S)$_3$]$_2$}$_2$ • 2 thf (**<u>14b</u>**) Sn[OC(C_4H_3S)$_3$]$_2$(thf) (**<u>15</u>**)

Figure 5.3. Example of molecular structures of new tin(II) alkoxides.

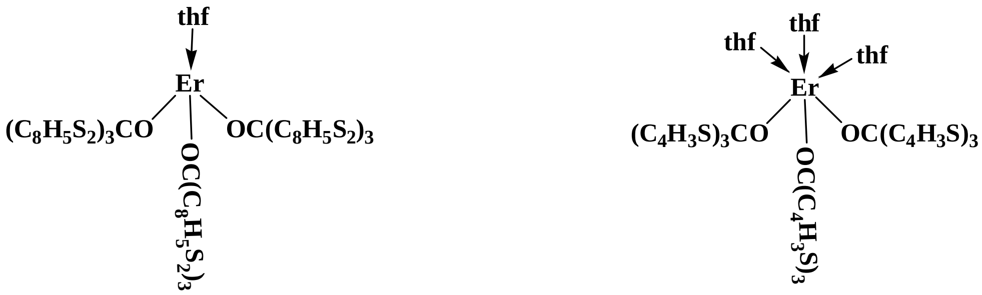
Novel rare earth alkoxides of yttrium, neodymium and erbium were synthesized by the reactions between Ln[N($SiMe_3$)$_2$]$_3$ (Ln = Y, Nd and Er) and acidic carbinols. The structure determinations revealed the exclusive formation of mononuclear compounds. The bulkiness of the ligands combined with their high electron density is supposed to prevent the formation of polynuclear products. For all the yttrium alkoxides under study, the coordination sphere around the metal centre is distorted trigonal–bipyramidal, whereas the determinations of the molecular structures of the neodymium compounds have revealed octahedral geometries around the metal centre. The modification of the stereoelectronic parameters of the organic ligands did not lead to a different geometry around the yttrium or neodymium metal centre: only some minor variations of angles and bond lengths have been observed.



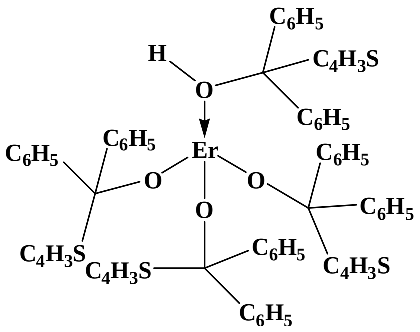
{Y[OC($C_{16}H_{13}S$)]$_3$(thf)$_2$} • toluene (**<u>26</u>**) {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**<u>10</u>**)

Figure 5.4. Examples of molecular structures of new yttrium and neodymium alkoxides.

Unfortunately, the X–ray structure determinations of the new erbium alkoxides could not be refined in a satisfying manner because of the poor quality of the crystals. Nevertheless, the preliminary data allows us to conclude that octahedral or tetrahedral coordination spheres around the metal centre are present (for example see Figure 5.5).



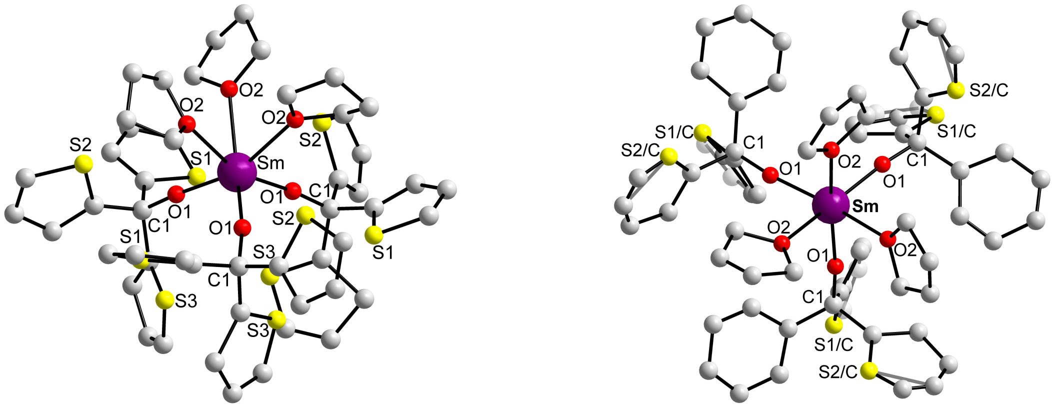
$Er[OC(C_8H_5S_2)]_3(thf)$ (**<u>11</u>**) $Er[OC(C_4H_3S)_3]_3(thf)_3$ (**<u>20</u>**)



$Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$ (**<u>44</u>**)

Figure 5.5. The different coordination spheres found around the erbium metal centre.

The samarium alkoxides $\{Sm[OC(C_4H_3S)_3]_3 (thf)_3\}$ • thf (**<u>19</u>**) and $\{Sm[OC(C_{16}H_{13}S)]_3(thf)_3\}$ • thf (**<u>29</u>**) were not accessible via the previous route. Fortunately, the salt metathesis reactions between the potassium $\{[KOC(C_4H_3S)_3]_4(thf)_2\}$ • thf (**<u>12</u>**) and $\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (**<u>25</u>**) or/and sodium $[NaOC(C_4H_3S)_3]_4(thf)_2$ (**<u>13</u>**) alcoholates and samarium(III) chloride allowed the synthesis of the targeted complexes. Again, the determination of their molecular structures revealed, like in the case of their neodymium analogues, only the occurrence of mononuclear compounds. The octahedral geometry around the samarium atom bearing three carbinolato ligands is completed by three tetrahydrofuran molecules (Figure 5.6).



{Sm[OC(C_4H_3S)$_3$]$_3$ (thf)$_3$} • thf (**<u>19</u>**) {Sm[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (**<u>29</u>**)

Figure 5.6. Molecular structure of the new samarium alkoxides.

The second part deals on the electrochemical behavior of the carbinols and their derived metal derivatives. The voltammograms are dominated by the oxidation wave of the thiophene groups. In addition, reduction waves could be obtained due to the reduction of a carbocation. Contrarily to the other compounds, the cycling of potentials of HO–C($C_8H_5S_2$)$_3$ (**<u>1</u>**), {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$} • 4 thf (**<u>10</u>**) and Er[OC($C_8H_5S_2$)$_3$]$_3$(thf) (**<u>11</u>**) lead to the formation of electroactive polymeric films (Figure 5.7 and Figure 5.8).

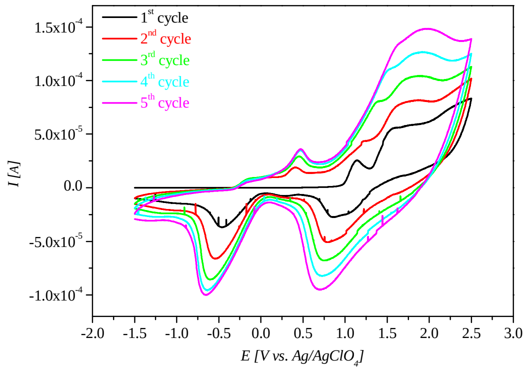


Figure 5.7. Repetitive cyclic voltammograms recorded on a platinum electrode in a dichloromethane solution containing <u>10</u> (10^{-3} M) and [NBu_4][PF_6] (0.1 M), vs. Ag/AgClO$_4$, scan rate 500 mV.s^{-1}.

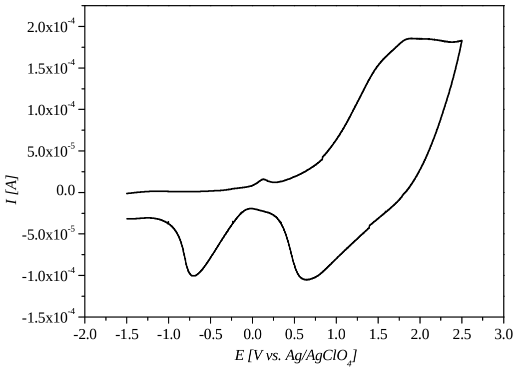
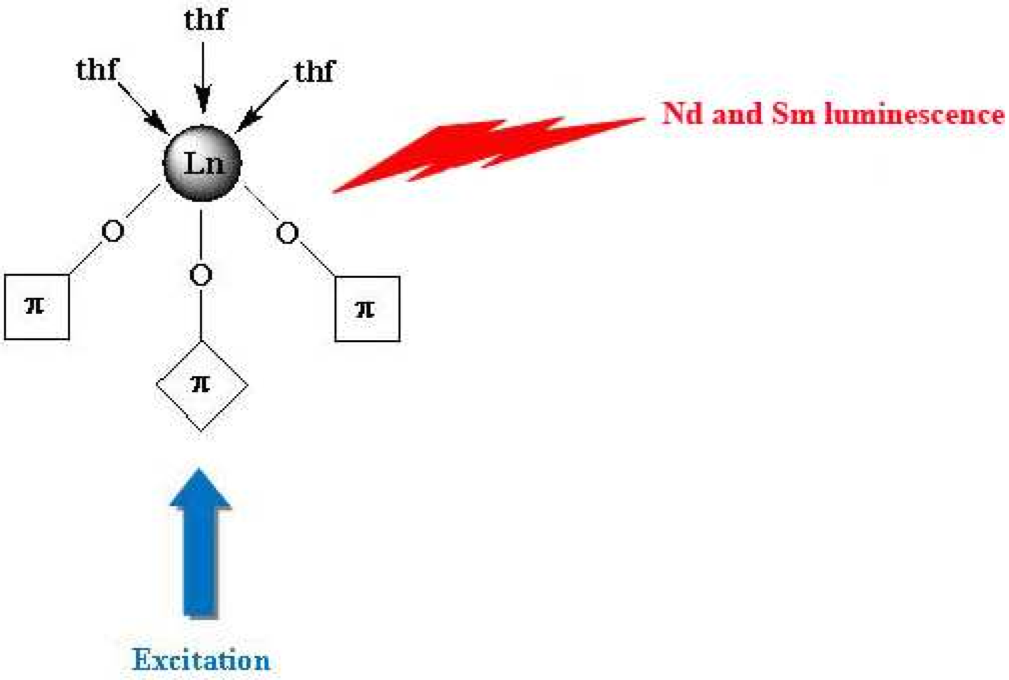


Figure 5.8. Cyclic voltammogram of poly (<u>10</u>), prepared by 5 oxidation–reductions on a platinum electrode at 500 mV.s^{-1}, in dichloromethane [NBu_4][PF_6] (0.1 M), vs. Ag/AgClO$_4$, scan rate 500 mV.s^{-1}.

No reduction or oxidation of the yttrium, neodymium, samarium and erbium metal centres has been noticed. We have also demonstrated that the introduction of the yttrium or neodymium metals increases the oxidation peak values of the thienyl units. These lanthanides decrease the electronic density of the heterocycles, which are therefore more difficult to oxidize.

The third part presents the photophysical properties of the carbinols and their derived metal complexes. The UV−Vis absorption properties are dominated by the organic ligands ($\pi \rightarrow \pi^*$ transitions of the aromatic groups). The alkali metal alcoholates and yttrium luminescence properties were investigated to get some information about the position of the electronic excited states of the bonded ligands in relation to the free ones because, K^+, Na^+ and Y^{3+} possess no excited *f*−state. Their emission spectra reveal broad bands attributed to the $\pi^* \rightarrow \pi$ transitions of the aromatic ligands. The luminescence investigations of the neodymium and samarium alkoxides indicate energy transfer from the excited states of the ligand to the excited states of the lanthanide ion (Scheme 5.1) in accordance with a dipole−dipole energy transfer mechanism.



Scheme 5.1 Schematic representation of the "energy transfer".

A promising continuation of these works will consist to center the future research on the synthesis of carbinol−containing thiophene derivatives substituted at the 3− and/or

4−positions by organic groups. This strategy could lead to lanthanide complexes in which the electrochemical and luminescence properties are modulated by the different donor or acceptor functional groups.

The second idea consists in to coordinate the lanthanide alkoxides to metals whose nature will be judiciously chosen according to the functional and physical properties desired.

Another aspect is to use 2T or 3T derivatives in order to form, via cyclovoltametry, polymeric films. Indeed, lanthanides polymers deposited on a surface and emitting in the visible after application of electric potential or environmental stimulus constitute a very interesting field of research. Last, not but least, the experimental findings and photophysical results should be completed by theoretical calculations (DFT and TD−DFT) to get a deeper insight on the electronic structure of these interesting compounds.

Chapter 6 Experimental Section

Part 1 Experimental Methods

All **reactions** were carried out under inert dinitrogen atmosphere in a modified “Stockschen vacuum apparatus”. The necessary vacuum was obtained with a rotary vane pump of the Vacuumbrand Company (model R75, 5.4 m^3/h, 4 x 10^{-4} mbar). Tetrahydrofuran, toluene, diethyl ether and acetonitrile were distilled from sodium/benzophenone and kept under nitrogen. Dichloromethane was distilled from $CaCl_2$ and kept under nitrogen. Pyridine was distilled from KOH and kept under nitrogen.

Analytical data were measured on an all−automatic CHN−900 Elemental Analysator from LECO *Corporation*, by Helga Feuerhake and by Susanne Harling (Anorganische Chemie, Saarbrücken). Calculations of theoretical molar masses were done with relative atomic masses IUPAC 2001. Some samples repeatedly showed a considerably difference content of carbon, hydrogen and nitrogen than calculated. The irreproducibility of analytical data may be due in part to the high sensitivity of the compounds to air.

Mass spectra (EI, 150 V) of compounds **11**, **18** and **20** were obtained with a Finnigan MAT 95 S spectrometer. Only characteristic fragments containing the isotopes of highest abundance are listed.

The **NMR spectra** were recorded on Bruker 200 NMR ACF or on Bruker 400 NMR ACF and ACP spectrometers. Samples were prepared with appropriate solvent and approximately 5 Vol. % C_6D_6 or $CDCl_3$ used as lock solvent. Chemical shifts are given according to the δ−scale in ppm. The reference corresponds to the signal of benzene [$\delta(^1H, C_6D_5H) = 7.15$ ppm, $\delta(^{13}C) = 128.0$ ppm] or of chloroform [$\delta(^1H, CDCl_3) = 7.24$ ppm, $\delta(^{13}C) = 77.0$ ppm]. Coupling constants ^nJ are given in Hertz (Hz). To characterize the spin multiplicity, abbreviations are used: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The notation used to attribute the different signals of the thienyl and bithienyl units, is given in Figure 6.1. For the protons of the phenyl groups, the notation φ−H are used. Additionally an “a” superscript (^{a}) is used for the free carbinol coordinated to the metal centre.

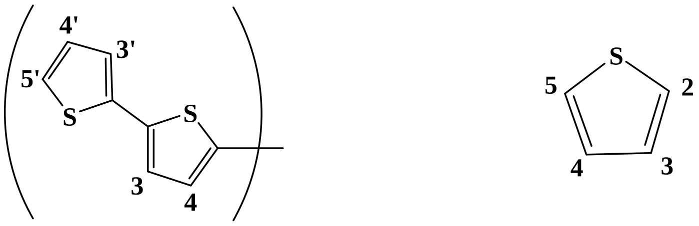


Figure 6.1. Notation used.

The **ATR−IR spectra** were performed using a Bruker Vector 22 Spectrometer equipped with Golden Gate.

The **X−Ray crystallography** was performed with a STOE IPDS diffractometer with Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods and refined by full−matrix least−square methods on F^2 with SHELX−97.[1] Hydrogen atoms were refined as rigid groups with the attached carbon atoms. Drawings were made with Diamond 2.1.[2]

Cyclic voltammetric experiments were performed on an Autolab PGSTAT 20 Potentiostat Galvanostat (Ecochemie) equipped with a three−electrode assembly with 0.1 M $[NBu_4][PF_6]$ (TBAF) as supporting electrolyte and freshly distilled dichloromethane or acetonitrile as solvent. The working electrode used is a 1 mm platinum disk. It was polished consecutively with polishing alumina and diamond suspension between runs. The reference electrode was $Ag/AgClO_4$ (0.1 M in CH_3CN). A 1 mm platinum disk was used as an auxiliary electrode. The solvent was freshly distilled and the solutions were prepared under dinitrogen atmosphere and blanketed with N_2 before the first scan. Measurements were made at room temperature. The scan rates employed were 100 and/or 500 mV.s^{-1}. Under these conditions, the $E_{1/2}$ of $Cp_2Fe^{+/0}$ was found to be 0.160 V (CH_2Cl_2) and 0.025 V (CH_3CN) vs. an $Ag/AgClO_4$ reference.

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The **UV−Vis absorption spectra** were recorded at room temperature using a Lambda 35 spectrometer. For these measurements, the samples were solved in UV−grade dichloromethane or tetrahydrofuran in 1 cm silica cells.

Solid−state emission and excitation spectra were recorded at room temperature on a Jobin−Yvon Fluorolog−3 spectrometer or on a Spectrofluorometer Fluorolog®−3 FL3−22 Jobin−Yvon (USA), equipped with a 1000W Xenon lamp, two double grated monochromators for emission and excitation, respectively, and a photomultiplier with a photon counting system. The emission spectra were corrected for photomultiplier sensitivity, the excitation spectra for lamp intensity and both for the transmission of the monochromators.

Part 2 Synthesis of the Starting Materials

The following compounds were prepared according to well−established procedures. Excepting elemental analyses, which were not systematically proceeding, all compounds were fully characterized.

Name	**Formula**	**Reference**
tris[bis(trimethylsilyl)amido]yttrium	$Y[N(SiMe_3)_2]_3$	3
tris[bis(trimethylsilyl)amido]neodymium	$Nd[N(SiMe_3)_2]_3$	3
tris[bis(trimethylsilyl)amido]erbium	$Er[N(SiMe_3)_2]_3$	3
bis[bis(trimethylsilyl)amido]tin	$Sn[N(SiMe_3)_2]_2$	4
tris(2,2’–bithienyl–5–yl)methanol (**1**)	$HO-C(C_8H_5S_2)_3$	5
tris(2–thienyl)methanol (**2**)	$HO-C(C_4H_3S)_3$	6
phenylbis(2–thienyl)methanol (**3**)	$HO-C(C_{14}H_{11}S_2)$	6
diphenyl(2–thienyl)methanol (**4**)	$HO-C(C_{16}H_{13}S)$	6
phenylbis(3−thienyl)methanol (**7**)	$HO-C(C_{14}H_{11}S_2)$	6
diphenyl(3−thienyl)methanol (**8**)	$HO-C(C_{16}H_{13}S)$	6

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Part 3 Synthesis of the New Compounds

1 Synthesis of $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (9)

To a solution of three equivalents of tris(2,2'–bithienyl–5–yl)methanol (**1**) (0.300 g, 0.57 mmol) in thf (20 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (0.108 g, 0.19 mmol) in thf (10 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated; a green solid was obtained. The product was subsequently recrystallized as green crystals from toluene at 5°C. The isolated yield is 2 % (6 mg). ^{1}H−NMR (200.13 MHz, C_6D_6): δ = 6.9 (dd, $^3J_{H5',H4'}$ = 4.5 Hz and $^4J_{H5', H3'}$= 0.8 Hz, 9H, 5'−H), 6.8 (d, $^3J_{H3,H4}$ = 3.7 Hz, 9H, 3−H), 6.8 (d, $^3J_{H4,H3}$ = 3.7 Hz, 9H, 4−H), 6.7 (dd, $^3J_{H3',H4'}$ = 3.7 Hz and $^4J_{H3',H5'}$ = 0.8 Hz, 9H, 3'−H), 6.6 (dd, $^3J_{H4',H5'}$ = 5.0 Hz and $^3J_{H4',H3'}$ = 3.7 Hz, 9H, 4'−H), 3.6 (thf), 1.4 (thf) ppm. Elemental analysis for $C_{83}H_{62}O_5S_{18}Y$ (1805.32 g/mol): calcd. %C 55.22, %H 3.43; found %C 55.48, %H 3.10.

2 Synthesis of $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\} \cdot 4$ thf (10)

To a solution of three equivalents of tris(2,2'–bithienyl–5–yl)methanol (**1**) (0.400 g, 0.70 mmol) in thf (15 mL) was added one equivalent of $Nd[N(SiMe_3)_2]_3$ (0.158 g, 0.25 mmol) in thf (10 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Green crystals were obtained at 5°C several days later. The isolated yield is 50 % (278 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.1 (m, 45H, 3−H, 4−H, 3'−H, 4'−H, 5'−H), 3.7 (br s, 14H, thf), 1.8 (br s, 14H, thf), 1.2 (br s, 21H, thf), 0.8 (br s, 7H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 8.70×10^{-5} M): λ = 232, 262, 312 nm. Elemental analysis for $C_{103}H_{101}O_{10}S_{18}Nd$ (2220.16 g/mol) calcd. %C 55.71, %H 4.54, %Nd 6.49; found %C 56.20, %H 2.96, %Nd 8.10 (the considerably difference content of hydrogen than calculated may be due in part to the high sensitivity of the compounds to air).

3 Synthesis of $Er[OC(C_8H_5S_2)_3]_3(thf)$ (11)

To a solution of three equivalents of tris(2,2'–bithienyl–5–yl)methanol (**1**) (0.590 g, 1.1 mmol) in thf (20 mL) was added one equivalent of $Er[N(SiMe_3)_2]_3$ (0.242 g, 0.37 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Brown crystals were obtained at 5°C several days later. The isolated yield is 15 % (100 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.1 (m, 45H, 3−H, 4−H, 3'−H, 4'−H, 5'−H), 3.7 (br s, 5H, thf), 1.9 (br s, 5H, thf), 1.2 (br s, 10H, thf), 0.8 (br s, 4H, thf) ppm. Mass spectrum: MS (EI, ^{167}Er): m/z (%) = 523 (10) $[M - Er - [OC(C_8H_5S_2)_3]_2 - thf]^+$, 166 (17) $[M - [OC(C_8H_5S_2)_3]_3 - thf]^+$. UV/Vis (190–1100 nm, CH_2Cl_2, M = 1.07×10^{-6} M): λ = 233, 262, 304 nm. Elemental analysis for $C_{79}H_{53}O_4S_{18}Er$ (1810.73 g/mol) calcd. %C 52.40, %H 2.95; found %C 49.99, %H 3.38.

4 Synthesis of $\{[KOC(C_4H_3S)_3]_4(thf)_2\} \bullet thf$ (12)

To a suspension of KH (0.254g, 6.35 mmol) in thf (5 mL) was slowly added tris(2–thienyl)methanol (**2**) (1.76 g, 6.35 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. All the KH has reacted. The solvent was evaporated, a solid was obtained (quantitative yield). Colourless crystals could be obtained in thf at 5°C (yield 20%, 460 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 6.9 (dd, $^{3}J_{H5,H4}$ = 4.7 Hz and $^{4}J_{H5,H3}$ = 1.3 Hz, 12H, 5−H), 6.8 (dd, $^{3}J_{H3,H4}$ = 3.3 Hz and $^{4}J_{H3,H5}$ = 1.3 Hz, 12H, 3−H), 6.7 (dd, $^{3}J_{H4,H3}$ = 3.3 Hz and $^{3}J_{H4,H5}$ = 4.7 Hz, 12H, 4−H) ppm. UV/Vis (190–1100 nm, thf, 0.949×10^{-5} M): λ = 238 nm (ε = 123.95×10^{3} $M^{-1}.cm^{-1}$). Elemental analysis for $C_{64}H_{60}O_7S_{12}K$ (1482.24 g/mol) calcd. %C 51.81, %H 4.05; found %C 53.02, %H 3.31.

5 Synthesis of $[NaOC(C_4H_3S)_3]_4(thf)_2$ (13)

To a suspension of NaH (0.121g, 5 mmol) in thf (5 mL) was slowly added tris(2–thienyl)methanol (**2**) (1.40 g, 5 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. All the NaH has reacted. The solvent was evaporated, a solid was obtained (quantitative yield). Colourless crystals could be obtained in thf at 5°C. (yield 15%, 243 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 6.9 (dd, $^{3}J_{H5,H4}$ = 4.9 Hz and $^{4}J_{H5,H3}$ = 1.2 Hz, 12H, 5−H), 6.8 (dd, $^{3}J_{H3,H4}$ = 3.4 Hz and $^{4}J_{H3,H5}$ = 1.2 Hz, 12H, 3−H), 6.7 (dd, $^{3}J_{H4,H3}$ = 3.7 Hz and $^{3}J_{H4,H5}$ = 4.9 Hz, 12H, 4−H). UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 235 nm (ε = 138.2×10^{3} $M^{-1}.cm^{-1}$). Elemental analysis for $C_{60}H_{52}O_6S_{12}Na_4$ (1345.60 g/mol) calcd. %C 53.50, %H 3.86; found %C 52.24, %H 3.56.

6 Synthesis of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 toluene (14a)

To a solution of four equivalents of tris(2–thienyl)methanol (**2**) (0.889 g, 3.00 mmol) in toluene (20 mL) was added two equivalents of $Sn[N(SiMe_3)_2]_2$ (0.702 g, 1.6 mmol) in toluene (5 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and colourless crystals were obtained at 5°C several days later. The isolated yield is 36% (435 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): Dimer: δ = 7.3 (dd, $^3J_{H5,H4}$ = 3.6 Hz and $^4J_{H5,H3}$ = 2.4 Hz, 12H, 5−H), 7.1 (dd, $^3J_{H3,H4}$ = 4.8 Hz and $^4J_{H3,H5}$ = 1.2 Hz, 12H, 3−H), 6.7 (dd, $^3J_{H4,H3}$ = 5.2 Hz and $^4J_{H4,H5}$ = 3.6 Hz, 12H, 4−H), 7.2 (toluene), 2.1 (toluene) ppm ; Monomer: δ = 7.2 (dd, $^3J_{H5,H4}$ = 4.8 Hz and $^4J_{H5,H3}$ = 1.2 Hz, 12H, 5−H), 6.8 (dd, $^3J_{H4,H3}$ = 3.6 Hz and $^4J_{H4,H5}$ = 4.8 Hz, 12H, 4−H), 6.6 (dd, $^3J_{H3,H4}$ = 3.6 Hz and $^4J_{H3,H5}$ = 1.2 Hz, 12H, 3−H) ppm. ^{119}Sn−NMR (149.1 MHz, $CDCl_3$): Dimer: δ = −236.5 ppm ; Monomer: δ = −244.5 ppm. Elemental analysis for $C_{66}H_{52}O_4S_{12}Sn_2$ (1531.18 g/mol) calcd. %C 51.72, %H 3.39; found %C 49.68, %H 3.22.

7 Synthesis of $\{Sn[OC(C_4H_3S)_3]_2\}_2$ • 2 thf (14b) and $Sn[OC(C_4H_3S)_3]_2$(thf) (15)

To a solution of six equivalents of tris(2–thienyl)methanol (**2**) (0.994 g, 3.33 mmol) in thf (20 mL) was added three equivalents of $Sn[N(SiMe_3)_2]_2$ (0.745 g, 1.69 mmol) in thf (5 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and colourless crystals were obtained at 5°C several days later (1.033 g). ^{1}H−NMR (400.13 MHz, $CDCl_3$): Dimer: δ = 7.3 (dd, $^3J_{H5,H4}$ = 4.7 Hz and $^4J_{H5,H3}$ = 1.2 Hz, 12H, 5−H), 7.1 (dd, $^3J_{H3,H4}$ = 4.7 Hz and $^4J_{H3,H5}$ = 1.2 Hz, 12H, 3−H), 6.7 (dd, $^3J_{H4,H3}$ = 4.7 Hz and $^4J_{H4,H5}$ = 3.5 Hz, 12H, 4−H), 3.6 (thf), 1.4 (thf) ppm ; Monomer: δ = 7.2 (dd, $^3J_{H5,H4}$ = 4.7 Hz and $^4J_{H5,H3}$ = 1.2 Hz, 12H, 5−H), 6.8 (dd, $^3J_{H4,H3}$ = 4.7 Hz and $^4J_{H4,H5}$ = 3.5 Hz, 12H, 4−H), 6.6 (dd, $^3J_{H3,H4}$ = 3.5 Hz and $^4J_{H3,H5}$ = 1.2 Hz, 12H, 3−H) ppm. ^{119}Sn−NMR (149.1 MHz, $CDCl_3$): Dimer: δ = −236.5 ppm, Monomer: δ = −244.5 ppm. ^{13}C−NMR (60 MHz, $CDCl_3$): δ = 153.7, 153.3, 128.3, 127.2, 126.5, 126.0, 125.6, 125.3, 68.3, 68.0, 67.6, 30.0, 25.5 ppm. Formulas: Dimer: $C_{60}H_{52}O_6S_{12}Sn_2$, Monomer: $C_{30}H_{26}O_3S_6Sn$. Molecular weights: Dimer: 1491.12 g/mol, Monomer 745.56 g/mol. Compound **14b** can be separated from **15** by crystal sorting under a microscope using their different habitus.

8 Synthesis of $Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a) and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (16b)

To a solution of three equivalents of tris(2–thienyl)methanol (2) (1.46 g, 5.2 mmol) in thf (20 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (1 g, 1.7 mmol) in thf (30 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated, a brown solid was obtained. The product was subsequently recrystallized as colourless crystals from toluene at 5°C.

$Y[OC(C_4H_3S)_3]_3(thf)_2$ (16a): The isolated yield is 23 % (420 mg). ^{1}H−NMR (400.13 MHz, C_6D_6): δ = 7.1 (br s, 9H, 5−H), 6.9 (br s, 9H, 3−H), 6.7 (br s, 9H, 4−H), 3.7 (thf), 1.4 (thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ = 257 nm (ε = 309.5 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{47}H_{43}O_5S_9Y$ (1065.26 g/mol) calcd. %C 52.99, %H 4.07; found %C 49.43, %H 4.04.

$\{Y[OC(C_4H_3S)_3]_3(thf)_2\}$ • toluene (16b): The isolated yield is 37 % (722 mg). ^{1}H−NMR (400.13 MHz, C_6D_6): δ = 7.1 (dd, $^3J_{H5,H4}$ = 6 Hz and $^4J_{H5,H3}$ = 1.2 Hz, 9H, 5−H), 6.9 (dd, $^3J_{H3,H4}$ = 5.2 Hz and $^4J_{H3,H5}$ = 0.8 Hz, 9H, 3−H), 6.7 (dd, $^3J_{H4,H5}$ = 8 Hz and $^3J_{H4,H3}$ = 4 Hz, 9H, 4−H), 7.0 (toluene), 3.7 (thf), 2.5 (toluene), 1.4 (thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ = 251 nm (ε = 291 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{54}H_{51}O_5S_9Y$ (1157.40 g/mol) calcd. %C 56.03, %H 4.44; found %C 54.34, %H 4.08.

9 Synthesis of $Y[OC(C_4H_3S)_3]_3(py)_2$ (17a) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (17b)

To a solution of three equivalents of tris(2–thienyl)methanol (2) (1.46 g, 5.2 mmol) in toluene (25 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (1 g, 1.7 mmol) in toluene (25 mL) and pyridine (5 mL). The mixture was stirred at room temperature for two days. A brown solution was obtained. It was concentrated, and light–brown crystals were grown at 5°C several days later.

$Y[OC(C_4H_3S)_3]_3(py)_2$ (17a): The isolated yield is 10 % (185 mg). ^{1}H−NMR (400.13 MHz, C_6D_6): δ = 6.9 (dd, $^3J_{H5,H4}$ = 3.5 Hz and $^4J_{H5,H3}$ = 0.8 Hz, 9H, 5−H), 6.8 (dd, $^3J_{H3,H4}$ = 4.7 Hz and ${}^{4}J_{H3,H5}$ = 0.8 Hz, 9H, 3−H), 6.6 (dd, ${}^{3}J_{H4,H3}$ = 4.7 Hz and ${}^{3}J_{H4,H5}$ = 3.5 Hz, 9H, 4−H), 8.4 (py), 6.9 (py), 6.6 (py) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ = 250 nm (ε = 290 × 10^{2} $M^{-1}.cm^{-1}$). Elemental analysis for $C_{49}H_{37}N_2O_3S_9Y$ (1079.26 g/mol) calcd. %C 54.53, %H 3.46, %N 2.60; found %C 52.80, %H 3.42, %N 2.62.

$\{Y[OC(C_4H_3S)_3]_3(py)_2\}$ • toluene (17b): The isolated yield is 61 % (1.22 g). ^{1}H−NMR (400.13 MHz, C_6D_6): δ = 6.9 (d, ${}^{3}J_{H5,H3}$ = 3.2 Hz, 9H, 5−H), 6.8 (d, ${}^{3}J_{H3,H4}$ = 4.8 Hz, 9H, 3−H), 6.6 (dd, ${}^{3}J_{H4,H3}$ = 4.8 Hz and ${}^{3}J_{H5,H3}$ = 3.2 Hz, 9H, 4−H), 8.4 (py), 6.9 (py), 6.6 (py), 7.0 (toluene), 2.1 (toluene) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ = 252 nm (ε = 249 × 10^{2} $M^{-1}.cm^{-1}$). Elemental analysis for $C_{56}H_{45}N_2O_3S_9Y$ (1171.39 g/mol) calcd. %C 57.29, %H 3.87, %N 2.39; found %C 57.06, %H 3.51, %N 3.52.

10 Synthesis of $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}$ • thf (18)

Method 1: To a solution of tris(2–thienyl)methanol (1) (0.244 g, 0.87 mmol) in thf (10 mL) was added $Nd[N(SiMe_3)_2]_3$ (0.547 g, 0.87 mmol) in thf (15 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and blue crystals were obtained at 5°C several days later. The isolated yield is 16 % (172 mg).

Method 2: To a solution of three equivalents of tris(2–thienyl)methanol (1) (0.498 g, 1.79 mmol) in thf (20 mL) was added one equivalent of $Nd[N(SiMe_3)_2]_3$ (0.372 g, 0.59 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and blue crystals were obtained at 5°C several days later. The isolated yield is 12 % (91 mg).

Method 3: To a solution of six equivalents of tris(2–thienyl)methanol (1) (0.534 g, 1.92 mmol) in thf (20 mL) was added one equivalent of $Nd[N(SiMe_3)_2]_3$ (0.200 g, 0.32 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. Blue crystals were obtained at 5°C several days later. The isolated yield is 72 % (222 mg).

^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.5 (br s, 27H, 3−H, 4−H, 5−H), 3.4 (br s, 7H, thf), 2.7 (br s, 17H, thf), 0.8 (br s, 9H, thf) ppm. Mass spectrum: MS (EI, ^{144}Nd): m/z (%) = 960 (16) $[M - CH_3 - (thf)_3 - thf]^{+}$, 1180 (0.5) $[M - thf]^{\bullet +}$. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 239 nm (ε = 104.5 × 10^{3} $M^{-1}.cm^{-1}$). Elemental analysis for $C_{55}H_{59}O_9S_9Nd$ (1264.80 g/mol) calcd. %C 52.22, %H 4.66, %Nd 11.40; found %C 51.67, %H 4.69, %Nd 11.26.

11 Synthesis of $\{Sm[OC(C_4H_3S)_3]_3(thf)_3\} \bullet thf$ (19)

Method 1: To a suspension of NaH (0.104 g, 4.3 mmol) in thf (5 mL) was slowly added tris(2–thienyl)methanol (**2**) (1.21 g, 4.3 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. Then, it was added to a suspension of $SmCl_3$ (0.373 g, 1.4 mmol) in thf (5 mL). The mixture was stirred at room temperature for two days. NaCl was filtered. The solution was concentrated and brown–light crystals were obtained at 5°C few days later. The isolated yield is 24% (430 mg).

Method 2: To a suspension of KH (0.154 g, 3.8 mmol) in thf (5 mL) was slowly added tris(2–thienyl)methanol (**2**) (1.07 g, 3.8 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. Then, it was added to a suspension of $SmCl_3$ (0.328 g, 1.3 mmol) in thf (5 mL). The mixture was stirred at room temperature for two days. KCl was filtered. The solution was concentrated and brown–light crystals were obtained at 5°C few days later. The isolated yield is 13 % (217 mg).

^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br. s, 27H, 3−H, 4−H, 5−H), 3.6 (br. s, 8H, thf), 3.4 (br. s, 3H, thf), 1.7 (br s, 10H, thf), 1.2 (br s, 8H, thf), 0.9 (br s, 3H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 236 nm (815×10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{55}H_{59}O_7S_9Sm$ (1270.91 g/mol): calcd. %C 51.93, %H 4.64; found %C 49.32, %H 4.57.

12 Synthesis of $Er[OC(C_4H_3S)_3]_3(thf)_3$ (20)

To a solution of three equivalents of tris(2–thienyl)methanol (**2**) (1.185 g, 4.26 mmol) in thf (20 mL) was added one equivalent of $Er[N(SiMe_3)_2]_3$ (0.920 g, 1.47 mmol) in thf (50 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and pink crystals were obtained at 5°C several days later. The isolated yield is 14 % (243 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.0 (m, 27H, 3−H, 4−H, 5−H), 3.5 (br s, 3H, thf), 1.2 (br s, 14H, thf), 0.9 (br s, 7H, thf) ppm. Mass spectrum: MS (EI, 167Er): m/z (%) = 166 (1.5) $[M -(OC(C_4H_3S)_3)_3-(thf)_3]^+$, 277 (5) $[M -Er -(OC(C_4H_3S)_3)_2 -(thf)_3]^+$. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-6} M): λ = 239 nm (ε = 175.4×10^3 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{47}H_{43}O_5S_9Er$ (1143.71 g/mol): calcd. %C 52.93, %H 3.15; found %C 50.40, %H 4.20 (the considerably difference content of hydrogen than calculated may be due in part to the high sensitivity of the compounds to air).

13 Synthesis of [KOC($C_{14}H_{11}S_2$)]$_4$(thf)$_3$ (21)

To a suspension of KH (0.202g, 5.0 mmol) in thf (5 mL) was slowly added phenylbis(2–thienyl)methanol (**3**) (1.37 g, 5.0 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. All the KH has reacted. The solvent was concentrated and colourless crystals were grown in thf at 5°C (yield 30 %, 580 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 7.5 (m, 8H, 5−H), 6.9 (m, 20H, φ−H), 6.7 (m, 8H, 4−H), 6.5 (m, 8H, 3−H) ppm. UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 237 nm ($\varepsilon = 101.7 \times 10^3$ $M^{-1}.cm^{-1}$). Elemental analysis for $C_{72}H_{68}O_7S_8K_4$ (1458.14 g/mol): calcd. %C 59.25, %H 4.66; found %C 54.50, %H 4.42 (the considerably difference content of carbon than calculated may be due in part to the high sensitivity of the compounds to air).

14 Synthesis of [NaOC($C_{14}H_{11}S_2$)]$_4$(thf)$_2$ (22)

To a suspension of NaH (0.160 g, 6.6 mmol) in thf (5 mL) was slowly added phenylbis(2–thienyl)methanol (**3**) (1.81 g, 6.6 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. The unreacted NaH was filtered. The solvent was slowly evaporated, a light−brown solid precipitated, it was filtered. The isolated yield is 32% (698 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 7.6 (dd, $^3J_{H5,H4}$ = 6.6 Hz and $^4J_{H5,H3}$ = 1.3 Hz, 8H, 5−H), 7.0 (m, 28H, 4−H, φ−H), 6.7 (dd, $^3J_{H4,H3}$ = 4.0 Hz , 8H, 3−H) ppm. UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 237 nm ($\varepsilon = 212 \times 10^3$ $M^{-1}.cm^{-1}$). Elemental analysis for $C_{68}H_{60}O_6S_8Na_4$ (1320 g/mol): calcd. %C 61.81, %H 4.54; found %C 60.61, %H 4.39.

15 Synthesis of {Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$} • thf (23)

To a solution of three equivalents of phenylbis(2–thienyl)methanol (**3**) (1.009 g, 3.70 mmol) in thf (20 mL) was added one equivalent of Nd[N($SiMe_3$)$_2$]$_3$ (0.771 g, 1.20 mmol) in thf (25 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Blue crystals were obtained at 5°C several days later. The isolated yield is 60 % (897 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.3 (br s, 21H, 5−H, φ−H), 6.9 (br s, 12H, 4−H, 3−H), 3.7 (br s, 8H, thf), 1.8 (br s, 8H, thf), 1.2 (br s, 12H, thf), 0.8 (br s, 4H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 237 nm ($\varepsilon = 650 \times 10^3$ $M^{-1}.cm^{-1}$). Elemental analysis for $C_{61}H_{65}O_7S_6Nd$ (1246.73 g/mol): calcd. %C 58.87, %H 5.21, %Nd 11.56; found %C 58.41, %H 5.11, %Nd 11.00.

16 Synthesis of $Er[OC(C_{14}H_{11}S_2)]_3(thf)$ (24)

To a solution of three equivalents of phenylbis(2–thienyl)methanol (**3**) (0.840 g, 3.0 mmol) in thf (20 mL) was added one equivalent of $Er[N(SiMe_3)_2]_3$ (0.667 g, 1.0 mmol) in thf (40 mL). The mixture was stirred at room temperature for two days. The pink solution was concentrated. Pink crystals were obtained at 5°C several days later. The isolated yield is 15 % (162 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.3 (br s, 21H, 5−H, φ−H), 6.9 (br s, 12H, 4−H, 3−H), 3.1 (br s, 4H, thf), 1.2 (br s, 4H, thf) ppm. Elemental analysis for $C_{49}H_{41}O_4S_6Er$ (1052 g/mol): calcd. %C 55.89, %H 3.89, %Er 15.89; found %C 54.13, %H 5.00, %Er 15.59 (the considerably difference content of hydrogen than calculated may be due in part to the high sensitivity of the compounds to air).

17 Synthesis of $\{[KOC(C_{16}H_{13}S)]_4(thf)_3\}$ • ½ thf (25)

To a suspension of KH (0.136 g, 3.4 mmol) in thf (5 mL) was slowly added diphenyl(2–thienyl)methanol (**4**) (0.904 g, 6.35 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. All the KH has reacted. The solvent was evaporated, a solid was obtained (quantitative yield). Colourless crystals could be obtained in thf at 5°C (yield 34%, 415 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 7.3 (m, 12H, 5−H, φ−H), 6.9 (m, 32H, φ−H), 6.7 (m, 4H, 4−H), 6.4 (m, 4H, 3−H) ppm. UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 235 nm (ε = 517 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{82}H_{80}O_{7.5}S_4K_4$ (1468 g/mol): calcd. %C 67.02, %H 5.40; found %C 65.74, %H 4.60 (the considerably difference content of hydrogen than calculated may be due in part to the high sensitivity of the compounds to air).

18 Synthesis of $\{Y[OC(C_{16}H_{13}S)]_3(thf)_2\}$ • toluene (26)

To a solution of three equivalents of diphenyl(2–thienyl)methanol (**4**) (1.18 g, 4.4 mmol) in thf (20 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (0.844 g, 1.5 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated, a white solid was obtained. The product was subsequently recrystallized as colourless crystals from toluene at 5°C.The isolated yield is 55 % (906 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.3 (m, 33H, 5−H, φ−H), 6.9 (m, 3H, 4−H), 6.7 (d, $^3J_{H4,H3,5}$ = 2.92 Hz, 3H, 3−H), 3.7 (thf), 1.8 (thf), 7.1 (toluene), 2.3 (toluene) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 236 nm (ε = 267 × 10^3 M^{-1}.cm^{-1}). Elemental analysis for $C_{66}H_{63}O_5S_3Y$ (1121.25 g/mol): calcd. %C 70.63, %H 5.61; found %C 72.74, %H 5.89.

19 Synthesis of {Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$} • toluene (27)

To a solution of three equivalents of diphenyl(2–thienyl)methanol (**4**) (1.31 g, 4.9 mmol) in toluene (25 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (0.939 g, 1.6 mmol) in toluene (25 mL) and pyridine (5 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated, a white solid was obtained. The product was subsequently recrystallized as colourless crystals from toluene at 5°C.The isolated yield is 42 % (766 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (m, 33H, 5−H, φ−H), 6.8 (br s, 3H, 4−H), 6.6 (br s, 3H, 3−H), 8.4 (py), 6.9 (py), 6.6 (py), 7.1 (toluene), 2.3 (toluene) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 235 nm (ε = 153.5 × 10^3 M^{-1}.cm^{-1}). Elemental analysis for $C_{68}H_{57}N_2O_3S_3Y$ (1226 g/mol): calcd. %C 71.87, %H 5.02, %N 2.46; found %C 68.30, %H 4.22, %N 2.50.

20 Synthesis of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (28)

To a solution of three equivalents of diphenyl(2–thienyl)methanol (**4**) (0.634 g, 2.38 mmol) in thf (20 mL) was added one equivalent of $Nd[N(SiMe_3)_2]_3$ (0.496 g, 0.79 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Blue crystals were obtained at 5°C several days later. The isolated yield is 34 % (328 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.3 (br s, 33H, 5−H, φ−H), 6.9 (br s, 3H, 4−H), 6.7 (br s, 3H, 3−H), 3.6 (br s, 5H, thf), 1.7 (br s, 6H, thf), 1.2 (br s, 10H, thf), 0.8 (br s, 12H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 232 nm (ε = 787 × 10^2 M^{-1}.cm^{-1}). Elemental analysis for $C_{67}H_{71}O_7S_3Nd$ (1228.66 g/mol): calcd. %C 65.43, %H 5.77, %Nd 11.73; found %C 60.22, %H 5.20, %Nd 12.50 (the considerably difference content of carbon than calculated may be due in part to the high sensitivity of the compounds to air).

21 Synthesis of {$Sm[OC(C_4H_3S)_3]_3(thf)_3$} • thf (29)

To a suspension of KH (0.193 g, 4.8 mmol) in thf (5 mL) was slowly added diphenyl(2–thienyl)methanol (**4**) (1.28 g, 4.8 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. Then, it was added to a suspension of $SmCl_3$ (0.410 g, 1.6 mmol) in thf (5 mL). The mixture was stirred at room temperature for two days. KCl was filtered. The solution was concentrated and white crystals were obtained at 5°C few days later. The isolated yield is 10 % (190 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.3 (m, 33H, φ─H, 5─H), 6.9 (dd, $^3J_{H4,H5}$ = 5.14 Hz , $^3J_{H4,H3}$ = 3.97 Hz, 3H, 4─H), 6.7 (dd, $^3J_{H3,H4}$ = 3.42 Hz , $^3J_{H3,H5}$ = 1.22 Hz, 3H, 3─H), 3.7 (m, 12H, thf), 1.8 (m, 12H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 233 nm ($\varepsilon = 567 \times 10^2$ $M^{-1}.cm^{-1}$). Elemental analysis for $C_{67}H_{71}O_7S_3Sm$ (1234.77 g/mol): calcd. %C 65.11, %H 5.75; found %C 65.18, %H 6.19.

22 Synthesis of $Er[OC(C_{16}H_{13}S)]_3[HOC(C_{16}H_{13}S)]$ (30)

To a solution of three equivalents of diphenyl(2–thienyl)methanol (**4**) (1.13 g, 4.2 mmol) in thf (20 mL) was added one equivalent of $Er[N(SiMe_3)_2]_3$ (0.918 g, 1.4 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. A pink solid precipitated and was filtered (0.312 g, 18 %). It was dissolved by heating on tetrahydrofuran. Pink crystals were obtained at 5°C several days later. The isolated yield is 7 % (120 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.3 (br s, 52H, φ−H, 5−H, 5^a−H, 4−H, 4^a−H, 3−H, 3^a−H), 3.0 (br s, 1H, −OH) ppm. Elemental analysis for $C_{68}H_{53}O_4S_4Er$ (1228 g/mol): calcd. %C 66.45, %H 4.31, %Er 13.62; found %C 62.23, %H 5.55, %Er 13.68 (the considerably difference content of hydrogen and carbon than calculated may be due in part to the high sensitivity of the compounds to air).

23 Synthesis of $HO-C(C_{17}H_{15}S)$ (5)

To a solution of 2−methylthiophene (1.57 g, 16 mmol, 1.53 mL) in diethyl ether (20 mL) was added *n*−butyl lithium (16 mmol, 10 mL, 1.6 M solution in hexane) at –15°C. The solution was stirred for 1 h and then benzophenone (2.91 g,16 mmol) in diethyl ether was added and the mixture was allowed to reach room temperature and was stirred overnight. It was hydrolysed with an aqueous saturated sodium hydrogenocarbonate solution. The mixture was extracted with diethyl ether and the organic layer was dried over Na_2SO_4 and evaporated. The solid was washed in hexane. A white solid was obtained (yield 67%, 3 g). ^{1}H−NMR (200.13 MHz, $CDCl_3$): δ = 7.3 (m, 10H, φ−H), 6.5 (m, $^3J_{H4,H3}$ = 3.4 Hz and $^4J_{H4,HMe}$ = 1.03 Hz, 1H, 4−H), 6.4 (d, $^3J_{H3,H4}$ = 3.4 Hz, 1H, 3−H), 2.9 (br s, 1H, −OH), 2.4 (d, $^4J_{HMe,H4}$ = 0.7 Hz, 3H, $-CH_3$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.3, 29.7, 79.9, 124.4, 126.8, 127.2, 127.5, 127.9, 140.4, 146.5, 149.5 ppm. ATR−IR: $\bar{\nu}$ (OH) = 3448 cm^{-1}. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ = 241 nm (ε = 125 × 10^2 M^{-1}.cm^{-1}). Elemental analysis for $C_{18}H_{16}OS$ (280 g/mol): calcd. %C 77.14, %H 5.71; found %C 77.10, %H 4.46.

24 Synthesis of [KOC($C_{17}H_{15}S$)]$_4$(thf)$_2$ (31)

To a suspension of KH (0.139 g, 3.4 mmol) in thf (5 mL) was slowly added diphenyl(5−methyl−2−thienyl)methanol (5) (0.973 g, 3.4 mmol) in thf (15 mL). The mixture was stirred at room temperature overnight. All the KH has reacted. The solvent was evaporated, a solid was obtained (quantitative yield). Colourless crystals could be obtained in thf at 5°C (yield 29%, 350 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 7.3 (m, 16H, φ−H), 7.0 (m, 24H, φ−H), 6.4 (m, 4H, 4−H), 6.2 (m, 4H, 3−H), 2.2 (s, 12H, $-CH_3$) ppm. UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 242 nm (ε = 104.8 × 10^3 M^{-1}.cm^{-1}). Elemental analysis for $C_{80}H_{76}O_6S_4K_4$ (1418.05 g/mol): calcd. %C 67.69, %H 5.35; found %C 66.60, %H 6.60.

25 Synthesis of [NaOC($C_{17}H_{15}S$)]$_4$(thf)$_2$ (32)

To a suspension of NaH (0.095 g, 3.9 mmol) in thf (5 mL) was slowly added diphenyl(5−methyl−2−thienyl)methanol (5) (1.108 g, 3.9 mmol) in thf (15 mL). The mixture was stirred at room temperature overnight. All the NaH has reacted. The solvent was slowly evaporated, a white solid precipitated, it was filtered (yield 14%, 188 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 7.3 (m, 16H, φ−H), 7.0 (m, 24H, φ−H), 6.4 (m, 4H, 4−H), 6.2 (m, 4H, 3−H), 2.2 (s, 12H, $-CH_3$) ppm. UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 240 nm (ε = 579 × 10^2 M^{-1}.cm^{-1}). Elemental analysis for $C_{80}H_{76}O_6S_4Na_4$ (1352 g/mol): calcd. %C 71.00, %H 5.62; found %C 71.00, %H 5.59.

26 Synthesis of {Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (33)

To a solution of three equivalents of diphenyl(5−methyl−2−thienyl)methanol (**5**) (0.986 g, 3.5 mmol) in tetrahydrofuran (20 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (0.668 g, 1.17 mmol) in tetrahydrofuran. The mixture was stirred at room temperature two days. The solvent was evaporated. The white solid was re−dissolved in toluene and placed at 5°C. Colourless crystals were grown. The isolated yield is 11 % (144 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.4 (m, 12 H, φ−H), 7.3 (m, 18H, φ−H), 6.6 (m, $^3J_{H4,H3}$ = 2.7 Hz, 3H, 4−H), 6.4 (m, $^3J_{H3,H4}$ = 3.4 Hz, 3H, 3−H), 2.7 (s, 9H, $-CH_3$), 3.7 (thf), 1.8 (thf), 7.1 (toluene), 2.3 (toluene) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 241 nm (ε = 138 ×10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{69}H_{69}O_3S_3Y$ (1163.33 g/mol): calcd. %C 71.17, %H 5.93; found %C 72.41, %H 6.19.

27 Synthesis of {Y[OC($C_{17}H_{15}S$)]$_3$(thf)$_2$} • toluene (34)

To a solution of three equivalents of diphenyl(5−methyl−2−thienyl)methanol (**5**) (0.857 g, 3.0 mmol) in toluene (25 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (0.581 g, 1.0 mmol) in toluene (25 mL) and pyridine (5 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated. The white solid was re−dissolved in toluene and placed at 5°C. Colourless crystals were grown. The isolated yield is 61 % (707 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.6 (br s, 12 H, φ−H), 7.2 (br s, 18H, φ−H), 6.5 (m, $^3J_{H4,H3}$ = 37.9 Hz, 3H, 4−H), 6.4 (m, $^3J_{H3,H4}$ = 29.3 Hz, 3H, 3−H), 2.9 (s, 9H, $-CH_3$), 8.4 (py), 6.9 (py), 7.1 (toluene), 2.4 (py) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 244 nm (ε = 637 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{71}H_{63}N_2O_3S_3Y$ (1177.32 g/mol): calcd. %C 72.36, %H 5.35, %N 2.37; found %C 71.37, %H 4.83, %N 2.45.

28 Synthesis of Er[OC($C_{17}H_{15}S$)]$_3$[HOC($C_{17}H_{15}S$)] (35)

To a solution of three equivalents of diphenyl(5−methyl−2−thienyl)methanol (**5**) (0.602 g, 2.1 mmol) in thf (15 mL) was added one equivalent of $Er[N(SiMe_3)_2]_3$ (0.463 g, 0.7 mmol) in thf (25 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Brown crystals were obtained at 5°C several days later. The isolated yield is 10 % (86 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br s, 40H, φ−H), 6.5 (br s, 8H, 4−H,

4^a−H, 3−H, 3^a−H), 3.7 (br s, 1H, −OH), 2.8 (br s, 3H, $-CH_3$), 2.3 (br s, 9H, $-CH_3$) ppm. Elemental analysis for $C_{72}H_{61}O_4S_4Er$ (1284 g/mol): calcd. %C 67.29, %H 4.75; found %C 66.59, %H 5.04.

29 Synthesis of HO−C($C_{17}H_{15}S$) (6)

To a solution of 3−methylthiophene (1.57 g, 16 mmol, 1.54 mL) in diethyl ether (20 mL) was added *n*−butyl lithium (16 mmol, 10 mL, 1.6 M solution in hexane) at –15°C. The solution was stirred for 1 h and then benzophenone (2.91 g, 16 mmol) in diethyl ether was added and the mixture was allowed to reach room temperature and was stirred overnight. It was hydrolysed with an aqueous saturated sodium hydrogenocarbonate solution. The mixture was extracted with diethyl ether and the organic layer was dried over Na_2SO_4 and evaporated. The solid was washed in hexane. A white solid was obtained (yield 56%, 2.5 g). ^{1}H−NMR (200.13 MHz, $CDCl_3$): δ = 7.3 (m, 10H, φ−H), 6.8 (m, 1H, 5−H), 6.4 (m, $^3J_{H3,HMe}$ = 1.3 Hz, 1H, 3−H), 2.9 (br s, 1H, −OH), 2.2 (m, 3H, $-CH_3$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.8, 80.0, 120.9, 123.0, 127.2, 127.3, 127.5, 127.9, 129.2, 131.9, 137.0 145.9, 146.5, 151,9 ppm. ATR−IR: $\bar{\nu}$ (OH) = 3460 cm^{-1}. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ = 231 nm (ε = 117 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{18}H_{16}OS$ (280 g/mol): calcd. %C 77.14, %H 5.71; found %C 77.94, %H 4.92.

30 Synthesis of Er[OC($C_{17}H_{15}S$)]$_3$[HOC($C_{17}H_{15}S$)] (36)

To a solution of three equivalents of diphenyl(4−methyl−2−thienyl)methanol (**6**) (0.766 g, 2.7 mmol) in thf (25 mL) was added one equivalent of $Er[N(SiMe_3)_2]_3$ (0.591 g, 0.91 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Pink crystals were obtained at 5°C several days later. The isolated yield is 7 % (80 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br s, 48H, φ−H, 5−H, 5^a−H, 3−H, 3^a−H), 3.7 (br s, 1H, −OH), 2.1 (br s, 9H, $-CH_3$), 1.8 (br s, 3H, $-CH_3$) ppm. Elemental analysis for $C_{72}H_{61}O_4S_4Er$ (1284 g/mol): calcd. %C 67.29, %H 4.75; found %C 66.10, %H 5.00.

31 Synthesis of $[NaOC(C_{14}H_{11}S_2)]_4(thf)_2$ (37)

To a suspension of NaH (0.145 g, 6.0 mmol) in thf (5 mL) was slowly added phenylbis(3−thienyl)methanol (7) (1.640 g, 6.0 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. The unreacted NaH was filtered. The solvent was slowly evaporated; colourless crystals were obtained (yield 22 %, 434 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 7.2 (m, 16H, φ−H, 5−H), 7.0 (m, 12H, φ−H), 6.8 (m, 8H, 4−H), 6.2 (m, 8H, 2−H) ppm. UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 236 nm (ε = 477 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{68}H_{60}O_6S_8Na_4$ (1320 g/mol): calcd. %C 61.81, %H 4.54; found %C 59.54, %H 5.08.

32 Synthesis of $\{Y[OC(C_{14}H_{11}S_2)]_3(thf)_2\}$ • ½ toluene (38)

To a solution of three equivalents of phenylbis(3−thienyl)methanol (7) (1.008 g, 3.7 mmol) in tetrahydrofuran (20 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (0.703 g, 1.2 mmol) in tetrahydrofuran (20 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated. The white solid obtained was re−dissolved in toluene, and the solution was placed at 5°C. Colourless crystals were obtained few days later. The isolated yield is 40 % (521 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.3 (m, 6H, φ−H), 7.1 (m, 15H, φ−H, 5−H), 6.9 (m, 8H, 4−H), 6.8 (m, 8H, 2−H), 3.4 (thf), 1.5 (thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 236 nm (ε = 510 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{56.5}H_{53}O_5S_6Y$ (1093.26 g/mol): calcd. %C 62.01, %H 4.84; found %C 64.01, %H 4.87.

33 Synthesis of $Y[OC(C_{14}H_{11}S_2)]_3(py)_2$ (39)

To a solution of three equivalents of phenylbis(3−thienyl)methanol (7) (0.955 g, 3.5 mmol) in toluene (20 mL) was added one equivalent of $Y[N(SiMe_3)_2]_3$ (0.666 g, 1.1 mmol) in toluene (20 mL) and pyridine (4 mL). The mixture was stirred at room temperature for two days. The solvent was slowly evaporated. A white solid precipitated, it was filtered. The isolated yield is 70% (813 mg).). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br s, 21H, 5−H, φ−H), 6.9 (br s, 12H, 4−H, 2−H), 8.4 (py), 7.6 (py) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 245 nm (ε = 934 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{55}H_{43}N_2O_3S_6Y$ (1060 g/mol): calcd. %C 62.26, %H 4.06, %N 2.64; found %C 63.51, %H 4.15, %N 3.16.

34 Synthesis of Nd[OC($C_{14}H_{11}S_2$)]$_3$(thf)$_3$ (40)

To a solution of three equivalents of phenylbis(3−thienyl)methanol (**7**) (0.623 g, 2.3 mmol) in tetrahydrofuran (10 mL) was added one equivalent of Nd[N($SiMe_3$)$_2$]$_3$ (0.477 g, 0.8 mmol) in tetrahydrofuran (20 mL). The mixture was stirred at room temperature for two days. The solvent was concentrated and placed at 5°C. Few weeks later, a blue solid precipitated, it was filtered and washed with tetrahydrofuran. The isolated yield is 26 % (231 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br s, 21H, 5−H, φ−H), 6.9 (br s, 12H, 4−H, 2−H), 3.7 (br s, 12H, thf), 1.8 (br s, 12H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 235, 264 nm (ε = 746 × 10^2, 114.5 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{57}H_{57}O_6S_6Nd$ (1173 g/mol): calcd. %C 58.31, %H 4.85, %Nd 12.29; found %C 56.93, %H 4.80, %Nd 12.43.

35 Synthesis of [NaOC($C_{16}H_{13}S$)]$_4$(thf)$_2$ (41)

To a suspension of NaH (0.099 g, 4.1 mmol) in thf (5 mL) was slowly added diphenyl(3−thienyl)methanol (**8**) (1.097 g, 4.1 mmol) in thf (20 mL). The mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was slowly evaporated, a white solid precipitated, it was filtered (yield 31 %, 402 mg). ^{1}H−NMR (200.13 MHz, thf/C_6D_6): δ = 7.3 (m, 12H, 5−H, φ−H), 7.0 (m, 24H, φ−H), 6.9 (d, 4H, 4−H), 6.2 (s, 4H, 2−H) ppm. UV/Vis (190–1100 nm, thf, 10^{-5} M): λ = 235 nm (ε = 615 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{76}H_{68}O_6S_4Na_4$ (1296 g/mol): calcd. %C 70.37, %H 5.24; found %C 71.03, %H 5.09.

36 Synthesis of Y[OC($C_{16}H_{13}S$)]$_3$(py)$_2$ (42)

To a solution of three equivalents of diphenyl(3−thienyl)methanol (**8**) (0.935 g, 3.5 mmol) in toluene (20 mL) was added one equivalent of Y[N($SiMe_3$)$_2$]$_3$ (0.667 g, 1.1 mmol) in toluene (20 mL) and pyridine (4 mL). The mixture was stirred at room temperature for two days. The solvent was slowly evaporated. A white solid precipitated, it was filtered. The isolated yield is 75 % (860 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br s, 33H, 5−H, φ−H), 6.9 (br s, 6H, 4−H, 2−H), 8.4 (py), 7.6 (py), 7.2 (py) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ = 244 nm (ε = 110.5 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{61}H_{49}N_2O_3S_3Y$ (1042 g/mol): calcd. %C 70.25, %H 4.70, %N 2.69; found %C 70.88, %H 5.19, %N 3.60 (the considerably difference content of nitrogen than calculated may be due in part to the high sensitivity of the compounds to air).

37 Synthesis of {Nd[OC($C_{16}H_{13}S$)]$_3$(thf)$_3$} • thf (43)

To a solution of three equivalents of diphenyl(3−thienyl)methanol (**8**) (0.806 g, 3.0 mmol) in tetrahydrofuran (20 mL) was added one equivalent of Nd[N($SiMe_3$)$_2$]$_3$ (0.631 g, 1.0 mmol) in tetrahydrofuran (20 mL). The mixture was stirred at room temperature two days. The solvent was concentrated and placed at 5°C. Few days later, blue crystals were grown. The isolated yield is 26 % (317 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br s, 33H, 5−H, φ−H), 6.9 (br s, 6H, 2−H, 4−H), 3.6 (br s, 12H, thf), 2.8 (br s, 4H, thf), 1.7 (br s, 12H, thf), 1.2 (br s, 4H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-5} M): λ = 229 nm (ε = 501 × 10^2 $M^{-1}.cm^{-1}$). Elemental analysis for $C_{67}H_{71}O_7S_3Nd$ (1228.66 g/mol): calcd. %C 55.67, %H 5.70, %Nd 11.73; found %C 55.79, %H 5.60, %Nd 11.53.

38 Synthesis of Er[OC($C_{16}H_{13}S$)]$_3$[HOC($C_{16}H_{13}S$)] (44)

To a solution of three equivalents of diphenyl(3–thienyl)methanol (**8**) (0.622 g, 2.3 mmol) in thf (20 mL) was added one equivalent of Er[N($SiMe_3$)$_2$]$_3$ (0.505 g, 0.8 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. A pink solid precipitated and was filtered (0.312 g, 33 %). It was dissolved by heating on tetrahydrofuran. Pink crystals were obtained at 5°C several days later. The isolated yield is 3 % (25 mg). ^{1}H−NMR (400.13 MHz, $CDCl_3$): δ = 7.2 (br s, 52H, φ−H, 5−H, 5^a−H, 4−H, 4^a−H, 2−H, 2^a−H), 2.8 (br s, 1H, −OH) ppm. Elemental analysis for $C_{68}H_{53}O_4S_4Er$ (1228 g/mol): calcd. %C 66.45, %H 4.31; the analysis could not be performed because of the air−sensivity of the crystals.

Appendix Additional Informations on the X−Ray Crystal Structures

In this appendix, the data are issued directly from the computer program. The standard deviations which contain two digit numbers, the bond length and angle values with four or three decimal places, respectively, have not physical sense. Therefore, we must take in consideration these comments during the reading.

Compound 1

Table 1. Crystal data and structure refinement for sh2294.

Identification code	sh2294	
Empirical formula	C25 H16 O S6	
Formula weight	524.74	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.217(2) Å	α = 90°.
	b = 6.0586(7) Å	β = 98.824(5)°.
	c = 23.280(3) Å	γ = 90°.
Volume	2260.2(5) $Å^3$	
Z	4	
Density (calculated)	1.542 Mg/m^3	
Absorption coefficient	0.623 mm^{-1}	
F(000)	1080	
Crystal size	0.25 x 0.5 x 0.65 mm^3	
Theta range for data collection	1.27 to 23.25°.	
Index ranges	−17<=h<=17. −6<=k<=6. −25<=l<=25	
Reflections collected	26879	
Independent reflections	3243 [R(int) = 0.1379]	
Completeness to theta = 23.25°	99.7 %	
Absorption correction	None	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	3243 / 8 / 305	
Goodness−of−fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0594. wR2 = 0.1297	
R indices (all data)	R1 = 0.1443. wR2 = 0.1765	
Largest diff. peak and hole	0.408 and −0.537 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2294. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4868(1)	5449(3)	1080(1)	30(1)
S(2A)	6125(2)	2087(5)	2631(1)	36(1)
S(2B)	6316(13)	6160(20)	2138(7)	21(3)
S(3)	2306(1)	8018(3)	204(1)	34(1)
S(4)	157(1)	8891(4)	1128(1)	49(1)
S(5)	2324(1)	3454(3)	−741(1)	33(1)
S(6A)	1223(6)	2500(17)	−2068(3)	33(2)
S(6B)	1955(10)	−1770(20)	−1970(6)	48(3)

O(1)	3926(3)	6581(8)	−31(2)	33(1)
C(1)	3552(4)	4681(11)	196(3)	29(2)
C(2)	4162(4)	3685(12)	683(3)	27(2)
C(3)	4198(4)	1640(12)	929(3)	30(2)
C(4)	4792(4)	1489(13)	1446(3)	34(2)
C(5)	5206(4)	3429(12)	1590(3)	29(2)
C(6)	5846(4)	3904(11)	2076(3)	30(2)
C(7A)	6358(12)	5780(30)	2194(8)	50
C(7B)	6210(50)	2630(70)	2590(20)	50
C(8)	6905(4)	5747(15)	2712(3)	43(2)
C(9)	6843(5)	3814(15)	2985(3)	46(2)
C(10)	2805(4)	5619(12)	463(3)	30(2)
C(11)	2435(4)	4641(13)	881(3)	36(2)
C(12)	1722(5)	5870(13)	997(3)	38(2)
C(13)	1566(4)	7717(13)	674(3)	31(2)
C(14)	931(4)	9398(14)	698(3)	36(2)
C(15)	791(5)	11383(13)	431(3)	39(2)
C(16)	93(5)	12545(13)	576(3)	43(2)
C(17)	−307(5)	11385(14)	954(3)	46(2)
C(18)	3260(4)	3084(12)	−290(3)	29(2)
C(19)	3692(5)	1358(12)	−473(3)	32(2)
C(20)	3273(5)	339(12)	−984(3)	32(2)
C(21)	2529(4)	1272(12)	−1185(3)	28(2)
C(22)	1940(4)	675(13)	−1697(3)	31(2)
C(23B)	1300(30)	2100(70)	−2024(17)	61(17)
C(23A)	1860(40)	−1300(110)	−1970(30)	50
C(24)	854(5)	585(16)	−2543(3)	49(2)
C(25)	1230(5)	−1398(15)	−2478(3)	43(2)

Table 3. Bond lengths [Å] and angles [°] for sh2294.

S(1)−C(5)	1.735(7)	C(5)−C(6)	1.442(9)
S(2A)−C(9)	1.683(8)	C(6)−C(7A)	1.409(15)
S(2A)−C(6)	1.705(7)	C(6)−C(7B)	1.46(2)
S(2B)−C(8)	1.538(15)	C(7A)−C(8)	1.383(15)
S(2B)−C(6)	1.561(15)	C(7B)−C(9)	1.46(2)
S(3)−C(10)	1.727(7)	C(8)−C(9)	1.343(11)
S(3)−C(13)	1.754(7)	C(10)−C(11)	1.356(9)
S(4)−C(17)	1.709(9)	C(11)−C(12)	1.435(10)
S(4)−C(14)	1.747(7)	C(12)−C(13)	1.350(10)
S(5)−C(18)	1.722(7)	C(13)−C(14)	1.456(10)
S(5)−C(21)	1.742(7)	C(14)−C(15)	1.357(11)
S(6A)−C(24)	1.650(12)	C(15)−C(16)	1.418(10)
S(6A)−C(22)	1.737(14)	C(16)−C(17)	1.364(10)
S(6B)−C(25)	1.551(19)	C(18)−C(19)	1.363(10)
S(6B)−C(22)	1.616(16)	C(19)−C(20)	1.417(10)
O(1)−C(1)	1.440(8)	C(20)−C(21)	1.350(9)
C(1)−C(18)	1.509(10)	C(21)−C(22)	1.452(10)
C(1)−C(2)	1.511(10)	C(22)−C(23A)	1.35(6)
C(1)−C(10)	1.550(10)	C(22)−C(23B)	1.47(4)
C(2)−C(3)	1.362(10)	C(23B)−C(24)	1.60(4)
C(3)−C(4)	1.425(9)	C(23A)−C(25)	1.44(7)
C(4)−C(5)	1.370(10)	C(24)−C(25)	1.345(11)

C(2)−S(1)−C(5)	92.5(3)	C(11)−C(10)−C(1)	125.9(6)
C(9)−S(2A)−C(6)	93.0(4)	C(11)−C(10)−S(3)	112.5(5)
C(8)−S(2B)−C(6)	99.7(8)	C(1)−C(10)−S(3)	121.5(5)
C(10)−S(3)−C(13)	91.3(4)	C(10)−C(11)−C(12)	111.5(7)
C(17)−S(4)−C(14)	92.2(4)	C(13)−C(12)−C(11)	114.4(7)
C(18)−S(5)−C(21)	91.9(3)	C(12)−C(13)−C(14)	129.2(6)
C(24)−S(6A)−C(22)	91.8(7)	C(12)−C(13)−S(3)	110.3(6)
C(25)−S(6B)−C(22)	96.3(7)	C(14)−C(13)−S(3)	120.5(6)
O(1)−C(1)−C(18)	109.8(5)	C(15)−C(14)−C(13)	132.2(7)
O(1)−C(1)−C(2)	109.3(5)	C(15)−C(14)−S(4)	109.5(6)
C(18)−C(1)−C(2)	113.6(6)	C(13)−C(14)−S(4)	118.3(6)
O(1)−C(1)−C(10)	104.7(5)	C(14)−C(15)−C(16)	114.4(7)
C(18)−C(1)−C(10)	111.1(6)	C(17)−C(16)−C(15)	111.9(7)
C(2)−C(1)−C(10)	107.9(5)	C(16)−C(17)−S(4)	111.9(6)
C(3)−C(2)−C(1)	131.2(6)	C(19)−C(18)−C(1)	127.5(7)
C(3)−C(2)−S(1)	110.9(5)	C(19)−C(18)−S(5)	110.9(5)
C(1)−C(2)−S(1)	117.3(5)	C(1)−C(18)−S(5)	121.3(5)
C(2)−C(3)−C(4)	113.1(7)	C(18)−C(19)−C(20)	113.2(7)
C(5)−C(4)−C(3)	113.2(7)	C(21)−C(20)−C(19)	113.4(7)
C(4)−C(5)−C(6)	129.1(7)	C(20)−C(21)−C(22)	128.4(6)

C(4)−C(5)−S(1)	110.3(5)	C(20)−C(21)−S(5)	110.7(5)
C(6)−C(5)−S(1)	120.7(5)	C(22)−C(21)−S(5)	120.9(5)
C(7A)−C(6)−C(5)	130.2(9)	C(23A)−C(22)−C(21)	127(3)
C(7A)−C(6)−C(7B)	96.5(13)	C(23A)−C(22)−C(23B)	106(3)
C(5)−C(6)−C(7B)	133.2(12)	C(21)−C(22)−C(23B)	127.0(18)
C(7A)−C(6)−S(2B)	8.6(11)	C(23A)−C(22)−S(6B)	7(3)
C(5)−C(6)−S(2B)	122.0(7)	C(21)−C(22)−S(6B)	120.2(7)
C(7B)−C(6)−S(2B)	104.8(12)	C(23B)−C(22)−S(6B)	112.7(18)
C(7A)−C(6)−S(2A)	107.0(8)	C(23A)−C(22)−S(6A)	109(3)
C(5)−C(6)−S(2A)	122.8(5)	C(21)−C(22)−S(6A)	123.8(6)
C(7B)−C(6)−S(2A)	10.6(13)	C(23B)−C(22)−S(6A)	3.6(19)
S(2B)−C(6)−S(2A)	115.2(6)	S(6B)−C(22)−S(6A)	115.9(7)
C(8)−C(7A)−C(6)	116.1(13)	C(22)−C(23B)−C(24)	105(3)
C(9)−C(7B)−C(6)	114.5(19)	C(22)−C(23A)−C(25)	115(4)
C(9)−C(8)−C(7A)	109.8(10)	C(25)−C(24)−C(23B)	106.3(17)
C(9)−C(8)−S(2B)	118.1(8)	C(25)−C(24)−S(6A)	116.2(8)
C(7A)−C(8)−S(2B)	8.6(11)	C(23B)−C(24)−S(6A)	10.0(19)
C(8)−C(9)−C(7B)	102.9(12)	C(24)−C(25)−C(23A)	108(3)
C(8)−C(9)−S(2A)	114.0(6)	C(24)−C(25)−S(6B)	119.6(8)
C(7B)−C(9)−S(2A)	11.2(13)	C(23A)−C(25)−S(6B)	12(3)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2294. The anisotropic displacement factor exponent takes the form: $-2p^2$[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	43(1)	32(1)	17(1)	0(1)	12(1)	−3(1)
S(2A)	49(2)	38(2)	23(1)	5(1)	10(1)	−1(1)
S(2B)	40(7)	18(8)	6(6)	−3(6)	13(5)	3(7)
S(3)	41(1)	40(1)	24(1)	3(1)	15(1)	0(1)
S(4)	51(1)	69(2)	32(1)	11(1)	24(1)	11(1)
S(5)	42(1)	42(1)	17(1)	−3(1)	10(1)	0(1)
S(6A)	40(3)	45(3)	14(2)	−1(2)	9(2)	2(3)
S(6B)	60(5)	64(8)	24(3)	−13(4)	19(3)	−11(5)
O(1)	39(3)	35(3)	30(3)	0(2)	18(2)	−1(3)
C(1)	41(4)	25(4)	24(4)	6(3)	17(4)	−6(4)
C(2)	39(4)	34(5)	11(4)	−4(3)	12(3)	0(4)
C(3)	28(4)	36(5)	27(4)	1(4)	10(3)	−4(4)
C(4)	44(5)	35(5)	26(4)	9(4)	12(4)	5(4)
C(5)	34(4)	34(5)	23(4)	−3(3)	18(3)	2(4)
C(6)	36(4)	43(5)	14(4)	−4(3)	11(3)	8(4)
C(8)	42(5)	64(6)	27(5)	−20(5)	15(4)	−3(5)
C(9)	50(5)	72(7)	17(4)	−1(4)	8(4)	21(5)
C(10)	36(4)	34(4)	20(4)	−4(3)	6(3)	−4(4)
C(11)	44(5)	43(5)	24(4)	1(4)	14(4)	1(4)
C(12)	49(5)	47(5)	20(4)	4(4)	15(4)	−4(4)
C(13)	36(4)	48(5)	12(4)	−4(4)	11(3)	−1(4)
C(14)	35(4)	54(6)	23(4)	−7(4)	16(3)	−3(4)
C(15)	46(5)	47(5)	25(4)	2(4)	15(4)	4(4)
C(16)	57(5)	45(5)	30(5)	−1(4)	16(4)	11(5)
C(17)	38(5)	71(6)	30(5)	−11(5)	13(4)	1(5)
C(18)	44(4)	29(4)	16(4)	5(3)	13(3)	−3(4)
C(19)	47(5)	33(5)	19(4)	2(4)	13(4)	6(4)
C(20)	46(5)	33(5)	19(4)	4(4)	16(4)	−4(4)
C(21)	41(5)	32(4)	15(4)	1(3)	16(4)	−3(4)
C(22)	39(4)	40(5)	18(4)	1(4)	16(4)	−2(4)
C(24)	46(5)	80(7)	23(5)	−1(5)	11(4)	−7(5)
C(25)	56(5)	57(6)	18(4)	−14(4)	14(4)	−8(5)

Compound 2

Table 1. Crystal data and structure refinement for sh2302.

Identification code	sh2302	
Empirical formula	C13 H10 O S3	
Formula weight	278.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.147(2) Å	α = 90°.

	b = 7.4240(10) Å	β = 100.24(3)°.
	c = 15.623(3) Å	γ = 90°.
Volume	1272.3(4) Å^3	
Z	4	
Density (calculated)	1.453 Mg/m	
Absorption coefficient	0.561 mm^{-1}	
F(000)	576	
Crystal size	0.7 x 0.6 x 0.3 mm^3	
Theta range for data collection	1.86 to 23.93°.	
Index ranges	−12<=h<=12, −8<=k<=8, −17<=l<=17	
Reflections collected	7714	
Independent reflections	1967 [R(int) = 0.2185]	
Completeness to theta = 23.93°	99.2 %	
Absorption correction	None	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	1967 / 0 / 158	
Goodness−of−fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0567, wR2 = 0.1498	
R indices (all data)	R1 = 0.0676, wR2 = 0.1686	
Largest diff. peak and hole	0.717 and −0.376 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2302. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5086(1)	1283(1)	1192(1)	37(1)
S(2)	8166(1)	−1574(1)	1167(1)	37(1)
S(3)	8513(1)	−387(1)	4071(1)	38(1)
O(1)	6488(3)	−1255(3)	2332(2)	31(1)
C(1)	7174(3)	399(4)	2416(2)	22(1)
C(2)	6397(3)	1864(4)	1892(2)	23(1)
C(3)	6632(3)	3745(4)	1877(3)	27(1)
C(4)	5673(4)	4601(5)	1281(3)	34(1)
C(5)	4807(4)	3467(5)	877(3)	37(1)
C(6)	7526(3)	928(4)	3364(2)	23(1)
C(7)	7022(3)	2349(4)	3832(2)	16(1)
C(8)	7510(4)	2183(5)	4746(3)	36(1)
C(9)	8302(3)	819(5)	4957(3)	32(1)
C(10)	8268(3)	22(4)	1983(2)	23(1)
C(11)	9364(3)	928(5)	2090(3)	31(1)
C(12)	10118(4)	279(5)	1513(3)	40(1)
C(13)	9586(4)	−1047(5)	974(3)	40(1)

Table 3. Bond lengths [Å] and angles [°] for sh2302.

S(1)−C(5)	1.707(4)	C(1)−C(2)	1.534(5)
S(1)−C(2)	1.718(4)	C(2)−C(3)	1.422(5)
S(2)−C(13)	1.709(4)	C(3)−C(4)	1.435(6)
S(2)−C(10)	1.729(3)	C(4)−C(5)	1.350(6)
S(3)−C(9)	1.700(4)	C(6)−C(7)	1.452(5)
S(3)−C(6)	1.718(4)	C(7)−C(8)	1.440(6)
O(1)−C(1)	1.440(4)	C(8)−C(9)	1.346(6)
C(1)−C(6)	1.514(5)	C(10)−C(11)	1.378(5)
C(1)−C(10)	1.523(5)	C(11)−C(12)	1.421(6)
C(1)−C(2)	1.534(5)	C(12)−C(13)	1.362(7)
C(5)−S(1)−C(2)	92.04(19)	C(4)−C(5)−S(1)	112.3(3)
C(13)−S(2)−C(10)	91.81(19)	C(7)−C(6)−C(1)	128.6(3)
C(9)−S(3)−C(6)	93.36(18)	C(7)−C(6)−S(3)	110.5(3)
O(1)−C(1)−C(6)	110.6(3)	C(1)−C(6)−S(3)	120.4(2)
O(1)−C(1)−C(10)	104.9(3)	C(8)−C(7)−C(6)	109.0(3)
C(6)−C(1)−C(10)	113.2(3)	C(9)−C(8)−C(7)	115.0(3)
O(1)−C(1)−C(2)	108.4(3)	C(8)−C(9)−S(3)	112.1(3)
C(6)−C(1)−C(2)	111.2(3)	C(11)−C(10)−C(1)	128.2(3)
C(10)−C(1)−C(2)	108.3(3)	C(11)−C(10)−S(2)	111.4(3)
C(3)−C(2)−C(1)	128.1(3)	C(1)−C(10)−S(2)	120.0(2)
C(3)−C(2)−S(1)	112.0(3)	C(10)−C(11)−C(12)	111.6(4)
C(1)−C(2)−S(1)	119.9(2)	C(13)−C(12)−C(11)	113.3(4)
C(2)−C(3)−C(4)	109.2(3)	C(12)−C(13)−S(2)	111.8(3)
C(5)−C(4)−C(3)	114.5(3)		

Compound 9

Table 1. Crystal data and structure refinement for sh2375.

Identification code	sh2375	
Empirical formula	C83 H62 O5 S18 Y	
Formula weight	1805.32	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.5246(16) Å	α = 90°.
	b = 15.182(2) Å	β = 97.480(2)°.
	c = 41.606(5) Å	γ = 90°.
Volume	7843.9(18) Å^3	
Z	4	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	1.276 mm^{-1}	
F(000)	3708	
Crystal size	0.3 x 0.5 x 0.65 mm^3	
Theta range for data collection	0.99 to 29.79°.	
Index ranges	−17<=h<=12, −21<=k<=21, −56<=l<=57	
Reflections collected	104589	
Independent reflections	22216 [R(int) = 0.0785]	
Completeness to theta = 29.79°	98.9 %	
Absorption correction	Semi−empirical from equivalents	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	22216 / 32 / 994	
Goodness−of−fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0533, wR2 = 0.1207	
R indices (all data)	R1 = 0.1014, wR2 = 0.1436	
Largest diff. peak and hole	1.392 and −1.073 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2375. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	933(1)	7672(1)	1233(1)	13(1)
S(1)	−607(1)	8076(1)	304(1)	16(1)
S(2)	−2261(1)	9677(1)	39(1)	25(1)
S(3)	−316(1)	5360(1)	856(1)	19(1)
S(4)	−3232(1)	3813(1)	734(1)	41(1)
S(5)	2707(1)	7062(1)	354(1)	20(1)
S(6A)	5838(1)	5874(1)	296(1)	31(1)
S(6B)	5122(6)	7601(5)	340(3)	29(2)
S(7)	−1217(1)	9773(1)	991(1)	18(1)
S(8A)	−3795(2)	9728(2)	741(1)	24(1)
S(8B)	−3721(3)	11452(2)	497(1)	25(1)
S(9)	2850(1)	10288(1)	1691(1)	22(1)
S(10A)	5391(1)	10687(1)	1974(1)	30(1)
S(10B)	5723(4)	11184(5)	1366(1)	23(1)
S(11)	1021(1)	9045(1)	1985(1)	20(1)
S(12A)	1413(2)	8471(2)	2783(1)	28(1)
S(12B)	−866(2)	8534(2)	2740(1)	27(1)
S(13)	2843(1)	7286(1)	2090(1)	18(1)
S(14)	5446(1)	7504(1)	2892(1)	36(1)
S(15)	2219(1)	5182(1)	1384(1)	18(1)
S(16)	1633(1)	3058(1)	800(1)	36(1)
S(17)	−946(1)	5653(1)	1730(1)	17(1)
S(18)	−3877(1)	6268(1)	2151(1)	31(1)
O(1)	694(2)	7051(2)	785(1)	16(1)
O(2)	863(2)	9055(2)	1263(1)	18(1)
O(3)	1250(2)	6758(2)	1607(1)	16(1)
O(4)	−933(2)	7661(2)	1252(1)	19(1)
O(5)	2789(2)	7836(2)	1206(1)	20(1)
C(1)	650(3)	6609(2)	491(1)	15(1)
C(2)	243(3)	7244(2)	218(1)	15(1)
C(3)	478(3)	7314(3)	−95(1)	20(1)
C(4)	−21(3)	8049(3)	−261(1)	21(1)
C(5)	−640(3)	8526(2)	−78(1)	17(1)

C(6)	−1208(3)	9342(2)	−162(1)	17(1)
C(7)	−998(3)	9966(2)	−384(1)	20(1)
C(8)	−1698(3)	10697(3)	−393(1)	23(1)
C(9)	−2409(3)	10639(3)	−176(1)	23(1)
C(10)	−137(3)	5842(2)	491(1)	16(1)
C(11)	−829(3)	5490(2)	243(1)	20(1)
C(12)	−1515(3)	4836(2)	348(1)	20(1)
C(13)	−1337(3)	4694(2)	673(1)	19(1)
C(14)	−1921(3)	4120(2)	869(1)	22(1)
C(15)	−1598(4)	3784(3)	1178(1)	26(1)
C(16)	−2439(4)	3274(3)	1290(1)	34(1)
C(17)	−3344(4)	3237(3)	1079(1)	37(1)
C(19)	1774(3)	6289(2)	445(1)	15(1)
C(20)	2249(3)	5484(2)	495(1)	19(1)
C(21)	3362(3)	5489(3)	460(1)	21(1)
C(22)	3737(3)	6304(2)	387(1)	18(1)
C(23)	4810(3)	6590(2)	336(1)	19(1)
C(24A)	5185(10)	7457(9)	312(4)	50
C(24B)	5780(17)	6115(15)	287(11)	50
C(25)	6293(3)	7496(3)	267(1)	29(1)
C(26)	6708(3)	6689(3)	251(1)	34(1)
C(27)	743(3)	9905(2)	1383(1)	16(1)
C(28)	−158(3)	10390(2)	1174(1)	19(1)
C(29)	−359(3)	11269(2)	1134(1)	20(1)
C(30)	−1385(3)	11445(3)	955(1)	21(1)
C(31)	−1955(3)	10701(2)	867(1)	19(1)
C(32)	−3048(3)	10626(3)	703(1)	22(1)
C(33A)	−3669(12)	11274(10)	511(4)	50
C(33B)	−3778(13)	9898(13)	690(6)	50
C(34)	−4774(4)	10948(4)	413(1)	42(1)
C(35)	−4858(4)	10125(4)	520(1)	39(1)
C(36)	1795(3)	10405(2)	1380(1)	18(1)
C(37)	2138(3)	10842(3)	1126(1)	23(1)
C(38)	3235(3)	11077(3)	1176(1)	25(1)
C(39)	3749(3)	10808(2)	1471(1)	21(1)
C(40)	4881(3)	10887(3)	1590(1)	22(1)
C(41A)	5746(11)	11111(13)	1402(4)	50
C(41B)	5479(14)	10569(19)	1902(5)	50
C(42)	6758(3)	11112(3)	1611(1)	38(1)
C(43)	6640(4)	10867(4)	1913(1)	42(1)
C(44)	404(3)	9827(2)	1722(1)	17(1)
C(45)	−427(3)	10210(3)	1847(1)	23(1)
C(46)	−565(3)	9883(3)	2159(1)	26(1)
C(47)	159(3)	9248(3)	2268(1)	21(1)
C(48)	237(3)	8764(3)	2570(1)	21(1)
C(49A)	−625(13)	8463(14)	2735(4)	50
C(49B)	1165(12)	8431(14)	2765(4)	50
C(50)	−209(4)	8010(3)	3040(1)	38(1)
C(51)	862(4)	7977(3)	3059(1)	38(1)
C(52)	1241(3)	6111(2)	1845(1)	15(1)
C(53)	2127(3)	6330(2)	2124(1)	17(1)
C(54)	2479(3)	5897(3)	2403(1)	24(1)
C(55)	3341(3)	6340(3)	2593(1)	23(1)
C(56)	3639(3)	7105(2)	2456(1)	19(1)
C(57)	4497(3)	7721(3)	2563(1)	20(1)
C(58)	4688(3)	8585(2)	2400(1)	15(1)
C(59)	5684(4)	8927(3)	2591(1)	30(1)
C(60)	6123(3)	8434(3)	2840(1)	31(1)
C(61)	1466(3)	5215(2)	1702(1)	17(1)
C(62)	1148(3)	4390(3)	1777(1)	21(1)
C(63)	1496(3)	3724(3)	1573(1)	21(1)
C(64)	2092(3)	4052(2)	1347(1)	19(1)
C(65)	2515(3)	3608(2)	1079(1)	19(1)
C(66)	3667(3)	3615(2)	1007(1)	19(1)
C(67)	3594(4)	3135(3)	693(1)	29(1)
C(68)	2618(4)	2815(3)	573(1)	28(1)
C(69)	156(3)	6104(2)	1969(1)	16(1)
C(70)	−161(3)	6509(3)	2235(1)	20(1)
C(71)	−1287(3)	6455(3)	2246(1)	22(1)
C(72)	−1830(3)	6009(2)	1989(1)	18(1)
C(73)	−2975(3)	5810(2)	1921(1)	19(1)
C(74)	−3496(3)	5248(3)	1676(1)	21(1)
C(75)	−4632(3)	5242(3)	1699(1)	32(1)

C(76)	−4935(3)	5736(3)	1937(1)	30(1)
C(77)	−1399(3)	7962(3)	1537(1)	20(1)
C(78)	−2608(3)	7904(3)	1448(1)	33(1)
C(79)	−2735(3)	7223(3)	1173(1)	32(1)
C(80)	−1789(3)	7424(3)	999(1)	23(1)
C(81)	3558(3)	7117(3)	1271(1)	27(1)
C(82)	4619(4)	7553(4)	1344(3)	111(4)
C(83)	4492(4)	8474(3)	1297(1)	45(1)
C(84)	3389(3)	8591(3)	1116(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for sh2375.

Y(1)−O(1)	2.075(2)
Y(1)−O(3)	2.086(2)
Y(1)−O(2)	2.106(3)
Y(1)−O(4)	2.348(2)
Y(1)−O(5)	2.356(2)
S(1)−C(2)	1.720(4)
S(1)−C(5)	1.728(3)
S(2)−C(9)	1.710(4)
S(2)−C(6)	1.727(4)
S(3)−C(10)	1.725(3)
S(3)−C(13)	1.727(4)
S(4)−C(17)	1.702(5)
S(4)−C(14)	1.728(4)
S(5)−C(22)	1.722(4)
S(5)−C(19)	1.734(4)
S(6A)−C(26)	1.676(5)
S(6A)−C(23)	1.710(4)
S(6B)−C(25)	1.544(8)
S(6B)−C(23)	1.584(9)
S(7)−C(28)	1.719(4)
S(7)−C(31)	1.727(4)
S(8A)−C(35)	1.631(5)
S(8A)−C(32)	1.673(5)
S(8B)−C(34)	1.526(7)
S(8B)−C(32)	1.681(5)
S(9)−C(39)	1.731(4)
S(9)−C(36)	1.734(4)
S(10A)−C(43)	1.640(5)
S(10A)−C(40)	1.669(4)
S(10B)−C(42)	1.546(7)
S(10B)−C(40)	1.562(6)
S(11)−C(44)	1.728(4)
S(11)−C(47)	1.725(4)
S(12A)−C(51)	1.604(6)
S(12A)−C(48)	1.676(4)
S(12B)−C(50)	1.613(6)
S(12B)−C(48)	1.669(5)
S(13)−C(53)	1.722(4)
S(13)−C(56)	1.731(4)
S(14)−C(60)	1.675(5)
S(14)−C(57)	1.721(4)
S(15)−C(61)	1.722(4)
S(15)−C(64)	1.728(4)
S(16)−C(68)	1.691(4)
S(16)−C(65)	1.712(4)
S(17)−C(72)	1.728(4)
S(17)−C(69)	1.732(3)
S(18)−C(76)	1.700(5)
S(18)−C(73)	1.717(4)
O(1)−C(1)	1.390(4)
O(2)−C(27)	1.400(4)
O(3)−C(52)	1.397(4)
O(4)−C(80)	1.447(4)
O(4)−C(77)	1.462(4)
O(5)−C(84)	1.446(4)
O(5)−C(81)	1.457(5)
C(1)−C(19)	1.525(5)
C(1)−C(10)	1.525(5)
C(1)−C(2)	1.526(5)
C(2)−C(3)	1.374(5)
C(3)−C(4)	1.414(5)
C(4)−C(5)	1.362(5)
C(15)−C(16)	1.435(6)
C(16)−C(17)	1.342(7)
C(19)−C(20)	1.362(5)
C(20)−C(21)	1.420(5)
C(21)−C(22)	1.371(5)
C(22)−C(23)	1.453(5)
C(23)−C(24A)	1.407(12)
C(23)−C(24B)	1.450(18)
C(24A)−C(25)	1.426(12)
C(24B)−C(26)	1.475(19)
C(25)−C(26)	1.336(6)
C(27)−C(28)	1.522(5)
C(27)−C(36)	1.522(5)
C(27)−C(44)	1.528(5)
C(28)−C(29)	1.365(5)
C(29)−C(30)	1.422(5)
C(30)−C(31)	1.361(5)
C(31)−C(32)	1.452(5)
C(32)−C(33A)	1.431(13)
C(32)−C(33B)	1.431(15)
C(33A)−C(34)	1.477(15)
C(33B)−C(35)	1.484(16)
C(34)−C(35)	1.334(7)
C(36)−C(37)	1.363(5)
C(37)−C(38)	1.408(5)
C(38)−C(39)	1.372(5)
C(39)−C(40)	1.446(5)
C(40)−C(41A)	1.457(14)
C(40)−C(41B)	1.491(17)
C(41A)−C(42)	1.442(14)
C(41B)−C(43)	1.517(18)
C(42)−C(43)	1.335(7)
C(44)−C(45)	1.354(5)
C(45)−C(46)	1.424(5)
C(46)−C(47)	1.360(5)
C(47)−C(48)	1.449(5)
C(48)−C(49B)	1.422(14)
C(48)−C(49A)	1.429(14)
C(49A)−C(50)	1.475(15)
C(49B)−C(51)	1.495(15)
C(50)−C(51)	1.335(7)
C(52)−C(69)	1.515(5)
C(52)−C(61)	1.527(5)
C(52)−C(53)	1.533(5)
C(53)−C(54)	1.360(5)
C(54)−C(55)	1.420(5)
C(55)−C(56)	1.367(5)
C(56)−C(57)	1.450(5)
C(57)−C(58)	1.510(5)
C(58)−C(59)	1.484(5)
C(59)−C(60)	1.339(6)
C(61)−C(62)	1.363(5)
C(62)−C(63)	1.424(5)
C(63)−C(64)	1.366(5)
C(64)−C(65)	1.461(5)
C(65)−C(66)	1.512(5)
C(66)−C(67)	1.489(5)
C(67)−C(68)	1.349(6)
C(69)−C(70)	1.367(5)
C(70)−C(71)	1.420(5)
C(71)−C(72)	1.370(5)
C(72)−C(73)	1.457(5)

C(5)−C(6)	1.448(5)
C(6)−C(7)	1.372(5)
C(7)−C(8)	1.413(5)
C(8)−C(9)	1.349(5)
C(10)−C(11)	1.367(5)
C(11)−C(12)	1.418(5)
C(12)−C(13)	1.361(5)
C(13)−C(14)	1.454(5)
C(14)−C(15)	1.392(6)

O(1)−Y(1)−O(3)	111.10(10)
O(1)−Y(1)−O(2)	120.25(9)
O(3)−Y(1)−O(2)	128.64(9)
O(1)−Y(1)−O(4)	89.98(9)
O(3)−Y(1)−O(4)	93.68(9)
O(2)−Y(1)−O(4)	87.46(9)
O(1)−Y(1)−O(5)	91.93(9)
O(3)−Y(1)−O(5)	90.65(9)
O(2)−Y(1)−O(5)	86.92(9)
O(4)−Y(1)−O(5)	174.28(9)
C(2)−S(1)−C(5)	92.23(17)
C(9)−S(2)−C(6)	92.03(19)
C(10)−S(3)−C(13)	92.09(18)
C(17)−S(4)−C(14)	92.5(2)
C(22)−S(5)−C(19)	92.75(18)
C(26)−S(6A)−C(23)	92.9(2)
C(25)−S(6B)−C(23)	97.9(5)
C(28)−S(7)−C(31)	92.30(18)
C(35)−S(8A)−C(32)	94.1(2)
C(34)−S(8B)−C(32)	96.0(3)
C(39)−S(9)−C(36)	92.46(18)
C(43)−S(10A)−C(40)	94.3(2)
C(42)−S(10B)−C(40)	99.1(3)
C(44)−S(11)−C(47)	92.36(18)
C(51)−S(12A)−C(48)	94.1(2)
C(50)−S(12B)−C(48)	93.6(2)
C(53)−S(13)−C(56)	92.33(18)
C(60)−S(14)−C(57)	92.6(2)
C(61)−S(15)−C(64)	92.41(18)
C(68)−S(16)−C(65)	91.9(2)
C(72)−S(17)−C(69)	92.67(17)
C(76)−S(18)−C(73)	92.4(2)
C(1)−O(1)−Y(1)	173.9(2)
C(27)−O(2)−Y(1)	161.4(2)
C(52)−O(3)−Y(1)	168.4(2)
C(80)−O(4)−C(77)	109.3(3)
C(80)−O(4)−Y(1)	128.6(2)
C(77)−O(4)−Y(1)	121.9(2)
C(84)−O(5)−C(81)	106.8(3)
C(84)−O(5)−Y(1)	130.2(2)
C(81)−O(5)−Y(1)	123.0(2)
O(1)−C(1)−C(19)	109.3(3)
O(1)−C(1)−C(10)	108.7(3)
C(19)−C(1)−C(10)	111.3(3)
O(1)−C(1)−C(2)	108.7(3)
C(19)−C(1)−C(2)	109.5(3)
C(10)−C(1)−C(2)	109.3(3)
C(3)−C(2)−C(1)	131.4(3)
C(3)−C(2)−S(1)	110.8(3)
C(1)−C(2)−S(1)	117.7(2)
C(2)−C(3)−C(4)	112.8(3)
C(5)−C(4)−C(3)	113.3(3)
C(4)−C(5)−C(6)	128.3(3)
C(4)−C(5)−S(1)	110.8(3)
C(6)−C(5)−S(1)	120.7(3)
C(7)−C(6)−C(5)	128.3(3)
C(7)−C(6)−S(2)	110.4(3)
C(5)−C(6)−S(2)	121.2(3)
C(6)−C(7)−C(8)	112.7(3)
C(9)−C(8)−C(7)	113.1(3)
C(8)−C(9)−S(2)	111.7(3)
C(11)−C(10)−C(1)	130.1(3)
C(11)−C(10)−S(3)	110.8(3)

C(73)−C(74)	1.423(5)
C(74)−C(75)	1.438(5)
C(75)−C(76)	1.337(6)
C(77)−C(78)	1.515(5)
C(78)−C(79)	1.532(6)
C(79)−C(80)	1.500(5)
C(81)−C(82)	1.480(7)
C(82)−C(83)	1.417(8)
C(83)−C(84)	1.495(6)

C(33A)−C(32)−S(8B)	4.8(8)
C(33B)−C(32)−S(8B)	106.3(7)
C(31)−C(32)−S(8B)	124.1(3)
S(8A)−C(32)−S(8B)	113.9(3)
C(32)−C(33A)−C(34)	110.3(11)
C(32)−C(33B)−C(35)	112.1(12)
C(35)−C(34)−C(33A)	109.4(7)
C(35)−C(34)−S(8B)	119.7(4)
C(33A)−C(34)−S(8B)	10.6(6)
C(34)−C(35)−C(33B)	105.7(7)
C(34)−C(35)−S(8A)	116.1(4)
C(33B)−C(35)−S(8A)	11.1(7)
C(37)−C(36)−C(27)	127.6(3)
C(37)−C(36)−S(9)	110.0(3)
C(27)−C(36)−S(9)	121.2(3)
C(36)−C(37)−C(38)	114.2(3)
C(39)−C(38)−C(37)	113.0(3)
C(38)−C(39)−C(40)	127.4(4)
C(38)−C(39)−S(9)	110.3(3)
C(40)−C(39)−S(9)	122.2(3)
C(39)−C(40)−C(41A)	126.8(7)
C(39)−C(40)−C(41B)	129.1(8)
C(41A)−C(40)−C(41B)	102.7(10)
C(39)−C(40)−S(10B)	121.9(3)
C(41A)−C(40)−S(10B)	5.8(8)
C(41B)−C(40)−S(10B)	108.1(8)
C(39)−C(40)−S(10A)	123.3(3)
C(41A)−C(40)−S(10A)	109.8(6)
C(41B)−C(40)−S(10A)	12.1(11)
S(10B)−C(40)−S(10A)	114.8(3)
C(42)−C(41A)−C(40)	109.3(10)
C(40)−C(41B)−C(43)	107.5(13)
C(43)−C(42)−C(41A)	111.9(7)
C(43)−C(42)−S(10B)	117.1(4)
C(41A)−C(42)−S(10B)	5.9(8)
C(42)−C(43)−C(41B)	106.1(8)
C(42)−C(43)−S(10A)	114.6(3)
C(41B)−C(43)−S(10A)	13.0(10)
C(45)−C(44)−C(27)	129.8(3)
C(45)−C(44)−S(11)	110.8(3)
C(27)−C(44)−S(11)	118.8(3)
C(44)−C(45)−C(46)	113.0(3)
C(47)−C(46)−C(45)	113.3(4)
C(46)−C(47)−C(48)	127.9(4)
C(46)−C(47)−S(11)	110.5(3)
C(48)−C(47)−S(11)	121.6(3)
C(49B)−C(48)−C(49A)	103.0(9)
C(49B)−C(48)−C(47)	129.3(7)
C(49A)−C(48)−C(47)	127.6(7)
C(49B)−C(48)−S(12B)	110.2(7)
C(49A)−C(48)−S(12B)	8.1(8)
C(47)−C(48)−S(12B)	120.5(3)
C(49B)−C(48)−S(12A)	6.9(7)
C(49A)−C(48)−S(12A)	109.2(7)
C(47)−C(48)−S(12A)	123.2(3)
S(12B)−C(48)−S(12A)	116.2(2)
C(48)−C(49A)−C(50)	111.0(11)
C(48)−C(49B)−C(51)	110.8(11)
C(51)−C(50)−C(49A)	108.0(7)
C(51)−C(50)−S(12B)	118.3(4)
C(49A)−C(50)−S(12B)	10.9(6)
C(50)−C(51)−C(49B)	107.1(7)
C(50)−C(51)−S(12A)	117.5(4)

C(1)−C(10)−S(3)	118.9(2)
C(10)−C(11)−C(12)	113.1(3)
C(13)−C(12)−C(11)	112.9(3)
C(12)−C(13)−C(14)	128.6(3)
C(12)−C(13)−S(3)	111.1(3)
C(14)−C(13)−S(3)	120.2(3)
C(15)−C(14)−C(13)	129.0(4)
C(15)−C(14)−S(4)	110.6(3)
C(13)−C(14)−S(4)	120.3(3)
C(14)−C(15)−C(16)	111.1(4)
C(17)−C(16)−C(15)	113.7(4)
C(16)−C(17)−S(4)	112.1(3)
C(20)−C(19)−C(1)	131.3(3)
C(20)−C(19)−S(5)	110.3(3)
C(1)−C(19)−S(5)	118.1(3)
C(19)−C(20)−C(21)	113.3(3)
C(22)−C(21)−C(20)	113.4(3)
C(21)−C(22)−C(23)	130.7(3)
C(21)−C(22)−S(5)	110.3(3)
C(23)−C(22)−S(5)	119.1(3)
C(24A)−C(23)−C(24B)	99.3(10)
C(24A)−C(23)−C(22)	127.9(6)
C(24B)−C(23)−C(22)	132.9(9)
C(24A)−C(23)−S(6B)	7.5(8)
C(24B)−C(23)−S(6B)	105.8(9)
C(22)−C(23)−S(6B)	121.3(4)
C(24A)−C(23)−S(6A)	109.0(6)
C(24B)−C(23)−S(6A)	9.9(9)
C(22)−C(23)−S(6A)	123.1(3)
S(6B)−C(23)−S(6A)	115.4(3)
C(23)−C(24A)−C(25)	112.8(10)
C(23)−C(24B)−C(26)	114.0(15)
C(26)−C(25)−C(24A)	111.1(6)
C(26)−C(25)−S(6B)	119.3(4)
C(24A)−C(25)−S(6B)	9.1(8)
C(25)−C(26)−C(24B)	102.7(9)
C(25)−C(26)−S(6A)	114.2(3)
C(24B)−C(26)−S(6A)	11.6(9)
O(2)−C(27)−C(28)	110.3(3)
O(2)−C(27)−C(36)	108.9(3)
C(28)−C(27)−C(36)	109.4(3)
O(2)−C(27)−C(44)	108.3(3)
C(28)−C(27)−C(44)	106.9(3)
C(36)−C(27)−C(44)	113.0(3)
C(29)−C(28)−C(27)	130.9(3)
C(29)−C(28)−S(7)	111.0(3)
C(27)−C(28)−S(7)	117.5(3)
C(28)−C(29)−C(30)	112.8(3)
C(31)−C(30)−C(29)	113.1(3)
C(30)−C(31)−C(32)	128.4(3)
C(30)−C(31)−S(7)	110.7(3)
C(32)−C(31)−S(7)	120.8(3)
C(33A)−C(32)−C(33B)	102.2(10)
C(33A)−C(32)−C(31)	128.2(7)
C(33B)−C(32)−C(31)	129.6(7)
C(33A)−C(32)−S(8A)	110.0(7)
C(33B)−C(32)−S(8A)	8.6(8)
C(31)−C(32)−S(8A)	121.7(3)
C(49B)−C(51)−S(12A)	11.0(6)
O(3)−C(52)−C(69)	109.7(3)
O(3)−C(52)−C(61)	109.3(3)
C(69)−C(52)−C(61)	110.3(3)
O(3)−C(52)−C(53)	108.1(3)
C(69)−C(52)−C(53)	109.8(3)
C(61)−C(52)−C(53)	109.7(3)
C(54)−C(53)−C(52)	131.6(3)
C(54)−C(53)−S(13)	111.3(3)
C(52)−C(53)−S(13)	117.1(2)
C(53)−C(54)−C(55)	112.6(4)
C(56)−C(55)−C(54)	113.6(3)
C(55)−C(56)−C(57)	130.7(3)
C(55)−C(56)−S(13)	110.1(3)
C(57)−C(56)−S(13)	119.1(3)
C(56)−C(57)−C(58)	125.1(3)
C(56)−C(57)−S(14)	121.8(3)
C(58)−C(57)−S(14)	113.0(3)
C(59)−C(58)−C(57)	103.5(3)
C(60)−C(59)−C(58)	116.8(4)
C(59)−C(60)−S(14)	114.0(3)
C(62)−C(61)−C(52)	130.9(3)
C(62)−C(61)−S(15)	110.8(3)
C(52)−C(61)−S(15)	118.3(3)
C(61)−C(62)−C(63)	113.2(3)
C(64)−C(63)−C(62)	112.8(3)
C(63)−C(64)−C(65)	129.9(3)
C(63)−C(64)−S(15)	110.8(3)
C(65)−C(64)−S(15)	119.1(3)
C(64)−C(65)−C(66)	126.8(3)
C(64)−C(65)−S(16)	118.5(3)
C(66)−C(65)−S(16)	114.7(3)
C(67)−C(66)−C(65)	102.7(3)
C(68)−C(67)−C(66)	116.8(4)
C(67)−C(68)−S(16)	113.9(3)
C(70)−C(69)−C(52)	129.7(3)
C(70)−C(69)−S(17)	110.4(3)
C(52)−C(69)−S(17)	119.4(2)
C(69)−C(70)−C(71)	113.3(3)
C(72)−C(71)−C(70)	113.4(3)
C(71)−C(72)−C(73)	129.1(3)
C(71)−C(72)−S(17)	110.3(3)
C(73)−C(72)−S(17)	120.6(3)
C(74)−C(73)−C(72)	127.7(3)
C(74)−C(73)−S(18)	111.7(3)
C(72)−C(73)−S(18)	120.7(3)
C(73)−C(74)−C(75)	108.7(3)
C(76)−C(75)−C(74)	115.2(4)
C(75)−C(76)−S(18)	112.1(3)
O(4)−C(77)−C(78)	106.0(3)
C(77)−C(78)−C(79)	103.0(3)
C(80)−C(79)−C(78)	102.2(3)
O(4)−C(80)−C(79)	104.8(3)
O(5)−C(81)−C(82)	104.9(4)
C(83)−C(82)−C(81)	109.4(4)
C(82)−C(83)−C(84)	105.4(4)
O(5)−C(84)−C(83)	104.6(3)

Compound <u>10</u>

Table 1. Crystal data and structure refinement for sh2385.

Identification code	sh2385	
Empirical formula	C103 H101 Nd O10 S18	
Formula weight	2220.16	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P−1	
Unit cell dimensions	a = 13.9062(3) Å	α = 90.9370(10)°.
	b = 17.7968(4) Å	β = 102.8770(10)°.
	c = 20.7081(4) Å	γ = 93.1290(10)°.

Volume	4986.48(18) Å^3
Z	2
Density (calculated)	1.479 Mg/m^3
Absorption coefficient	0.957 mm^{-1}
F(000)	2294
Crystal size	0.3 x 0.6 x 0.7 mm^3
Theta range for data collection	1.01 to 19.61°.
Index ranges	−13<=h<=13, −16<=k<=16, −19<=l<=19
Reflections collected	46816
Independent reflections	8779 [R(int) = 0.0331]
Completeness to theta = 19.61°	99.9 %
Absorption correction	Semi−empirical from equivalents
Refinement method	Full−matrix least−squares on F^2
Data / restraints / parameters	8779 / 50 / 1164
Goodness−of−fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1201
R indices (all data)	R1 = 0.0589, wR2 = 0.1308
Largest diff. peak and hole	1.574 and −0.804 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2385. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nd	5212(1)	8500(1)	7598(1)	23(1)
S(1)	6267(2)	5443(1)	7020(1)	27(1)
S(2A)	6308(6)	4946(5)	4987(3)	31(2)
S(2B)	7548(7)	4453(5)	6146(3)	33(1)
S(3)	3701(2)	5438(1)	7084(1)	25(1)
S(4A)	904(3)	4631(2)	7505(2)	43(1)
S(4B)	1709(7)	4505(7)	6298(5)	33(3)
S(5)	6036(2)	5441(1)	8620(1)	43(1)
S(6)	8658(2)	5280(2)	10213(1)	69(1)
S(7)	4077(2)	7650(1)	5157(1)	29(1)
S(8)	6309(2)	7622(1)	4018(1)	56(1)
S(9)	1515(2)	8048(1)	5524(1)	26(1)
S(10A)	−806(3)	7323(2)	5239(4)	32(1)
S(10B)	−50(7)	5917(5)	5577(9)	38(2)
S(11)	3092(2)	9921(1)	6714(1)	30(1)
S(12A)	2883(4)	11536(3)	7423(3)	57(2)
S(12B)	1365(12)	11875(8)	6336(5)	61(3)
S(13)	1956(2)	7768(1)	8696(1)	30(1)
S(14)	−424(2)	6955(1)	8423(1)	48(1)
S(15)	2350(2)	9897(1)	8649(1)	34(1)
S(16A)	913(3)	11296(2)	8560(4)	50(1)
S(16B)	2514(10)	12234(7)	9283(12)	42(3)
S(17)	4800(2)	7622(1)	9474(1)	26(1)
S(18)	5340(2)	6819(2)	11485(1)	62(1)
O(1)	5230(4)	7283(3)	7666(3)	29(1)
O(2)	4195(4)	8628(3)	6631(2)	25(1)
O(3)	4435(4)	8721(3)	8393(2)	26(1)
O(4)	5582(4)	9916(3)	7506(3)	34(1)
O(5)	6613(4)	8338(3)	6999(3)	35(1)
O(6)	6820(4)	8887(3)	8427(3)	36(2)
C(1)	5276(6)	6511(4)	7676(4)	27(2)
C(2)	5615(5)	6240(4)	7060(4)	24(2)
C(3)	5396(6)	6553(5)	6459(4)	29(2)
C(4)	5747(6)	6170(5)	5959(4)	28(2)
C(5)	6235(5)	5552(4)	6184(4)	25(2)
C(6)	6665(5)	5018(4)	5808(4)	26(2)
C(7A)	7410(30)	4470(20)	6019(12)	50
C(7B)	6410(30)	4850(20)	5103(11)	50
C(8)	7600(7)	4055(5)	5455(5)	43(3)
C(9)	7009(7)	4283(5)	4907(5)	40(2)
C(10)	4246(6)	6134(4)	7659(4)	24(2)
C(11)	3624(6)	6314(5)	8046(4)	38(2)
C(12)	2715(6)	5888(5)	7890(4)	37(2)
C(13)	2634(6)	5387(4)	7380(4)	24(2)
C(14)	1787(6)	4885(4)	7071(4)	28(2)
C(15A)	1515(15)	4561(15)	6422(10)	50

C(15B)	870(20)	4720(20)	7269(17)	50
C(16)	595(6)	4125(5)	6294(5)	38(2)
C(17)	213(7)	4170(5)	6822(5)	46(3)
C(18)	6009(6)	6309(5)	8302(4)	35(2)
C(19)	6792(6)	6707(6)	8687(4)	32(2)
C(20)	7326(8)	6427(5)	9164(6)	49(3)
C(21)	7084(5)	5682(4)	9245(4)	23(2)
C(22)	7508(7)	5147(6)	9716(4)	46(3)
C(23)	7075(8)	4460(6)	9852(5)	56(3)
C(24)	7738(11)	4074(7)	10359(6)	76(4)
C(25)	8553(10)	4494(8)	10565(6)	87(4)
C(26)	3491(6)	8662(4)	6033(4)	23(2)
C(27)	3986(6)	8547(4)	5453(4)	25(2)
C(28)	4508(6)	9059(5)	5167(4)	30(2)
C(29)	5007(6)	8725(5)	4716(4)	32(2)
C(30)	4845(6)	7964(5)	4652(4)	29(2)
C(31)	5222(6)	7419(5)	4248(4)	32(2)
C(32)	4807(6)	6708(4)	4001(4)	33(2)
C(33)	5419(8)	6364(5)	3640(5)	55(3)
C(34)	6218(8)	6785(5)	3596(4)	49(3)
C(35)	2691(5)	8020(4)	6015(4)	22(2)
C(36)	2816(6)	7359(4)	6327(4)	24(2)
C(37)	1961(6)	6867(4)	6173(4)	25(2)
C(38)	1186(6)	7149(4)	5746(4)	24(2)
C(39)	187(6)	6819(4)	5519(4)	27(2)
C(40A)	−175(15)	6053(12)	5550(20)	50
C(40B)	−763(16)	7140(16)	5260(30)	50
C(41)	−1210(6)	5942(6)	5317(4)	48(3)
C(42)	−1593(7)	6577(6)	5146(5)	48(3)
C(43)	3036(6)	9422(4)	5986(4)	25(2)
C(44)	2536(6)	9793(5)	5459(4)	31(2)
C(45)	2193(6)	10480(5)	5639(5)	36(2)
C(46)	2434(6)	10631(4)	6306(5)	33(2)
C(47)	2219(6)	11285(5)	6670(4)	41(2)
C(48A)	1530(30)	11865(16)	6468(14)	50
C(48B)	2530(30)	11527(16)	7346(13)	50
C(49)	1587(11)	12430(6)	6982(6)	90(5)
C(50)	2257(10)	12270(5)	7493(7)	74(4)
C(51)	3695(5)	8729(4)	8748(4)	22(2)
C(52)	2756(6)	8313(4)	8344(4)	22(2)
C(53)	2426(6)	8313(4)	7677(4)	27(2)
C(54)	1522(6)	7884(5)	7445(4)	30(2)
C(55)	1172(6)	7548(4)	7933(4)	27(2)
C(56)	307(6)	7029(5)	7850(4)	32(2)
C(57)	−70(6)	6539(5)	7309(4)	36(2)
C(58)	−915(7)	6119(5)	7387(5)	45(3)
C(59)	−1187(7)	6271(5)	7949(5)	49(3)
C(60)	3493(6)	9545(4)	8896(4)	24(2)
C(61)	4150(6)	10087(4)	9227(4)	26(2)
C(62)	3754(6)	10783(5)	9288(4)	29(2)
C(63)	2777(7)	10776(4)	9004(4)	30(2)
C(64)	2113(6)	11388(4)	8960(4)	35(2)
C(65A)	2315(16)	12159(11)	9201(17)	50
C(65B)	1080(30)	11450(20)	8630(40)	50
C(66)	1492(8)	12606(6)	9029(5)	60(3)
C(67)	724(9)	12198(6)	8690(5)	61(3)
C(68)	4011(6)	8349(4)	9409(4)	23(2)
C(69)	3673(6)	8426(4)	9970(4)	26(2)
C(70)	4040(6)	7900(4)	10457(4)	28(2)
C(71)	4660(6)	7422(4)	10267(4)	24(2)
C(72)	5207(6)	6832(5)	10644(4)	29(2)
C(73)	5692(6)	6234(4)	10404(4)	29(2)
C(74)	6151(8)	5822(6)	10955(6)	57(3)
C(75)	6025(9)	6067(6)	11546(6)	66(3)
C(76)	5417(7)	10458(5)	7991(4)	39(2)
C(77)	5701(9)	11218(5)	7757(5)	58(3)
C(78)	5481(9)	11109(5)	7029(5)	62(3)
C(79)	5740(7)	10310(5)	6928(4)	45(3)
C(80)	6657(7)	8636(5)	6361(4)	42(2)
C(81)	7049(7)	8029(6)	6010(5)	49(3)
C(82)	7752(7)	7653(6)	6552(5)	50(3)
C(83)	7400(6)	7832(5)	7178(4)	39(2)
C(84)	6967(7)	8883(6)	9135(4)	51(3)

C(85)	8066(10)	8846(11)	9373(6)	128(7)
C(86)	8531(8)	9130(7)	8795(5)	78(4)
C(87)	7643(7)	9353(5)	8295(5)	46(3)
O(7)	1104(6)	539(5)	3074(4)	85(3)
C(88)	894(11)	535(11)	3722(6)	142(8)
C(89)	−98(9)	323(9)	3672(6)	94(5)
C(90)	−546(8)	199(8)	2960(6)	75(4)
C(91)	197(7)	527(7)	2610(5)	63(3)
O(8)	1784(8)	9267(6)	471(6)	115(3)
C(92)	1724(10)	8611(9)	876(6)	92(4)
C(93)	1237(12)	7978(10)	393(8)	121(6)
C(94)	443(12)	8393(12)	−89(9)	135(7)
C(95)	913(13)	9169(12)	−75(8)	138(7)
O(9)	2750(14)	6298(11)	2095(9)	235(8)
C(96)	2348(15)	6806(11)	1561(10)	160(7)
C(97)	1363(16)	6312(13)	1230(12)	182(9)
C(98)	988(19)	5897(18)	1697(14)	256(14)
C(99)	1874(14)	5823(10)	2184(9)	134(6)
O(10)	1683(17)	8782(12)	2963(11)	284(10)
C(100)	1582(14)	8143(11)	2564(9)	139(6)
C(101)	940(20)	7840(20)	3005(13)	303(17)
C(102)	1644(14)	7753(10)	3668(10)	143(6)
C(103)	2064(17)	8564(12)	3674(12)	187(9)

Table 3. Bond lengths [Å] and angles [°] for sh2385.

Nd−O(1)	2.173(5)	C(22)−C(23)	1.394(13)
Nd−O(3)	2.202(5)	C(23)−C(24)	1.444(15)
Nd−O(2)	2.203(5)	C(24)−C(25)	1.306(16)
Nd−O(6)	2.550(5)	C(26)−C(43)	1.520(11)
Nd−O(5)	2.558(5)	C(26)−C(27)	1.527(11)
Nd−O(4)	2.563(5)	C(26)−C(35)	1.544(11)
S(1)−C(2)	1.736(8)	C(27)−C(28)	1.357(11)
S(1)−C(5)	1.737(8)	C(28)−C(29)	1.423(11)
S(2A)−C(9)	1.601(11)	C(29)−C(30)	1.361(11)
S(2A)−C(6)	1.663(10)	C(30)−C(31)	1.462(12)
S(2B)−C(8)	1.605(11)	C(31)−C(32)	1.402(11)
S(2B)−C(6)	1.668(10)	C(32)−C(33)	1.409(12)
S(3)−C(10)	1.723(8)	C(33)−C(34)	1.327(13)
S(3)−C(13)	1.725(8)	C(35)−C(36)	1.352(11)
S(4A)−C(17)	1.694(9)	C(36)−C(37)	1.411(11)
S(4A)−C(14)	1.722(8)	C(37)−C(38)	1.358(11)
S(4B)−C(16)	1.654(12)	C(38)−C(39)	1.452(11)
S(4B)−C(14)	1.705(12)	C(39)−C(40A)	1.435(18)
S(5)−C(18)	1.687(9)	C(39)−C(40B)	1.46(2)
S(5)−C(21)	1.747(8)	C(40A)−C(41)	1.415(18)
S(6)−C(25)	1.601(14)	C(40B)−C(42)	1.46(2)
S(6)−C(22)	1.699(10)	C(41)−C(42)	1.297(13)
S(7)−C(27)	1.722(8)	C(43)−C(44)	1.360(11)
S(7)−C(30)	1.733(8)	C(44)−C(45)	1.410(12)
S(8)−C(34)	1.699(10)	C(45)−C(46)	1.366(12)
S(8)−C(31)	1.705(9)	C(46)−C(47)	1.457(12)
S(9)−C(35)	1.726(8)	C(47)−C(48B)	1.42(2)
S(9)−C(38)	1.737(8)	C(47)−C(48A)	1.453(19)
S(10A)−C(42)	1.654(10)	C(48A)−C(49)	1.437(19)
S(10A)−C(39)	1.686(9)	C(48B)−C(50)	1.44(2)
S(10B)−C(41)	1.586(13)	C(49)−C(50)	1.290(16)
S(10B)−C(39)	1.634(12)	C(51)−C(68)	1.523(11)
S(11)−C(46)	1.722(9)	C(51)−C(52)	1.529(11)
S(11)−C(43)	1.722(8)	C(51)−C(60)	1.532(11)
S(12A)−C(50)	1.631(12)	C(52)−C(53)	1.355(10)
S(12A)−C(47)	1.664(10)	C(53)−C(54)	1.417(11)
S(12B)−C(49)	1.611(15)	C(54)−C(55)	1.350(11)
S(12B)−C(47)	1.669(12)	C(55)−C(56)	1.453(12)
S(13)−C(52)	1.726(8)	C(56)−C(57)	1.396(11)
S(13)−C(55)	1.732(8)	C(57)−C(58)	1.398(12)
S(14)−C(59)	1.710(9)	C(58)−C(59)	1.330(13)
S(14)−C(56)	1.728(9)	C(60)−C(61)	1.356(11)
S(15)−C(60)	1.715(8)	C(61)−C(62)	1.398(11)
S(15)−C(63)	1.733(8)	C(62)−C(63)	1.354(11)
S(16A)−C(67)	1.668(10)	C(63)−C(64)	1.458(12)
S(16A)−C(64)	1.687(9)	C(64)−C(65A)	1.443(17)
S(16B)−C(66)	1.586(15)	C(64)−C(65B)	1.46(2)
S(16B)−C(64)	1.654(14)	C(65A)−C(66)	1.413(17)

S(17)−C(68)	1.730(8)	C(65B)−C(67)	1.46(2)
S(17)−C(71)	1.736(8)	C(66)−C(67)	1.313(14)
S(18)−C(75)	1.675(11)	C(68)−C(69)	1.353(11)
S(18)−C(72)	1.709(8)	C(69)−C(70)	1.418(11)
O(1)−C(1)	1.380(9)	C(70)−C(71)	1.357(11)
O(2)−C(26)	1.401(9)	C(71)−C(72)	1.463(11)
O(3)−C(51)	1.393(9)	C(72)−C(73)	1.430(11)
O(4)−C(76)	1.444(10)	C(73)−C(74)	1.415(13)
O(4)−C(79)	1.450(10)	C(74)−C(75)	1.343(14)
O(5)−C(80)	1.443(10)	C(76)−C(77)	1.505(12)
O(5)−C(83)	1.444(10)	C(77)−C(78)	1.478(13)
O(6)−C(84)	1.436(10)	C(78)−C(79)	1.508(13)
O(6)−C(87)	1.454(10)	C(80)−C(81)	1.487(12)
C(1)−C(18)	1.521(12)	C(81)−C(82)	1.505(13)
C(1)−C(2)	1.536(11)	C(82)−C(83)	1.520(12)
C(1)−C(10)	1.542(11)	C(84)−C(85)	1.503(16)
C(2)−C(3)	1.349(11)	C(85)−C(86)	1.560(16)
C(3)−C(4)	1.419(11)	C(86)−C(87)	1.501(14)
C(4)−C(5)	1.359(11)	O(7)−C(91)	1.404(12)
C(5)−C(6)	1.454(11)	O(7)−C(88)	1.436(14)
C(6)−C(7B)	1.45(2)	C(88)−C(89)	1.390(16)
C(6)−C(7A)	1.46(2)	C(89)−C(90)	1.476(15)
C(7A)−C(8)	1.45(2)	C(90)−C(91)	1.487(14)
C(7B)−C(9)	1.45(2)	O(8)−C(92)	1.458(16)
C(8)−C(9)	1.328(12)	O(8)−C(95)	1.462(17)
C(10)−C(11)	1.350(11)	C(92)−C(93)	1.520(18)
C(11)−C(12)	1.408(12)	C(93)−C(94)	1.54(2)
C(12)−C(13)	1.354(11)	C(94)−C(95)	1.49(2)
C(13)−C(14)	1.457(11)	O(9)−C(96)	1.471(16)
C(14)−C(15A)	1.415(17)	O(9)−C(99)	1.492(16)
C(14)−C(15B)	1.45(2)	C(96)−C(97)	1.598(17)
C(15A)−C(16)	1.430(17)	C(97)−C(98)	1.400(18)
C(15B)−C(17)	1.46(2)	C(98)−C(99)	1.421(18)
C(16)−C(17)	1.322(12)	O(10)−C(100)	1.377(17)
C(18)−C(19)	1.354(11)	O(10)−C(103)	1.514(17)
C(19)−C(20)	1.226(12)	C(100)−C(101)	1.497(19)
C(20)−C(21)	1.372(12)	C(101)−C(102)	1.510(19)
C(21)−C(22)	1.429(12)	C(102)−C(103)	1.527(17)

O(1)−Nd−O(3)	98.31(18)	C(36)−C(35)−S(9)	111.4(6)
O(1)−Nd−O(2)	102.00(19)	C(26)−C(35)−S(9)	122.1(6)
O(3)−Nd−O(2)	109.13(18)	C(35)−C(36)−C(37)	112.7(7)
O(1)−Nd−O(6)	99.88(19)	C(38)−C(37)−C(36)	114.1(7)
O(3)−Nd−O(6)	87.61(17)	C(37)−C(38)−C(39)	128.5(7)
O(2)−Nd−O(6)	149.97(18)	C(37)−C(38)−S(9)	110.0(6)
O(1)−Nd−O(5)	83.52(18)	C(39)−C(38)−S(9)	121.3(6)
O(3)−Nd−O(5)	160.70(18)	C(40A)−C(39)−C(38)	128.9(11)
O(2)−Nd−O(5)	89.10(17)	C(40A)−C(39)−C(40B)	97.9(14)
O(6)−Nd−O(5)	73.18(17)	C(38)−C(39)−C(40B)	133.0(12)
O(1)−Nd−O(4)	167.65(18)	C(40A)−C(39)−S(10B)	8.6(11)
O(3)−Nd−O(4)	90.40(17)	C(38)−C(39)−S(10B)	120.6(7)
O(2)−Nd−O(4)	83.19(17)	C(40B)−C(39)−S(10B)	106.3(12)
O(6)−Nd−O(4)	71.61(18)	C(40A)−C(39)−S(10A)	106.9(10)
O(5)−Nd−O(4)	85.38(17)	C(38)−C(39)−S(10A)	123.9(6)
C(2)−S(1)−C(5)	92.3(4)	C(40B)−C(39)−S(10A)	9.1(11)
C(9)−S(2A)−C(6)	95.1(5)	S(10B)−C(39)−S(10A)	115.4(6)
C(8)−S(2B)−C(6)	94.6(5)	C(41)−C(40A)−C(39)	113.4(16)
C(10)−S(3)−C(13)	92.5(4)	C(42)−C(40B)−C(39)	112.7(18)
C(17)−S(4A)−C(14)	90.1(5)	C(42)−C(41)−C(40A)	110.2(12)
C(16)−S(4B)−C(14)	90.2(6)	C(42)−C(41)−S(10B)	119.7(8)
C(18)−S(5)−C(21)	93.3(4)	C(40A)−C(41)−S(10B)	9.6(11)
C(25)−S(6)−C(22)	92.2(6)	C(41)−C(42)−C(40B)	105.8(13)
C(27)−S(7)−C(30)	92.4(4)	C(41)−C(42)−S(10A)	115.8(7)
C(34)−S(8)−C(31)	91.8(5)	C(40B)−C(42)−S(10A)	10.1(11)
C(35)−S(9)−C(38)	91.8(4)	C(44)−C(43)−C(26)	131.6(7)
C(42)−S(10A)−C(39)	93.6(5)	C(44)−C(43)−S(11)	110.7(6)
C(41)−S(10B)−C(39)	95.4(6)	C(26)−C(43)−S(11)	117.6(6)
C(46)−S(11)−C(43)	92.3(4)	C(43)−C(44)−C(45)	113.2(7)
C(50)−S(12A)−C(47)	94.2(6)	C(46)−C(45)−C(44)	113.2(8)
C(49)−S(12B)−C(47)	93.8(7)	C(45)−C(46)−C(47)	128.7(8)
C(52)−S(13)−C(55)	92.4(4)	C(45)−C(46)−S(11)	110.5(6)
C(59)−S(14)−C(56)	91.5(5)	C(47)−C(46)−S(11)	120.8(7)
C(60)−S(15)−C(63)	92.1(4)	C(48B)−C(47)−C(48A)	96.8(15)

C(67)−S(16A)−C(64)	93.4(5)
C(66)−S(16B)−C(64)	95.0(7)
C(68)−S(17)−C(71)	92.2(4)
C(75)−S(18)−C(72)	92.1(5)
C(1)−O(1)−Nd	176.1(5)
C(26)−O(2)−Nd	174.9(4)
C(51)−O(3)−Nd	161.1(4)
C(76)−O(4)−C(79)	109.0(6)
C(76)−O(4)−Nd	122.0(4)
C(79)−O(4)−Nd	127.4(5)
C(80)−O(5)−C(83)	107.8(6)
C(80)−O(5)−Nd	125.4(5)
C(83)−O(5)−Nd	126.0(5)
C(84)−O(6)−C(87)	105.6(6)
C(84)−O(6)−Nd	125.7(5)
C(87)−O(6)−Nd	126.3(5)
O(1)−C(1)−C(18)	108.7(6)
O(1)−C(1)−C(2)	109.0(6)
C(18)−C(1)−C(2)	110.2(6)
O(1)−C(1)−C(10)	110.1(6)
C(18)−C(1)−C(10)	110.5(7)
C(2)−C(1)−C(10)	108.3(6)
C(3)−C(2)−C(1)	125.3(7)
C(3)−C(2)−S(1)	110.0(6)
C(1)−C(2)−S(1)	124.6(6)
C(2)−C(3)−C(4)	114.5(7)
C(5)−C(4)−C(3)	112.8(7)
C(4)−C(5)−C(6)	127.7(7)
C(4)−C(5)−S(1)	110.5(6)
C(6)−C(5)−S(1)	121.7(6)
C(7B)−C(6)−C(5)	128.5(11)
C(7B)−C(6)−C(7A)	100.0(14)
C(5)−C(6)−C(7A)	131.4(11)
C(7B)−C(6)−S(2A)	8.3(14)
C(5)−C(6)−S(2A)	120.8(6)
C(7A)−C(6)−S(2A)	107.7(10)
C(7B)−C(6)−S(2B)	107.4(11)
C(5)−C(6)−S(2B)	124.1(6)
C(7A)−C(6)−S(2B)	7.5(11)
S(2A)−C(6)−S(2B)	115.1(5)
C(8)−C(7A)−C(6)	111.3(17)
C(6)−C(7B)−C(9)	112.6(18)
C(9)−C(8)−C(7A)	108.5(12)
C(9)−C(8)−S(2B)	117.8(7)
C(7A)−C(8)−S(2B)	9.4(11)
C(8)−C(9)−C(7B)	107.5(12)
C(8)−C(9)−S(2A)	117.3(7)
C(7B)−C(9)−S(2A)	10.2(13)
C(11)−C(10)−C(1)	126.8(7)
C(11)−C(10)−S(3)	110.4(6)
C(1)−C(10)−S(3)	122.7(6)
C(10)−C(11)−C(12)	113.4(7)
C(13)−C(12)−C(11)	113.8(8)
C(12)−C(13)−C(14)	128.4(7)
C(12)−C(13)−S(3)	110.0(6)
C(14)−C(13)−S(3)	121.6(6)
C(15A)−C(14)−C(15B)	98.3(14)
C(15A)−C(14)−C(13)	130.2(10)
C(15B)−C(14)−C(13)	130.0(11)
C(15A)−C(14)−S(4B)	11.5(10)
C(15B)−C(14)−S(4B)	109.4(12)
C(13)−C(14)−S(4B)	120.0(6)
C(15A)−C(14)−S(4A)	109.8(10)
C(15B)−C(14)−S(4A)	15.5(18)
C(13)−C(14)−S(4A)	120.0(6)
S(4B)−C(14)−S(4A)	120.0(6)
C(14)−C(15A)−C(16)	113.6(14)
C(14)−C(15B)−C(17)	112.5(18)
C(17)−C(16)−C(15A)	108.6(11)
C(17)−C(16)−S(4B)	121.2(8)
C(15A)−C(16)−S(4B)	13.5(9)
C(16)−C(17)−C(15B)	105.1(13)
C(16)−C(17)−S(4A)	117.7(7)
C(48B)−C(47)−C(46)	132.3(12)
C(48A)−C(47)−C(46)	130.7(11)
C(48B)−C(47)−S(12A)	15.3(17)
C(48A)−C(47)−S(12A)	107.1(11)
C(46)−C(47)−S(12A)	121.9(6)
C(48B)−C(47)−S(12B)	105.0(12)
C(48A)−C(47)−S(12B)	8.4(11)
C(46)−C(47)−S(12B)	122.4(7)
S(12A)−C(47)−S(12B)	115.5(6)
C(49)−C(48A)−C(47)	112.0(17)
C(47)−C(48B)−C(50)	114.8(19)
C(50)−C(49)−C(48A)	109.4(13)
C(50)−C(49)−S(12B)	119.2(9)
C(48A)−C(49)−S(12B)	9.8(11)
C(49)−C(50)−C(48B)	104.9(15)
C(49)−C(50)−S(12A)	117.0(10)
C(48B)−C(50)−S(12A)	16.4(16)
O(3)−C(51)−C(68)	110.9(6)
O(3)−C(51)−C(52)	109.4(6)
C(68)−C(51)−C(52)	109.1(6)
O(3)−C(51)−C(60)	109.5(6)
C(68)−C(51)−C(60)	107.6(6)
C(52)−C(51)−C(60)	110.2(6)
C(53)−C(52)−C(51)	126.6(7)
C(53)−C(52)−S(13)	110.2(6)
C(51)−C(52)−S(13)	123.2(5)
C(52)−C(53)−C(54)	113.6(7)
C(55)−C(54)−C(53)	113.4(7)
C(54)−C(55)−C(56)	126.4(7)
C(54)−C(55)−S(13)	110.3(6)
C(56)−C(55)−S(13)	123.1(6)
C(57)−C(56)−C(55)	126.6(8)
C(57)−C(56)−S(14)	110.2(6)
C(55)−C(56)−S(14)	123.2(6)
C(56)−C(57)−C(58)	111.8(8)
C(59)−C(58)−C(57)	114.3(8)
C(58)−C(59)−S(14)	112.2(7)
C(61)−C(60)−C(51)	127.2(7)
C(61)−C(60)−S(15)	110.0(6)
C(51)−C(60)−S(15)	122.7(6)
C(60)−C(61)−C(62)	114.6(7)
C(63)−C(62)−C(61)	112.6(7)
C(62)−C(63)−C(64)	128.8(8)
C(62)−C(63)−S(15)	110.7(6)
C(64)−C(63)−S(15)	120.5(6)
C(65A)−C(64)−C(65B)	97.6(14)
C(65A)−C(64)−C(63)	129.7(10)
C(65B)−C(64)−C(63)	132.7(12)
C(65A)−C(64)−S(16B)	8.6(11)
C(65B)−C(64)−S(16B)	106.1(12)
C(63)−C(64)−S(16B)	121.1(7)
C(65A)−C(64)−S(16A)	107.3(9)
C(65B)−C(64)−S(16A)	9.8(12)
C(63)−C(64)−S(16A)	123.0(6)
S(16B)−C(64)−S(16A)	115.9(6)
C(66)−C(65A)−C(64)	113.6(15)
C(64)−C(65B)−C(67)	114(2)
C(67)−C(66)−C(65A)	110.1(12)
C(67)−C(66)−S(16B)	120.1(9)
C(65A)−C(66)−S(16B)	10.0(11)
C(66)−C(67)−C(65B)	105.2(14)
C(66)−C(67)−S(16A)	115.6(8)
C(65B)−C(67)−S(16A)	10.5(12)
C(69)−C(68)−C(51)	129.4(7)
C(69)−C(68)−S(17)	110.7(6)
C(51)−C(68)−S(17)	119.5(6)
C(68)−C(69)−C(70)	113.5(7)
C(71)−C(70)−C(69)	113.4(7)
C(70)−C(71)−C(72)	128.9(7)
C(70)−C(71)−S(17)	110.3(6)
C(72)−C(71)−S(17)	120.8(6)
C(73)−C(72)−C(71)	128.3(7)
C(73)−C(72)−S(18)	112.0(6)

C(15B)−C(17)−S(4A)	16.5(18)	C(71)−C(72)−S(18)	119.7(6)
C(19)−C(18)−C(1)	131.4(9)	C(74)−C(73)−C(72)	107.9(8)
C(19)−C(18)−S(5)	105.0(7)	C(75)−C(74)−C(73)	115.5(9)
C(1)−C(18)−S(5)	123.4(7)	C(74)−C(75)−S(18)	112.5(8)
C(20)−C(19)−C(18)	121.5(11)	O(4)−C(76)−C(77)	105.9(7)
C(19)−C(20)−C(21)	114.2(11)	C(78)−C(77)−C(76)	103.2(7)
C(20)−C(21)−C(22)	132.7(9)	C(77)−C(78)−C(79)	103.8(8)
C(20)−C(21)−S(5)	105.9(7)	O(4)−C(79)−C(78)	105.5(7)
C(22)−C(21)−S(5)	121.4(7)	O(5)−C(80)−C(81)	105.1(7)
C(23)−C(22)−C(21)	127.4(9)	C(80)−C(81)−C(82)	104.3(7)
C(23)−C(22)−S(6)	109.5(7)	C(81)−C(82)−C(83)	104.6(7)
C(21)−C(22)−S(6)	123.1(8)	O(5)−C(83)−C(82)	107.0(7)
C(22)−C(23)−C(24)	111.1(10)	O(6)−C(84)−C(85)	103.8(8)
C(25)−C(24)−C(23)	109.3(11)	C(84)−C(85)−C(86)	106.3(10)
C(24)−C(25)−S(6)	117.8(11)	C(87)−C(86)−C(85)	102.3(9)
O(2)−C(26)−C(43)	109.9(6)	O(6)−C(87)−C(86)	105.0(7)
O(2)−C(26)−C(27)	109.5(6)	C(91)−O(7)−C(88)	107.5(9)
C(43)−C(26)−C(27)	109.6(6)	C(89)−C(88)−O(7)	109.7(10)
O(2)−C(26)−C(35)	108.1(6)	C(88)−C(89)−C(90)	106.7(10)
C(43)−C(26)−C(35)	110.6(6)	C(89)−C(90)−C(91)	105.2(9)
C(27)−C(26)−C(35)	109.1(6)	O(7)−C(91)−C(90)	105.4(8)
C(28)−C(27)−C(26)	128.8(7)	C(92)−O(8)−C(95)	104.6(12)
C(28)−C(27)−S(7)	110.9(6)	O(8)−C(92)−C(93)	105.4(12)
C(26)−C(27)−S(7)	119.7(6)	C(92)−C(93)−C(94)	101.6(14)
C(27)−C(28)−C(29)	113.1(7)	C(95)−C(94)−C(93)	102.6(13)
C(30)−C(29)−C(28)	113.3(7)	O(8)−C(95)−C(94)	110.7(16)
C(29)−C(30)−C(31)	130.2(7)	C(96)−O(9)−C(99)	104.5(16)
C(29)−C(30)−S(7)	110.3(6)	O(9)−C(96)−C(97)	98.3(16)
C(31)−C(30)−S(7)	119.5(6)	C(98)−C(97)−C(96)	112(2)
C(32)−C(31)−C(30)	128.8(7)	C(97)−C(98)−C(99)	100(2)
C(32)−C(31)−S(8)	111.2(6)	C(98)−C(99)−O(9)	115.7(19)
C(30)−C(31)−S(8)	120.0(6)	C(100)−O(10)−C(103)	108(2)
C(31)−C(32)−C(33)	110.4(8)	O(10)−C(100)−C(101)	85(2)
C(34)−C(33)−C(32)	114.2(8)	C(100)−C(101)−C(102)	105(2)
C(33)−C(34)−S(8)	112.4(7)	C(101)−C(102)−C(103)	92(2)
C(36)−C(35)−C(26)	126.4(7)	O(10)−C(103)−C(102)	102.2(18)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for sh2385. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nd	22(1)	26(1)	22(1)	−7(1)	6(1)	−1(1)
S(1)	27(1)	26(1)	28(1)	−6(1)	7(1)	6(1)
S(2A)	22(3)	37(4)	33(3)	−17(3)	9(3)	−3(2)
S(2B)	37(4)	35(3)	26(3)	−11(3)	5(3)	9(2)
S(3)	29(1)	22(1)	25(1)	−5(1)	6(1)	2(1)
S(4A)	37(2)	45(2)	49(3)	−12(2)	21(2)	−11(2)
S(4B)	29(5)	24(5)	42(6)	−1(4)	−1(4)	−5(4)
S(5)	55(2)	32(1)	43(2)	−2(1)	11(1)	1(1)
S(6)	74(2)	63(2)	59(2)	2(2)	−11(2)	28(2)
S(7)	37(1)	23(1)	27(1)	−3(1)	12(1)	−3(1)
S(8)	67(2)	45(2)	67(2)	−8(1)	40(2)	−2(1)
S(9)	28(1)	25(1)	24(1)	3(1)	2(1)	−2(1)
S(10A)	27(2)	28(2)	40(2)	−4(2)	6(2)	2(2)
S(10B)	43(5)	34(5)	34(4)	0(5)	6(4)	−8(4)
S(11)	37(1)	26(1)	30(1)	−1(1)	13(1)	4(1)
S(12A)	84(5)	45(3)	52(3)	0(2)	37(3)	14(3)
S(12B)	79(8)	65(5)	54(6)	21(4)	35(5)	50(5)
S(13)	31(1)	35(1)	23(1)	−2(1)	5(1)	−5(1)
S(14)	40(2)	54(2)	49(2)	−9(1)	14(1)	−8(1)
S(15)	34(1)	27(1)	37(1)	−9(1)	−2(1)	3(1)
S(16A)	40(2)	41(2)	69(3)	−9(2)	8(2)	11(2)
S(16B)	44(8)	33(6)	46(8)	−5(5)	1(6)	7(6)
S(17)	31(1)	25(1)	24(1)	−3(1)	9(1)	3(1)
S(18)	98(2)	54(2)	38(2)	14(1)	15(2)	29(2)
O(1)	32(3)	21(4)	37(3)	−9(3)	14(3)	1(3)
O(2)	29(3)	23(3)	23(3)	−5(2)	7(3)	−1(2)
O(3)	29(3)	27(3)	23(3)	−5(2)	10(3)	−1(2)
O(4)	41(4)	30(3)	29(3)	−2(3)	10(3)	−7(3)
O(5)	30(3)	46(4)	31(4)	0(3)	13(3)	6(3)
O(6)	29(3)	50(4)	26(4)	−6(3)	7(3)	−10(3)

C(1)	29(5)	26(6)	27(5)	−6(4)	5(4)	8(4)
C(2)	19(5)	24(5)	25(6)	−11(4)	−2(4)	−4(4)
C(3)	26(5)	33(5)	25(6)	−7(5)	2(4)	8(4)
C(4)	30(5)	31(5)	20(5)	−6(4)	3(4)	2(4)
C(5)	15(4)	27(5)	31(5)	−5(4)	6(4)	−7(4)
C(6)	21(5)	24(5)	35(5)	−12(4)	14(4)	−7(4)
C(8)	37(6)	30(6)	70(8)	−8(5)	30(6)	6(5)
C(9)	47(6)	38(6)	38(6)	−21(5)	22(5)	−20(5)
C(10)	29(5)	26(5)	17(5)	−4(4)	6(4)	2(4)
C(11)	40(6)	39(6)	36(6)	−18(5)	13(5)	−15(5)
C(12)	40(6)	40(6)	35(6)	−9(5)	18(5)	−3(5)
C(13)	29(5)	19(5)	23(5)	1(4)	5(4)	2(4)
C(14)	37(5)	20(5)	31(5)	8(4)	8(4)	11(4)
C(16)	37(6)	32(6)	44(6)	−6(4)	7(5)	−3(4)
C(17)	28(5)	46(6)	61(7)	−12(5)	9(5)	−7(5)
C(18)	37(6)	50(6)	20(5)	−1(4)	8(5)	21(5)
C(19)	0(4)	90(8)	2(5)	−23(5)	−3(4)	−20(5)
C(20)	57(7)	28(7)	77(9)	−6(5)	47(8)	−6(5)
C(21)	21(5)	26(6)	22(5)	4(4)	5(4)	7(4)
C(22)	53(6)	63(8)	24(5)	3(5)	9(5)	24(6)
C(23)	60(7)	44(7)	66(8)	10(6)	18(6)	−4(6)
C(24)	131(12)	45(7)	62(8)	35(6)	34(8)	37(8)
C(25)	97(10)	107(11)	57(8)	−32(8)	31(7)	−42(9)
C(26)	25(5)	28(5)	15(5)	0(4)	4(4)	−1(4)
C(27)	31(5)	20(5)	19(5)	−2(4)	1(4)	−3(4)
C(28)	42(5)	17(5)	34(5)	−6(4)	18(5)	−3(4)
C(29)	43(6)	25(6)	32(5)	5(4)	17(5)	−2(4)
C(30)	37(5)	24(6)	27(5)	0(4)	10(4)	−1(4)
C(31)	47(6)	28(6)	25(5)	2(4)	16(4)	−1(4)
C(32)	50(6)	12(5)	47(6)	−13(4)	39(5)	−9(4)
C(33)	75(8)	29(6)	67(7)	−16(5)	31(6)	−7(6)
C(34)	67(8)	52(7)	39(6)	−2(5)	31(5)	19(6)
C(35)	24(5)	24(5)	17(5)	−2(4)	4(4)	3(4)
C(36)	20(5)	30(5)	21(5)	−3(4)	5(4)	0(4)
C(37)	32(6)	21(5)	23(5)	2(4)	9(4)	3(5)
C(38)	29(6)	24(5)	18(5)	−1(4)	6(4)	2(4)
C(39)	27(5)	32(5)	21(5)	−7(4)	5(4)	−5(4)
C(41)	46(7)	56(7)	41(6)	−12(5)	14(5)	−26(6)
C(42)	28(6)	77(8)	38(6)	−11(6)	3(5)	4(6)
C(43)	29(5)	22(5)	25(5)	−2(4)	10(4)	−3(4)
C(44)	41(5)	29(6)	22(5)	1(4)	6(4)	−2(4)
C(45)	37(6)	32(6)	39(7)	11(5)	7(5)	5(4)
C(46)	36(5)	24(5)	43(7)	6(5)	21(5)	2(4)
C(47)	48(6)	28(6)	58(7)	17(5)	29(5)	13(5)
C(49)	134(13)	65(9)	107(11)	44(9)	83(10)	64(9)
C(50)	137(12)	34(7)	76(9)	−4(6)	74(9)	12(7)
C(51)	20(5)	30(5)	20(5)	−2(4)	9(4)	0(4)
C(52)	28(5)	24(5)	16(5)	2(4)	7(4)	5(4)
C(53)	34(6)	31(5)	18(6)	1(4)	11(4)	−3(4)
C(54)	35(6)	36(5)	15(5)	−2(4)	0(4)	4(5)
C(55)	35(5)	23(5)	22(5)	−6(4)	6(4)	3(4)
C(56)	28(5)	33(5)	37(6)	−5(5)	9(4)	0(5)
C(57)	28(5)	38(6)	40(6)	−3(5)	5(4)	−15(5)
C(58)	43(6)	47(6)	44(7)	−18(5)	11(5)	−6(5)
C(59)	39(6)	42(6)	64(8)	−7(5)	13(5)	−13(5)
C(60)	27(5)	29(5)	17(4)	−2(4)	8(4)	0(4)
C(61)	21(5)	26(5)	29(5)	−7(4)	4(4)	0(4)
C(62)	26(6)	31(6)	28(5)	−7(4)	6(4)	−8(4)
C(63)	45(7)	26(5)	20(5)	−7(4)	8(4)	2(5)
C(64)	45(6)	32(6)	32(5)	−2(4)	13(4)	10(5)
C(66)	98(10)	36(6)	52(7)	−7(5)	31(7)	13(7)
C(67)	62(8)	53(7)	71(8)	3(6)	15(6)	31(6)
C(68)	25(5)	24(5)	20(5)	−6(4)	5(4)	−2(4)
C(69)	26(5)	28(5)	22(5)	−5(4)	4(4)	5(4)
C(70)	36(5)	30(5)	22(5)	−4(4)	13(4)	−1(4)
C(71)	28(5)	26(5)	18(5)	−5(4)	6(4)	−3(4)
C(72)	32(5)	29(5)	29(5)	7(4)	11(4)	−4(4)
C(73)	33(5)	29(5)	29(5)	20(4)	14(4)	8(4)
C(74)	69(7)	39(6)	71(8)	7(6)	28(6)	21(5)
C(75)	100(9)	46(7)	55(8)	22(6)	19(7)	26(6)
C(76)	56(6)	35(6)	26(5)	−8(5)	11(5)	−1(5)
C(77)	95(9)	31(6)	48(7)	−6(5)	18(6)	−3(6)
C(78)	112(9)	40(7)	37(7)	−3(5)	25(6)	−12(6)

C(79)	66(7)	38(6)	34(6)	−6(5)	21(5)	−11(5)
C(80)	34(6)	65(7)	34(6)	3(5)	18(5)	7(5)
C(81)	43(6)	66(7)	43(6)	−6(5)	23(5)	0(5)
C(82)	43(6)	63(7)	51(7)	−4(5)	21(5)	13(5)
C(83)	26(5)	50(6)	41(6)	−1(5)	9(4)	7(5)
C(84)	48(7)	70(7)	33(6)	−5(5)	11(5)	−14(5)
C(85)	76(10)	240(20)	55(9)	32(10)	6(8)	−52(11)
C(86)	62(8)	106(10)	62(8)	3(7)	13(6)	−21(7)
O(7)	59(5)	130(7)	66(6)	−14(5)	22(5)	−26(5)
C(88)	94(12)	270(20)	48(9)	−9(10)	18(8)	−99(13)
C(89)	62(9)	163(14)	55(9)	−17(8)	18(7)	−24(9)
C(90)	43(7)	117(10)	68(9)	23(7)	16(6)	6(7)
C(91)	49(7)	82(8)	52(7)	11(6)	0(6)	0(6)
O(8)	125(9)	112(8)	120(9)	−11(7)	52(8)	5(7)
C(92)	85(10)	125(12)	66(9)	−15(9)	24(7)	−13(9)
C(93)	79(11)	170(17)	120(13)	−32(13)	49(10)	−27(11)
C(94)	89(12)	210(20)	111(14)	−74(14)	40(11)	−25(14)
C(95)	112(14)	190(20)	92(12)	−36(13)	−7(11)	−4(14)

Compound 12

Table 1. Crystal data and structure refinement for sh2389.

Identification code	sh2389	
Empirical formula	C64 H60 K4 O7 S12	
Formula weight	1482.24	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 14.2460(7) Å	α = 90°.
	b = 16.7427(9) Å	β = 90°.
	c = 27.7073(13) Å	γ = 90°.
Volume	6608.6(6) Å^3	
Z	4	
Density (calculated)	1.490 Mg/m^3	
Absorption coefficient	0.701 mm^{-1}	
F(000)	3072	
Crystal size	0.55 x 0.3 x 0.25 mm^3	
Theta range for data collection	1.47 to 29.40°.	
Index ranges	−16<=h<=19, −23<=k<=18, −36<=l<=38	
Reflections collected	46554	
Independent reflections	9114 [R(int) = 0.0290]	
Completeness to theta = 29.40°	99.9 %	
Absorption correction	None	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	9114 / 0 / 460	
Goodness−of−fit on F^2	2.785	
Final R indices [I>2sigma(I)]	R1 = 0.0951, wR2 = 0.2853	
R indices (all data)	R1 = 0.1251, wR2 = 0.3074	
Largest diff. peak and hole	2.130 and −1.303 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2389. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
K(1)	6185(1)	2370(1)	2908(1)	20(1)
K(2)	7752(1)	1369(1)	3813(1)	26(1)
S(1A)	4714(2)	3541(2)	3718(1)	47(1)
S(2A)	6449(2)	2401(2)	4903(1)	53(1)
S(1B)	4625(9)	3267(6)	3531(7)	83(5)
S(2B)	5840(3)	3138(2)	4944(2)	48(1)
S(3)	5541(1)	674(1)	3638(1)	40(1)
S(4)	8725(1)	2010(1)	1797(1)	37(1)
S(5)	5939(1)	783(1)	2276(1)	25(1)
S(6)	7685(1)	−316(1)	3121(1)	28(1)
O(1)	6236(2)	2285(2)	3858(1)	28(1)
O(2)	7606(2)	1337(2)	2829(1)	18(1)
C(1)	5430(4)	2124(3)	4103(2)	36(1)

C(2)	4630(5)	2610(4)	3881(5)	98(4)
C(3A)	3863(8)	2283(7)	3567(4)	79(3)
C(4A)	3331(10)	2955(10)	3363(7)	138(7)
C(5A)	3659(7)	3673(5)	3416(4)	64(3)
C(3B)	3781(13)	2640(20)	4289(7)	43(9)
C(4B)	3163(15)	3200(20)	4089(10)	40(8)
C(5B)	3596(16)	3621(12)	3802(8)	18(4)
C(6)	5525(8)	2348(5)	4626(3)	89(4)
C(7A)	4655(8)	2563(7)	4897(4)	52(3)
C(8A)	4913(14)	2649(8)	5386(4)	84(5)
C(9)	6099(11)	2689(6)	5449(3)	129(6)
C(7B)	6200(30)	1651(11)	5014(6)	121(14)
C(8B)	6400(30)	2028(12)	5436(6)	133(15)
C(10)	5195(4)	1220(3)	4096(2)	40(1)
C(11)	4606(3)	733(2)	4427(1)	17(1)
C(12)	4635(6)	−83(4)	4246(3)	61(2)
C(13)	5043(6)	−156(4)	3817(2)	57(2)
C(14)	7867(3)	885(2)	2434(2)	18(1)
C(15)	8749(3)	1242(2)	2203(2)	19(1)
C(16)	9767(2)	1043(2)	2388(1)	7(1)
C(17)	10332(3)	1686(3)	2134(2)	33(1)
C(18)	9877(4)	2186(3)	1835(2)	35(1)
C(19)	7061(3)	844(2)	2058(2)	18(1)
C(20)	7081(3)	789(3)	1545(2)	25(1)
C(21)	6131(4)	689(4)	1371(2)	37(1)
C(22)	5465(3)	675(3)	1714(2)	30(1)
C(23)	8074(3)	11(2)	2568(2)	20(1)
C(24)	8460(3)	−602(3)	2307(2)	28(1)
C(25)	8051(4)	−1279(3)	3002(2)	34(1)
C(26)	8445(4)	−1337(3)	2564(2)	34(1)
O(3)	7877(3)	114(3)	4414(2)	47(1)
C(27)	7277(6)	−28(8)	4777(4)	107(4)
C(28)	7795(9)	−110(20)	5197(5)	312(19)
C(29)	8733(8)	−236(13)	5078(4)	155(7)
C(30)	8793(7)	−146(9)	4512(4)	117(5)
C(31)	2642(16)	2328(13)	1068(5)	57(5)
C(32)	2541(16)	2044(11)	762(9)	83(5)
C(33)	1864(16)	1670(15)	997(9)	111(8)

Table 3. Bond lengths [Å] and angles [°] for sh2389.

K(1)−O(1)	2.636(3)	C(2)−C(3A)	1.500(14)
K(1)−O(2)	2.671(3)	C(2)−C(3B)	1.66(2)
K(1)−O(2)#1	2.775(3)	C(3A)−C(4A)	1.470(16)
K(1)−C(15)#1	3.038(4)	C(4A)−C(5A)	1.298(19)
K(1)−S(1B)	3.190(9)	C(3B)−C(4B)	1.39(4)
K(1)−S(5)	3.2016(14)	C(4B)−C(5B)	1.23(4)
K(1)−S(4)#1	3.2521(17)	C(6)−C(7A)	1.494(13)
K(1)−C(16)#1	3.314(3)	C(6)−C(7B)	1.86(3)
K(1)−C(18)#1	3.418(5)	C(7A)−C(8A)	1.409(16)
K(1)−C(17)#1	3.432(5)	C(8A)−C(9)	1.70(2)
K(1)−C(14)#1	3.478(4)	C(9)−C(8B)	1.19(3)
K(1)−C(1)	3.505(6)	C(7B)−C(8B)	1.36(3)
K(2)−O(1)	2.652(4)	C(10)−C(11)	1.488(6)
K(2)−O(1)#1	2.679(4)	C(11)−C(12)	1.457(8)
K(2)−O(3)	2.687(4)	C(12)−C(13)	1.327(10)
K(2)−O(2)	2.736(3)	C(14)−C(15)	1.531(6)
K(2)−S(3)	3.3932(19)	C(14)−C(23)	1.538(6)
K(2)−S(6)	3.4120(16)	C(14)−C(19)	1.550(6)
K(2)−C(30)	3.519(10)	C(14)−K(1)#1	3.478(4)
K(2)−K(1)#1	3.6114(13)	C(15)−C(16)	1.573(5)
K(2)−S(1A)#1	3.622(3)	C(15)−K(1)#1	3.038(4)
K(2)−K(2)#1	3.855(2)	C(16)−C(17)	1.519(6)
S(1A)−C(2)	1.626(8)	C(16)−K(1)#1	3.314(3)
S(1A)−C(5A)	1.735(10)	C(17)−C(18)	1.344(8)
S(1A)−K(2)#1	3.622(3)	C(17)−K(1)#1	3.432(5)
S(2A)−C(6)	1.526(11)	C(18)−K(1)#1	3.418(5)
S(2A)−C(9)	1.665(8)	C(19)−C(20)	1.426(6)
S(1B)−C(2)	1.465(18)	C(20)−C(21)	1.447(7)
S(1B)−C(5B)	1.75(3)	C(21)−C(22)	1.343(7)
S(2B)−C(9)	1.630(9)	C(23)−C(24)	1.372(6)
S(2B)−C(6)	1.652(7)	C(24)−C(26)	1.423(7)
S(3)−C(13)	1.638(7)	C(25)−C(26)	1.341(8)
S(3)−C(10)	1.641(5)	O(3)−C(27)	1.341(9)

S(4)−C(18)	1.670(6)	O(3)−C(30)	1.403(10)
S(4)−C(15)	1.709(4)	C(27)−C(28)	1.386(16)
S(4)−K(1)#1	3.2519(17)	C(28)−C(29)	1.392(17)
S(5)−C(22)	1.705(5)	C(29)−C(30)	1.577(14)
S(5)−C(19)	1.712(4)	C(31)−C(31)#2	0.70(3)
S(6)−C(23)	1.720(4)	C(31)−C(32)	0.98(2)
S(6)−C(25)	1.727(5)	C(31)−C(32)#2	1.38(3)
O(1)−C(1)	1.361(6)	C(31)−C(33)	1.58(4)
O(1)−K(2)#1	2.679(4)	C(31)−C(33)#2	1.83(3)
O(2)−C(14)	1.383(5)	C(32)−C(33)	1.32(3)
O(2)−K(1)#1	2.775(3)	C(32)−C(31)#2	1.38(3)
C(1)−C(6)	1.502(9)	C(32)−C(32)#2	1.53(4)
C(1)−C(2)	1.530(10)	C(33)−C(31)#2	1.83(3)
C(1)−C(10)	1.550(7)		

O(1)−K(1)−O(2)	91.51(10)	C(15)−S(4)−K(1)#1	67.43(15)
O(1)−K(1)−O(2)#1	95.96(10)	C(22)−S(5)−C(19)	93.1(2)
O(2)−K(1)−O(2)#1	91.59(9)	C(22)−S(5)−K(1)	129.11(18)
O(1)−K(1)−C(15)#1	133.01(11)	C(19)−S(5)−K(1)	92.34(15)
O(2)−K(1)−C(15)#1	114.75(10)	C(23)−S(6)−C(25)	91.7(2)
O(2)#1−K(1)−C(15)#1	48.15(10)	C(23)−S(6)−K(2)	103.25(15)
O(1)−K(1)−S(1B)	60.3(4)	C(25)−S(6)−K(2)	150.52(19)
O(2)−K(1)−S(1B)	151.3(3)	C(1)−O(1)−K(1)	119.1(3)
O(2)#1−K(1)−S(1B)	96.2(2)	C(1)−O(1)−K(2)	126.6(3)
C(15)#1−K(1)−S(1B)	90.5(3)	K(1)−O(1)−K(2)	90.41(10)
O(1)−K(1)−S(5)	120.32(8)	C(1)−O(1)−K(2)#1	130.0(3)
O(2)−K(1)−S(5)	60.09(7)	K(1)−O(1)−K(2)#1	85.61(10)
O(2)#1−K(1)−S(5)	132.21(7)	K(2)−O(1)−K(2)#1	92.64(11)
C(15)#1−K(1)−S(5)	106.63(9)	C(14)−O(2)−K(1)	128.5(2)
S(1B)−K(1)−S(5)	127.7(3)	K(1)−O(2)−K(2)	87.90(9)
O(1)−K(1)−S(4)#1	163.97(8)	C(14)−O(2)−K(1)#1	108.9(2)
O(2)−K(1)−S(4)#1	95.68(7)	K(1)−O(2)−K(1)#1	87.67(9)
O(2)#1−K(1)−S(4)#1	69.59(7)	K(2)−O(2)−K(1)#1	81.89(8)
C(15)#1−K(1)−S(4)#1	31.30(8)	O(1)−C(1)−C(6)	110.9(5)
S(1B)−K(1)−S(4)#1	112.9(3)	O(1)−C(1)−C(2)	108.8(5)
S(5)−K(1)−S(4)#1	75.58(4)	C(6)−C(1)−C(2)	108.9(7)
O(1)−K(1)−C(16)#1	119.24(10)	O(1)−C(1)−C(10)	111.6(4)
O(2)−K(1)−C(16)#1	142.51(9)	C(6)−C(1)−C(10)	106.0(5)
O(2)#1−K(1)−C(16)#1	66.02(8)	C(2)−C(1)−C(10)	110.7(5)
C(15)#1−K(1)−C(16)#1	28.26(9)	O(1)−C(1)−K(1)	41.1(2)
S(1B)−K(1)−C(16)#1	64.7(3)	C(6)−C(1)−K(1)	148.6(4)
S(5)−K(1)−C(16)#1	112.50(7)	C(2)−C(1)−K(1)	77.6(5)
S(4)#1−K(1)−C(16)#1	49.32(7)	C(10)−C(1)−K(1)	99.7(3)
O(1)−K(1)−C(18)#1	153.16(13)	C(3A)−C(2)−S(1B)	83.6(10)
O(2)−K(1)−C(18)#1	113.88(12)	C(3A)−C(2)−C(1)	125.6(7)
O(2)#1−K(1)−C(18)#1	92.05(11)	S(1B)−C(2)−C(1)	132.0(7)
C(15)#1−K(1)−C(18)#1	44.58(11)	C(3A)−C(2)−S(1A)	104.1(8)
S(1B)−K(1)−C(18)#1	93.5(4)	S(1B)−C(2)−S(1A)	25.6(6)
S(5)−K(1)−C(18)#1	69.87(9)	C(1)−C(2)−S(1A)	124.5(5)
S(4)#1−K(1)−C(18)#1	28.87(10)	C(3A)−C(2)−C(3B)	82.8(10)
C(16)#1−K(1)−C(18)#1	42.78(11)	S(1B)−C(2)−C(3B)	115.0(13)
O(1)−K(1)−C(17)#1	131.79(12)	C(1)−C(2)−C(3B)	106.6(12)
O(2)−K(1)−C(17)#1	136.39(12)	S(1A)−C(2)−C(3B)	102.2(14)
O(2)#1−K(1)−C(17)#1	88.97(10)	C(3A)−C(2)−K(1)	88.5(7)
C(15)#1−K(1)−C(17)#1	42.69(11)	S(1B)−C(2)−K(1)	65.3(5)
S(1B)−K(1)−C(17)#1	71.5(4)	C(1)−C(2)−K(1)	77.2(4)
S(5)−K(1)−C(17)#1	88.32(10)	S(1A)−C(2)−K(1)	81.4(4)
S(4)#1−K(1)−C(17)#1	44.41(9)	C(3B)−C(2)−K(1)	171.2(10)
C(16)#1−K(1)−C(17)#1	25.96(10)	C(4A)−C(3A)−C(2)	108.6(11)
C(18)#1−K(1)−C(17)#1	22.63(13)	C(5A)−C(4A)−C(3A)	118.7(13)
O(1)−K(1)−C(14)#1	114.34(10)	C(4A)−C(5A)−S(1A)	104.3(8)
O(2)−K(1)−C(14)#1	102.60(9)	C(4B)−C(3B)−C(2)	102(2)
O(2)#1−K(1)−C(14)#1	22.10(9)	C(5B)−C(4B)−C(3B)	109(2)
C(15)#1−K(1)−C(14)#1	26.07(10)	C(4B)−C(5B)−S(1B)	120.1(19)
S(1B)−K(1)−C(14)#1	94.6(2)	C(7A)−C(6)−C(1)	118.1(9)
S(5)−K(1)−C(14)#1	122.17(8)	C(7A)−C(6)−S(2A)	116.7(6)
S(4)#1−K(1)−C(14)#1	50.06(7)	C(1)−C(6)−S(2A)	125.2(6)
C(16)#1−K(1)−C(14)#1	47.18(8)	C(7A)−C(6)−S(2B)	76.3(6)
C(18)#1−K(1)−C(14)#1	70.11(11)	C(1)−C(6)−S(2B)	137.6(6)
C(17)#1−K(1)−C(14)#1	67.73(11)	S(2A)−C(6)−S(2B)	56.7(3)
O(1)−K(1)−C(1)	19.84(12)	C(7A)−C(6)−C(7B)	107.0(10)
O(2)−K(1)−C(1)	103.55(12)	C(1)−C(6)−C(7B)	116.7(8)
O(2)#1−K(1)−C(1)	110.89(11)	S(2A)−C(6)−C(7B)	45.3(9)

C(15)#1−K(1)−C(1)	134.95(12)
S(1B)−K(1)−C(1)	48.0(3)
S(5)−K(1)−C(1)	112.73(9)
S(4)#1−K(1)−C(1)	160.70(10)
C(16)#1−K(1)−C(1)	112.28(11)
C(18)#1−K(1)−C(1)	135.36(14)
C(17)#1−K(1)−C(1)	116.84(13)
C(14)#1−K(1)−C(1)	125.10(11)
O(1)−K(2)−O(1)#1	87.12(11)
O(1)−K(2)−O(3)	118.49(13)
O(1)#1−K(2)−O(3)	126.47(12)
O(1)−K(2)−O(2)	89.74(10)
O(1)#1−K(2)−O(2)	95.92(10)
O(3)−K(2)−O(2)	127.40(12)
O(1)−K(2)−S(3)	56.55(8)
O(1)#1−K(2)−S(3)	142.64(8)
O(3)−K(2)−S(3)	83.21(10)
O(2)−K(2)−S(3)	77.27(7)
O(1)−K(2)−S(6)	118.75(8)
O(1)#1−K(2)−S(6)	137.45(8)
O(3)−K(2)−S(6)	72.75(10)
O(2)−K(2)−S(6)	54.65(7)
S(3)−K(2)−S(6)	67.01(4)
O(1)−K(2)−C(30)	137.25(18)
O(1)#1−K(2)−C(30)	110.8(2)
O(3)−K(2)−C(30)	21.17(19)
O(2)−K(2)−C(30)	124.5(2)
S(3)−K(2)−C(30)	102.9(2)
S(6)−K(2)−C(30)	74.1(2)
O(1)−K(2)−K(1)#1	92.05(8)
O(1)#1−K(2)−K(1)#1	46.70(7)
O(3)−K(2)−K(1)#1	149.32(11)
O(2)−K(2)−K(1)#1	49.53(6)
S(3)−K(2)−K(1)#1	119.35(4)
S(6)−K(2)−K(1)#1	96.02(3)
C(30)−K(2)−K(1)#1	128.84(16)
O(1)−K(2)−S(1A)#1	142.27(9)
O(1)#1−K(2)−S(1A)#1	55.38(9)
O(3)−K(2)−S(1A)#1	90.71(11)
O(2)−K(2)−S(1A)#1	90.23(7)
S(3)−K(2)−S(1A)#1	158.26(6)
S(6)−K(2)−S(1A)#1	91.25(5)
C(30)−K(2)−S(1A)#1	69.54(18)
K(1)#1−K(2)−S(1A)#1	60.47(5)
O(1)−K(2)−K(1)	44.62(7)
O(1)#1−K(2)−K(1)	88.58(7)
O(3)−K(2)−K(1)	143.36(10)
O(2)−K(2)−K(1)	45.34(6)
S(3)−K(2)−K(1)	60.32(3)
S(6)−K(2)−K(1)	88.65(3)
C(30)−K(2)−K(1)	160.1(2)
K(1)#1−K(2)−K(1)	61.60(3)
S(1A)#1−K(2)−K(1)	121.71(5)
O(1)−K(2)−K(2)#1	43.95(8)
O(1)#1−K(2)−K(2)#1	43.41(8)
O(3)−K(2)−K(2)#1	141.34(10)
O(2)−K(2)−K(2)#1	90.27(6)
S(3)−K(2)−K(2)#1	99.43(5)
S(6)−K(2)−K(2)#1	143.78(3)
C(30)−K(2)−K(2)#1	141.9(2)
K(1)#1−K(2)−K(2)#1	60.24(2)
S(1A)#1−K(2)−K(2)#1	98.32(6)
K(1)−K(2)−K(2)#1	56.66(2)
C(2)−S(1A)−C(5A)	101.1(5)
C(2)−S(1A)−K(2)#1	95.3(3)
C(5A)−S(1A)−K(2)#1	153.3(4)
C(2)−S(1A)−K(1)	72.4(4)
C(5A)−S(1A)−K(1)	105.7(4)
K(2)#1−S(1A)−K(1)	59.62(5)
C(6)−S(2A)−C(9)	102.4(6)
C(2)−S(1B)−C(5B)	88.6(10)
C(2)−S(1B)−K(1)	90.0(5)
C(5B)−S(1B)−K(1)	167.1(11)
S(2B)−C(6)−C(7B)	93.0(8)
C(8A)−C(7A)−C(6)	106.9(11)
C(7A)−C(8A)−C(9)	111.3(11)
C(8B)−C(9)−S(2B)	119.0(10)
C(8B)−C(9)−S(2A)	66.1(8)
S(2B)−C(9)−S(2A)	54.7(3)
C(8B)−C(9)−C(8A)	108(2)
S(2B)−C(9)−C(8A)	72.9(7)
S(2A)−C(9)−C(8A)	101.1(8)
C(8B)−C(7B)−C(6)	108.2(17)
C(9)−C(8B)−C(7B)	113(2)
C(11)−C(10)−C(1)	130.4(4)
C(11)−C(10)−S(3)	110.0(4)
C(1)−C(10)−S(3)	119.3(4)
C(12)−C(11)−C(10)	106.5(4)
C(13)−C(12)−C(11)	114.1(6)
C(12)−C(13)−S(3)	112.6(5)
O(2)−C(14)−C(15)	109.7(3)
O(2)−C(14)−C(23)	112.4(3)
C(15)−C(14)−C(23)	108.3(3)
O(2)−C(14)−C(19)	110.9(3)
C(15)−C(14)−C(19)	110.2(3)
C(23)−C(14)−C(19)	105.2(3)
O(2)−C(14)−K(1)#1	49.04(18)
C(15)−C(14)−K(1)#1	60.7(2)
C(23)−C(14)−K(1)#1	129.3(3)
C(19)−C(14)−K(1)#1	125.3(3)
C(14)−C(15)−C(16)	122.5(3)
C(14)−C(15)−S(4)	123.5(3)
C(16)−C(15)−S(4)	113.1(3)
C(14)−C(15)−K(1)#1	93.2(2)
C(16)−C(15)−K(1)#1	85.6(2)
S(4)−C(15)−K(1)#1	81.28(15)
C(17)−C(16)−C(15)	100.8(3)
C(17)−C(16)−K(1)#1	81.4(2)
C(15)−C(16)−K(1)#1	66.09(18)
C(18)−C(17)−C(16)	118.1(4)
C(18)−C(17)−K(1)#1	78.1(3)
C(16)−C(17)−K(1)#1	72.7(2)
C(17)−C(18)−S(4)	113.8(4)
C(17)−C(18)−K(1)#1	79.3(3)
S(4)−C(18)−K(1)#1	70.04(17)
C(20)−C(19)−C(14)	131.1(4)
C(20)−C(19)−S(5)	111.4(3)
C(14)−C(19)−S(5)	117.3(3)
C(19)−C(20)−C(21)	108.8(4)
C(22)−C(21)−C(20)	115.3(4)
C(21)−C(22)−S(5)	111.4(4)
C(24)−C(23)−C(14)	131.4(4)
C(24)−C(23)−S(6)	111.2(3)
C(14)−C(23)−S(6)	117.1(3)
C(23)−C(24)−C(26)	112.1(5)
C(26)−C(25)−S(6)	111.6(4)
C(25)−C(26)−C(24)	113.4(5)
C(27)−O(3)−C(30)	113.1(6)
C(27)−O(3)−K(2)	124.1(5)
C(30)−O(3)−K(2)	115.1(5)
O(3)−C(27)−C(28)	108.1(9)
C(27)−C(28)−C(29)	109.1(11)
C(28)−C(29)−C(30)	105.9(10)
O(3)−C(30)−C(29)	99.9(8)
O(3)−C(30)−K(2)	43.7(4)
C(29)−C(30)−K(2)	126.4(9)
C(31)#2−C(31)−C(32)	108(3)
C(31)#2−C(31)−C(32)#2	42.8(19)
C(32)−C(31)−C(32)#2	79(2)
C(31)#2−C(31)−C(33)	100(5)
C(32)−C(31)−C(33)	57(2)
C(32)#2−C(31)−C(33)	108.9(18)
C(31)#2−C(31)−C(33)#2	58(4)
C(32)−C(31)−C(33)#2	114(2)
C(32)#2−C(31)−C(33)#2	46.1(14)
C(33)−C(31)−C(33)#2	154.0(14)

C(9)−S(2B)−C(6)	98.6(6)	C(31)−C(32)−C(33)	85(3)
C(13)−S(3)−C(10)	96.1(3)	C(31)−C(32)−C(31)#2	29.1(14)
C(13)−S(3)−K(2)	130.5(3)	C(33)−C(32)−C(31)#2	85(2)
C(10)−S(3)−K(2)	88.7(2)	C(31)−C(32)−C(32)#2	61.9(15)
C(13)−S(3)−K(1)	161.7(2)	C(33)−C(32)−C(32)#2	115(2)
C(10)−S(3)−K(1)	94.1(2)	C(31)#2−C(32)−C(32)#2	39.1(11)
K(2)−S(3)−K(1)	64.79(3)	C(32)−C(33)−C(31)	38.4(12)
C(18)−S(4)−C(15)	94.1(3)	C(32)−C(33)−C(31)#2	48.5(12)
C(14)−O(2)−K(2)	141.3(2)	C(31)−C(33)−C(31)#2	22.2(11)

Symmetry transformations used to generate equivalent atoms:
#1 −x+3/2,−y+1/2,z #2 −x+1/2,−y+1/2,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2389. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K(1)	18(1)	19(1)	21(1)	1(1)	0(1)	1(1)
K(2)	29(1)	21(1)	26(1)	4(1)	−5(1)	−2(1)
S(1A)	47(1)	55(2)	39(1)	5(1)	−1(1)	−2(1)
S(2A)	83(2)	42(1)	35(1)	−11(1)	−19(1)	8(1)
S(1B)	55(7)	24(5)	170(14)	−21(6)	78(8)	2(4)
S(2B)	53(2)	33(2)	57(2)	−20(2)	−4(2)	−1(2)
S(3)	42(1)	35(1)	44(1)	−8(1)	1(1)	−2(1)
S(4)	37(1)	32(1)	42(1)	−2(1)	8(1)	−2(1)
S(5)	20(1)	23(1)	31(1)	−4(1)	1(1)	−2(1)
S(6)	29(1)	21(1)	33(1)	10(1)	0(1)	2(1)
O(1)	36(2)	24(2)	25(2)	−3(1)	7(1)	2(2)
O(2)	18(1)	16(1)	19(1)	0(1)	4(1)	3(1)
C(1)	36(3)	26(2)	47(3)	−11(2)	12(2)	−5(2)
C(2)	26(3)	32(4)	236(13)	18(5)	7(5)	−6(3)
C(3A)	73(7)	64(7)	100(8)	9(6)	−22(6)	2(6)
C(4A)	80(9)	132(15)	201(18)	49(13)	−26(10)	60(10)
C(5A)	59(6)	35(5)	99(8)	17(5)	−7(5)	5(4)
C(3B)	0(8)	130(30)	1(8)	−7(12)	4(6)	2(12)
C(4B)	0(8)	90(20)	34(13)	−31(15)	−11(9)	17(11)
C(5B)	26(11)	4(8)	24(11)	3(8)	−11(9)	−1(8)
C(6)	159(9)	57(4)	50(4)	−38(3)	63(5)	−62(5)
C(7A)	65(7)	60(7)	32(5)	−8(4)	16(5)	23(6)
C(8A)	157(15)	69(9)	28(5)	−3(5)	10(7)	58(10)
C(9)	281(18)	83(7)	24(3)	−1(4)	10(6)	93(9)
C(7B)	310(40)	26(8)	28(8)	8(6)	45(14)	1(15)
C(8B)	340(50)	39(10)	18(7)	−4(7)	48(15)	−14(18)
C(10)	45(3)	29(3)	45(3)	−11(2)	14(2)	−11(2)
C(11)	25(2)	8(2)	17(2)	−6(1)	18(2)	−7(2)
C(12)	68(5)	36(3)	79(5)	−2(3)	15(4)	−21(3)
C(13)	80(5)	33(3)	56(4)	−20(3)	−20(4)	−2(3)
C(14)	15(2)	17(2)	22(2)	0(2)	2(2)	1(2)
C(15)	16(2)	14(2)	26(2)	−2(2)	5(2)	0(2)
C(16)	4(1)	2(1)	14(2)	−8(1)	5(1)	−9(1)
C(17)	18(2)	25(2)	57(3)	−14(2)	4(2)	−1(2)
C(18)	39(3)	22(2)	42(3)	−8(2)	19(2)	−8(2)
C(19)	17(2)	14(2)	24(2)	0(2)	1(2)	1(2)
C(20)	16(2)	33(2)	25(2)	−8(2)	0(2)	−2(2)
C(21)	37(3)	46(3)	26(2)	1(2)	−4(2)	−3(2)
C(22)	22(2)	29(3)	40(3)	−5(2)	−9(2)	4(2)
C(23)	17(2)	15(2)	28(2)	2(2)	−4(2)	1(2)
C(24)	25(2)	20(2)	38(3)	−2(2)	3(2)	3(2)
C(25)	32(3)	16(2)	54(3)	12(2)	−10(2)	2(2)
C(26)	26(2)	18(2)	60(3)	0(2)	−9(2)	5(2)
O(3)	50(2)	46(2)	45(2)	19(2)	−10(2)	−7(2)
C(27)	68(6)	154(10)	98(7)	87(7)	31(5)	36(6)
C(28)	85(9)	800(60)	53(7)	40(17)	2(6)	−80(20)
C(29)	99(9)	310(20)	59(6)	16(9)	3(6)	−3(12)
C(30)	71(6)	190(13)	89(7)	82(8)	4(5)	28(7)
C(31)	52(13)	72(19)	47(7)	13(8)	6(7)	3(9)
C(32)	88(14)	58(11)	102(16)	7(11)	8(13)	17(10)
C(33)	85(14)	113(18)	140(20)	46(16)	−49(14)	−15(13)

Compound <u>13</u>

Table 1. Crystal data and structure refinement for sh2386.

Identification code	sh2386	
Empirical formula	C60 H52 Na4 O6 S12	
Formula weight	1345.70	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.1895(13) Å	α = 90°.
	b = 13.3431(6) Å	β = 119.965(5)°.
	c = 22.9756(11) Å	γ = 90°.
Volume	6158.8(5) Å^3	
Z	4	
Density (calculated)	1.451 Mg/m^3	
Absorption coefficient	0.504 mm^{-1}	
F(000)	2784	
Crystal size	0.4 x 0.28 x 0.22 mm^3	
Theta range for data collection	1.83 to 34.67°.	
Index ranges	−36<=h<=36, −21<=k<=21, −36<=l<=36	
Reflections collected	105170	
Independent reflections	12917 [R(int) = 0.0356]	
Completeness to theta = 34.67°	97.5 %	
Absorption correction	Multiscan	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	12917 / 0 / 360	
Goodness−of−fit on F^2	2.755	
Final R indices [I>2sigma(I)]	R1 = 0.1052, wR2 = 0.2969	
R indices (all data)	R1 = 0.1603, wR2 = 0.3197	
Largest diff. peak and hole	4.195 and −2.547 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2386. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Na(1)	9347(1)	7997(1)	6825(1)	19(1)
Na(2)	10350(1)	9728(1)	7037(1)	18(1)
S(1)	10840(1)	8701(1)	6107(1)	35(1)
S(2)	11766(1)	6780(1)	8166(1)	44(1)
S(3)	9506(1)	6081(1)	6350(1)	46(1)
S(4)	9141(1)	11947(1)	6760(1)	40(1)
S(5)	7359(1)	10473(1)	6005(1)	45(1)
S(6A)	9109(1)	9224(2)	5463(1)	47(1)
S(6B)	8020(2)	8465(3)	5395(2)	33(1)
S(6C)	7934(6)	8839(10)	5220(6)	35(2)
O(1)	10442(1)	7869(2)	7093(1)	18(1)
O(2)	9282(1)	9733(2)	6843(1)	17(1)
C(1)	10692(2)	7149(2)	6845(2)	21(1)
C(2)	11127(2)	7636(2)	6593(2)	24(1)
C(3)	11734(2)	7381(3)	6678(2)	35(1)
C(4)	11957(2)	8030(4)	6340(2)	44(1)
C(5)	11533(3)	8778(3)	6019(2)	44(1)
C(6)	11134(2)	6394(3)	7395(2)	30(1)
C(7)	11089(2)	5318(2)	7384(2)	32(1)
C(8)	11609(3)	4931(4)	8021(4)	63(2)
C(9)	11979(3)	5590(5)	8466(3)	59(2)
C(10)	10145(2)	6560(2)	6271(2)	28(1)
C(11)	10084(2)	6333(2)	5602(2)	25(1)
C(12)	9463(3)	5724(4)	5257(3)	62(2)
C(13)	9125(3)	5571(4)	5593(3)	60(2)
C(14)	8686(2)	10025(2)	6295(2)	18(1)
C(15)	8700(2)	11129(2)	6130(2)	23(1)
C(16)	8342(2)	11659(3)	5499(2)	30(1)
C(17)	8486(3)	12659(4)	5574(3)	56(1)
C(18)	8886(3)	12948(3)	6218(3)	57(1)
C(19)	8115(2)	9880(2)	6441(2)	21(1)
C(20)	8136(2)	9344(3)	6960(2)	26(1)
C(21)	7523(2)	9352(3)	6960(2)	34(1)

C(22)	7060(2)	9927(3)	6475(2)	41(1)
C(23A)	8531(2)	9351(3)	5692(2)	19(1)
C(24A)	8254(4)	8446(5)	5387(3)	32(1)
C(25A)	8227(6)	7975(8)	4909(6)	69(3)
C(26A)	8744(5)	8331(6)	4917(4)	33(2)
C(23B)	8673(7)	9568(10)	5651(7)	19(2)
C(26B)	8499(10)	8193(11)	4834(8)	27(3)
C(25B)	8859(8)	8740(13)	4917(8)	32(3)
O(3)	10648(1)	11066(2)	6593(2)	34(1)
C(27)	11322(2)	11401(3)	6877(2)	43(1)
C(28)	11295(3)	12513(4)	6738(3)	60(2)
C(29)	10587(3)	12719(4)	6318(4)	86(2)
C(30)	10244(3)	11718(4)	6058(3)	55(1)

Table 3. Bond lengths [Å] and angles [°] for sh2386.

Na(1)−O(1)#1	2.287(2)	S(6C)−C(26B)	2.10(2)
Na(1)−O(1)	2.302(2)	O(1)−C(1)	1.383(3)
Na(1)−O(2)	2.323(2)	O(1)−Na(1)#1	2.287(2)
Na(1)−S(3)	2.8750(16)	O(2)−C(14)	1.382(3)
Na(1)−C(23A)	2.950(5)	O(2)−Na(2)#1	2.271(2)
Na(1)−C(24A)	3.056(7)	C(1)−C(10)	1.514(5)
Na(1)−C(14)	3.048(3)	C(1)−C(6)	1.538(5)
Na(1)−S(2)#1	3.0564(16)	C(1)−C(2)	1.536(4)
Na(1)−Na(1)#1	3.068(2)	C(2)−C(3)	1.363(5)
Na(1)−Na(2)	3.1395(17)	C(3)−C(4)	1.422(6)
Na(1)−S(6B)	3.249(4)	C(4)−C(5)	1.337(7)
Na(1)−Na(2)#1	3.2902(17)	C(6)−C(7)	1.440(5)
Na(2)−O(2)#1	2.271(2)	C(7)−C(8)	1.449(7)
Na(2)−O(2)	2.286(2)	C(8)−C(9)	1.295(9)
Na(2)−O(3)	2.325(3)	C(10)−C(11)	1.503(5)
Na(2)−O(1)	2.488(2)	C(11)−C(12)	1.491(6)
Na(2)−S(1)	3.1882(15)	C(12)−C(13)	1.363(8)
Na(2)−Na(2)#1	3.256(2)	C(14)−C(15)	1.525(4)
Na(2)−Na(1)#1	3.2902(17)	C(14)−C(19)	1.533(4)
Na(2)−S(6A)	3.379(2)	C(14)−C(23A)	1.536(5)
S(1)−C(5)	1.721(4)	C(14)−C(23B)	1.585(13)
S(1)−C(2)	1.723(4)	C(15)−C(16)	1.444(4)
S(2)−C(9)	1.702(5)	C(16)−C(17)	1.365(7)
S(2)−C(6)	1.720(5)	C(17)−C(18)	1.351(9)
S(2)−Na(1)#1	3.0564(16)	C(19)−C(20)	1.371(4)
S(3)−C(13)	1.653(6)	C(20)−C(21)	1.421(5)
S(3)−C(10)	1.706(4)	C(21)−C(22)	1.338(6)
S(4)−C(15)	1.690(4)	C(23A)−C(24A)	1.382(8)
S(4)−C(18)	1.717(5)	C(24A)−C(25A)	1.238(12)
S(5)−C(22)	1.712(4)	C(24A)−C(26A)	1.927(11)
S(5)−C(19)	1.716(3)	C(25A)−C(26A)	1.283(13)
S(6A)−C(26A)	1.628(9)	C(26B)−C(25B)	1.05(2)
S(6A)−C(23A)	1.675(5)	O(3)−C(30)	1.412(6)
S(6A)−C(24A)	2.166(8)	O(3)−C(27)	1.432(5)
S(6B)−S(6C)	0.609(12)	C(27)−C(28)	1.512(6)
S(6B)−C(23B)	1.979(15)	C(28)−C(29)	1.456(9)
S(6B)−C(26B)	2.111(18)	C(29)−C(30)	1.517(8)
S(6C)−C(23B)	1.780(19)		

O(1)#1−Na(1)−O(1)	95.45(8)	C(26A)−S(6A)−C(24A)	59.0(4)
O(1)#1−Na(1)−O(2)	92.10(8)	C(23A)−S(6A)−C(24A)	39.6(2)
O(1)−Na(1)−O(2)	98.13(8)	C(26A)−S(6A)−Na(1)	98.3(3)
O(1)#1−Na(1)−S(3)	110.35(7)	C(23A)−S(6A)−Na(1)	62.40(17)
O(1)−Na(1)−S(3)	72.63(6)	C(24A)−S(6A)−Na(1)	63.57(19)
O(2)−Na(1)−S(3)	156.17(8)	C(26A)−S(6A)−Na(2)	143.9(3)
O(1)#1−Na(1)−C(23A)	134.44(11)	C(23A)−S(6A)−Na(2)	91.79(17)
O(1)−Na(1)−C(23A)	114.65(12)	C(24A)−S(6A)−Na(2)	116.0(2)
O(2)−Na(1)−C(23A)	52.13(10)	Na(1)−S(6A)−Na(2)	55.84(4)
S(3)−Na(1)−C(23A)	110.89(10)	S(6C)−S(6B)−C(23B)	62.3(13)
O(1)#1−Na(1)−C(24A)	143.32(16)	S(6C)−S(6B)−C(26B)	80.5(13)
O(1)−Na(1)−C(24A)	120.79(16)	C(23B)−S(6B)−C(26B)	75.6(6)
O(2)−Na(1)−C(24A)	78.30(14)	S(6C)−S(6B)−Na(1)	131.1(13)
S(3)−Na(1)−C(24A)	87.59(14)	C(23B)−S(6B)−Na(1)	69.2(4)
C(23A)−Na(1)−C(24A)	26.54(15)	C(26B)−S(6B)−Na(1)	93.6(5)
O(1)#1−Na(1)−C(14)	107.06(9)	S(6B)−S(6C)−C(23B)	100.0(15)
O(1)−Na(1)−C(14)	116.11(9)	S(6B)−S(6C)−C(26B)	82.9(13)
O(2)−Na(1)−C(14)	25.55(8)	C(23B)−S(6C)−C(26B)	80.2(8)
S(3)−Na(1)−C(14)	140.50(8)	C(1)−O(1)−Na(1)#1	126.39(19)

C(23A)−Na(1)−C(14)	29.61(10)
C(24A)−Na(1)−C(14)	54.09(14)
O(1)#1−Na(1)−S(2)#1	71.15(6)
O(1)−Na(1)−S(2)#1	141.34(7)
O(2)−Na(1)−S(2)#1	117.90(7)
S(3)−Na(1)−S(2)#1	78.40(4)
C(23A)−Na(1)−S(2)#1	99.19(11)
C(24A)−Na(1)−S(2)#1	82.21(15)
C(14)−Na(1)−S(2)#1	102.53(7)
O(1)#1−Na(1)−Na(1)#1	48.26(6)
O(1)−Na(1)−Na(1)#1	47.83(6)
O(2)−Na(1)−Na(1)#1	91.27(6)
S(3)−Na(1)−Na(1)#1	97.72(4)
C(23A)−Na(1)−Na(1)#1	140.03(10)
C(24A)−Na(1)−Na(1)#1	163.74(15)
C(14)−Na(1)−Na(1)#1	116.73(6)
S(2)#1−Na(1)−Na(1)#1	113.86(6)
O(1)#1−Na(1)−Na(2)	98.43(7)
O(1)−Na(1)−Na(2)	51.68(6)
O(2)−Na(1)−Na(2)	46.58(6)
S(3)−Na(1)−Na(2)	119.16(5)
C(23A)−Na(1)−Na(2)	77.59(10)
C(24A)−Na(1)−Na(2)	99.98(14)
C(14)−Na(1)−Na(2)	66.07(7)
S(2)#1−Na(1)−Na(2)	162.27(5)
Na(1)#1−Na(1)−Na(2)	64.01(4)
O(1)#1−Na(1)−S(6B)	133.98(10)
O(1)−Na(1)−S(6B)	130.22(10)
O(2)−Na(1)−S(6B)	77.84(9)
S(3)−Na(1)−S(6B)	91.32(8)
C(23A)−Na(1)−S(6B)	28.80(12)
C(24A)−Na(1)−S(6B)	9.44(14)
C(14)−Na(1)−S(6B)	52.55(9)
S(2)#1−Na(1)−S(6B)	74.48(8)
Na(1)#1−Na(1)−S(6B)	168.72(7)
Na(2)−Na(1)−S(6B)	105.64(8)
O(1)#1−Na(1)−Na(2)#1	49.05(6)
O(1)−Na(1)−Na(2)#1	94.02(7)
O(2)−Na(1)−Na(2)#1	43.63(6)
S(3)−Na(1)−Na(2)#1	155.35(6)
C(23A)−Na(1)−Na(2)#1	93.43(9)
C(24A)−Na(1)−Na(2)#1	117.02(13)
C(14)−Na(1)−Na(2)#1	63.89(6)
S(2)#1−Na(1)−Na(2)#1	102.39(5)
Na(1)#1−Na(1)−Na(2)#1	59.05(4)
Na(2)−Na(1)−Na(2)#1	60.80(4)
S(6B)−Na(1)−Na(2)#1	112.80(8)
O(2)#1−Na(2)−O(2)	88.79(8)
O(2)#1−Na(2)−O(3)	117.98(10)
O(2)−Na(2)−O(3)	116.25(10)
O(2)#1−Na(2)−O(1)	88.30(8)
O(2)−Na(2)−O(1)	93.99(8)
O(3)−Na(2)−O(1)	138.70(10)
O(2)#1−Na(2)−Na(1)	90.45(7)
O(2)−Na(2)−Na(1)	47.56(6)
O(3)−Na(2)−Na(1)	148.91(9)
O(1)−Na(2)−Na(1)	46.54(6)
O(2)#1−Na(2)−S(1)	134.65(8)
O(2)−Na(2)−S(1)	125.73(7)
O(3)−Na(2)−S(1)	75.68(8)
O(1)−Na(2)−S(1)	63.61(6)
Na(1)−Na(2)−S(1)	93.68(4)
O(2)#1−Na(2)−Na(2)#1	44.58(6)
O(2)−Na(2)−Na(2)#1	44.21(6)
O(3)−Na(2)−Na(2)#1	129.85(7)
O(1)−Na(2)−Na(2)#1	91.39(5)
Na(1)−Na(2)−Na(2)#1	61.89(4)
S(1)−Na(2)−Na(2)#1	153.96(3)
O(2)#1−Na(2)−Na(1)#1	44.90(6)
O(2)−Na(2)−Na(1)#1	86.47(6)
O(3)−Na(2)−Na(1)#1	153.48(9)
O(1)−Na(2)−Na(1)#1	43.95(6)
Na(1)−Na(2)−Na(1)#1	56.94(5)
C(1)−O(1)−Na(1)	125.11(19)
Na(1)#1−O(1)−Na(1)	83.91(8)
C(1)−O(1)−Na(2)	135.57(18)
Na(1)#1−O(1)−Na(2)	87.00(8)
Na(1)−O(1)−Na(2)	81.79(7)
C(14)−O(2)−Na(2)#1	132.23(17)
C(14)−O(2)−Na(2)	132.21(18)
Na(2)#1−O(2)−Na(2)	91.21(8)
C(14)−O(2)−Na(1)	108.00(17)
Na(2)#1−O(2)−Na(1)	91.47(8)
Na(2)−O(2)−Na(1)	85.86(8)
O(1)−C(1)−C(10)	112.2(3)
O(1)−C(1)−C(6)	111.1(3)
C(10)−C(1)−C(6)	107.5(3)
O(1)−C(1)−C(2)	110.6(2)
C(10)−C(1)−C(2)	108.2(3)
C(6)−C(1)−C(2)	107.0(3)
C(3)−C(2)−C(1)	131.8(3)
C(3)−C(2)−S(1)	109.6(3)
C(1)−C(2)−S(1)	118.6(2)
C(2)−C(3)−C(4)	113.7(4)
C(5)−C(4)−C(3)	112.8(4)
C(4)−C(5)−S(1)	111.3(3)
C(7)−C(6)−C(1)	128.8(4)
C(7)−C(6)−S(2)	109.5(3)
C(1)−C(6)−S(2)	121.7(3)
C(6)−C(7)−C(8)	108.7(4)
C(9)−C(8)−C(7)	116.4(4)
C(8)−C(9)−S(2)	111.7(4)
C(11)−C(10)−C(1)	127.3(3)
C(11)−C(10)−S(3)	113.0(3)
C(1)−C(10)−S(3)	119.7(2)
C(12)−C(11)−C(10)	103.1(3)
C(13)−C(12)−C(11)	117.1(4)
C(12)−C(13)−S(3)	112.3(4)
O(2)−C(14)−C(15)	111.3(3)
O(2)−C(14)−C(19)	110.2(2)
C(15)−C(14)−C(19)	107.7(2)
O(2)−C(14)−C(23A)	109.5(3)
C(15)−C(14)−C(23A)	111.5(3)
C(19)−C(14)−C(23A)	106.6(3)
O(2)−C(14)−C(23B)	106.6(5)
C(15)−C(14)−C(23B)	97.6(5)
C(19)−C(14)−C(23B)	122.7(6)
C(23A)−C(14)−C(23B)	17.7(5)
O(2)−C(14)−Na(1)	46.45(13)
C(15)−C(14)−Na(1)	152.6(2)
C(19)−C(14)−Na(1)	96.71(17)
C(23A)−C(14)−Na(1)	71.6(2)
C(23B)−C(14)−Na(1)	78.6(5)
C(16)−C(15)−C(14)	130.5(3)
C(16)−C(15)−S(4)	110.0(3)
C(14)−C(15)−S(4)	119.3(2)
C(17)−C(16)−C(15)	111.7(4)
C(18)−C(17)−C(16)	114.1(4)
C(17)−C(18)−S(4)	111.8(4)
C(20)−C(19)−C(14)	126.7(3)
C(20)−C(19)−S(5)	109.4(2)
C(14)−C(19)−S(5)	123.7(2)
C(19)−C(20)−C(21)	113.2(3)
C(22)−C(21)−C(20)	113.1(4)
C(21)−C(22)−S(5)	111.1(3)
C(24A)−C(23A)−C(14)	144.0(5)
C(24A)−C(23A)−S(6A)	89.7(4)
C(14)−C(23A)−S(6A)	118.6(3)
C(24A)−C(23A)−Na(1)	81.0(3)
C(14)−C(23A)−Na(1)	78.8(2)
S(6A)−C(23A)−Na(1)	87.38(18)
C(25A)−C(24A)−C(23A)	134.2(8)
C(25A)−C(24A)−C(26A)	41.0(6)
C(23A)−C(24A)−C(26A)	95.7(5)
C(25A)−C(24A)−S(6A)	87.4(7)
C(23A)−C(24A)−S(6A)	50.7(3)

S(1)−Na(2)−Na(1)#1	102.94(4)	C(26A)−C(24A)−S(6A)	46.4(3)
Na(2)#1−Na(2)−Na(1)#1	57.31(3)	C(25A)−C(24A)−Na(1)	120.4(7)
O(2)#1−Na(2)−S(6A)	148.28(8)	C(23A)−C(24A)−Na(1)	72.5(3)
O(2)−Na(2)−S(6A)	62.04(7)	C(26A)−C(24A)−Na(1)	100.8(4)
O(3)−Na(2)−S(6A)	87.95(9)	S(6A)−C(24A)−Na(1)	77.0(2)
O(1)−Na(2)−S(6A)	82.06(7)	C(24A)−C(25A)−C(26A)	99.7(9)
Na(1)−Na(2)−S(6A)	61.21(5)	C(25A)−C(26A)−S(6A)	113.7(7)
S(1)−Na(2)−S(6A)	66.10(5)	C(25A)−C(26A)−C(24A)	39.3(5)
Na(2)#1−Na(2)−S(6A)	105.26(6)	S(6A)−C(26A)−C(24A)	74.6(4)
Na(1)#1−Na(2)−S(6A)	116.12(5)	C(14)−C(23B)−S(6C)	107.1(9)
C(5)−S(1)−C(2)	92.5(2)	C(14)−C(23B)−S(6B)	102.6(8)
C(5)−S(1)−Na(2)	136.01(15)	S(6C)−C(23B)−S(6B)	17.6(4)
C(2)−S(1)−Na(2)	94.13(11)	C(25B)−C(26B)−S(6C)	104.2(13)
C(9)−S(2)−C(6)	93.7(3)	C(25B)−C(26B)−S(6B)	112.5(13)
C(9)−S(2)−Na(1)#1	124.64(17)	S(6C)−C(26B)−S(6B)	16.6(4)
C(6)−S(2)−Na(1)#1	82.97(11)	C(30)−O(3)−C(27)	107.6(3)
C(13)−S(3)−C(10)	94.5(2)	C(30)−O(3)−Na(2)	129.9(3)
C(13)−S(3)−Na(1)	131.6(2)	C(27)−O(3)−Na(2)	122.4(2)
C(10)−S(3)−Na(1)	89.47(11)	O(3)−C(27)−C(28)	106.8(4)
C(15)−S(4)−C(18)	92.2(2)	C(29)−C(28)−C(27)	103.9(4)
C(22)−S(5)−C(19)	93.04(18)	C(28)−C(29)−C(30)	106.9(5)
C(26A)−S(6A)−C(23A)	97.3(4)	O(3)−C(30)−C(29)	102.2(5)

Symmetry transformations used to generate equivalent atoms:
#1 −x+2,y,−z+3/2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2386. The anisotropic displacement factor exponent takes the form: $-2p^2[\, h^2 a^{*2}U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Na(1)	17(1)	18(1)	19(1)	−2(1)	7(1)	−1(1)
Na(2)	19(1)	19(1)	17(1)	−1(1)	10(1)	−2(1)
S(1)	56(1)	24(1)	41(1)	2(1)	38(1)	0(1)
S(2)	36(1)	50(1)	48(1)	18(1)	21(1)	20(1)
S(3)	51(1)	35(1)	61(1)	−18(1)	35(1)	−14(1)
S(4)	53(1)	26(1)	42(1)	4(1)	25(1)	0(1)
S(5)	27(1)	56(1)	52(1)	25(1)	21(1)	20(1)
O(1)	20(1)	16(1)	23(1)	−4(1)	13(1)	2(1)
O(2)	16(1)	20(1)	15(1)	5(1)	6(1)	5(1)
C(1)	25(2)	17(1)	31(2)	−1(1)	20(1)	2(1)
C(2)	27(2)	23(1)	28(2)	−6(1)	19(1)	−4(1)
C(3)	32(2)	44(2)	41(2)	−4(2)	26(2)	1(2)
C(4)	36(2)	68(3)	38(2)	−13(2)	27(2)	−17(2)
C(5)	62(3)	44(2)	47(2)	−15(2)	42(2)	−24(2)
C(6)	35(2)	25(2)	47(2)	9(1)	32(2)	11(1)
C(7)	45(2)	17(1)	48(2)	8(1)	35(2)	14(1)
C(8)	76(4)	44(3)	102(5)	46(3)	70(4)	41(3)
C(9)	54(3)	73(4)	62(3)	37(3)	39(3)	39(3)
C(10)	36(2)	17(1)	39(2)	−6(1)	25(2)	−4(1)
C(12)	87(4)	53(3)	53(3)	−37(2)	41(3)	−36(3)
C(13)	67(4)	38(2)	84(4)	−24(2)	44(3)	−29(2)
C(14)	17(1)	20(1)	16(1)	3(1)	7(1)	6(1)
C(15)	25(2)	24(1)	24(2)	10(1)	15(1)	11(1)
C(16)	33(2)	38(2)	22(2)	19(1)	16(2)	11(1)
C(17)	60(3)	50(3)	68(3)	42(3)	40(3)	30(2)
C(18)	79(4)	23(2)	93(4)	17(2)	62(4)	12(2)
C(19)	18(1)	23(1)	21(2)	0(1)	8(1)	4(1)
C(20)	13(1)	34(2)	28(2)	14(1)	8(1)	4(1)
C(21)	28(2)	33(2)	47(2)	−2(2)	22(2)	−8(1)
C(22)	25(2)	48(2)	55(3)	9(2)	24(2)	2(2)
O(3)	35(2)	25(1)	45(2)	−1(1)	23(1)	−8(1)
C(27)	40(2)	47(2)	44(2)	2(2)	23(2)	−19(2)
C(28)	87(4)	46(3)	60(3)	−12(2)	47(3)	−34(3)
C(29)	79(5)	38(3)	139(7)	36(3)	54(5)	−7(3)
C(30)	41(3)	79(4)	49(3)	21(2)	25(2)	−9(2)

Compound 14a

Table 1. Crystal data and structure refinement for sh2438.

Identification code	sh2438

Empirical formula	C66 H52 O4 S12 Sn2	
Formula weight	1531.18	
Temperature	148(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.8475(16) Å	α = 90°.
	b = 23.425(3) Å	β = 100.275(5)°.
	c = 21.625(3) Å	γ = 90°.
Volume	6403.9(13) $Å^3$	
Z	4	
Density (calculated)	1.588 Mg/m^3	
Absorption coefficient	1.220 mm^{-1}	
F(000)	3088	
Crystal size	0.15 x 0.36 x 0.52 mm^3	
Theta range for data collection	1.29 to 34.90°.	
Index ranges	−20<=h<=20, −37<=k<=30, −34<=l<=34	
Reflections collected	146369	
Independent reflections	27903 [R(int) = 0.0343]	
Completeness to theta = 34.90°	99.7 %	
Absorption correction	Multi scan	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	27903 / 37 / 715	
Goodness−of−fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1599	
R indices (all data)	R1 = 0.0757, wR2 = 0.1737	
Largest diff. peak and hole	5.241 and −2.285 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2438. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	1928(1)	1817(1)	6891(1)	17(1)
Sn(2)	2019(1)	3347(1)	6814(1)	17(1)
S(1)	5140(1)	3493(1)	6824(1)	34(1)
S(2)	5183(1)	2617(1)	5612(1)	49(1)
S(3)	4908(1)	1646(1)	7332(1)	62(1)
S(4)	2625(1)	2181(1)	8543(1)	34(1)
S(5)	−1248(1)	2791(1)	8083(1)	39(1)
S(6)	2045(2)	3495(1)	8560(1)	59(1)
S(7)	−1872(1)	1106(1)	5463(1)	57(1)
S(8)	1670(1)	1555(1)	4890(1)	41(1)
S(9)	1387(1)	372(1)	6276(1)	29(1)
S(10A)	−1416(1)	3529(1)	6047(1)	38(1)
S(11A)	473(1)	2985(1)	4707(1)	33(1)
S(12A)	742(1)	4775(1)	6399(1)	34(1)
S(10B)	−1256(3)	4404(2)	5110(2)	19(1)
S(11B)	949(5)	4140(2)	4497(2)	53(1)
S(12B)	2400(2)	4385(1)	5739(1)	25(1)
O(1)	2749(2)	2534(1)	6548(1)	19(1)
O(2)	1286(2)	2626(1)	7221(1)	21(1)
O(3)	957(2)	1843(1)	6027(1)	25(1)
O(4)	798(2)	3321(1)	6053(1)	26(1)
C(1)	3861(2)	2502(1)	6513(1)	18(1)
C(2)	4455(2)	2908(1)	7005(2)	20(1)
C(3)	4411(3)	2909(2)	7644(2)	25(1)
C(4)	4940(3)	3379(2)	7967(2)	36(1)
C(5)	5369(4)	3727(2)	7587(2)	41(1)
C(6)	3998(3)	2667(2)	5854(2)	23(1)
C(7)	3172(3)	2880(2)	5354(2)	27(1)
C(8)	3630(6)	2950(3)	4804(2)	60(2)
C(9)	4673(6)	2826(3)	4877(3)	60(2)
C(10)	4226(2)	1885(2)	6631(2)	23(1)
C(11)	3929(2)	1413(1)	6133(2)	25(1)
C(12)	4350(4)	892(2)	6489(3)	42(1)
C(13)	4882(5)	970(2)	7084(3)	57(2)
C(14)	818(3)	2686(1)	7776(1)	20(1)
C(15)	1279(3)	2230(1)	8251(1)	21(1)
C(16)	758(3)	1786(2)	8475(2)	29(1)

C(17)	1444(4)	1424(2)	8888(2)	36(1)
C(18)	2468(4)	1584(2)	8963(2)	34(1)
C(19)	−377(3)	2607(2)	7592(2)	25(1)
C(20)	−916(3)	2396(2)	7034(2)	30(1)
C(21)	−2041(4)	2386(2)	7001(3)	41(1)
C(22)	−2324(4)	2588(2)	7537(3)	45(1)
C(23)	1045(4)	3292(2)	8020(2)	30(1)
C(24)	437(2)	3828(1)	7693(1)	11(1)
C(25)	1012(8)	4303(2)	8023(3)	76(3)
C(26)	1846(7)	4164(3)	8473(3)	72(2)
C(27)	334(3)	1374(1)	5768(2)	23(1)
C(28)	−815(3)	1574(2)	5587(2)	28(1)
C(29)	−1151(4)	2124(2)	5460(2)	35(1)
C(30)	−2253(4)	2168(2)	5277(2)	45(1)
C(31)	−2754(4)	1653(3)	5255(3)	58(2)
C(32)	721(3)	1183(2)	5173(2)	28(1)
C(33)	321(4)	704(1)	4749(2)	37(1)
C(34)	932(5)	685(2)	4260(2)	49(1)
C(35)	1645(4)	1105(3)	4278(2)	49(1)
C(36)	418(3)	886(1)	6239(2)	23(1)
C(37)	−79(3)	848(2)	6754(2)	33(1)
C(38)	339(4)	394(2)	7169(2)	40(1)
C(39)	1127(4)	105(2)	6970(2)	36(1)
C(40)	501(3)	3793(1)	5658(1)	21(1)
C(41)	−677(2)	3918(1)	5634(1)	24(1)
C(42A)	−1353(3)	4346(2)	5280(2)	14(1)
C(42B)	−1442(5)	3737(3)	6007(4)	52
C(43)	−2412(2)	4301(2)	5371(2)	36(1)
C(44)	−2523(3)	3893(2)	5769(2)	45(1)
C(45)	640(3)	3644(1)	4986(2)	33(1)
C(46A)	561(4)	4013(2)	4430(2)	32(1)
C(46B)	285(7)	3145(2)	4593(3)	82
C(47)	831(7)	3722(3)	3890(2)	81(2)
C(48)	612(5)	3153(3)	3982(2)	67(2)
C(49)	1150(2)	4320(1)	5891(1)	22(1)
C(50A)	2239(3)	4473(2)	5860(2)	16(1)
C(50B)	951(5)	4820(3)	6239(4)	52
C(51)	2616(4)	4946(2)	6242(2)	48(1)
C(52)	1882(4)	5125(2)	6527(2)	51(1)
C(53)	241(5)	9485(3)	−265(3)	50(1)
C(54)	422(4)	9545(3)	370(3)	49(1)
C(55)	177(5)	10057(3)	642(3)	50(1)
C(56)	345(9)	10089(5)	1280(5)	48(2)
C(57)	991(5)	5227(3)	10024(3)	55(1)
C(58)	778(4)	4687(2)	9790(3)	45(1)
C(59)	−206(4)	4450(2)	9763(3)	45(1)
C(60)	−401(9)	3873(5)	9502(5)	46(2)
C(61)	2546(6)	4434(4)	2664(4)	68(2)
C(62)	2384(6)	4449(4)	2055(4)	71(2)
C(63)	1969(7)	4922(4)	1688(5)	84(2)
C(64)	1854(7)	5441(5)	1978(5)	86(2)
C(65)	2000(10)	5386(6)	2619(6)	116(4)
C(66)	2312(8)	4947(4)	2980(5)	87(2)
C(67)	2920(9)	3932(6)	3019(6)	113(4)

Table 3. Bond lengths [Å] and angles [°] for sh2438.

Sn(1)−O(3)	2.053(2)	C(16)−C(17)	1.419(5)
Sn(1)−O(1)	2.182(2)	C(17)−C(18)	1.350(6)
Sn(1)−O(2)	2.233(2)	C(19)−C(20)	1.371(6)
Sn(2)−O(4)	2.062(3)	C(20)−C(21)	1.435(6)
Sn(2)−O(2)	2.194(2)	C(21)−C(22)	1.359(8)
Sn(2)−O(1)	2.243(2)	C(23)−C(24)	1.578(5)
S(1)−C(2)	1.711(3)	C(24)−C(25)	1.451(8)
S(1)−C(5)	1.713(5)	C(25)−C(26)	1.352(12)
S(2)−C(9)	1.680(7)	C(27)−C(36)	1.521(5)
S(2)−C(6)	1.700(4)	C(27)−C(32)	1.527(5)
S(3)−C(13)	1.670(6)	C(27)−C(28)	1.532(5)
S(3)−C(10)	1.703(4)	C(28)−C(29)	1.371(5)
S(4)−C(18)	1.699(4)	C(29)−C(30)	1.404(7)
S(4)−C(15)	1.736(4)	C(30)−C(31)	1.364(9)
S(5)−C(22)	1.718(6)	C(32)−C(33)	1.481(5)
S(5)−C(19)	1.729(4)	C(33)−C(34)	1.425(7)
S(6)−C(26)	1.595(8)	C(34)−C(35)	1.340(9)

S(6)−C(23)	1.644(5)	C(36)−C(37)	1.380(6)
S(7)−C(31)	1.717(6)	C(37)−C(38)	1.433(6)
S(7)−C(28)	1.728(4)	C(38)−C(39)	1.351(7)
S(8)−C(35)	1.688(6)	C(40)−C(49)	1.525(4)
S(8)−C(32)	1.698(4)	C(40)−C(41)	1.533(4)
S(9)−C(39)	1.712(4)	C(40)−C(45)	1.535(5)
S(9)−C(36)	1.724(4)	C(41)−C(42B)	1.442(4)
S(10A)−C(44)	1.675(4)	C(41)−C(42A)	1.451(3)
S(10A)−C(41)	1.684(3)	C(42A)−C(43)	1.413(4)
S(11A)−C(48)	1.656(4)	C(42B)−C(44)	1.440(5)
S(11A)−C(45)	1.659(3)	C(43)−C(44)	1.311(7)
S(12A)−C(52)	1.659(4)	C(45)−C(46A)	1.468(4)
S(12A)−C(49)	1.679(3)	C(45)−C(46B)	1.471(5)
S(10B)−C(41)	1.681(3)	C(46A)−C(47)	1.448(4)
S(10B)−C(43)	1.697(4)	C(46B)−C(48)	1.455(5)
S(11B)−C(47)	1.622(4)	C(47)−C(48)	1.385(5)
S(11B)−C(45)	1.665(4)	C(49)−C(50B)	1.439(4)
S(12B)−C(51)	1.696(4)	C(49)−C(50A)	1.457(4)
S(12B)−C(49)	1.703(3)	C(50A)−C(51)	1.414(4)
O(1)−C(1)	1.446(4)	C(50B)−C(52)	1.437(5)
O(2)−C(14)	1.443(4)	C(51)−C(52)	1.285(8)
O(3)−C(27)	1.416(4)	C(53)−C(54)	1.357(8)
O(4)−C(40)	1.409(4)	C(53)−C(55)#1	1.395(8)
C(1)−C(6)	1.517(4)	C(54)−C(55)	1.398(8)
C(1)−C(10)	1.526(4)	C(55)−C(56)	1.361(12)
C(1)−C(2)	1.526(4)	C(55)−C(53)#1	1.395(8)
C(2)−C(3)	1.394(5)	C(57)−C(58)	1.371(8)
C(3)−C(4)	1.411(5)	C(57)−C(59)#2	1.403(8)
C(4)−C(5)	1.344(7)	C(58)−C(59)	1.373(7)
C(6)−C(7)	1.461(5)	C(59)−C(57)#2	1.403(8)
C(7)−C(8)	1.427(7)	C(59)−C(60)	1.468(12)
C(8)−C(9)	1.353(10)	C(61)−C(62)	1.298(11)
C(10)−C(11)	1.544(5)	C(61)−C(67)	1.439(14)
C(11)−C(12)	1.493(6)	C(61)−C(66)	1.442(12)
C(12)−C(13)	1.357(7)	C(62)−C(63)	1.411(12)
C(14)−C(23)	1.524(5)	C(63)−C(64)	1.386(13)
C(14)−C(15)	1.527(5)	C(64)−C(65)	1.372(14)
C(14)−C(19)	1.528(5)	C(65)−C(66)	1.309(15)
C(15)−C(16)	1.370(5)		

O(3)−Sn(1)−O(1)	85.44(9)	C(33)−C(32)−S(8)	111.0(3)
O(3)−Sn(1)−O(2)	93.78(10)	C(27)−C(32)−S(8)	121.1(3)
O(1)−Sn(1)−O(2)	71.65(9)	C(34)−C(33)−C(32)	107.8(4)
O(4)−Sn(2)−O(2)	88.69(10)	C(35)−C(34)−C(33)	114.8(4)
O(4)−Sn(2)−O(1)	93.62(10)	C(34)−C(35)−S(8)	113.4(4)
O(2)−Sn(2)−O(1)	71.22(9)	C(37)−C(36)−C(27)	126.9(3)
C(2)−S(1)−C(5)	92.5(2)	C(37)−C(36)−S(9)	110.6(3)
C(9)−S(2)−C(6)	93.0(3)	C(27)−C(36)−S(9)	121.3(3)
C(13)−S(3)−C(10)	92.8(2)	C(36)−C(37)−C(38)	112.2(4)
C(18)−S(4)−C(15)	92.54(19)	C(39)−C(38)−C(37)	112.9(4)
C(22)−S(5)−C(19)	92.2(2)	C(38)−C(39)−S(9)	111.8(3)
C(26)−S(6)−C(23)	96.4(4)	O(4)−C(40)−C(49)	111.2(2)
C(31)−S(7)−C(28)	91.8(3)	O(4)−C(40)−C(41)	109.2(3)
C(35)−S(8)−C(32)	92.7(3)	C(49)−C(40)−C(41)	109.6(2)
C(39)−S(9)−C(36)	92.5(2)	O(4)−C(40)−C(45)	109.4(3)
C(44)−S(10A)−C(41)	93.2(2)	C(49)−C(40)−C(45)	110.4(3)
C(48)−S(11A)−C(45)	95.3(2)	C(41)−C(40)−C(45)	107.0(3)
C(52)−S(12A)−C(49)	93.1(2)	C(42B)−C(41)−C(42A)	95.5(3)
C(41)−S(10B)−C(43)	89.3(2)	C(42B)−C(41)−C(40)	133.8(3)
C(47)−S(11B)−C(45)	95.5(3)	C(42A)−C(41)−C(40)	130.1(3)
C(51)−S(12B)−C(49)	89.8(2)	C(42B)−C(41)−S(10B)	108.2(3)
C(1)−O(1)−Sn(1)	121.29(18)	C(42A)−C(41)−S(10B)	13.33(14)
C(1)−O(1)−Sn(2)	121.34(18)	C(40)−C(41)−S(10B)	117.9(2)
Sn(1)−O(1)−Sn(2)	108.42(10)	C(42B)−C(41)−S(10A)	16.0(2)
C(14)−O(2)−Sn(2)	122.00(18)	C(42A)−C(41)−S(10A)	108.2(2)
C(14)−O(2)−Sn(1)	125.62(18)	C(40)−C(41)−S(10A)	121.7(2)
Sn(2)−O(2)−Sn(1)	108.39(10)	S(10B)−C(41)−S(10A)	120.0(2)
C(27)−O(3)−Sn(1)	123.1(2)	C(43)−C(42A)−C(41)	112.0(3)
C(40)−O(4)−Sn(2)	123.1(2)	C(44)−C(42B)−C(41)	115.8(5)
O(1)−C(1)−C(6)	108.4(2)	C(44)−C(43)−C(42A)	111.5(3)
O(1)−C(1)−C(10)	108.5(2)	C(44)−C(43)−S(10B)	121.7(3)
C(6)−C(1)−C(10)	108.3(3)	C(42A)−C(43)−S(10B)	11.93(15)
O(1)−C(1)−C(2)	107.9(2)	C(43)−C(44)−C(42B)	102.0(4)

C(6)−C(1)−C(2)	111.6(3)
C(10)−C(1)−C(2)	111.9(2)
C(3)−C(2)−C(1)	126.0(3)
C(3)−C(2)−S(1)	109.8(2)
C(1)−C(2)−S(1)	123.6(2)
C(2)−C(3)−C(4)	113.0(3)
C(5)−C(4)−C(3)	112.6(4)
C(4)−C(5)−S(1)	112.1(3)
C(7)−C(6)−C(1)	126.3(3)
C(7)−C(6)−S(2)	111.5(2)
C(1)−C(6)−S(2)	122.2(3)
C(8)−C(7)−C(6)	107.7(4)
C(9)−C(8)−C(7)	115.2(5)
C(8)−C(9)−S(2)	112.6(4)
C(1)−C(10)−C(11)	122.0(3)
C(1)−C(10)−S(3)	123.6(3)
C(11)−C(10)−S(3)	114.2(2)
C(12)−C(11)−C(10)	101.7(3)
C(13)−C(12)−C(11)	116.9(4)
C(12)−C(13)−S(3)	114.2(4)
O(2)−C(14)−C(23)	107.3(3)
O(2)−C(14)−C(15)	108.8(3)
C(23)−C(14)−C(15)	113.1(3)
O(2)−C(14)−C(19)	108.6(3)
C(23)−C(14)−C(19)	108.9(3)
C(15)−C(14)−C(19)	110.0(3)
C(16)−C(15)−C(14)	127.8(3)
C(16)−C(15)−S(4)	109.8(3)
C(14)−C(15)−S(4)	122.2(2)
C(15)−C(16)−C(17)	112.8(4)
C(18)−C(17)−C(16)	113.2(4)
C(17)−C(18)−S(4)	111.6(3)
C(20)−C(19)−C(14)	126.8(3)
C(20)−C(19)−S(5)	110.5(3)
C(14)−C(19)−S(5)	122.7(3)
C(19)−C(20)−C(21)	113.3(4)
C(22)−C(21)−C(20)	111.9(4)
C(21)−C(22)−S(5)	112.2(4)
C(14)−C(23)−C(24)	122.5(3)
C(14)−C(23)−S(6)	126.2(3)
C(24)−C(23)−S(6)	110.5(2)
C(25)−C(24)−C(23)	102.8(4)
C(26)−C(25)−C(24)	116.0(5)
C(25)−C(26)−S(6)	114.2(4)
O(3)−C(27)−C(36)	110.5(3)
O(3)−C(27)−C(32)	108.4(3)
C(36)−C(27)−C(32)	110.5(3)
O(3)−C(27)−C(28)	108.3(3)
C(36)−C(27)−C(28)	110.5(3)
C(32)−C(27)−C(28)	108.6(3)
C(29)−C(28)−C(27)	126.4(4)
C(29)−C(28)−S(7)	110.7(3)
C(27)−C(28)−S(7)	122.7(3)
C(28)−C(29)−C(30)	113.0(4)
C(31)−C(30)−C(29)	113.0(4)
C(30)−C(31)−S(7)	111.5(4)
C(33)−C(32)−C(27)	127.9(4)
C(43)−C(44)−S(10A)	115.0(3)
C(42B)−C(44)−S(10A)	16.2(2)
C(46A)−C(45)−C(46B)	91.5(3)
C(46A)−C(45)−C(40)	129.7(3)
C(46B)−C(45)−C(40)	130.6(4)
C(46A)−C(45)−S(11A)	105.3(2)
C(46B)−C(45)−S(11A)	16.6(2)
C(40)−C(45)−S(11A)	121.7(3)
C(46A)−C(45)−S(11B)	19.92(17)
C(46B)−C(45)−S(11B)	105.8(3)
C(40)−C(45)−S(11B)	121.6(3)
S(11A)−C(45)−S(11B)	116.6(2)
C(47)−C(46A)−C(45)	113.2(4)
C(48)−C(46B)−C(45)	113.8(5)
C(48)−C(47)−C(46A)	104.5(5)
C(48)−C(47)−S(11B)	117.1(4)
C(46A)−C(47)−S(11B)	20.62(17)
C(47)−C(48)−C(46B)	104.1(5)
C(47)−C(48)−S(11A)	115.2(4)
C(46B)−C(48)−S(11A)	16.5(2)
C(50B)−C(49)−C(50A)	94.9(3)
C(50B)−C(49)−C(40)	134.0(3)
C(50A)−C(49)−C(40)	131.1(3)
C(50B)−C(49)−S(12A)	15.6(2)
C(50A)−C(49)−S(12A)	106.7(2)
C(40)−C(49)−S(12A)	121.0(2)
C(50B)−C(49)−S(12B)	106.8(3)
C(50A)−C(49)−S(12B)	12.26(15)
C(40)−C(49)−S(12B)	119.2(2)
S(12A)−C(49)−S(12B)	119.0(2)
C(51)−C(50A)−C(49)	113.4(3)
C(52)−C(50B)−C(49)	114.8(5)
C(52)−C(51)−C(50A)	109.4(4)
C(52)−C(51)−S(12B)	120.7(3)
C(50A)−C(51)−S(12B)	11.35(14)
C(51)−C(52)−C(50B)	104.7(4)
C(51)−C(52)−S(12A)	117.3(4)
C(50B)−C(52)−S(12A)	16.1(2)
C(54)−C(53)−C(55)#1	119.4(6)
C(53)−C(54)−C(55)	120.2(6)
C(56)−C(55)−C(53)#1	121.8(7)
C(56)−C(55)−C(54)	117.9(7)
C(53)#1−C(55)−C(54)	120.4(5)
C(58)−C(57)−C(59)#2	120.8(6)
C(57)−C(58)−C(59)	120.7(5)
C(58)−C(59)−C(57)#2	118.5(5)
C(58)−C(59)−C(60)	118.8(6)
C(57)#2−C(59)−C(60)	122.6(6)
C(62)−C(61)−C(67)	122.8(9)
C(62)−C(61)−C(66)	116.6(8)
C(67)−C(61)−C(66)	120.5(9)
C(61)−C(62)−C(63)	124.7(9)
C(64)−C(63)−C(62)	119.6(9)
C(65)−C(64)−C(63)	111.6(11)
C(66)−C(65)−C(64)	130.5(13)
C(65)−C(66)−C(61)	116.0(10)

Symmetry transformations used to generate equivalent atoms:
#1 −x,−y+2,−z #2 −x,−y+1,−z+2

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for sh2438. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	19(1)	12(1)	19(1)	1(1)	0(1)	−1(1)
Sn(2)	22(1)	12(1)	15(1)	1(1)	2(1)	−1(1)
S(1)	40(1)	27(1)	34(1)	3(1)	3(1)	−12(1)
S(2)	45(1)	65(1)	44(1)	−1(1)	26(1)	2(1)
S(3)	65(1)	31(1)	71(1)	6(1)	−37(1)	−1(1)
S(4)	31(1)	41(1)	28(1)	10(1)	1(1)	−6(1)

S(5)	36(1)	42(1)	43(1)	0(1)	19(1)	6(1)
S(6)	75(1)	55(1)	51(1)	−16(1)	20(1)	−27(1)
S(7)	30(1)	34(1)	97(1)	−10(1)	−18(1)	−2(1)
S(8)	38(1)	44(1)	37(1)	−6(1)	0(1)	0(1)
S(9)	33(1)	19(1)	32(1)	2(1)	0(1)	3(1)
S(10A)	41(1)	30(1)	44(1)	9(1)	12(1)	11(1)
S(11A)	38(1)	27(1)	33(1)	−3(1)	7(1)	2(1)
S(12A)	40(1)	26(1)	32(1)	2(1)	−2(1)	−7(1)
S(10B)	19(2)	22(2)	15(2)	10(1)	−1(1)	1(1)
S(11B)	49(3)	78(4)	29(2)	9(2)	−1(2)	−6(3)
S(12B)	21(1)	24(1)	33(1)	15(1)	15(1)	6(1)
O(1)	15(1)	16(1)	26(1)	1(1)	2(1)	−1(1)
O(2)	33(1)	15(1)	16(1)	0(1)	10(1)	−2(1)
O(3)	32(1)	16(1)	24(1)	1(1)	−5(1)	−7(1)
O(4)	30(1)	13(1)	32(1)	5(1)	−7(1)	−1(1)
C(1)	16(1)	18(1)	18(1)	1(1)	1(1)	0(1)
C(2)	17(1)	21(1)	22(1)	0(1)	0(1)	−2(1)
C(3)	22(1)	31(2)	21(1)	0(1)	−1(1)	−2(1)
C(4)	36(2)	40(2)	29(2)	−9(2)	−4(1)	−3(2)
C(5)	45(2)	29(2)	44(2)	−9(2)	−4(2)	−11(2)
C(6)	27(1)	24(2)	20(1)	0(1)	5(1)	−3(1)
C(7)	26(1)	35(2)	19(1)	−3(1)	1(1)	−9(1)
C(8)	93(5)	58(3)	23(2)	6(2)	−2(2)	−11(3)
C(9)	95(5)	60(4)	36(2)	−9(2)	38(3)	−25(3)
C(10)	18(1)	22(1)	27(1)	2(1)	−1(1)	2(1)
C(11)	17(1)	5(1)	50(2)	4(1)	2(1)	6(1)
C(12)	47(2)	23(2)	54(3)	−5(2)	−3(2)	1(2)
C(13)	56(3)	30(2)	69(4)	2(2)	−28(3)	13(2)
C(14)	29(1)	17(1)	17(1)	1(1)	9(1)	−1(1)
C(15)	28(1)	20(1)	17(1)	1(1)	9(1)	0(1)
C(16)	34(2)	21(2)	34(2)	10(1)	15(1)	5(1)
C(17)	39(2)	27(2)	42(2)	15(2)	12(2)	4(2)
C(18)	39(2)	35(2)	29(2)	10(2)	7(2)	4(2)
C(19)	27(1)	20(1)	28(2)	5(1)	9(1)	1(1)
C(20)	30(2)	30(2)	31(2)	4(1)	4(1)	−1(1)
C(21)	33(2)	40(2)	49(3)	12(2)	1(2)	−2(2)
C(22)	30(2)	42(3)	62(3)	16(2)	9(2)	5(2)
C(23)	47(2)	20(2)	28(2)	−5(1)	21(2)	−7(1)
C(24)	22(1)	2(1)	13(1)	−2(1)	11(1)	5(1)
C(25)	158(8)	19(2)	73(4)	0(2)	83(5)	7(3)
C(26)	117(6)	52(3)	62(4)	−35(3)	55(4)	−53(4)
C(27)	26(1)	16(1)	24(1)	0(1)	−5(1)	−2(1)
C(28)	29(2)	23(2)	28(2)	−3(1)	−7(1)	0(1)
C(29)	40(2)	20(2)	50(2)	3(2)	21(2)	7(1)
C(30)	49(3)	49(3)	38(2)	8(2)	9(2)	25(2)
C(31)	36(2)	58(3)	69(4)	−21(3)	−19(2)	15(2)
C(32)	37(2)	19(2)	24(1)	2(1)	−2(1)	3(1)
C(33)	85(3)	8(1)	17(1)	−4(1)	9(2)	−9(2)
C(34)	79(4)	37(2)	27(2)	−10(2)	−6(2)	12(2)
C(35)	47(3)	64(3)	33(2)	6(2)	4(2)	22(2)
C(36)	23(1)	16(1)	29(2)	1(1)	−3(1)	−4(1)
C(37)	35(2)	23(2)	40(2)	5(1)	9(2)	−5(1)
C(38)	52(3)	31(2)	37(2)	9(2)	12(2)	−3(2)
C(39)	47(2)	25(2)	33(2)	9(1)	−3(2)	−1(2)
C(40)	25(1)	16(1)	20(1)	2(1)	−3(1)	3(1)
C(41)	24(1)	17(1)	27(1)	−3(1)	−2(1)	1(1)
C(43)	28(2)	38(2)	37(2)	−7(2)	−6(1)	11(2)
C(44)	42(2)	45(3)	49(3)	−10(2)	15(2)	−6(2)
C(45)	36(2)	36(2)	25(2)	−9(1)	−4(1)	10(2)
C(47)	116(7)	96(6)	31(3)	10(3)	14(3)	−7(5)
C(48)	60(4)	96(5)	47(3)	−39(3)	16(3)	−19(3)
C(49)	25(1)	18(1)	22(1)	6(1)	−1(1)	0(1)
C(51)	34(2)	41(3)	62(3)	20(2)	−9(2)	−19(2)
C(52)	76(4)	27(2)	39(2)	5(2)	−19(2)	−12(2)

Compound 14b

Table 1. Crystal data and structure refinement for sh2349.

Identification code	sh2349
Empirical formula	C60 H52 O6 S12 Sn2
Formula weight	1491.12
Temperature	293(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.043(4) Å	α = 90°.
	b = 17.317(4) Å	β = 110.90(3)°.
	c = 23.051(5) Å	γ = 90°.
Volume	6728(2) Å^3	
Z	4	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	1.161 mm^{-1}	
F(000)	3008	
Crystal size	0.6 x 0.44 x 0.3 mm^3	
Theta range for data collection	1.89 to 24.10°.	
Index ranges	−20<=h<=20, −19<=k<=19, −26<=l<=26	
Reflections collected	41568	
Independent reflections	10449 [R(int) = 0.0409]	
Completeness to theta = 24.10°	97.8 %	
Absorption correction	None	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	10449 / 16 / 707	
Goodness−of−fit on F^2	1.764	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1753	
R indices (all data)	R1 = 0.0583, wR2 = 0.1808	
Largest diff. peak and hole	1.887 and −1.114 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2349. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	3899(1)	1866(1)	1970(1)	23(1)
Sn(2)	1815(1)	1740(1)	1125(1)	28(1)
S(1)	2743(1)	3314(1)	768(1)	46(1)
S(2)	1304(1)	4178(1)	1526(1)	66(1)
S(3)	2917(1)	3536(1)	3223(1)	59(1)
S(4)	2933(2)	−695(1)	236(1)	57(1)
S(5)	2477(1)	1814(1)	−430(1)	44(1)
S(6)	4572(1)	418(1)	554(1)	45(1)
S(7)	649(2)	877(2)	2878(1)	71(1)
S(8)	102(1)	536(1)	648(1)	61(1)
S(9)	712(2)	−854(2)	2199(2)	101(1)
S(11)	4840(1)	530(1)	4339(1)	53(1)
S(10A)	5752(4)	1586(4)	3298(3)	33(1)
S(12A)	4871(4)	−893(2)	3285(3)	35(1)
S(10B)	5279(4)	497(3)	2305(3)	47(1)
S(12B)	3257(5)	−496(4)	2878(5)	38(2)
O(1)	2747(2)	2394(2)	1874(2)	25(1)
O(2)	2992(2)	1327(2)	1150(2)	24(1)
O(3)	1837(3)	813(2)	1690(2)	33(1)
O(4)	3720(2)	1042(2)	2552(2)	27(1)
C(1)	2669(4)	3219(3)	1973(3)	28(1)
C(2)	2870(4)	3699(3)	1487(3)	31(1)
C(3)	3041(4)	4490(4)	1509(3)	42(2)
C(4)	3085(5)	4748(4)	924(4)	54(2)
C(5)	2941(5)	4184(4)	492(4)	49(2)
C(6)	1816(4)	3374(4)	1915(3)	36(2)
C(7)	1373(5)	2978(4)	2190(4)	48(2)
C(8)	627(5)	3331(5)	2095(5)	63(2)
C(9)	513(6)	3968(7)	1754(5)	83(3)
C(10)	3241(4)	3435(3)	2615(3)	31(1)
C(11)	4158(4)	3525(3)	2816(2)	26(1)
C(12)	4409(5)	3743(4)	3468(4)	50(2)
C(13)	3841(5)	3753(4)	3718(3)	50(2)
C(14)	3113(4)	888(3)	658(2)	25(1)
C(15)	3119(4)	15(3)	800(3)	32(1)
C(16)	3360(4)	−321(3)	1385(3)	35(2)
C(17)	3393(5)	−1144(4)	1359(4)	55(2)
C(18)	3176(6)	−1420(4)	768(4)	62(2)
C(19)	2426(4)	1075(3)	55(3)	30(1)
C(20)	1664(4)	739(4)	−147(3)	37(2)

C(21)	1154(5)	1128(5)	−690(3)	53(2)
C(22)	1512(5)	1694(5)	−884(3)	56(2)
C(23)	3913(4)	1115(3)	620(2)	26(1)
C(24)	4231(4)	1838(3)	634(3)	29(1)
C(25)	5000(4)	1833(4)	601(3)	39(2)
C(26)	5265(4)	1098(4)	555(3)	47(2)
C(27)	1193(4)	580(4)	1856(3)	35(1)
C(28)	1343(4)	872(4)	2520(3)	41(2)
C(29)	2069(4)	1114(3)	2933(3)	33(1)
C(30)	2046(6)	1309(5)	3519(4)	56(2)
C(31)	1337(6)	1209(5)	3558(4)	69(3)
C(32)	419(4)	901(4)	1391(3)	42(2)
C(33)	−64(5)	1557(4)	1429(4)	51(2)
C(34)	−652(6)	1697(7)	842(7)	89(4)
C(35)	−620(6)	1201(7)	377(5)	79(3)
C(36)	1173(4)	−310(4)	1839(3)	41(2)
C(37)	1565(3)	−796(2)	1440(2)	13(1)
C(38)	1341(7)	−1617(5)	1572(5)	76(3)
C(39)	909(7)	−1671(5)	1929(5)	80(3)
C(40)	4356(4)	674(3)	3029(2)	27(1)
C(41)	5132(4)	842(3)	2923(3)	31(1)
C(42A)	5414(19)	580(20)	2459(15)	140(20)
C(42B)	5725(13)	1409(13)	3155(10)	19(5)
C(43)	6043(5)	998(6)	2381(4)	64(2)
C(44)	6266(5)	1503(6)	2828(5)	69(3)
C(46)	4394(4)	1014(3)	3648(3)	30(1)
C(47)	4092(5)	1712(4)	3745(3)	41(2)
C(48)	4229(5)	1851(4)	4386(3)	49(2)
C(49)	4621(5)	1268(4)	4758(3)	53(2)
C(50)	4180(4)	−188(3)	3022(3)	31(1)
C(51A)	3452(11)	−591(9)	2850(17)	25(6)
C(51B)	4634(14)	−885(10)	3204(17)	101(17)
C(52)	3511(7)	−1400(4)	2964(4)	69(3)
C(53)	4241(7)	−1596(4)	3164(4)	62(3)
O(5)	−2340(9)	3018(8)	456(6)	164(4)
C(54)	3137(12)	−3306(10)	−262(9)	137(6)
C(55)	3096(10)	5923(9)	−582(7)	120(5)
C(56)	2185(12)	5865(11)	−992(9)	148(6)
C(57)	−1806(13)	3417(13)	1031(10)	161(7)
O(6)	7656(12)	604(12)	1432(9)	172(7)
C(58)	7352(12)	1312(12)	1414(9)	103(5)
C(59)	7738(13)	1692(11)	1933(10)	108(6)
C(60)	8268(15)	1202(15)	2354(12)	139(8)
C(61)	1625(14)	5468(13)	2972(10)	120(7)

Table 3. Bond lengths [Å] and angles [°] for sh2349.

Sn(1)−O(4)	2.062(4)	C(15)−C(16)	1.389(9)
Sn(1)−O(1)	2.209(4)	C(16)−C(17)	1.428(9)
Sn(1)−O(2)	2.217(4)	C(17)−C(18)	1.362(12)
Sn(2)−O(3)	2.059(4)	C(19)−C(20)	1.410(9)
Sn(2)−O(2)	2.223(4)	C(20)−C(21)	1.431(10)
Sn(2)−O(1)	2.241(4)	C(21)−C(22)	1.335(12)
S(1)−C(5)	1.722(7)	C(23)−C(24)	1.373(8)
S(1)−C(2)	1.725(6)	C(24)−C(25)	1.416(9)
S(2)−C(9)	1.727(11)	C(25)−C(26)	1.376(10)
S(2)−C(6)	1.733(7)	C(27)−C(32)	1.529(10)
S(3)−C(13)	1.693(8)	C(27)−C(28)	1.539(9)
S(3)−C(10)	1.709(6)	C(27)−C(36)	1.542(9)
S(4)−C(18)	1.701(9)	C(28)−C(29)	1.382(10)
S(4)−C(15)	1.733(6)	C(29)−C(30)	1.408(9)
S(5)−C(22)	1.694(9)	C(30)−C(31)	1.324(12)
S(5)−C(19)	1.724(6)	C(32)−C(33)	1.452(11)
S(6)−C(26)	1.717(8)	C(33)−C(34)	1.412(14)
S(6)−C(23)	1.737(6)	C(34)−C(35)	1.391(16)
S(7)−C(31)	1.716(10)	C(36)−C(37)	1.586(9)
S(7)−C(28)	1.729(7)	C(37)−C(38)	1.537(11)
S(8)−C(35)	1.683(11)	C(38)−C(39)	1.325(15)
S(8)−C(32)	1.720(7)	C(40)−C(46)	1.524(8)
S(9)−C(39)	1.635(12)	C(40)−C(50)	1.524(8)
S(9)−C(36)	1.661(7)	C(40)−C(41)	1.532(9)
S(11)−C(46)	1.725(6)	C(41)−C(42B)	1.410(15)
S(11)−C(49)	1.732(7)	C(41)−C(42A)	1.413(19)
S(10A)−C(44)	1.663(10)	C(42A)−C(43)	1.409(19)

S(10A)−C(41)	1.722(8)	C(42B)−C(44)	1.439(16)
S(12A)−C(53)	1.621(11)	C(43)−C(44)	1.300(13)
S(12A)−C(50)	1.695(7)	C(46)−C(47)	1.376(9)
S(10B)−C(43)	1.584(11)	C(47)−C(48)	1.430(9)
S(10B)−C(41)	1.651(7)	C(48)−C(49)	1.349(10)
S(12B)−C(52)	1.623(11)	C(50)−C(51A)	1.415(17)
S(12B)−C(50)	1.666(10)	C(50)−C(51B)	1.436(18)
O(1)−C(1)	1.462(6)	C(51A)−C(52)	1.422(17)
O(2)−C(14)	1.444(6)	C(51B)−C(53)	1.407(18)
O(3)−C(27)	1.407(7)	C(52)−C(53)	1.277(14)
O(4)−C(40)	1.425(7)	O(5)−C(54)#1	1.44(2)
C(1)−C(10)	1.518(9)	O(5)−C(57)	1.50(2)
C(1)−C(6)	1.521(9)	C(54)−O(5)#1	1.44(2)
C(1)−C(2)	1.539(8)	C(54)−C(55)#2	1.51(2)
C(2)−C(3)	1.400(9)	C(55)−C(54)#3	1.51(2)
C(3)−C(4)	1.449(10)	C(55)−C(56)	1.58(2)
C(4)−C(5)	1.353(11)	C(56)−C(57)#4	1.41(2)
C(6)−C(7)	1.368(10)	C(57)−C(56)#4	1.41(2)
C(7)−C(8)	1.422(11)	O(6)−C(58)	1.34(2)
C(8)−C(9)	1.326(14)	O(6)−C(61)#5	1.53(3)
C(10)−C(11)	1.559(9)	C(58)−C(59)	1.33(3)
C(11)−C(12)	1.456(9)	C(59)−C(60)	1.38(3)
C(12)−C(13)	1.343(11)	C(60)−C(61)#5	1.52(3)
C(14)−C(23)	1.530(8)	C(61)−C(60)#6	1.52(3)
C(14)−C(19)	1.530(8)	C(61)−O(6)#6	1.53(3)
C(14)−C(15)	1.545(8)		

O(4)−Sn(1)−O(1)	89.49(15)	O(3)−C(27)−C(36)	107.1(5)
O(4)−Sn(1)−O(2)	91.38(15)	C(32)−C(27)−C(36)	109.7(5)
O(1)−Sn(1)−O(2)	72.95(14)	C(28)−C(27)−C(36)	110.4(5)
O(3)−Sn(2)−O(2)	85.96(15)	C(29)−C(28)−C(27)	125.0(6)
O(3)−Sn(2)−O(1)	93.77(15)	C(29)−C(28)−S(7)	109.8(5)
O(2)−Sn(2)−O(1)	72.22(13)	C(27)−C(28)−S(7)	125.1(5)
C(5)−S(1)−C(2)	92.4(3)	C(28)−C(29)−C(30)	112.9(7)
C(9)−S(2)−C(6)	91.1(5)	C(31)−C(30)−C(29)	113.2(8)
C(13)−S(3)−C(10)	91.8(4)	C(30)−C(31)−S(7)	112.5(6)
C(18)−S(4)−C(15)	92.9(3)	C(33)−C(32)−C(27)	131.2(6)
C(22)−S(5)−C(19)	91.7(4)	C(33)−C(32)−S(8)	110.6(6)
C(26)−S(6)−C(23)	92.5(3)	C(27)−C(32)−S(8)	117.5(5)
C(31)−S(7)−C(28)	91.5(4)	C(34)−C(33)−C(32)	109.9(8)
C(35)−S(8)−C(32)	93.3(5)	C(35)−C(34)−C(33)	114.0(9)
C(39)−S(9)−C(36)	94.9(5)	C(34)−C(35)−S(8)	112.1(7)
C(46)−S(11)−C(49)	91.8(3)	C(27)−C(36)−C(37)	122.3(5)
C(44)−S(10A)−C(41)	91.2(5)	C(27)−C(36)−S(9)	124.4(5)
C(53)−S(12A)−C(50)	95.7(5)	C(37)−C(36)−S(9)	113.3(5)
C(43)−S(10B)−C(41)	96.1(5)	C(38)−C(37)−C(36)	100.0(6)
C(52)−S(12B)−C(50)	93.8(6)	C(39)−C(38)−C(37)	116.3(8)
C(1)−O(1)−Sn(1)	121.9(3)	C(38)−C(39)−S(9)	115.5(7)
C(1)−O(1)−Sn(2)	121.8(3)	O(4)−C(40)−C(46)	107.7(4)
Sn(1)−O(1)−Sn(2)	106.79(15)	O(4)−C(40)−C(50)	108.8(5)
C(14)−O(2)−Sn(1)	128.2(3)	C(46)−C(40)−C(50)	109.2(4)
C(14)−O(2)−Sn(2)	124.0(3)	O(4)−C(40)−C(41)	108.8(4)
Sn(1)−O(2)−Sn(2)	107.16(15)	C(46)−C(40)−C(41)	109.7(5)
C(27)−O(3)−Sn(2)	124.4(4)	C(50)−C(40)−C(41)	112.5(5)
C(40)−O(4)−Sn(1)	122.8(3)	C(42B)−C(41)−C(42A)	94.7(12)
O(1)−C(1)−C(10)	108.9(5)	C(42B)−C(41)−C(40)	133.2(8)
O(1)−C(1)−C(6)	108.1(5)	C(42A)−C(41)−C(40)	131.0(11)
C(10)−C(1)−C(6)	110.9(5)	C(42B)−C(41)−S(10B)	104.3(8)
O(1)−C(1)−C(2)	110.7(4)	C(42A)−C(41)−S(10B)	11.1(14)
C(10)−C(1)−C(2)	108.8(5)	C(40)−C(41)−S(10B)	120.4(5)
C(6)−C(1)−C(2)	109.5(5)	C(42B)−C(41)−S(10A)	11.3(7)
C(3)−C(2)−C(1)	127.5(5)	C(42A)−C(41)−S(10A)	105.9(11)
C(3)−C(2)−S(1)	111.4(5)	C(40)−C(41)−S(10A)	122.0(5)
C(1)−C(2)−S(1)	120.4(4)	S(10B)−C(41)−S(10A)	115.3(5)
C(2)−C(3)−C(4)	110.7(6)	C(43)−C(42A)−C(41)	117.0(18)
C(5)−C(4)−C(3)	113.7(6)	C(41)−C(42B)−C(44)	116.3(11)
C(4)−C(5)−S(1)	111.8(5)	C(44)−C(43)−C(42A)	106.3(12)
C(7)−C(6)−C(1)	127.6(6)	C(44)−C(43)−S(10B)	117.9(7)
C(7)−C(6)−S(2)	110.5(5)	C(42A)−C(43)−S(10B)	13.0(13)
C(1)−C(6)−S(2)	121.6(5)	C(43)−C(44)−C(42B)	105.3(9)
C(6)−C(7)−C(8)	113.0(7)	C(43)−C(44)−S(10A)	119.1(7)
C(9)−C(8)−C(7)	112.8(8)	C(42B)−C(44)−S(10A)	14.0(6)
C(8)−C(9)−S(2)	112.6(7)	C(47)−C(46)−C(40)	127.2(5)

C(1)−C(10)−C(11)	126.5(5)	C(47)−C(46)−S(11)	111.0(5)
C(1)−C(10)−S(3)	120.8(5)	C(40)−C(46)−S(11)	121.8(4)
C(11)−C(10)−S(3)	112.5(4)	C(46)−C(47)−C(48)	112.5(6)
C(12)−C(11)−C(10)	103.9(5)	C(49)−C(48)−C(47)	112.9(6)
C(13)−C(12)−C(11)	116.2(7)	C(48)−C(49)−S(11)	111.7(5)
C(12)−C(13)−S(3)	115.3(5)	C(51A)−C(50)−C(51B)	92.4(13)
O(2)−C(14)−C(23)	108.7(4)	C(51A)−C(50)−C(40)	130.9(9)
O(2)−C(14)−C(19)	107.5(4)	C(51B)−C(50)−C(40)	136.5(11)
C(23)−C(14)−C(19)	111.6(4)	C(51A)−C(50)−S(12B)	12.2(10)
O(2)−C(14)−C(15)	109.9(4)	C(51B)−C(50)−S(12B)	102.3(10)
C(23)−C(14)−C(15)	109.1(5)	C(40)−C(50)−S(12B)	120.4(5)
C(19)−C(14)−C(15)	109.9(5)	C(51A)−C(50)−S(12A)	103.6(9)
C(16)−C(15)−C(14)	126.2(5)	C(51B)−C(50)−S(12A)	11.2(10)
C(16)−C(15)−S(4)	109.9(5)	C(40)−C(50)−S(12A)	125.3(5)
C(14)−C(15)−S(4)	123.4(4)	S(12B)−C(50)−S(12A)	113.3(5)
C(15)−C(16)−C(17)	112.4(6)	C(50)−C(51A)−C(52)	115.7(15)
C(18)−C(17)−C(16)	113.0(7)	C(53)−C(51B)−C(50)	119.7(17)
C(17)−C(18)−S(4)	111.7(6)	C(53)−C(52)−C(51A)	109.2(10)
C(20)−C(19)−C(14)	126.3(5)	C(53)−C(52)−S(12B)	120.7(8)
C(20)−C(19)−S(5)	111.2(5)	C(51A)−C(52)−S(12B)	13.6(10)
C(14)−C(19)−S(5)	122.2(4)	C(52)−C(53)−C(51B)	102.8(11)
C(19)−C(20)−C(21)	110.0(6)	C(52)−C(53)−S(12A)	115.6(7)
C(22)−C(21)−C(20)	113.7(7)	C(51B)−C(53)−S(12A)	12.9(9)
C(21)−C(22)−S(5)	113.3(6)	C(54)#1−O(5)−C(57)	111.7(15)
C(24)−C(23)−C(14)	128.9(5)	O(5)#1−C(54)−C(55)#2	106.6(15)
C(24)−C(23)−S(6)	110.1(5)	C(54)#3−C(55)−C(56)	102.0(14)
C(14)−C(23)−S(6)	121.1(4)	C(57)#4−C(56)−C(55)	111.1(17)
C(23)−C(24)−C(25)	113.6(6)	C(56)#4−C(57)−O(5)	101.9(17)
C(26)−C(25)−C(24)	112.6(6)	C(58)−O(6)−C(61)#5	112.0(19)
C(25)−C(26)−S(6)	111.1(5)	C(59)−C(58)−O(6)	110(2)
O(3)−C(27)−C(32)	110.0(5)	C(58)−C(59)−C(60)	110(2)
O(3)−C(27)−C(28)	107.8(5)	C(59)−C(60)−C(61)#5	110(2)
C(32)−C(27)−C(28)	111.8(6)	C(60)#6−C(61)−O(6)#6	95.7(18)

Symmetry transformations used to generate equivalent atoms:
#1 −x,−y,−z #2 x,y−1,z #3 x,y+1,z #4 −x,−y+1,−z
#5 −x+1,y−1/2,−z+1/2 #6 −x+1,y+1/2,−z+1/2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2349. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	25(1)	23(1)	21(1)	1(1)	8(1)	−1(1)
Sn(2)	24(1)	29(1)	29(1)	−2(1)	9(1)	−2(1)
S(1)	72(1)	33(1)	40(1)	4(1)	30(1)	3(1)
S(2)	53(1)	64(1)	82(2)	17(1)	27(1)	30(1)
S(3)	70(2)	64(1)	44(1)	−12(1)	23(1)	6(1)
S(4)	88(2)	37(1)	49(1)	−17(1)	29(1)	−10(1)
S(5)	46(1)	55(1)	29(1)	10(1)	10(1)	−5(1)
S(6)	43(1)	38(1)	60(1)	2(1)	27(1)	11(1)
S(7)	66(2)	92(2)	75(2)	−18(1)	50(1)	−19(1)
S(8)	51(1)	68(1)	53(1)	−2(1)	5(1)	−18(1)
S(9)	131(3)	80(2)	96(2)	7(2)	47(2)	−35(2)
S(11)	94(2)	37(1)	23(1)	6(1)	16(1)	19(1)
S(10A)	36(2)	31(3)	26(3)	−8(2)	6(2)	−11(2)
S(12A)	43(3)	25(2)	38(2)	1(1)	15(2)	8(1)
S(10B)	48(3)	46(3)	58(3)	10(2)	32(3)	15(2)
S(12B)	40(4)	28(3)	51(3)	1(3)	22(3)	7(3)
O(1)	30(2)	17(2)	29(2)	−3(2)	12(2)	−1(2)
O(2)	26(2)	25(2)	21(2)	−3(2)	9(2)	−2(2)
O(3)	30(2)	37(2)	36(2)	−1(2)	16(2)	−6(2)
O(4)	28(2)	29(2)	23(2)	4(2)	9(2)	3(2)
C(1)	28(3)	22(3)	36(3)	−6(2)	15(3)	0(2)
C(2)	34(4)	25(3)	32(3)	3(2)	10(3)	3(3)
C(3)	48(4)	35(4)	34(3)	5(3)	5(3)	−6(3)
C(4)	57(5)	41(4)	55(5)	21(4)	9(4)	−11(4)
C(5)	63(5)	42(4)	47(4)	13(3)	25(4)	−4(4)
C(6)	35(4)	31(3)	44(4)	−11(3)	16(3)	4(3)
C(7)	44(5)	40(4)	70(5)	−8(4)	33(4)	−1(3)
C(8)	49(5)	52(5)	104(7)	−18(5)	45(5)	−1(4)
C(9)	45(6)	94(8)	112(8)	−26(7)	31(6)	21(5)

C(10)	43(4)	21(3)	30(3)	−2(2)	15(3)	3(3)
C(11)	62(4)	14(3)	5(2)	−11(2)	13(2)	−33(3)
C(12)	59(5)	38(4)	51(4)	−11(3)	17(4)	−14(4)
C(13)	67(5)	49(4)	28(3)	−15(3)	10(3)	−5(4)
C(14)	30(3)	29(3)	18(3)	−3(2)	10(2)	−1(2)
C(15)	38(4)	26(3)	33(3)	−6(3)	15(3)	−5(3)
C(16)	49(4)	24(3)	36(3)	2(3)	22(3)	−1(3)
C(17)	76(6)	35(4)	61(5)	13(4)	33(4)	2(4)
C(18)	92(7)	23(4)	84(6)	−11(4)	47(5)	−4(4)
C(19)	38(4)	31(3)	26(3)	−2(2)	17(3)	−2(3)
C(20)	31(4)	48(4)	27(3)	−4(3)	4(3)	−3(3)
C(21)	41(5)	70(5)	39(4)	−9(4)	3(3)	−13(4)
C(22)	55(5)	70(5)	33(4)	8(4)	2(4)	2(4)
C(23)	33(3)	29(3)	18(3)	2(2)	11(2)	4(3)
C(24)	29(3)	33(3)	27(3)	2(2)	14(3)	3(3)
C(25)	36(4)	50(4)	35(4)	2(3)	17(3)	−5(3)
C(26)	38(4)	58(5)	53(4)	1(4)	24(4)	4(3)
C(27)	35(4)	37(3)	38(3)	−3(3)	20(3)	−11(3)
C(28)	46(4)	37(4)	46(4)	0(3)	25(3)	−3(3)
C(29)	37(4)	30(3)	31(3)	−5(3)	12(3)	−4(3)
C(30)	73(6)	55(5)	45(4)	−14(4)	26(4)	−6(4)
C(31)	102(8)	68(6)	56(5)	−14(4)	52(5)	−7(5)
C(32)	30(4)	44(4)	52(4)	3(3)	16(3)	−11(3)
C(33)	46(5)	52(4)	55(5)	−3(4)	18(4)	−2(4)
C(34)	54(6)	79(7)	131(10)	35(7)	30(7)	14(5)
C(35)	49(6)	90(7)	72(6)	24(6)	−11(5)	−14(5)
C(36)	40(4)	41(4)	37(4)	−1(3)	9(3)	−11(3)
C(37)	15(3)	0(2)	27(3)	−6(2)	12(2)	−11(2)
C(38)	83(8)	49(5)	92(7)	−8(5)	27(6)	−1(5)
C(39)	101(9)	48(5)	84(7)	9(5)	25(6)	−31(5)
C(40)	35(4)	27(3)	17(3)	4(2)	8(2)	8(3)
C(41)	34(4)	30(3)	28(3)	6(3)	9(3)	8(3)
C(42A)	140(30)	70(20)	130(30)	−10(20)	−40(20)	−10(19)
C(42B)	33(9)	18(10)	0(9)	−22(6)	−2(7)	4(7)
C(43)	53(6)	85(7)	67(6)	23(5)	38(5)	19(5)
C(44)	37(5)	68(6)	99(8)	31(6)	19(5)	−4(4)
C(46)	36(4)	27(3)	24(3)	2(2)	9(3)	3(3)
C(47)	60(5)	36(4)	25(3)	−2(3)	11(3)	13(3)
C(48)	67(6)	46(4)	29(4)	−11(3)	10(3)	16(4)
C(49)	90(6)	44(4)	24(3)	−3(3)	18(4)	4(4)
C(50)	47(4)	29(3)	20(3)	2(2)	15(3)	11(3)
C(51A)	11(10)	19(8)	47(10)	−14(6)	14(8)	20(6)
C(51B)	33(16)	190(40)	80(20)	−27(19)	23(14)	−8(16)
C(52)	98(8)	46(5)	82(6)	−20(4)	58(6)	−32(5)
C(53)	107(9)	35(4)	49(5)	7(3)	35(5)	16(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for sh2349.

	x	y	z	U(eq)
H(3)	3116	4806	1851	50
H(4)	3201	5255	852	65
H(5)	2948	4257	94	59
H(7)	1542	2525	2415	57
H(8)	259	3137	2254	76
H(9)	57	4268	1649	99
H(11)	4472	3456	2576	32
H(12)	4934	3867	3699	60
H(13)	3948	3870	4134	60
H(16)	3487	−42	1752	41
H(17)	3546	−1458	1709	66
H(18)	3163	−1942	669	74
H(20)	1515	324	44	45
H(21)	623	1000	−889	64
H(22)	1256	1993	−1234	68
H(24)	3967	2289	664	34
H(25)	5293	2277	609	47
H(26)	5755	985	528	57
H(29)	2525	1145	2835	39
H(30)	2484	1489	3846	67
H(31)	1225	1308	3915	83
H(33)	5	1842	1786	61

H(34)	−1029	2087	772	107
H(35)	−958	1232	−35	95
H(37)	1849	−631	1197	15
H(38)	1501	−2051	1409	91
H(39)	730	−2143	2020	96
H(42A)	5195	151	2216	165
H(42B)	5765	1707	3501	23
H(43)	6255	927	2072	77
H(44)	6706	1813	2884	83
H(47)	3828	2056	3428	50
H(48)	4065	2296	4532	59
H(49)	4756	1263	5187	64
H(51A)	2965	−343	2674	30
H(51B)	5185	−868	3348	121
H(52)	3085	−1733	2902	82
H(53)	4401	−2109	3236	74

Compound 15

Table 1. Crystal data and structure refinement for sh2400.

Identification code	sh2400	
Empirical formula	C30 H26 O3 S6 Sn	
Formula weight	745.56	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 13.9406(11) Å	α = 90°.
	b = 23.572(2) Å	β = 90°.
	c = 9.2198(7) Å	γ = 90°.
Volume	3029.7(4) Å^3	
Z	4	
Density (calculated)	1.635 Mg/m^3	
Absorption coefficient	1.289 mm^{-1}	
F(000)	1504	
Crystal size	0.17 x 0.38 x 0.76 mm^3	
Theta range for data collection	1.73 to 41.46°.	
Index ranges	−25<=h<=24, −43<=k<=43, −16<=l<=16	
Reflections collected	136807	
Independent reflections	10184 [R(int) = 0.0400]	
Completeness to theta = 41.46°	97.8 %	
Absorption correction	Multi scan	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	10184 / 0 / 196	
Goodness−of−fit on F^2	1.249	
Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.1488	
R indices (all data)	R1 = 0.0785, wR2 = 0.1566	
Largest diff. peak and hole	2.838 and −5.639 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2400. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn	3326(1)	2500	7242(1)	13(1)
S(1)	3459(1)	944(1)	4249(1)	22(1)
S(2)	5983(1)	1640(1)	5205(1)	23(1)
S(3)	4790(1)	1670(1)	9619(1)	22(1)
O(1)	4365(1)	1937(1)	6664(2)	16(1)
C(1)	4357(2)	1342(1)	6785(3)	13(1)
C(2)	3474(2)	1084(1)	6074(3)	15(1)
C(3)	2541(2)	1007(1)	6683(3)	16(1)
C(4)	1894(2)	800(1)	5609(4)	23(1)
C(5)	2277(2)	763(1)	4269(4)	23(1)
C(6)	5266(2)	1140(1)	6021(3)	14(1)
C(7)	5612(2)	570(2)	5843(3)	22(1)
C(8)	6477(2)	597(1)	4952(4)	20(1)
C(9)	6746(2)	1133(1)	4564(4)	23(1)
C(10)	4394(2)	1174(1)	8388(3)	14(1)

C(11)	4187(2)	641(1)	9045(3)	19(1)
C(12)	4371(2)	688(1)	10604(4)	21(1)
C(13)	4693(2)	1209(2)	11023(4)	22(1)
O(2)	2903(2)	2500	4874(4)	29(1)
C(14)	3540(4)	2500	3621(5)	23(1)
C(15)	2874(5)	2500	2312(6)	36(1)
C(16)	1890(6)	2353(4)	2936(8)	33(2)
C(17)	1937(5)	2372(3)	4403(9)	27(1)

Table 3. Bond lengths [Å] and angles [°] for sh2400.

Sn−O(1)	2.0359(19)	C(3)−C(4)	1.425(4)
Sn−O(1)#1	2.0360(19)	C(4)−C(5)	1.349(5)
Sn−O(2)	2.261(4)	C(6)−C(7)	1.436(4)
S(1)−C(5)	1.703(3)	C(7)−C(8)	1.460(4)
S(1)−C(2)	1.715(3)	C(8)−C(9)	1.366(4)
S(2)−C(9)	1.706(3)	C(10)−C(11)	1.423(4)
S(2)−C(6)	1.720(3)	C(11)−C(12)	1.464(4)
S(3)−C(13)	1.696(4)	C(12)−C(13)	1.363(5)
S(3)−C(10)	1.721(3)	O(2)−C(17)	1.446(7)
O(1)−C(1)	1.406(3)	O(2)−C(17)#1	1.446(7)
C(1)−C(2)	1.521(4)	O(2)−C(14)	1.457(6)
C(1)−C(6)	1.526(3)	C(14)−C(15)	1.523(8)
C(1)−C(10)	1.531(4)	C(15)−C(16)	1.527(11)
C(2)−C(3)	1.429(4)	C(16)−C(17)	1.355(11)

O(1)−Sn−O(1)#1	81.46(11)	C(1)−C(6)−S(2)	118.08(17)
O(1)−Sn−O(2)	86.16(9)	C(6)−C(7)−C(8)	107.6(3)
O(1)#1−Sn−O(2)	86.17(9)	C(9)−C(8)−C(7)	114.4(3)
C(5)−S(1)−C(2)	92.82(15)	C(8)−C(9)−S(2)	112.8(2)
C(9)−S(2)−C(6)	91.88(14)	C(11)−C(10)−C(1)	129.3(2)
C(13)−S(3)−C(10)	92.42(15)	C(11)−C(10)−S(3)	112.5(2)
C(1)−O(1)−Sn	128.60(16)	C(1)−C(10)−S(3)	118.12(17)
O(1)−C(1)−C(2)	111.8(2)	C(10)−C(11)−C(12)	108.4(3)
O(1)−C(1)−C(6)	105.52(19)	C(13)−C(12)−C(11)	113.8(3)
C(2)−C(1)−C(6)	110.4(2)	C(12)−C(13)−S(3)	112.8(2)
O(1)−C(1)−C(10)	109.5(2)	C(17)−O(2)−C(17)#1	24.0(5)
C(2)−C(1)−C(10)	109.9(2)	C(17)−O(2)−C(14)	109.2(4)
C(6)−C(1)−C(10)	109.7(2)	C(17)#1−O(2)−C(14)	109.2(4)
C(3)−C(2)−C(1)	128.2(2)	C(17)−O(2)−Sn	122.2(4)
C(3)−C(2)−S(1)	110.50(19)	C(17)#1−O(2)−Sn	122.2(4)
C(1)−C(2)−S(1)	120.65(19)	C(14)−O(2)−Sn	127.3(3)
C(4)−C(3)−C(2)	110.2(3)	O(2)−C(14)−C(15)	104.9(4)
C(5)−C(4)−C(3)	114.2(3)	C(14)−C(15)−C(16)	104.4(5)
C(4)−C(5)−S(1)	112.1(2)	C(17)−C(16)−C(15)	109.0(6)
C(7)−C(6)−C(1)	128.6(2)	C(16)−C(17)−O(2)	110.6(6)
C(7)−C(6)−S(2)	113.3(2)		

Symmetry transformations used to generate equivalent atoms:
#1 x,−y+1/2,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2400. The anisotropic displacement factor exponent takes the form: $-2p^2[\,h^2 a^{*2}U^{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn	13(1)	11(1)	16(1)	0	4(1)	0
S(1)	22(1)	23(1)	20(1)	0(1)	1(1)	−4(1)
S(2)	20(1)	18(1)	29(1)	3(1)	8(1)	0(1)
S(3)	23(1)	20(1)	23(1)	−3(1)	0(1)	−1(1)
O(1)	15(1)	8(1)	23(1)	1(1)	4(1)	0(1)
C(1)	12(1)	9(1)	18(1)	1(1)	3(1)	−1(1)
C(2)	14(1)	12(1)	18(1)	2(1)	0(1)	−1(1)
C(3)	14(1)	21(1)	14(1)	1(1)	−1(1)	−8(1)
C(4)	13(1)	21(1)	36(2)	0(1)	−2(1)	−1(1)
C(5)	26(1)	22(1)	23(1)	2(1)	−7(1)	−4(1)
C(6)	13(1)	10(1)	18(1)	0(1)	2(1)	0(1)
C(7)	8(1)	34(1)	22(1)	−18(1)	3(1)	1(1)
C(8)	19(1)	18(1)	23(1)	−3(1)	4(1)	4(1)
C(9)	18(1)	24(1)	26(1)	3(1)	6(1)	2(1)
C(10)	12(1)	12(1)	17(1)	0(1)	1(1)	0(1)
C(11)	11(1)	31(1)	14(1)	8(1)	2(1)	3(1)
C(12)	18(1)	23(1)	22(1)	5(1)	2(1)	0(1)

C(13)	20(1)	28(1)	20(1)	−3(1)	2(1)	0(1)
O(2)	16(1)	52(2)	19(1)	0	−3(1)	0
C(14)	26(2)	25(2)	18(2)	0	2(1)	0
C(15)	44(3)	43(3)	20(2)	0	−6(2)	0
C(16)	31(3)	39(4)	30(3)	0(2)	−16(3)	−4(2)
C(17)	18(2)	22(3)	40(3)	6(2)	−10(2)	−3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for sh2400.

	x	y	z	U(eq)
H(3)	2375	1082	7664	20
H(4)	1250	698	5818	28
H(5)	1928	648	3434	28
H(7)	5329	237	6233	26
H(8)	6824	268	4666	24
H(9)	7299	1215	3999	27
H(11)	3967	311	8556	22
H(12)	4274	384	11264	25
H(13)	4848	1304	11997	27
H(14A)	3953	2158	3621	28
H(14B)	3953	2842	3621	28
H(15A)	3078	2213	1591	43
H(15B)	2864	2877	1841	43
H(16A)	1406	2627	2582	40
H(16B)	1697	1969	2617	40
H(17A)	1735	2003	4810	32
H(17B)	1493	2667	4770	32

Compound 16a

Table 1. Crystal data and structure refinement for sh2359.

Identification code	sh2359	
Empirical formula	C47 H43 O5 S9 Y	
Formula weight	1065.26	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.889(4) Å	α = 90°.
	b = 14.421(3) Å	β = 94.75(3)°.
	c = 16.190(3) Å	γ = 90°.
Volume	4860.4(17) Å^3	
Z	4	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	1.631 mm^{-1}	
F(000)	2192	
Crystal size	0.25 x 0.4 x 0.55 mm^3	
Theta range for data collection	1.89 to 24.11°.	
Index ranges	−23<=h<=22, −16<=k<=16, −18<=l<=18	
Reflections collected	28041	
Independent reflections	7593 [R(int) = 0.0738]	
Completeness to theta = 24.11°	98.2 %	
Absorption correction	Empirical	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	7593 / 0 / 559	
Goodness−of−fit on F^2	1.972	
Final R indices [I>2sigma(I)]	R1 = 0.0742, wR2 = 0.2067	
R indices (all data)	R1 = 0.0876, wR2 = 0.2130	
Largest diff. peak and hole	1.981 and −1.057 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2359. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y	2592(1)	609(1)	7717(1)	20(1)
S(1)	4536(1)	3544(2)	7651(2)	77(1)
S(2)	4525(1)	725(2)	8918(2)	67(1)

S(3)	4244(1)	413(2)	6233(2)	58(1)
S(4)	1315(1)	−1312(2)	8435(2)	65(1)
S(5)	3205(1)	−3293(2)	8477(2)	54(1)
S(6)	1736(1)	−2403(2)	6292(1)	49(1)
S(7)	1753(1)	3517(2)	7231(2)	85(1)
S(8)	1182(1)	1238(1)	9334(1)	40(1)
S(9)	840(1)	284(2)	6757(2)	63(1)
O(1)	3503(2)	1203(3)	7689(3)	29(1)
O(2)	2471(2)	−824(3)	7739(3)	27(1)
O(3)	1837(2)	1561(3)	7833(3)	28(1)
O(4)	2446(2)	660(3)	6240(3)	31(1)
O(5)	2784(2)	542(3)	9200(3)	29(1)
C(1)	4051(3)	1692(4)	7501(4)	27(1)
C(2)	3950(3)	2731(4)	7660(4)	30(2)
C(3)	3313(3)	3106(3)	7867(3)	13(1)
C(4)	4054(5)	4403(6)	7866(6)	62(3)
C(5)	3443(4)	4134(5)	7961(5)	47(2)
C(6)	4634(3)	1373(4)	8050(4)	29(1)
C(7)	5270(3)	1541(6)	7994(5)	44(2)
C(8)	5672(4)	1155(6)	8659(5)	46(2)
C(9)	5326(4)	693(7)	9197(6)	64(3)
C(10)	4180(3)	1545(5)	6578(4)	30(2)
C(11)	4238(3)	2148(5)	5933(4)	32(2)
C(12)	4333(4)	1689(8)	5164(5)	56(2)
C(13)	4346(4)	762(7)	5245(6)	59(2)
C(14)	2457(3)	−1791(4)	7759(4)	22(1)
C(15)	1841(3)	−2098(4)	8161(4)	24(1)
C(16)	1628(2)	−3127(3)	8309(3)	7(1)
C(17)	807(4)	−2078(8)	8737(5)	57(2)
C(18)	977(4)	−2942(7)	8649(5)	57(2)
C(19)	3067(3)	−2154(4)	8245(4)	25(1)
C(20)	3627(3)	−1587(4)	8512(4)	28(1)
C(21)	4092(4)	−2167(7)	8916(6)	58(2)
C(22)	3947(4)	−3059(7)	8942(5)	56(2)
C(23)	2450(3)	−2177(4)	6871(4)	27(1)
C(24)	2974(4)	−2273(4)	6389(4)	31(2)
C(25)	2764(5)	−2534(5)	5557(5)	47(2)
C(26)	2135(5)	−2615(5)	5419(5)	53(2)
C(27)	1199(3)	1873(4)	7685(4)	27(1)
C(28)	1180(3)	2926(5)	7638(4)	35(2)
C(29)	596(2)	3573(3)	7904(3)	8(1)
C(30)	850(6)	4500(6)	7594(7)	76(3)
C(31)	1424(5)	4513(6)	7274(6)	65(3)
C(32)	799(3)	1543(5)	8399(4)	34(2)
C(33)	146(3)	1501(5)	8419(5)	42(2)
C(34)	−37(4)	1199(6)	9211(5)	47(2)
C(35)	467(4)	1028(6)	9765(5)	50(2)
C(36)	922(3)	1469(5)	6862(4)	31(2)
C(37)	783(3)	1968(5)	6077(4)	31(2)
C(38)	573(4)	1242(8)	5450(6)	62(3)
C(39)	594(4)	361(8)	5737(6)	67(3)
C(40)	2421(5)	−125(5)	5676(5)	54(2)
C(41)	2287(7)	236(6)	4833(5)	79(4)
C(42)	2362(6)	1221(6)	4864(5)	65(3)
C(43)	2457(3)	1499(4)	5753(4)	33(2)
C(44)	2938(4)	1358(5)	9699(4)	42(2)
C(45)	3059(6)	1013(6)	10584(5)	64(3)
C(46)	2645(4)	163(6)	10603(5)	48(2)
C(47)	2689(5)	−234(5)	9750(4)	48(2)

Table 3. Bond lengths [Å] and angles [°] for sh2359.

Y−O(2)	2.083(4)	C(6)−C(7)	1.361(9)
Y−O(1)	2.091(4)	C(7)−C(8)	1.423(11)
Y−O(3)	2.111(4)	C(8)−C(9)	1.352(11)
Y−O(4)	2.386(4)	C(10)−C(11)	1.372(10)
Y−O(5)	2.404(4)	C(11)−C(12)	1.437(11)
S(1)−C(4)	1.652(10)	C(12)−C(13)	1.343(13)
S(1)−C(2)	1.696(7)	C(14)−C(19)	1.533(9)
S(2)−C(9)	1.698(9)	C(14)−C(23)	1.541(8)
S(2)−C(6)	1.719(7)	C(14)−C(15)	1.554(8)
S(3)−C(13)	1.707(10)	C(15)−C(16)	1.574(7)
S(3)−C(10)	1.733(7)	C(16)−C(18)	1.532(10)
S(4)−C(17)	1.635(9)	C(17)−C(18)	1.305(13)

S(4)−C(15)	1.664(6)	C(19)−C(20)	1.461(9)
S(5)−C(22)	1.700(9)	C(20)−C(21)	1.402(11)
S(5)−C(19)	1.704(6)	C(21)−C(22)	1.322(13)
S(6)−C(23)	1.726(7)	C(23)−C(24)	1.401(9)
S(6)−C(26)	1.728(9)	C(24)−C(25)	1.432(10)
S(7)−C(31)	1.596(10)	C(25)−C(26)	1.320(13)
S(7)−C(28)	1.650(7)	C(27)−C(28)	1.521(9)
S(8)−C(32)	1.710(7)	C(27)−C(36)	1.525(9)
S(8)−C(35)	1.725(8)	C(27)−C(32)	1.555(9)
S(9)−C(39)	1.692(11)	C(28)−C(29)	1.623(7)
S(9)−C(36)	1.724(7)	C(29)−C(30)	1.537(11)
O(1)−C(1)	1.399(7)	C(30)−C(31)	1.344(14)
O(2)−C(14)	1.394(7)	C(32)−C(33)	1.369(10)
O(3)−C(27)	1.409(7)	C(33)−C(34)	1.436(11)
O(4)−C(43)	1.445(7)	C(34)−C(35)	1.348(12)
O(4)−C(40)	1.452(8)	C(36)−C(37)	1.468(10)
O(5)−C(44)	1.450(8)	C(37)−C(38)	1.498(12)
O(5)−C(47)	1.454(8)	C(38)−C(39)	1.352(14)
C(1)−C(6)	1.518(9)	C(40)−C(41)	1.466(12)
C(1)−C(2)	1.538(9)	C(41)−C(42)	1.430(12)
C(1)−C(10)	1.555(9)	C(42)−C(43)	1.492(11)
C(2)−C(3)	1.499(8)	C(44)−C(45)	1.518(11)
C(3)−C(5)	1.513(9)	C(45)−C(46)	1.502(12)
C(4)−C(5)	1.354(13)	C(46)−C(47)	1.504(10)

O(2)−Y−O(1)	121.24(17)	C(19)−C(14)−C(23)	107.4(5)
O(2)−Y−O(3)	123.48(16)	O(2)−C(14)−C(15)	108.3(5)
O(1)−Y−O(3)	115.03(17)	C(19)−C(14)−C(15)	111.7(5)
O(2)−Y−O(4)	92.44(15)	C(23)−C(14)−C(15)	110.1(5)
O(1)−Y−O(4)	90.43(17)	C(14)−C(15)−C(16)	126.0(5)
O(3)−Y−O(4)	92.00(17)	C(14)−C(15)−S(4)	120.3(4)
O(2)−Y−O(5)	87.28(15)	C(16)−C(15)−S(4)	113.6(4)
O(1)−Y−O(5)	87.78(16)	C(18)−C(16)−C(15)	99.3(5)
O(3)−Y−O(5)	90.05(16)	C(18)−C(17)−S(4)	115.0(6)
O(4)−Y−O(5)	177.72(15)	C(17)−C(18)−C(16)	117.6(7)
C(4)−S(1)−C(2)	93.6(4)	C(20)−C(19)−C(14)	124.8(5)
C(9)−S(2)−C(6)	92.2(4)	C(20)−C(19)−S(5)	111.0(5)
C(13)−S(3)−C(10)	92.5(4)	C(14)−C(19)−S(5)	124.1(4)
C(17)−S(4)−C(15)	94.5(4)	C(21)−C(20)−C(19)	108.1(6)
C(22)−S(5)−C(19)	92.1(4)	C(22)−C(21)−C(20)	116.4(8)
C(23)−S(6)−C(26)	91.3(4)	C(21)−C(22)−S(5)	112.4(7)
C(31)−S(7)−C(28)	96.8(4)	C(24)−C(23)−C(14)	127.4(6)
C(32)−S(8)−C(35)	92.6(4)	C(24)−C(23)−S(6)	111.0(5)
C(39)−S(9)−C(36)	92.9(5)	C(14)−C(23)−S(6)	121.0(5)
C(1)−O(1)−Y	166.8(4)	C(23)−C(24)−C(25)	111.0(7)
C(14)−O(2)−Y	174.3(4)	C(26)−C(25)−C(24)	113.9(7)
C(27)−O(3)−Y	153.6(4)	C(25)−C(26)−S(6)	112.8(6)
C(43)−O(4)−C(40)	108.2(5)	O(3)−C(27)−C(28)	110.3(5)
C(43)−O(4)−Y	124.4(4)	O(3)−C(27)−C(36)	108.2(5)
C(40)−O(4)−Y	126.9(4)	C(28)−C(27)−C(36)	109.3(6)
C(44)−O(5)−C(47)	108.5(5)	O(3)−C(27)−C(32)	109.6(5)
C(44)−O(5)−Y	122.4(4)	C(28)−C(27)−C(32)	109.3(5)
C(47)−O(5)−Y	128.6(4)	C(36)−C(27)−C(32)	110.2(5)
O(1)−C(1)−C(6)	110.5(5)	C(27)−C(28)−C(29)	125.3(5)
O(1)−C(1)−C(2)	109.2(5)	C(27)−C(28)−S(7)	121.3(5)
C(6)−C(1)−C(2)	108.2(5)	C(29)−C(28)−S(7)	113.2(4)
O(1)−C(1)−C(10)	110.5(5)	C(30)−C(29)−C(28)	97.2(5)
C(6)−C(1)−C(10)	109.1(5)	C(31)−C(30)−C(29)	118.8(7)
C(2)−C(1)−C(10)	109.3(5)	C(30)−C(31)−S(7)	113.9(7)
C(3)−C(2)−C(1)	121.7(5)	C(33)−C(32)−C(27)	128.9(7)
C(3)−C(2)−S(1)	114.0(4)	C(33)−C(32)−S(8)	111.2(5)
C(1)−C(2)−S(1)	124.2(5)	C(27)−C(32)−S(8)	119.7(5)
C(2)−C(3)−C(5)	102.8(5)	C(32)−C(33)−C(34)	111.9(7)
C(5)−C(4)−S(1)	114.0(6)	C(35)−C(34)−C(33)	113.5(7)
C(4)−C(5)−C(3)	115.5(7)	C(34)−C(35)−S(8)	110.7(6)
C(7)−C(6)−C(1)	130.3(6)	C(37)−C(36)−C(27)	127.1(6)
C(7)−C(6)−S(2)	110.3(5)	C(37)−C(36)−S(9)	112.9(5)
C(1)−C(6)−S(2)	119.3(5)	C(27)−C(36)−S(9)	119.5(5)
C(6)−C(7)−C(8)	113.5(6)	C(36)−C(37)−C(38)	105.6(7)
C(9)−C(8)−C(7)	111.5(7)	C(39)−C(38)−C(37)	115.1(8)
C(8)−C(9)−S(2)	112.5(6)	C(38)−C(39)−S(9)	113.3(7)
C(11)−C(10)−C(1)	132.7(6)	O(4)−C(40)−C(41)	107.6(6)
C(11)−C(10)−S(3)	109.7(5)	C(42)−C(41)−C(40)	107.9(7)

C(1)−C(10)−S(3)	117.5(5)	C(41)−C(42)−C(43)	107.9(7)
C(10)−C(11)−C(12)	113.3(7)	O(4)−C(43)−C(42)	107.1(5)
C(13)−C(12)−C(11)	112.1(8)	O(5)−C(44)−C(45)	105.8(6)
C(12)−C(13)−S(3)	112.4(7)	C(46)−C(45)−C(44)	103.6(7)
O(2)−C(14)−C(19)	109.6(5)	C(45)−C(46)−C(47)	102.3(6)
O(2)−C(14)−C(23)	109.8(5)	O(5)−C(47)−C(46)	106.9(6)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2359. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y	24(1)	17(1)	19(1)	0(1)	4(1)	0(1)
S(1)	71(2)	55(1)	107(2)	−13(1)	24(2)	−13(1)
S(2)	37(1)	96(2)	68(2)	53(1)	−1(1)	−6(1)
S(3)	74(2)	48(1)	53(1)	−17(1)	6(1)	9(1)
S(4)	53(1)	75(2)	68(2)	−2(1)	10(1)	9(1)
S(5)	58(1)	44(1)	58(1)	7(1)	−2(1)	11(1)
S(6)	60(1)	54(1)	31(1)	−8(1)	−6(1)	−10(1)
S(7)	78(2)	59(2)	121(3)	2(2)	21(2)	−1(1)
S(8)	41(1)	49(1)	33(1)	6(1)	7(1)	6(1)
S(9)	67(1)	54(1)	66(2)	−10(1)	−8(1)	−12(1)
O(1)	27(2)	30(2)	32(3)	−1(2)	7(2)	−4(2)
O(2)	36(2)	20(2)	25(2)	−4(2)	2(2)	−1(2)
O(3)	22(2)	30(2)	33(3)	0(2)	1(2)	3(2)
O(4)	51(3)	23(2)	18(2)	0(2)	5(2)	−4(2)
O(5)	45(3)	22(2)	19(2)	−1(2)	3(2)	−5(2)
C(1)	22(3)	31(3)	28(4)	0(3)	2(3)	−3(3)
C(2)	39(4)	27(3)	25(3)	2(3)	4(3)	−3(3)
C(3)	28(3)	4(2)	8(3)	0(2)	7(2)	13(2)
C(4)	96(7)	34(4)	56(6)	−7(4)	8(5)	−11(5)
C(5)	65(5)	35(4)	41(4)	1(3)	12(4)	9(4)
C(6)	33(3)	28(3)	24(3)	2(3)	−1(3)	−4(3)
C(7)	26(4)	59(5)	48(5)	23(4)	8(3)	1(3)
C(8)	32(4)	57(5)	49(5)	10(4)	−3(4)	−1(3)
C(9)	49(5)	88(7)	53(5)	36(5)	−11(4)	0(5)
C(10)	21(3)	38(4)	31(4)	−7(3)	1(3)	5(3)
C(11)	27(3)	46(4)	24(3)	2(3)	5(3)	3(3)
C(12)	44(5)	100(8)	26(4)	−4(4)	12(4)	4(5)
C(13)	45(5)	88(7)	45(5)	−26(5)	3(4)	5(5)
C(14)	35(3)	15(3)	17(3)	−1(2)	4(3)	−1(2)
C(15)	26(3)	23(3)	22(3)	−2(3)	0(3)	−5(2)
C(16)	7(2)	13(2)	1(2)	1(2)	7(2)	−16(2)
C(17)	28(4)	94(7)	52(5)	−11(5)	12(4)	−4(4)
C(18)	56(5)	71(6)	44(5)	2(4)	10(4)	−30(5)
C(19)	25(3)	30(3)	20(3)	−1(3)	7(3)	1(3)
C(20)	11(3)	33(3)	37(4)	−20(3)	−3(3)	8(2)
C(21)	36(4)	80(7)	57(6)	−30(5)	2(4)	−1(4)
C(22)	44(5)	79(7)	45(5)	−1(5)	2(4)	30(5)
C(23)	45(4)	17(3)	18(3)	1(2)	1(3)	−2(3)
C(24)	54(4)	24(3)	15(3)	−1(3)	6(3)	17(3)
C(25)	79(6)	40(4)	25(4)	0(3)	16(4)	9(4)
C(26)	99(7)	37(4)	21(4)	−9(3)	−7(4)	0(4)
C(27)	22(3)	28(3)	32(4)	2(3)	4(3)	6(3)
C(28)	37(4)	29(4)	41(4)	3(3)	11(3)	14(3)
C(29)	0(2)	0(2)	23(3)	5(2)	7(2)	8(2)
C(30)	97(8)	46(5)	87(8)	10(5)	27(7)	38(5)
C(31)	88(7)	37(5)	72(7)	−5(4)	28(6)	−20(5)
C(32)	38(4)	33(4)	31(4)	−1(3)	9(3)	0(3)
C(33)	30(4)	51(5)	45(5)	7(4)	5(3)	−5(3)
C(34)	35(4)	55(5)	54(5)	−6(4)	24(4)	−10(4)
C(35)	61(5)	49(5)	43(5)	3(4)	21(4)	−10(4)
C(36)	21(3)	41(4)	32(4)	−6(3)	4(3)	5(3)
C(37)	17(3)	61(5)	15(3)	−5(3)	−4(3)	17(3)
C(38)	40(4)	104(8)	39(5)	−3(5)	−4(4)	6(5)
C(39)	43(5)	88(7)	66(6)	−28(6)	−11(4)	−14(5)
C(40)	107(7)	27(4)	28(4)	−5(3)	0(4)	0(4)
C(41)	163(11)	45(5)	29(4)	−7(4)	8(6)	−17(6)
C(42)	125(9)	42(5)	30(4)	9(4)	7(5)	3(5)
C(43)	40(4)	26(3)	33(4)	5(3)	6(3)	−3(3)
C(44)	58(5)	36(4)	32(4)	−11(3)	1(4)	−10(4)
C(45)	112(8)	47(5)	35(5)	−10(4)	6(5)	−15(5)

C(46)	69(5)	43(4)	33(4)	−2(4)	5(4)	7(4)
C(47)	90(6)	33(4)	21(4)	6(3)	7(4)	−5(4)

Compound <u>16b</u>

Table 1. Crystal data and structure refinement for sh2443.

Identification code	sh2443	
Empirical formula	C54 H51 O5 S9 Y	
Formula weight	1157.40	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.7243(8) Å	α = 90°.
	b = 15.9300(9) Å	β = 114.404(2)°.
	c = 14.3268(9) Å	γ = 90°.
Volume	2644.6(3) Å^3	
Z	2	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	1.505 mm^{-1}	
F(000)	1196	
Crystal size	0.3 x 0.5 x 0.65 mm^3	
Theta range for data collection	1.56 to 36.80°.	
Index ranges	−20<=h<=21, −25<=k<=26, −24<=l<=21	
Reflections collected	63311	
Independent reflections	23073 [R(int) = 0.0342]	
Completeness to theta = 36.80°	99.0 %	
Absorption correction	Semi−empirical from equivalents	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	23073 / 9 / 629	
Goodness−of−fit on F^2	1.440	
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1460	
R indices (all data)	R1 = 0.0676, wR2 = 0.1489	
Absolute structure parameter	−0.002(3)	
Largest diff. peak and hole	3.226 and −1.747 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2443. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	−882(1)	5204(1)	1868(1)	11(1)
S(1)	300(1)	5341(1)	−620(1)	21(1)
S(2)	2565(1)	6244(1)	2552(1)	22(1)
S(3)	1837(1)	3103(1)	995(1)	54(1)
S(4)	1757(1)	5238(1)	4530(1)	37(1)
S(5)	511(1)	3006(1)	4602(1)	27(1)
S(6A)	−1327(2)	5092(1)	5744(1)	23(1)
S(6B)	−2040(2)	5867(2)	3922(2)	14(1)
S(7)	−3040(1)	7250(1)	1756(1)	22(1)
S(8)	−4857(1)	4228(1)	−186(1)	27(1)
S(9)	−3391(1)	5838(1)	−1104(1)	46(1)
O(1)	486(2)	5157(2)	1399(2)	18(1)
O(2)	−563(2)	4864(1)	3350(2)	18(1)
O(3)	−2541(2)	5664(1)	1035(2)	19(1)
O(4)	−1536(2)	3892(1)	1103(2)	18(1)
O(5)	−312(2)	6612(1)	2238(2)	16(1)
C(1)	1489(2)	4809(2)	1410(2)	15(1)
C(2)	1520(2)	4967(2)	362(2)	18(1)
C(3)	2406(3)	4860(2)	56(3)	26(1)
C(4)	2063(3)	5065(3)	−1001(2)	29(1)
C(5)	969(3)	5342(2)	−1454(2)	26(1)
C(6)	2553(2)	5194(2)	2252(2)	16(1)
C(7)	3948(3)	6175(2)	3500(2)	26(1)
C(8)	4359(3)	5388(2)	3577(2)	25(1)
C(9)	3575(3)	4831(2)	2865(3)	24(1)
C(10)	1501(2)	3860(2)	1616(2)	18(1)
C(11)	1225(2)	3532(1)	2534(2)	3(1)
C(12)	1304(3)	2562(2)	2379(3)	31(1)

C(13)	1588(4)	2344(3)	1618(4)	46(1)
C(14)	−367(2)	4654(2)	4344(2)	14(1)
C(15)	896(2)	4865(2)	5058(2)	15(1)
C(16)	1472(2)	4750(1)	6259(2)	7(1)
C(17)	2703(3)	5045(2)	6461(2)	25(1)
C(18)	2882(3)	5295(2)	5630(3)	25(1)
C(19)	−567(2)	3714(2)	4396(2)	14(1)
C(20)	−1723(2)	3299(1)	4093(2)	12(1)
C(21)	−1484(3)	2400(2)	4108(2)	26(1)
C(22)	−393(3)	2181(2)	4326(2)	25(1)
C(23)	−1194(2)	5155(2)	4659(2)	17(1)
C(24A)	−1958(12)	5822(11)	4010(11)	50
C(24B)	−1367(17)	5147(15)	5555(13)	50
C(25)	−2609(3)	6161(2)	4625(4)	44(1)
C(26)	−2284(4)	5797(3)	5506(4)	45(1)
C(27)	−3747(2)	5747(2)	680(2)	16(1)
C(28)	−4012(2)	6447(2)	1277(2)	16(1)
C(29)	−5013(3)	6565(2)	1458(3)	24(1)
C(30)	−4901(3)	7342(2)	2020(3)	26(1)
C(31)	−3894(3)	7773(2)	2211(3)	26(1)
C(32)	−4266(2)	4923(2)	810(2)	16(1)
C(33)	−4240(2)	4594(2)	1776(3)	20(1)
C(34)	−4762(3)	3751(2)	1537(3)	27(1)
C(35)	−5084(3)	3496(2)	573(3)	27(1)
C(36)	−4227(2)	5996(2)	−448(2)	17(1)
C(37)	−5267(3)	6342(2)	−1072(2)	24(1)
C(38)	−5366(3)	6482(2)	−2084(3)	31(1)
C(39)	−4423(4)	6243(4)	−2210(3)	49(1)
C(40)	−1872(3)	3167(2)	1539(2)	21(1)
C(41)	−2279(3)	2519(2)	699(3)	28(1)
C(42)	−1648(3)	2757(2)	31(3)	29(1)
C(43)	−1672(3)	3703(2)	68(2)	25(1)
C(44)	113(3)	7101(2)	3170(2)	24(1)
C(45)	6(4)	8006(2)	2837(3)	36(1)
C(46)	188(4)	7958(3)	1863(3)	39(1)
C(47)	−389(3)	7142(2)	1377(2)	22(1)
C(48)	−5989(4)	8629(2)	3925(3)	33(1)
C(49)	−6379(3)	8246(3)	4590(3)	32(1)
C(50)	−5633(4)	7868(3)	5496(3)	39(1)
C(51)	−4446(4)	7861(3)	5742(4)	44(1)
C(52)	−4038(4)	8217(3)	5119(4)	48(1)
C(53)	−4801(4)	8604(3)	4196(4)	44(1)
C(54)	−6781(5)	9041(4)	2954(4)	60(2)

Table 3. Bond lengths [Å] and angles [°] for sh2443.

Y(1)−O(2)	2.062(2)	C(11)−C(12)	1.571(4)
Y(1)−O(3)	2.082(2)	C(12)−C(13)	1.328(7)
Y(1)−O(1)	2.1104(18)	C(14)−C(19)	1.524(4)
Y(1)−O(4)	2.348(2)	C(14)−C(23)	1.529(4)
Y(1)−O(5)	2.349(2)	C(14)−C(15)	1.544(4)
S(1)−C(2)	1.714(3)	C(15)−C(16)	1.577(4)
S(1)−C(5)	1.729(3)	C(16)−C(17)	1.544(4)
S(2)−C(6)	1.725(3)	C(17)−C(18)	1.361(5)
S(2)−C(7)	1.726(3)	C(19)−C(20)	1.505(4)
S(3)−C(13)	1.610(5)	C(20)−C(21)	1.462(4)
S(3)−C(10)	1.655(3)	C(21)−C(22)	1.337(5)
S(4)−C(18)	1.637(3)	C(23)−C(24B)	1.389(14)
S(4)−C(15)	1.677(3)	C(23)−C(24A)	1.482(13)
S(5)−C(22)	1.683(4)	C(24A)−C(25)	1.536(14)
S(5)−C(19)	1.706(3)	C(24B)−C(26)	1.539(16)
S(6A)−C(26)	1.586(5)	C(25)−C(26)	1.292(7)
S(6A)−C(23)	1.635(3)	C(27)−C(32)	1.515(4)
S(6B)−C(25)	1.537(6)	C(27)−C(36)	1.525(4)
S(6B)−C(23)	1.620(4)	C(27)−C(28)	1.527(4)
S(7)−C(31)	1.698(4)	C(28)−C(29)	1.413(5)
S(7)−C(28)	1.713(3)	C(29)−C(30)	1.451(5)
S(8)−C(35)	1.699(4)	C(30)−C(31)	1.377(5)
S(8)−C(32)	1.714(3)	C(32)−C(33)	1.469(5)
S(9)−C(36)	1.704(3)	C(33)−C(34)	1.473(5)
S(9)−C(39)	1.712(5)	C(34)−C(35)	1.332(5)
O(1)−C(1)	1.386(3)	C(36)−C(37)	1.370(4)
O(2)−C(14)	1.382(3)	C(37)−C(38)	1.420(5)
O(3)−C(27)	1.409(3)	C(38)−C(39)	1.340(7)

O(4)−C(43)	1.452(4)	C(40)−C(41)	1.506(5)
O(4)−C(40)	1.458(4)	C(41)−C(42)	1.529(5)
O(5)−C(44)	1.444(4)	C(42)−C(43)	1.509(5)
O(5)−C(47)	1.464(4)	C(44)−C(45)	1.508(5)
C(1)−C(6)	1.521(4)	C(45)−C(46)	1.507(6)
C(1)−C(2)	1.538(4)	C(46)−C(47)	1.514(5)
C(1)−C(10)	1.540(4)	C(48)−C(49)	1.385(5)
C(2)−C(3)	1.379(4)	C(48)−C(53)	1.396(6)
C(3)−C(4)	1.430(5)	C(48)−C(54)	1.491(6)
C(4)−C(5)	1.344(5)	C(49)−C(50)	1.390(6)
C(6)−C(9)	1.362(4)	C(50)−C(51)	1.401(6)
C(7)−C(8)	1.345(5)	C(51)−C(52)	1.331(7)
C(8)−C(9)	1.408(4)	C(52)−C(53)	1.417(8)
C(10)−C(11)	1.583(4)		

O(2)−Y(1)−O(3)	113.85(9)	C(20)−C(19)−C(14)	125.5(2)
O(2)−Y(1)−O(1)	118.75(8)	C(20)−C(19)−C(14)	125.5(2)
O(3)−Y(1)−O(1)	127.17(8)	C(20)−C(19)−S(5)	112.29(19)
O(2)−Y(1)−O(4)	97.33(8)	C(14)−C(19)−S(5)	121.3(2)
O(3)−Y(1)−O(4)	88.04(8)	C(21)−C(20)−C(19)	104.7(2)
O(1)−Y(1)−O(4)	89.97(8)	C(22)−C(21)−C(20)	116.7(3)
O(2)−Y(1)−O(5)	96.17(8)	C(21)−C(22)−S(5)	113.2(3)
O(3)−Y(1)−O(5)	86.48(8)	C(24B)−C(23)−C(24A)	105.8(9)
O(1)−Y(1)−O(5)	83.55(8)	C(24B)−C(23)−C(14)	131.2(7)
O(4)−Y(1)−O(5)	166.50(7)	C(24A)−C(23)−C(14)	122.9(6)
C(2)−S(1)−C(5)	91.78(15)	C(24B)−C(23)−S(6B)	107.0(7)
C(6)−S(2)−C(7)	92.04(15)	C(24A)−C(23)−S(6B)	1.6(7)
C(13)−S(3)−C(10)	95.4(2)	C(14)−C(23)−S(6B)	121.8(2)
C(18)−S(4)−C(15)	93.41(15)	C(24B)−C(23)−S(6A)	4.2(8)
C(22)−S(5)−C(19)	93.05(15)	C(24A)−C(23)−S(6A)	110.0(6)
C(26)−S(6A)−C(23)	97.1(2)	C(14)−C(23)−S(6A)	127.1(2)
C(25)−S(6B)−C(23)	98.8(2)	S(6B)−C(23)−S(6A)	111.1(2)
C(31)−S(7)−C(28)	92.82(16)	C(23)−C(24A)−C(25)	105.2(9)
C(35)−S(8)−C(32)	92.44(16)	C(23)−C(24B)−C(26)	111.0(11)
C(36)−S(9)−C(39)	92.3(2)	C(26)−C(25)−C(24A)	111.8(6)
C(1)−O(1)−Y(1)	152.62(19)	C(26)−C(25)−S(6B)	117.1(3)
C(14)−O(2)−Y(1)	178.5(2)	C(24A)−C(25)−S(6B)	5.4(6)
C(27)−O(3)−Y(1)	159.16(18)	C(25)−C(26)−C(24B)	106.1(6)
C(43)−O(4)−C(40)	110.0(2)	C(25)−C(26)−S(6A)	115.8(3)
C(43)−O(4)−Y(1)	122.06(18)	C(24B)−C(26)−S(6A)	9.7(6)
C(40)−O(4)−Y(1)	127.96(17)	O(3)−C(27)−C(32)	109.9(2)
C(44)−O(5)−C(47)	109.7(2)	O(3)−C(27)−C(36)	107.9(2)
C(44)−O(5)−Y(1)	133.33(18)	C(32)−C(27)−C(36)	110.6(2)
C(47)−O(5)−Y(1)	116.92(16)	O(3)−C(27)−C(28)	109.0(2)
O(1)−C(1)−C(6)	111.2(2)	C(32)−C(27)−C(28)	110.8(2)
O(1)−C(1)−C(2)	108.5(2)	C(36)−C(27)−C(28)	108.6(2)
C(6)−C(1)−C(2)	109.6(2)	C(29)−C(28)−C(27)	128.7(3)
O(1)−C(1)−C(10)	109.3(2)	C(29)−C(28)−S(7)	112.5(2)
C(6)−C(1)−C(10)	108.0(2)	C(27)−C(28)−S(7)	118.6(2)
C(2)−C(1)−C(10)	110.2(2)	C(28)−C(29)−C(30)	109.0(3)
C(3)−C(2)−C(1)	130.1(3)	C(31)−C(30)−C(29)	113.9(3)
C(3)−C(2)−S(1)	111.3(2)	C(30)−C(31)−S(7)	111.7(3)
C(1)−C(2)−S(1)	118.64(19)	C(33)−C(32)−C(27)	125.8(2)
C(2)−C(3)−C(4)	112.1(3)	C(33)−C(32)−S(8)	112.7(2)
C(5)−C(4)−C(3)	112.9(3)	C(27)−C(32)−S(8)	121.3(2)
C(4)−C(5)−S(1)	111.9(2)	C(32)−C(33)−C(34)	105.9(3)
C(9)−C(6)−C(1)	129.8(3)	C(35)−C(34)−C(33)	115.8(3)
C(9)−C(6)−S(2)	110.1(2)	C(34)−C(35)−S(8)	113.1(3)
C(1)−C(6)−S(2)	120.1(2)	C(37)−C(36)−C(27)	130.7(3)
C(8)−C(7)−S(2)	111.1(2)	C(37)−C(36)−S(9)	110.8(2)
C(7)−C(8)−C(9)	113.1(3)	C(27)−C(36)−S(9)	118.5(2)
C(6)−C(9)−C(8)	113.7(3)	C(36)−C(37)−C(38)	112.6(3)
C(1)−C(10)−C(11)	119.6(2)	C(39)−C(38)−C(37)	112.7(3)
C(1)−C(10)−S(3)	126.6(2)	C(38)−C(39)−S(9)	111.7(3)
C(11)−C(10)−S(3)	113.7(2)	O(4)−C(40)−C(41)	105.4(2)
C(12)−C(11)−C(10)	99.1(2)	C(40)−C(41)−C(42)	103.5(3)
C(13)−C(12)−C(11)	115.3(3)	C(43)−C(42)−C(41)	101.7(3)
C(12)−C(13)−S(3)	116.2(3)	O(4)−C(43)−C(42)	104.3(3)
O(2)−C(14)−C(19)	109.0(2)	O(5)−C(44)−C(45)	105.8(3)
O(2)−C(14)−C(23)	108.9(2)	C(46)−C(45)−C(44)	102.5(3)
C(19)−C(14)−C(23)	110.5(2)	C(45)−C(46)−C(47)	103.9(3)
O(2)−C(14)−C(15)	109.0(2)	O(5)−C(47)−C(46)	104.8(3)
C(19)−C(14)−C(15)	109.3(2)	C(49)−C(48)−C(53)	116.8(4)

C(23)−C(14)−C(15)	110.2(2)	C(49)−C(48)−C(54)	122.6(4)
C(14)−C(15)−C(16)	125.8(2)	C(53)−C(48)−C(54)	120.7(4)
C(14)−C(15)−S(4)	118.3(2)	C(48)−C(49)−C(50)	122.2(4)
C(16)−C(15)−S(4)	115.94(18)	C(49)−C(50)−C(51)	119.2(4)
C(17)−C(16)−C(15)	98.5(2)	C(52)−C(51)−C(50)	120.4(5)
C(18)−C(17)−C(16)	116.7(3)	C(51)−C(52)−C(53)	120.2(4)
C(17)−C(18)−S(4)	115.5(2)	C(48)−C(53)−C(52)	121.2(4)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2443. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	11(1)	10(1)	11(1)	1(1)	4(1)	0(1)
S(1)	18(1)	24(1)	20(1)	2(1)	6(1)	4(1)
S(2)	22(1)	18(1)	26(1)	−4(1)	9(1)	−3(1)
S(3)	63(1)	45(1)	55(1)	−14(1)	26(1)	−8(1)
S(4)	35(1)	38(1)	38(1)	−2(1)	15(1)	−5(1)
S(5)	32(1)	19(1)	32(1)	2(1)	15(1)	1(1)
S(6A)	28(1)	22(1)	20(1)	2(1)	11(1)	5(1)
S(6B)	8(1)	15(1)	12(1)	1(1)	−2(1)	1(1)
S(7)	23(1)	16(1)	25(1)	−3(1)	8(1)	−2(1)
S(8)	25(1)	18(1)	34(1)	−5(1)	10(1)	−3(1)
S(9)	29(1)	85(1)	31(1)	18(1)	17(1)	12(1)
O(1)	16(1)	17(1)	24(1)	1(1)	12(1)	3(1)
O(2)	23(1)	16(1)	13(1)	2(1)	5(1)	−4(1)
O(3)	12(1)	14(1)	25(1)	0(1)	4(1)	0(1)
O(4)	22(1)	14(1)	18(1)	−4(1)	9(1)	−4(1)
O(5)	22(1)	12(1)	14(1)	−1(1)	7(1)	−4(1)
C(1)	13(1)	14(1)	19(1)	−3(1)	6(1)	1(1)
C(2)	14(1)	21(1)	17(1)	−4(1)	5(1)	1(1)
C(3)	19(1)	37(2)	23(1)	−1(1)	11(1)	5(1)
C(4)	30(1)	41(2)	22(1)	−4(1)	16(1)	0(2)
C(5)	30(2)	27(2)	20(1)	−1(1)	8(1)	−2(1)
C(6)	17(1)	17(1)	16(1)	−2(1)	9(1)	−2(1)
C(7)	23(1)	30(2)	20(1)	−5(1)	4(1)	−13(1)
C(8)	17(1)	30(2)	24(1)	1(1)	5(1)	−6(1)
C(9)	23(1)	21(1)	26(2)	0(1)	8(1)	1(1)
C(10)	11(1)	17(1)	22(1)	−3(1)	2(1)	0(1)
C(11)	0(1)	0(1)	6(1)	8(1)	−2(1)	2(1)
C(12)	16(1)	26(2)	40(2)	11(1)	1(1)	−2(1)
C(13)	39(2)	19(2)	72(3)	−17(2)	14(2)	−3(2)
C(14)	14(1)	12(1)	13(1)	1(1)	4(1)	−2(1)
C(15)	15(1)	12(1)	16(1)	−1(1)	6(1)	−2(1)
C(16)	0(1)	6(1)	7(1)	−7(1)	−7(1)	−3(1)
C(17)	26(1)	19(2)	22(1)	−2(1)	2(1)	−3(1)
C(18)	21(1)	19(1)	37(2)	1(1)	14(1)	0(1)
C(19)	17(1)	12(1)	12(1)	1(1)	5(1)	0(1)
C(20)	28(1)	4(1)	8(1)	2(1)	12(1)	2(1)
C(21)	27(2)	25(2)	20(1)	4(1)	6(1)	−10(1)
C(22)	36(2)	16(1)	19(1)	2(1)	9(1)	4(1)
C(23)	16(1)	11(1)	24(1)	−3(1)	7(1)	−4(1)
C(25)	22(2)	19(2)	86(3)	1(2)	19(2)	6(1)
C(26)	51(2)	39(2)	66(3)	−31(2)	46(2)	−24(2)
C(27)	13(1)	12(1)	19(1)	0(1)	3(1)	2(1)
C(28)	16(1)	13(1)	16(1)	1(1)	2(1)	3(1)
C(29)	30(2)	18(1)	26(2)	1(1)	15(1)	7(1)
C(30)	32(2)	22(2)	30(2)	−3(1)	17(1)	6(1)
C(31)	37(2)	17(1)	24(2)	−2(1)	14(1)	−2(1)
C(32)	12(1)	12(1)	22(1)	−1(1)	4(1)	2(1)
C(33)	13(1)	6(1)	43(2)	1(1)	13(1)	−2(1)
C(34)	23(1)	21(1)	37(2)	10(1)	13(1)	5(1)
C(35)	20(1)	16(1)	42(2)	−4(1)	10(1)	−4(1)
C(36)	16(1)	13(1)	20(1)	0(1)	5(1)	−1(1)
C(37)	19(1)	21(1)	23(1)	−2(1)	0(1)	7(1)
C(38)	32(2)	23(2)	23(2)	5(1)	−3(1)	−3(1)
C(39)	53(3)	67(3)	22(2)	13(2)	11(2)	−13(2)
C(40)	24(1)	16(1)	27(1)	−1(1)	15(1)	−3(1)
C(41)	31(2)	17(1)	39(2)	−6(1)	16(2)	−6(1)
C(42)	29(2)	26(2)	34(2)	−13(1)	16(1)	−7(1)
C(43)	34(2)	24(1)	19(1)	−4(1)	13(1)	−5(1)
C(44)	27(2)	24(2)	19(1)	−9(1)	8(1)	−8(1)

C(45)	37(2)	21(2)	51(2)	−15(2)	19(2)	−2(1)
C(46)	47(2)	22(2)	45(2)	2(2)	18(2)	−10(2)
C(47)	36(2)	15(1)	20(1)	3(1)	16(1)	−2(1)
C(48)	50(2)	28(2)	27(2)	−9(1)	21(2)	−10(2)
C(49)	26(2)	41(2)	32(2)	2(2)	14(1)	2(2)
C(50)	42(2)	41(2)	38(2)	−1(2)	20(2)	1(2)
C(51)	34(2)	44(2)	39(2)	−16(2)	1(2)	0(2)
C(52)	28(2)	59(3)	61(3)	−30(2)	24(2)	−16(2)
C(53)	55(3)	44(2)	51(2)	−24(2)	40(2)	−26(2)
C(54)	82(4)	70(4)	30(2)	12(2)	24(2)	5(3)

Compound 17a

Table 1. Crystal data and structure refinement for sh2344.

Identification code	sh2344	
Empirical formula	C49 H37 N2 O3 S9 Y	
Formula weight	1079.26	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.802(4) Å	α = 90°.
	b = 14.573(3) Å	β = 93.55(3)°.
	c = 16.041(3) Å	γ = 90°.
Volume	4853.6(17) Å^3	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	1.633 mm^{-1}	
F(000)	2208	
Crystal size	0.35 x 0.45 x 0.6 mm^3	
Theta range for data collection	1.89 to 24.13°.	
Index ranges	−23<=h<=23, −15<=k<=16, −18<=l<=18	
Reflections collected	30211	
Independent reflections	7590 [R(int) = 0.0517]	
Completeness to theta = 24.13°	98.0 %	
Absorption correction	Empirical	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	7590 / 48 / 620	
Goodness−of−fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1291	
R indices (all data)	R1 = 0.0620, wR2 = 0.1352	
Largest diff. peak and hole	1.813 and −1.397 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2344. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y	2596(1)	589(1)	7789(1)	22(1)
S(1)	3340(1)	3070(1)	8200(1)	45(1)
S(2A)	4560(1)	382(2)	8764(2)	71(1)
S(2B)	5271(3)	1938(4)	8472(4)	87(2)
S(3)	4159(1)	304(1)	6403(1)	88(1)
S(4A)	1685(1)	−3313(1)	8120(2)	42(1)
S(4B)	1273(4)	−1418(7)	8394(7)	41(2)
S(5A)	3272(1)	−3321(2)	8064(2)	46(1)
S(5B)	3556(3)	−1509(4)	8731(5)	38(1)
S(6A)	1730(1)	−2218(4)	6187(2)	56(1)
S(6B)	3089(2)	−1961(3)	6181(2)	28(1)
S(7A)	1746(1)	3372(1)	7200(2)	50(1)
S(7B)	531(3)	3495(3)	7965(4)	35(1)
S(8)	1146(1)	1227(1)	9439(1)	44(1)
S(9A)	772(1)	202(1)	6904(1)	46(1)
S(9B)	829(9)	2041(11)	6107(9)	63(6)
O(1)	3506(1)	1230(2)	7818(2)	35(1)
O(2)	2463(1)	−839(2)	7739(2)	28(1)
O(3)	1813(1)	1479(2)	7937(2)	30(1)
N(1)	2443(2)	789(2)	6246(2)	32(1)
N(2)	2772(2)	409(2)	9349(2)	30(1)

C(1)	4070(2)	1668(3)	7597(3)	29(1)
C(2)	3999(2)	2701(3)	7718(3)	31(1)
C(3)	4431(2)	3436(3)	7542(3)	40(1)
C(4)	4147(3)	4287(3)	7831(3)	49(1)
C(5)	3586(3)	4182(3)	8188(3)	49(1)
C(6)	4643(2)	1325(3)	8166(3)	33(1)
C(7A)	5280(5)	1607(7)	8231(7)	50
C(7B)	4699(9)	384(12)	8553(13)	50
C(8)	5666(2)	1115(4)	8870(3)	55(1)
C(9)	5348(3)	409(5)	9098(4)	73(2)
C(10)	4184(2)	1419(4)	6689(3)	43(1)
C(11)	4280(2)	2005(3)	5959(2)	29(1)
C(12)	4354(3)	1425(8)	5257(4)	90(3)
C(13)	4285(4)	535(7)	5408(5)	97(3)
C(14)	2453(2)	−1792(3)	7669(2)	24(1)
C(15)	1845(2)	−2165(3)	8051(2)	28(1)
C(16A)	1318(4)	−1648(6)	8307(6)	25(2)
C(16B)	1601(14)	−3078(15)	8180(30)	50
C(17)	814(3)	−2242(4)	8593(3)	54(1)
C(18)	962(3)	−3125(4)	8505(3)	49(1)
C(19)	3069(2)	−2191(3)	8116(2)	26(1)
C(20A)	3532(7)	−1685(10)	8628(11)	60
C(20B)	3372(17)	−3078(18)	8100(30)	60(20)
C(21)	4054(2)	−2319(4)	8942(3)	49(1)
C(22)	3946(2)	−3165(4)	8662(3)	47(1)
C(23)	2425(2)	−2055(3)	6745(2)	29(1)
C(24A)	2962(7)	−2084(12)	6193(8)	60
C(24B)	1902(10)	−2260(30)	6187(11)	35
C(25)	2679(4)	−2204(4)	5315(3)	61(2)
C(26)	2053(3)	−2304(3)	5319(3)	57(2)
C(27)	1177(2)	1789(3)	7779(3)	27(1)
C(28)	1168(2)	2836(3)	7675(3)	30(1)
C(29A)	624(6)	3494(9)	7822(9)	33(4)
C(29B)	1663(16)	3420(18)	7380(50)	230(30)
C(30)	856(3)	4419(3)	7553(4)	57(1)
C(31)	1428(3)	4356(3)	7233(4)	55(1)
C(32)	767(2)	1520(3)	8492(3)	31(1)
C(33)	109(2)	1502(3)	8530(3)	41(1)
C(34)	−85(2)	1256(3)	9333(3)	48(1)
C(35)	420(3)	1087(3)	9878(3)	50(1)
C(36)	899(2)	1364(3)	6956(3)	30(1)
C(37A)	791(3)	1753(4)	6168(3)	28(1)
C(37B)	1200(40)	301(15)	6600(20)	50
C(38)	595(3)	1099(4)	5555(3)	54(1)
C(39)	574(3)	253(4)	5861(4)	62(2)
C(40)	2263(3)	105(3)	5740(3)	60(2)
C(41)	2121(4)	218(4)	4892(3)	72(2)
C(42)	2160(3)	1052(4)	4553(3)	53(1)
C(43)	2340(3)	1763(4)	5056(3)	56(1)
C(44)	2484(3)	1611(3)	5892(3)	48(1)
C(45)	2499(2)	−270(3)	9754(3)	39(1)
C(46)	2537(3)	−360(4)	10611(3)	46(1)
C(47)	2882(2)	288(4)	11077(3)	48(1)
C(48)	3165(3)	981(4)	10677(3)	53(1)
C(49)	3111(2)	1025(3)	9818(3)	43(1)

Table 3. Bond lengths [Å] and angles [°] for sh2344.

Y−O(2)	2.100(3)	C(6)−C(7B)	1.507(17)
Y−O(3)	2.107(3)	C(7A)−C(8)	1.451(11)
Y−O(1)	2.109(3)	C(7B)−C(9)	1.562(17)
Y−N(1)	2.493(3)	C(8)−C(9)	1.289(8)
Y−N(2)	2.520(3)	C(10)−C(11)	1.472(7)
S(1)−C(5)	1.699(5)	C(11)−C(12)	1.424(9)
S(1)−C(2)	1.705(4)	C(12)−C(13)	1.329(12)
S(2A)−C(6)	1.690(5)	C(14)−C(23)	1.528(5)
S(2A)−C(9)	1.692(6)	C(14)−C(15)	1.538(6)
S(2B)−C(8)	1.567(8)	C(14)−C(19)	1.543(5)
S(2B)−C(6)	1.632(7)	C(15)−C(16A)	1.412(9)
S(3)−C(13)	1.668(9)	C(15)−C(16B)	1.444(19)
S(3)−C(10)	1.688(5)	C(16A)−C(17)	1.456(10)
S(4A)−C(18)	1.683(6)	C(16B)−C(18)	1.456(19)
S(4A)−C(15)	1.710(4)	C(17)−C(18)	1.332(8)
S(4B)−C(17)	1.579(11)	C(19)−C(20A)	1.431(13)

S(4B)−C(15)	1.728(10)	C(19)−C(20B)	1.44(2)
S(5A)−C(22)	1.664(6)	C(20A)−C(21)	1.489(14)
S(5A)−C(19)	1.703(5)	C(20B)−C(22)	1.45(2)
S(5B)−C(21)	1.593(8)	C(21)−C(22)	1.327(7)
S(5B)−C(19)	1.692(6)	C(23)−C(24B)	1.398(18)
S(6A)−C(26)	1.588(7)	C(23)−C(24A)	1.469(13)
S(6A)−C(23)	1.670(5)	C(24A)−C(25)	1.502(14)
S(6B)−C(25)	1.624(7)	C(24B)−C(26)	1.448(19)
S(6B)−C(23)	1.703(5)	C(25)−C(26)	1.312(8)
S(7A)−C(31)	1.581(6)	C(27)−C(32)	1.521(6)
S(7A)−C(28)	1.658(5)	C(27)−C(28)	1.535(6)
S(7B)−C(30)	1.663(8)	C(27)−C(36)	1.538(6)
S(7B)−C(28)	1.724(6)	C(28)−C(29B)	1.44(2)
S(8)−C(35)	1.717(5)	C(28)−C(29A)	1.511(12)
S(8)−C(32)	1.722(4)	C(29A)−C(30)	1.505(13)
S(9A)−C(39)	1.699(6)	C(29B)−C(31)	1.46(2)
S(9A)−C(36)	1.715(4)	C(30)−C(31)	1.328(8)
S(9B)−C(36)	1.680(15)	C(32)−C(33)	1.373(6)
S(9B)−C(38)	1.689(15)	C(33)−C(34)	1.419(7)
O(1)−C(1)	1.399(5)	C(34)−C(35)	1.349(8)
O(2)−C(14)	1.394(5)	C(36)−C(37A)	1.391(7)
O(3)−C(27)	1.406(5)	C(36)−C(37B)	1.77(4)
N(1)−C(40)	1.326(6)	C(37A)−C(38)	1.411(7)
N(1)−C(44)	1.331(6)	C(37B)−C(39)	1.71(4)
N(2)−C(45)	1.331(6)	C(38)−C(39)	1.329(8)
N(2)−C(49)	1.341(6)	C(40)−C(41)	1.382(7)
C(1)−C(2)	1.525(6)	C(41)−C(42)	1.337(8)
C(1)−C(10)	1.535(6)	C(42)−C(43)	1.352(8)
C(1)−C(6)	1.540(6)	C(43)−C(44)	1.373(7)
C(2)−C(3)	1.437(6)	C(45)−C(46)	1.378(7)
C(3)−C(4)	1.461(7)	C(46)−C(47)	1.377(7)
C(4)−C(5)	1.342(8)	C(47)−C(48)	1.351(8)
C(6)−C(7A)	1.386(11)	C(48)−C(49)	1.379(7)

O(2)−Y−O(3)	120.87(11)	C(20A)−C(19)−C(20B)	101.0(11)
O(2)−Y−O(1)	123.82(11)	C(20A)−C(19)−C(14)	125.7(6)
O(3)−Y−O(1)	115.05(11)	C(20B)−C(19)−C(14)	133.1(10)
O(2)−Y−N(1)	93.99(11)	C(20A)−C(19)−S(5B)	6.0(7)
O(3)−Y−N(1)	89.29(11)	C(20B)−C(19)−S(5B)	106.8(10)
O(1)−Y−N(1)	91.66(12)	C(14)−C(19)−S(5B)	120.0(3)
O(2)−Y−N(2)	86.91(11)	C(20A)−C(19)−S(5A)	111.4(6)
O(3)−Y−N(2)	91.03(11)	C(20B)−C(19)−S(5A)	11.6(14)
O(1)−Y−N(2)	87.08(12)	C(14)−C(19)−S(5A)	122.9(3)
N(1)−Y−N(2)	178.72(12)	S(5B)−C(19)−S(5A)	117.0(3)
C(5)−S(1)−C(2)	92.5(2)	C(19)−C(20A)−C(21)	109.0(9)
C(6)−S(2A)−C(9)	91.7(3)	C(19)−C(20B)−C(22)	114.4(17)
C(8)−S(2B)−C(6)	95.4(4)	C(22)−C(21)−C(20A)	110.9(6)
C(13)−S(3)−C(10)	93.6(4)	C(22)−C(21)−S(5B)	121.5(4)
C(18)−S(4A)−C(15)	92.6(3)	C(20A)−C(21)−S(5B)	10.8(6)
C(17)−S(4B)−C(15)	91.3(6)	C(21)−C(22)−C(20B)	104.1(10)
C(22)−S(5A)−C(19)	92.5(3)	C(21)−C(22)−S(5A)	116.1(4)
C(21)−S(5B)−C(19)	92.7(3)	C(20B)−C(22)−S(5A)	13.1(13)
C(26)−S(6A)−C(23)	94.7(3)	C(24B)−C(23)−C(24A)	101.4(11)
C(25)−S(6B)−C(23)	92.1(3)	C(24B)−C(23)−C(14)	130.9(9)
C(31)−S(7A)−C(28)	95.5(3)	C(24A)−C(23)−C(14)	127.5(6)
C(30)−S(7B)−C(28)	90.3(4)	C(24B)−C(23)−S(6A)	9.0(11)
C(35)−S(8)−C(32)	91.4(2)	C(24A)−C(23)−S(6A)	109.7(6)
C(39)−S(9A)−C(36)	91.9(3)	C(14)−C(23)−S(6A)	122.3(3)
C(36)−S(9B)−C(38)	87.5(8)	C(24B)−C(23)−S(6B)	107.5(9)
C(1)−O(1)−Y	164.0(3)	C(24A)−C(23)−S(6B)	7.9(7)
C(14)−O(2)−Y	172.7(3)	C(14)−C(23)−S(6B)	120.8(3)
C(27)−O(3)−Y	154.5(2)	S(6A)−C(23)−S(6B)	115.5(3)
C(40)−N(1)−C(44)	116.0(4)	C(23)−C(24A)−C(25)	107.5(9)
C(40)−N(1)−Y	122.3(3)	C(23)−C(24B)−C(26)	114.8(15)
C(44)−N(1)−Y	121.5(3)	C(26)−C(25)−C(24A)	109.8(7)
C(45)−N(2)−C(49)	116.7(4)	C(26)−C(25)−S(6B)	119.3(4)
C(45)−N(2)−Y	121.5(3)	C(24A)−C(25)−S(6B)	10.9(6)
C(49)−N(2)−Y	121.7(3)	C(25)−C(26)−C(24B)	105.9(9)
O(1)−C(1)−C(2)	109.2(3)	C(25)−C(26)−S(6A)	118.0(4)
O(1)−C(1)−C(10)	108.3(3)	C(24B)−C(26)−S(6A)	12.7(9)
C(2)−C(1)−C(10)	112.0(4)	O(3)−C(27)−C(32)	110.3(3)
O(1)−C(1)−C(6)	109.4(3)	O(3)−C(27)−C(28)	110.2(3)
C(2)−C(1)−C(6)	108.8(3)	C(32)−C(27)−C(28)	109.5(3)

C(10)−C(1)−C(6)	109.1(3)
C(3)−C(2)−C(1)	130.2(4)
C(3)−C(2)−S(1)	112.6(3)
C(1)−C(2)−S(1)	117.1(3)
C(2)−C(3)−C(4)	107.6(4)
C(5)−C(4)−C(3)	114.6(4)
C(4)−C(5)−S(1)	112.7(4)
C(7A)−C(6)−C(7B)	101.0(9)
C(7A)−C(6)−C(1)	130.6(5)
C(7B)−C(6)−C(1)	125.2(7)
C(7A)−C(6)−S(2B)	21.8(4)
C(7B)−C(6)−S(2B)	109.6(7)
C(1)−C(6)−S(2B)	125.2(4)
C(7A)−C(6)−S(2A)	109.3(5)
C(7B)−C(6)−S(2A)	15.1(9)
C(1)−C(6)−S(2A)	119.8(3)
S(2B)−C(6)−S(2A)	112.5(3)
C(6)−C(7A)−C(8)	113.0(8)
C(6)−C(7B)−C(9)	104.5(11)
C(9)−C(8)−C(7A)	108.9(6)
C(9)−C(8)−S(2B)	117.4(5)
C(7A)−C(8)−S(2B)	23.3(4)
C(8)−C(9)−C(7B)	107.6(8)
C(8)−C(9)−S(2A)	115.7(4)
C(7B)−C(9)−S(2A)	15.5(8)
C(11)−C(10)−C(1)	130.9(4)
C(11)−C(10)−S(3)	110.2(3)
C(1)−C(10)−S(3)	118.8(4)
C(12)−C(11)−C(10)	108.1(5)
C(13)−C(12)−C(11)	114.7(7)
C(12)−C(13)−S(3)	113.3(6)
O(2)−C(14)−C(23)	109.1(3)
O(2)−C(14)−C(15)	109.2(3)
C(23)−C(14)−C(15)	108.4(3)
O(2)−C(14)−C(19)	109.3(3)
C(23)−C(14)−C(19)	109.7(3)
C(15)−C(14)−C(19)	111.1(3)
C(16A)−C(15)−C(16B)	99.3(10)
C(16A)−C(15)−C(14)	126.8(5)
C(16B)−C(15)−C(14)	133.6(10)
C(16A)−C(15)−S(4A)	110.2(4)
C(16B)−C(15)−S(4A)	11.0(9)
C(14)−C(15)−S(4A)	122.7(3)
C(16A)−C(15)−S(4B)	7.6(6)
C(16B)−C(15)−S(4B)	106.1(10)
C(14)−C(15)−S(4B)	120.2(4)
S(4A)−C(15)−S(4B)	117.1(4)
C(15)−C(16A)−C(17)	111.2(6)
C(15)−C(16B)−C(18)	115.6(16)
C(18)−C(17)−C(16A)	111.4(6)
C(18)−C(17)−S(4B)	124.5(6)
C(16A)−C(17)−S(4B)	13.5(5)
C(17)−C(18)−C(16B)	102.4(10)
C(17)−C(18)−S(4A)	114.5(4)
C(16B)−C(18)−S(4A)	12.1(9)
O(3)−C(27)−C(36)	109.0(3)
C(32)−C(27)−C(36)	110.0(3)
C(28)−C(27)−C(36)	107.8(3)
C(29B)−C(28)−C(29A)	103.6(12)
C(29B)−C(28)−C(27)	128.2(11)
C(29A)−C(28)−C(27)	128.2(6)
C(29B)−C(28)−S(7A)	10(3)
C(29A)−C(28)−S(7A)	110.1(5)
C(27)−C(28)−S(7A)	120.9(3)
C(29B)−C(28)−S(7B)	109.7(12)
C(29A)−C(28)−S(7B)	8.0(6)
C(27)−C(28)−S(7B)	122.0(3)
S(7A)−C(28)−S(7B)	117.0(3)
C(30)−C(29A)−C(28)	105.5(8)
C(28)−C(29B)−C(31)	111.4(17)
C(31)−C(30)−C(29A)	111.1(6)
C(31)−C(30)−S(7B)	119.6(4)
C(29A)−C(30)−S(7B)	9.7(6)
C(30)−C(31)−C(29B)	107.5(12)
C(30)−C(31)−S(7A)	117.5(4)
C(29B)−C(31)−S(7A)	12(2)
C(33)−C(32)−C(27)	130.2(4)
C(33)−C(32)−S(8)	111.0(3)
C(27)−C(32)−S(8)	118.7(3)
C(32)−C(33)−C(34)	112.7(4)
C(35)−C(34)−C(33)	112.4(4)
C(34)−C(35)−S(8)	112.5(4)
C(37A)−C(36)−C(27)	130.3(4)
C(37A)−C(36)−C(37B)	96.2(11)
C(27)−C(36)−C(37B)	120.2(10)
C(37A)−C(36)−S(9B)	12.4(6)
C(27)−C(36)−S(9B)	117.9(6)
C(37B)−C(36)−S(9B)	105.6(14)
C(37A)−C(36)−S(9A)	110.0(4)
C(27)−C(36)−S(9A)	119.2(3)
C(37B)−C(36)−S(9A)	35(2)
S(9B)−C(36)−S(9A)	122.3(6)
C(36)−C(37A)−C(38)	112.4(5)
C(39)−C(37B)−C(36)	89(2)
C(39)−C(38)−C(37A)	112.6(5)
C(39)−C(38)−S(9B)	125.1(7)
C(37A)−C(38)−S(9B)	12.6(6)
C(38)−C(39)−C(37B)	100.3(12)
C(38)−C(39)−S(9A)	113.1(4)
C(37B)−C(39)−S(9A)	36(2)
N(1)−C(40)−C(41)	123.2(5)
C(42)−C(41)−C(40)	119.6(5)
C(41)−C(42)−C(43)	118.4(5)
C(42)−C(43)−C(44)	119.7(5)
N(1)−C(44)−C(43)	123.1(5)
N(2)−C(45)−C(46)	123.9(4)
C(45)−C(46)−C(47)	118.2(5)
C(48)−C(47)−C(46)	118.9(5)
C(47)−C(48)−C(49)	119.8(5)
N(2)−C(49)−C(48)	122.6(5)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for sh2344. The anisotropic displacement factor exponent takes the form: $-2p^2[\,h^2 a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y	24(1)	19(1)	24(1)	−2(1)	0(1)	1(1)
S(1)	50(1)	40(1)	46(1)	−1(1)	7(1)	6(1)
S(2A)	25(1)	71(2)	116(3)	65(2)	−6(1)	−5(1)
S(2B)	59(3)	92(4)	107(5)	0(3)	−22(3)	4(3)
S(3)	87(1)	86(1)	90(1)	−43(1)	−5(1)	13(1)
S(4A)	54(1)	31(1)	41(1)	2(1)	8(1)	−12(1)
S(4B)	34(4)	43(5)	47(5)	−15(4)	2(3)	4(4)
S(5A)	48(1)	32(1)	56(2)	1(1)	−10(1)	12(1)
S(5B)	21(2)	40(3)	52(3)	2(2)	−5(2)	2(2)
S(6A)	71(2)	56(2)	39(1)	−10(1)	−8(1)	1(2)
S(6B)	30(2)	38(2)	16(1)	−4(1)	7(1)	9(1)

S(7A)	55(1)	34(1)	61(2)	−2(1)	−2(1)	−3(1)
S(7B)	31(2)	19(2)	57(3)	−1(2)	19(2)	8(1)
S(8)	46(1)	51(1)	35(1)	6(1)	3(1)	5(1)
O(1)	25(2)	34(2)	46(2)	−4(1)	5(1)	−5(1)
O(2)	38(2)	21(1)	26(2)	−1(1)	1(1)	1(1)
O(3)	25(1)	33(2)	33(2)	−3(1)	−2(1)	5(1)
N(1)	39(2)	29(2)	28(2)	−1(2)	1(2)	2(2)
N(2)	35(2)	29(2)	26(2)	−3(2)	−2(2)	4(2)
C(1)	21(2)	33(2)	32(2)	−4(2)	2(2)	−5(2)
C(2)	30(2)	35(2)	27(2)	4(2)	−4(2)	1(2)
C(3)	47(3)	27(2)	45(3)	5(2)	−1(2)	−1(2)
C(4)	63(3)	32(3)	49(3)	7(2)	−10(3)	−9(2)
C(5)	70(4)	34(3)	44(3)	−1(2)	−3(3)	10(2)
C(6)	31(2)	35(2)	33(2)	−1(2)	3(2)	2(2)
C(8)	33(3)	66(4)	64(4)	−9(3)	−11(2)	7(3)
C(9)	42(3)	88(5)	88(5)	41(4)	6(3)	20(3)
C(10)	24(2)	63(3)	41(3)	−16(2)	−4(2)	2(2)
C(12)	58(4)	171(9)	40(3)	−13(5)	−1(3)	20(5)
C(13)	66(4)	157(9)	67(5)	−70(6)	−6(4)	23(5)
C(14)	37(2)	17(2)	18(2)	−2(2)	1(2)	1(2)
C(15)	34(2)	28(2)	22(2)	−1(2)	−4(2)	0(2)
C(17)	35(3)	78(4)	47(3)	−5(3)	1(2)	0(3)
C(18)	48(3)	57(4)	40(3)	4(3)	1(2)	−24(3)
C(19)	29(2)	26(2)	23(2)	0(2)	4(2)	3(2)
C(21)	36(3)	59(3)	52(3)	−11(3)	−5(2)	4(2)
C(22)	45(3)	47(3)	50(3)	2(2)	−1(2)	22(2)
C(23)	43(2)	20(2)	23(2)	1(2)	4(2)	4(2)
C(25)	96(5)	51(3)	38(3)	−13(3)	25(3)	1(3)
C(26)	98(5)	39(3)	30(3)	−4(2)	−20(3)	0(3)
C(27)	21(2)	29(2)	32(2)	−1(2)	1(2)	3(2)
C(28)	29(2)	28(2)	32(2)	−5(2)	2(2)	3(2)
C(30)	64(4)	35(3)	73(4)	2(3)	14(3)	14(2)
C(31)	69(4)	38(3)	60(3)	0(3)	16(3)	−7(3)
C(32)	35(2)	27(2)	31(2)	−1(2)	3(2)	0(2)
C(33)	35(3)	48(3)	41(3)	3(2)	6(2)	−2(2)
C(34)	40(3)	49(3)	57(3)	1(3)	18(2)	−5(2)
C(35)	68(4)	45(3)	40(3)	4(2)	20(3)	−5(3)
C(36)	20(2)	36(2)	34(2)	−3(2)	−1(2)	2(2)
C(38)	50(3)	77(4)	33(3)	−4(3)	−4(2)	−3(3)
C(39)	58(4)	67(4)	57(4)	−30(3)	−20(3)	−3(3)
C(40)	112(5)	30(3)	36(3)	8(2)	−15(3)	−8(3)
C(41)	127(6)	52(3)	35(3)	0(3)	−16(3)	−16(4)
C(42)	54(3)	72(4)	32(3)	19(3)	−3(2)	−8(3)
C(43)	76(4)	46(3)	47(3)	21(3)	15(3)	2(3)
C(44)	69(3)	33(3)	44(3)	2(2)	14(2)	1(2)
C(45)	48(3)	39(3)	28(2)	−6(2)	−2(2)	−5(2)
C(46)	60(3)	45(3)	33(3)	−2(2)	5(2)	1(2)
C(47)	54(3)	63(3)	26(2)	−8(2)	−3(2)	11(3)
C(48)	60(3)	58(3)	40(3)	−19(3)	−9(2)	−10(3)
C(49)	53(3)	39(3)	36(3)	−5(2)	−6(2)	−9(2)

Compound 17b

Table 1. Crystal data and structure refinement for sh2437.

Identification code	sh2437	
Empirical formula	C56 H45 N2 O3 S9 Y	
Formula weight	1171.39	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.4487(8) Å	α = 90°.
	b = 16.2321(10) Å	β = 112.311(2)°.
	c = 14.1860(7) Å	γ = 90°.
Volume	2651.9(3) Å^3	
Z	2	
Density (calculated)	1.467 Mg/m^3	
Absorption coefficient	1.501 mm^{-1}	
F(000)	1204	
Crystal size	0.2 x 0.4 x 0.55 mm^3	
Theta range for data collection	1.77 to 29.05°.	

Index ranges	−16<=h<=16, −22<=k<=21, −19<=l<=15
Reflections collected	24074
Independent reflections	11138 [R(int) = 0.0427]
Completeness to theta = 29.05°	85.9 %
Absorption correction	Multi scan
Refinement method	Full−matrix least−squares on F^2
Data / restraints / parameters	11138 / 9 / 647
Goodness−of−fit on F^2	0.999
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.0971
R indices (all data)	R1 = 0.0564, wR2 = 0.1000
Absolute structure parameter	0.001(4)
Largest diff. peak and hole	1.130 and −0.897 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2437. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	774(1)	5980(1)	−1784(1)	13(1)
S(1)	−2771(1)	6966(1)	−2483(1)	26(1)
S(2)	−1282(1)	4199(1)	−2278(1)	50(1)
S(3)	−429(1)	6144(1)	661(1)	23(1)
S(4)	−1660(1)	6046(1)	−4323(1)	48(1)
S(5)	−400(1)	3867(1)	−4410(1)	32(1)
S(6A)	1403(4)	5889(3)	−5724(2)	29(1)
S(6B)	2007(4)	6784(2)	−3958(3)	17(1)
S(7)	2885(1)	8043(1)	−1482(1)	24(1)
S(8)	3460(1)	6333(1)	1415(1)	35(1)
S(9)	4683(1)	5017(1)	241(1)	34(1)
N(1)	133(3)	7430(2)	−2184(2)	16(1)
N(2)	1535(3)	4619(2)	−1053(3)	18(1)
O(1)	−660(2)	5865(2)	−1366(2)	22(1)
O(2)	688(2)	5698(2)	−3232(2)	21(1)
O(3)	2363(2)	6465(2)	−790(2)	18(1)
C(1)	−1679(3)	5574(3)	−1298(3)	19(1)
C(2)	−2744(3)	5950(3)	−2158(3)	19(1)
C(3)	−3749(4)	5561(3)	−2749(3)	27(1)
C(4)	−4543(3)	6088(3)	−3476(3)	29(1)
C(5)	−4149(4)	6867(3)	−3427(3)	31(1)
C(6)	−1736(3)	4642(3)	−1391(3)	23(1)
C(7)	−2136(4)	4039(3)	−909(3)	31(1)
C(8)	−2038(6)	3259(4)	−1213(5)	62(2)
C(9)	−1577(5)	3235(3)	−1935(6)	68(2)
C(10)	−1699(3)	5819(2)	−270(3)	19(1)
C(11)	−2568(4)	5778(3)	77(3)	25(1)
C(12)	−2205(4)	6015(3)	1128(3)	32(1)
C(13)	−1092(4)	6219(3)	1543(3)	31(1)
C(14)	472(3)	5483(2)	−4254(3)	16(1)
C(15)	−796(3)	5689(2)	−4903(3)	18(1)
C(16)	−1366(3)	5618(2)	−6056(2)	3(1)
C(17)	−2620(3)	5875(3)	−6232(3)	28(1)
C(18)	−2810(4)	6090(3)	−5404(3)	30(1)
C(19)	688(3)	4562(2)	−4304(3)	18(1)
C(20)	1789(4)	4167(2)	−4158(2)	14(1)
C(21)	1582(4)	3277(3)	−4151(3)	28(1)
C(22)	499(4)	3056(3)	−4259(3)	29(1)
C(23)	1281(3)	5994(3)	−4603(3)	18(1)
C(24A)	1950(20)	6707(13)	−4104(16)	50
C(24B)	1461(18)	5979(13)	−5514(12)	50
C(25)	2562(4)	7057(3)	−4740(4)	41(1)
C(26)	2291(4)	6621(4)	−5581(5)	51(2)
C(27)	3570(3)	6537(2)	−502(3)	16(1)
C(28)	3835(3)	7230(3)	−1099(3)	20(1)
C(29)	4761(4)	7344(3)	−1389(4)	25(1)
C(30)	4678(4)	8094(3)	−1934(4)	30(1)
C(31)	3720(4)	8533(3)	−2031(3)	28(1)
C(32)	4096(3)	6741(3)	633(3)	23(1)
C(33)	5056(4)	7188(3)	1171(3)	27(1)
C(34)	5264(5)	7203(3)	2221(4)	48(2)
C(35)	4476(5)	6794(3)	2462(4)	45(1)
C(36)	4061(3)	5725(2)	−711(3)	21(1)
C(37)	3962(3)	5418(2)	−1714(3)	15(1)

C(38)	4478(4)	4609(3)	−1541(4)	30(1)
C(39)	4870(4)	4326(3)	−578(4)	30(1)
C(40)	152(3)	7888(3)	−1401(3)	22(1)
C(41)	61(3)	8734(3)	−1435(3)	22(1)
C(42)	−48(4)	9125(3)	−2315(3)	29(1)
C(43)	−102(4)	8670(3)	−3138(3)	30(1)
C(44)	−1(3)	7823(2)	−3051(3)	21(1)
C(45)	1683(4)	4424(3)	−87(3)	23(1)
C(46)	2033(4)	3659(3)	339(3)	25(1)
C(47)	2252(3)	3054(3)	−270(3)	24(1)
C(48)	2118(3)	3248(3)	−1254(3)	23(1)
C(49)	1761(3)	4033(3)	−1614(3)	20(1)
C(50)	5982(5)	9233(3)	−3894(4)	37(1)
C(51)	4806(5)	9383(3)	−4193(5)	48(2)
C(52)	4045(5)	9098(4)	−5104(5)	49(2)
C(53)	4439(5)	8632(4)	−5713(4)	49(2)
C(54)	5594(5)	8471(4)	−5434(4)	43(1)
C(55)	6367(4)	8765(3)	−4519(4)	41(1)
C(56)	6808(6)	9577(4)	−2928(5)	65(2)

Table 3. Bond lengths [Å] and angles [°] for sh2437.

Y(1)−O(2)	2.067(3)	C(12)−C(13)	1.325(6)
Y(1)−O(1)	2.092(2)	C(14)−C(19)	1.525(5)
Y(1)−O(3)	2.098(3)	C(14)−C(23)	1.526(5)
Y(1)−N(2)	2.471(3)	C(14)−C(15)	1.533(6)
Y(1)−N(1)	2.481(3)	C(15)−C(16)	1.520(5)
S(1)−C(2)	1.709(5)	C(16)−C(17)	1.542(5)
S(1)−C(5)	1.737(5)	C(17)−C(18)	1.329(6)
S(2)−C(9)	1.719(7)	C(19)−C(20)	1.455(5)
S(2)−C(6)	1.720(4)	C(20)−C(21)	1.468(6)
S(3)−C(10)	1.714(4)	C(21)−C(22)	1.346(6)
S(3)−C(13)	1.746(4)	C(23)−C(24B)	1.393(14)
S(4)−C(18)	1.655(4)	C(23)−C(24A)	1.445(16)
S(4)−C(15)	1.686(4)	C(24A)−C(25)	1.494(16)
S(5)−C(22)	1.687(5)	C(24B)−C(26)	1.496(16)
S(5)−C(19)	1.725(4)	C(25)−C(26)	1.316(7)
S(6A)−C(26)	1.583(7)	C(27)−C(28)	1.518(6)
S(6A)−C(23)	1.662(4)	C(27)−C(32)	1.527(6)
S(6B)−C(25)	1.576(7)	C(27)−C(36)	1.527(5)
S(6B)−C(23)	1.634(6)	C(28)−C(29)	1.376(6)
S(7)−C(31)	1.713(4)	C(29)−C(30)	1.425(6)
S(7)−C(28)	1.717(4)	C(30)−C(31)	1.350(6)
S(8)−C(35)	1.715(5)	C(32)−C(33)	1.359(6)
S(8)−C(32)	1.720(4)	C(33)−C(34)	1.411(7)
S(9)−C(39)	1.693(5)	C(34)−C(35)	1.332(7)
S(9)−C(36)	1.717(4)	C(36)−C(37)	1.467(6)
N(1)−C(40)	1.329(5)	C(37)−C(38)	1.443(6)
N(1)−C(44)	1.338(5)	C(38)−C(39)	1.346(7)
N(2)−C(49)	1.337(5)	C(40)−C(41)	1.378(6)
N(2)−C(45)	1.349(5)	C(41)−C(42)	1.361(6)
O(1)−C(1)	1.392(4)	C(42)−C(43)	1.362(6)
O(2)−C(14)	1.413(4)	C(43)−C(44)	1.381(6)
O(3)−C(27)	1.405(4)	C(45)−C(46)	1.378(6)
C(1)−C(6)	1.519(6)	C(46)−C(47)	1.401(6)
C(1)−C(10)	1.520(5)	C(47)−C(48)	1.378(6)
C(1)−C(2)	1.546(6)	C(48)−C(49)	1.382(6)
C(2)−C(3)	1.368(6)	C(50)−C(51)	1.382(7)
C(3)−C(4)	1.414(6)	C(50)−C(55)	1.383(7)
C(4)−C(5)	1.349(7)	C(50)−C(56)	1.476(8)
C(6)−C(7)	1.390(6)	C(51)−C(52)	1.361(8)
C(7)−C(8)	1.358(7)	C(52)−C(53)	1.371(8)
C(8)−C(9)	1.352(9)	C(53)−C(54)	1.364(7)
C(10)−C(11)	1.349(5)	C(54)−C(55)	1.375(7)
C(11)−C(12)	1.437(6)		

O(2)−Y(1)−O(1)	122.26(10)	C(20)−C(19)−S(5)	113.0(3)
O(2)−Y(1)−O(3)	115.56(10)	C(14)−C(19)−S(5)	119.9(3)
O(1)−Y(1)−O(3)	122.06(10)	C(19)−C(20)−C(21)	106.0(4)
O(2)−Y(1)−N(2)	94.94(11)	C(22)−C(21)−C(20)	115.6(4)
O(1)−Y(1)−N(2)	91.94(11)	C(21)−C(22)−S(5)	113.2(4)
O(3)−Y(1)−N(2)	86.56(11)	C(24B)−C(23)−C(24A)	101.7(10)
O(2)−Y(1)−N(1)	95.31(10)	C(24B)−C(23)−C(14)	130.6(8)
O(1)−Y(1)−N(1)	85.06(11)	C(24A)−C(23)−C(14)	127.3(8)

O(3)−Y(1)−N(1)	86.39(10)	C(24B)−C(23)−S(6B)	106.5(8)
N(2)−Y(1)−N(1)	169.34(11)	C(24A)−C(23)−S(6B)	4.8(8)
C(2)−S(1)−C(5)	91.8(2)	C(14)−C(23)−S(6B)	122.5(3)
C(9)−S(2)−C(6)	90.5(3)	C(24B)−C(23)−S(6A)	6.1(8)
C(10)−S(3)−C(13)	91.4(2)	C(24A)−C(23)−S(6A)	107.8(8)
C(18)−S(4)−C(15)	92.9(2)	C(14)−C(23)−S(6A)	124.5(3)
C(22)−S(5)−C(19)	92.2(2)	S(6B)−C(23)−S(6A)	112.6(3)
C(26)−S(6A)−C(23)	96.5(3)	C(23)−C(24A)−C(25)	109.9(12)
C(25)−S(6B)−C(23)	97.1(3)	C(23)−C(24B)−C(26)	113.9(12)
C(31)−S(7)−C(28)	92.1(2)	C(26)−C(25)−C(24A)	109.2(8)
C(35)−S(8)−C(32)	91.2(3)	C(26)−C(25)−S(6B)	117.2(4)
C(39)−S(9)−C(36)	92.4(2)	C(24A)−C(25)−S(6B)	8.0(7)
C(40)−N(1)−C(44)	117.3(3)	C(25)−C(26)−C(24B)	105.2(7)
C(40)−N(1)−Y(1)	115.9(3)	C(25)−C(26)−S(6A)	116.5(4)
C(44)−N(1)−Y(1)	125.4(3)	C(24B)−C(26)−S(6A)	11.3(6)
C(49)−N(2)−C(45)	117.4(4)	O(3)−C(27)−C(28)	109.5(3)
C(49)−N(2)−Y(1)	121.3(3)	O(3)−C(27)−C(32)	107.9(3)
C(45)−N(2)−Y(1)	121.2(3)	C(28)−C(27)−C(32)	109.3(3)
C(1)−O(1)−Y(1)	161.6(3)	O(3)−C(27)−C(36)	109.6(3)
C(14)−O(2)−Y(1)	172.4(2)	C(28)−C(27)−C(36)	110.1(3)
C(27)−O(3)−Y(1)	149.1(2)	C(32)−C(27)−C(36)	110.4(3)
O(1)−C(1)−C(6)	110.2(3)	C(29)−C(28)−C(27)	130.6(4)
O(1)−C(1)−C(10)	109.0(3)	C(29)−C(28)−S(7)	110.9(3)
C(6)−C(1)−C(10)	109.0(3)	C(27)−C(28)−S(7)	118.5(3)
O(1)−C(1)−C(2)	110.0(3)	C(28)−C(29)−C(30)	112.4(4)
C(6)−C(1)−C(2)	109.1(3)	C(31)−C(30)−C(29)	112.7(4)
C(10)−C(1)−C(2)	109.4(3)	C(30)−C(31)−S(7)	111.9(4)
C(3)−C(2)−C(1)	127.7(4)	C(33)−C(32)−C(27)	129.9(4)
C(3)−C(2)−S(1)	111.1(3)	C(33)−C(32)−S(8)	111.5(3)
C(1)−C(2)−S(1)	121.1(3)	C(27)−C(32)−S(8)	118.6(3)
C(2)−C(3)−C(4)	113.1(4)	C(32)−C(33)−C(34)	111.8(4)
C(5)−C(4)−C(3)	112.9(4)	C(35)−C(34)−C(33)	113.9(5)
C(4)−C(5)−S(1)	111.1(4)	C(34)−C(35)−S(8)	111.6(4)
C(7)−C(6)−C(1)	132.3(4)	C(37)−C(36)−C(27)	126.0(3)
C(7)−C(6)−S(2)	110.1(3)	C(37)−C(36)−S(9)	112.5(3)
C(1)−C(6)−S(2)	117.6(3)	C(27)−C(36)−S(9)	121.2(3)
C(8)−C(7)−C(6)	114.1(5)	C(38)−C(37)−C(36)	106.1(4)
C(9)−C(8)−C(7)	112.5(6)	C(39)−C(38)−C(37)	116.7(4)
C(8)−C(9)−S(2)	112.7(5)	C(38)−C(39)−S(9)	112.3(4)
C(11)−C(10)−C(1)	130.1(4)	N(1)−C(40)−C(41)	123.5(4)
C(11)−C(10)−S(3)	111.5(3)	C(42)−C(41)−C(40)	118.4(4)
C(1)−C(10)−S(3)	118.2(3)	C(41)−C(42)−C(43)	119.2(4)
C(10)−C(11)−C(12)	112.7(4)	C(42)−C(43)−C(44)	119.3(4)
C(13)−C(12)−C(11)	113.0(4)	N(1)−C(44)−C(43)	122.1(4)
C(12)−C(13)−S(3)	111.3(3)	N(2)−C(45)−C(46)	123.7(4)
O(2)−C(14)−C(19)	108.8(3)	C(45)−C(46)−C(47)	117.7(4)
O(2)−C(14)−C(23)	107.9(3)	C(48)−C(47)−C(46)	119.2(4)
C(19)−C(14)−C(23)	111.6(3)	C(47)−C(48)−C(49)	119.0(4)
O(2)−C(14)−C(15)	108.3(3)	N(2)−C(49)−C(48)	123.1(4)
C(19)−C(14)−C(15)	110.2(3)	C(51)−C(50)−C(55)	118.9(5)
C(23)−C(14)−C(15)	110.0(3)	C(51)−C(50)−C(56)	120.1(5)
C(16)−C(15)−C(14)	125.8(3)	C(55)−C(50)−C(56)	121.0(5)
C(16)−C(15)−S(4)	115.3(3)	C(52)−C(51)−C(50)	120.4(5)
C(14)−C(15)−S(4)	118.9(3)	C(51)−C(52)−C(53)	120.0(5)
C(15)−C(16)−C(17)	100.6(3)	C(54)−C(53)−C(52)	120.8(5)
C(18)−C(17)−C(16)	115.9(3)	C(53)−C(54)−C(55)	119.4(5)
C(17)−C(18)−S(4)	115.2(3)	C(54)−C(55)−C(50)	120.5(5)
C(20)−C(19)−C(14)	126.7(3)		

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2437. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	11(1)	13(1)	16(1)	−1(1)	6(1)	0(1)
S(1)	20(1)	24(1)	32(1)	2(1)	9(1)	4(1)
S(2)	25(1)	55(1)	73(1)	−42(1)	21(1)	−7(1)
S(3)	23(1)	24(1)	22(1)	−1(1)	6(1)	0(1)
S(4)	41(1)	56(1)	48(1)	−3(1)	17(1)	4(1)
S(5)	37(1)	23(1)	37(1)	−1(1)	15(1)	−2(1)
S(6A)	31(1)	36(2)	28(2)	−14(1)	19(1)	−12(1)
S(6B)	13(1)	17(1)	22(1)	−2(1)	6(1)	−2(1)

S(7)	19(1)	18(1)	34(1)	3(1)	11(1)	0(1)
S(8)	31(1)	45(1)	29(1)	2(1)	10(1)	4(1)
S(9)	27(1)	26(1)	51(1)	8(1)	16(1)	4(1)
N(1)	14(2)	18(2)	18(2)	0(2)	8(2)	0(1)
N(2)	14(2)	14(2)	25(2)	−1(2)	8(2)	−1(1)
O(1)	13(1)	29(2)	26(2)	−3(1)	9(1)	−4(1)
O(2)	20(2)	21(2)	20(2)	−1(1)	7(1)	3(1)
O(3)	10(1)	20(2)	26(2)	4(1)	8(1)	1(1)
C(1)	13(2)	23(2)	24(2)	−2(2)	12(2)	−3(2)
C(2)	15(2)	25(2)	22(2)	6(2)	12(2)	3(2)
C(3)	19(2)	31(3)	32(3)	−1(2)	11(2)	−3(2)
C(4)	16(2)	42(3)	23(2)	1(2)	0(2)	6(2)
C(5)	20(2)	42(3)	31(3)	4(2)	9(2)	14(2)
C(6)	9(2)	22(2)	30(2)	−3(2)	−1(2)	3(2)
C(7)	40(3)	22(3)	26(3)	0(2)	6(2)	−7(2)
C(8)	71(5)	30(3)	54(4)	−2(3)	−10(4)	−13(3)
C(9)	36(3)	26(3)	99(6)	−34(3)	−24(3)	9(3)
C(10)	18(2)	18(2)	22(2)	4(2)	9(2)	−3(2)
C(11)	19(2)	28(3)	31(2)	6(2)	13(2)	4(2)
C(12)	38(3)	37(3)	31(2)	9(3)	25(2)	12(3)
C(13)	43(3)	32(3)	20(2)	5(2)	14(2)	16(2)
C(14)	18(2)	16(2)	15(2)	−3(2)	8(2)	−1(2)
C(15)	16(2)	16(2)	28(2)	5(2)	16(2)	1(2)
C(16)	0(2)	0(2)	0(2)	1(1)	−11(1)	4(1)
C(17)	20(2)	32(3)	25(2)	3(2)	2(2)	−2(2)
C(18)	22(2)	33(3)	38(3)	−7(2)	15(2)	1(2)
C(19)	17(2)	23(2)	14(2)	−1(2)	7(2)	0(2)
C(20)	34(2)	8(2)	0(2)	−2(1)	6(2)	7(2)
C(21)	31(3)	33(3)	17(2)	−1(2)	7(2)	12(2)
C(22)	44(3)	21(2)	21(2)	1(2)	11(2)	3(2)
C(23)	14(2)	22(2)	19(2)	6(2)	7(2)	5(2)
C(25)	20(3)	19(3)	76(4)	12(3)	10(3)	0(2)
C(26)	34(3)	75(5)	57(4)	35(3)	33(3)	17(3)
C(27)	5(2)	18(2)	22(2)	1(2)	1(2)	−1(2)
C(28)	12(2)	20(2)	25(2)	−1(2)	5(2)	−3(2)
C(29)	18(2)	17(2)	41(3)	1(2)	13(2)	−1(2)
C(30)	26(3)	27(3)	44(3)	1(2)	21(2)	−7(2)
C(31)	28(3)	21(2)	32(3)	3(2)	9(2)	−5(2)
C(32)	13(2)	23(2)	34(3)	−1(2)	9(2)	5(2)
C(33)	20(2)	22(2)	30(3)	5(2)	−1(2)	2(2)
C(34)	30(3)	42(3)	45(3)	−11(3)	−14(3)	−2(3)
C(35)	43(3)	55(4)	26(3)	−2(3)	−1(3)	17(3)
C(36)	7(2)	21(2)	33(2)	5(2)	7(2)	−4(2)
C(37)	5(2)	2(2)	45(3)	3(2)	17(2)	0(1)
C(38)	21(3)	31(3)	39(3)	−7(2)	13(2)	−8(2)
C(39)	19(2)	18(2)	57(3)	1(2)	17(2)	0(2)
C(40)	19(2)	23(2)	25(2)	2(2)	10(2)	1(2)
C(41)	19(2)	21(2)	24(2)	−5(2)	6(2)	1(2)
C(42)	34(3)	12(2)	38(3)	1(2)	9(2)	2(2)
C(43)	45(3)	27(3)	18(2)	7(2)	11(2)	4(2)
C(44)	21(2)	17(2)	23(2)	−1(2)	7(2)	2(2)
C(45)	29(2)	19(2)	22(2)	0(2)	13(2)	0(2)
C(46)	31(3)	24(2)	24(2)	6(2)	14(2)	2(2)
C(47)	19(2)	17(2)	35(3)	10(2)	10(2)	2(2)
C(48)	20(2)	23(2)	31(3)	1(2)	14(2)	4(2)
C(49)	16(2)	26(2)	17(2)	7(2)	6(2)	3(2)
C(50)	46(3)	38(3)	32(3)	3(2)	20(3)	−9(2)
C(51)	59(4)	38(3)	60(4)	10(3)	39(4)	21(3)
C(52)	32(3)	60(4)	56(4)	21(3)	17(3)	17(3)
C(53)	57(4)	50(4)	34(3)	16(3)	10(3)	−6(3)
C(54)	38(3)	60(4)	36(3)	−8(3)	18(3)	−5(3)
C(55)	29(3)	61(4)	39(3)	−5(3)	21(3)	−1(3)
C(56)	87(5)	56(4)	56(4)	−1(3)	33(4)	−8(4)

Compound 18

Table 1. Crystal data and structure refinement for sh2390.

Identification code	sh2390
Empirical formula	C55 H59 Nd O7 S9
Formula weight	1264.80
Temperature	143(2) K
Wavelength	0.71073 Å

Crystal system	Rhombohedral	
Space group	R3	
Unit cell dimensions	a = 13.9688(6) Å	α = 90°.
	b = 13.9688(6) Å	β = 90°.
	c = 24.6314(10) Å	γ = 120°.
Volume	4162.3(3) Å^3	
Z	3	
Density (calculated)	1.514 Mg/m^3	
Absorption coefficient	1.325 mm^{-1}	
F(000)	1947	
Crystal size	0.3 x 0.5 x 0.55 mm^3	
Theta range for data collection	1.88 to 45.44°.	
Index ranges	−22<=h<=27, −28<=k<=27, −49<=l<=39	
Reflections collected	102475	
Independent reflections	14318 [R(int) = 0.0292]	
Completeness to theta = 45.44°	100.0 %	
Absorption correction	Semi−empirical from equivalents	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	14318 / 1 / 212	
Goodness−of−fit on F^2	1.491	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1203	
R indices (all data)	R1 = 0.0446, wR2 = 0.1204	
Absolute structure parameter	0.009(8)	
Largest diff. peak and hole	5.174 and −3.235 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2390. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nd(1)	6667	3333	433	10(1)
S(1)	3107(1)	878(1)	487(1)	30(1)
S(2)	6220(1)	279(1)	−188(1)	40(1)
S(3)	4966(1)	2336(1)	−1128(1)	48(1)
O(1)	5332(1)	1890(1)	28(1)	18(1)
C(1)	4632(1)	948(1)	−267(1)	15(1)
C(2)	3431(1)	564(2)	−129(1)	17(1)
C(3)	2475(2)	−49(2)	−442(1)	26(1)
C(4)	1503(2)	−272(3)	−157(2)	31(1)
C(5)	1715(2)	174(3)	353(2)	31(1)
C(6)	4888(1)	33(2)	−127(1)	17(1)
C(7)	4209(2)	−1001(2)	94(1)	25(1)
C(8)	4810(3)	−1567(2)	209(2)	31(1)
C(9)	5880(3)	−991(3)	66(2)	31(1)
C(10)	4773(2)	1156(2)	−877(1)	18(1)
C(11)	4495(2)	153(1)	−1350(1)	15(1)
C(12)	4797(4)	971(4)	−1851(2)	41(1)
C(13)	5001(3)	1998(3)	−1755(1)	33(1)
O(2)	5357(1)	3307(2)	1202(1)	19(1)
C(14)	4873(2)	2522(3)	1639(1)	27(1)
C(15)	4008(6)	2733(7)	1894(2)	79(3)
C(16)	3763(2)	3346(3)	1467(2)	32(1)
C(17)	4906(3)	4042(3)	1230(2)	37(1)
O(3)	10000	10000	1355(2)	36(1)
C(18)	9264(10)	10319(10)	1680(5)	62(2)
C(19)	9521(9)	10239(10)	2249(4)	58(2)

Table 3. Bond lengths [Å] and angles [°] for sh2390.

Nd(1)−O(1)	2.1861(13)	C(4)−C(5)	1.368(5)
Nd(1)−O(1)#1	2.1862(13)	C(6)−C(7)	1.383(3)
Nd(1)−O(1)#2	2.1862(13)	C(7)−C(8)	1.440(3)
Nd(1)−O(2)#1	2.6202(15)	C(8)−C(9)	1.343(4)
Nd(1)−O(2)#2	2.6202(15)	C(10)−C(11)	1.711(3)
Nd(1)−O(2)	2.6202(15)	C(11)−C(12)	1.589(5)
S(1)−C(2)	1.704(2)	C(12)−C(13)	1.337(6)
S(1)−C(5)	1.715(3)	O(2)−C(14)	1.442(3)
S(2)−C(9)	1.709(3)	O(2)−C(17)	1.451(3)
S(2)−C(6)	1.7208(19)	C(14)−C(15)	1.515(4)
S(3)−C(13)	1.621(4)	C(15)−C(16)	1.498(5)
S(3)−C(10)	1.652(2)	C(16)−C(17)	1.511(4)

O(1)−C(1)	1.389(2)
C(1)−C(2)	1.522(2)
C(1)−C(10)	1.523(3)
C(1)−C(6)	1.528(2)
C(2)−C(3)	1.402(3)
C(3)−C(4)	1.418(4)
O(3)−C(18)#3	1.535(12)
O(3)−C(18)	1.535(12)
O(3)−C(18)#4	1.535(12)
C(18)−C(19)	1.466(16)
C(19)−C(19)#4	1.533(19)
C(19)−C(19)#3	1.533(19)

O(1)−Nd(1)−O(1)#1	100.81(6)
O(1)−Nd(1)−O(1)#2	100.81(6)
O(1)#1−Nd(1)−O(1)#2	100.81(6)
O(1)−Nd(1)−O(2)#1	160.76(6)
O(1)#1−Nd(1)−O(2)#1	92.82(6)
O(1)#2−Nd(1)−O(2)#1	89.77(6)
O(1)−Nd(1)−O(2)#2	89.77(6)
O(1)#1−Nd(1)−O(2)#2	160.76(6)
O(1)#2−Nd(1)−O(2)#2	92.82(6)
O(2)#1−Nd(1)−O(2)#2	73.55(6)
O(1)−Nd(1)−O(2)	92.82(6)
O(1)#1−Nd(1)−O(2)	89.78(6)
O(1)#2−Nd(1)−O(2)	160.76(6)
O(2)#1−Nd(1)−O(2)	73.55(6)
O(2)#2−Nd(1)−O(2)	73.55(6)
C(2)−S(1)−C(5)	92.95(14)
C(9)−S(2)−C(6)	92.87(12)
C(13)−S(3)−C(10)	94.66(16)
C(1)−O(1)−Nd(1)	169.90(13)
O(1)−C(1)−C(2)	110.30(15)
O(1)−C(1)−C(10)	111.85(15)
C(2)−C(1)−C(10)	107.55(15)
O(1)−C(1)−C(6)	109.02(15)
C(2)−C(1)−C(6)	109.44(15)
C(10)−C(1)−C(6)	108.64(15)
C(3)−C(2)−C(1)	129.64(19)
C(3)−C(2)−S(1)	110.63(16)
C(1)−C(2)−S(1)	119.73(14)
C(2)−C(3)−C(4)	112.1(2)
C(5)−C(4)−C(3)	112.9(2)
C(4)−C(5)−S(1)	111.3(2)
C(7)−C(6)−C(1)	129.57(17)
C(7)−C(6)−S(2)	110.52(15)
C(1)−C(6)−S(2)	119.70(13)
C(6)−C(7)−C(8)	111.6(2)
C(9)−C(8)−C(7)	113.5(2)
C(8)−C(9)−S(2)	111.46(19)
C(1)−C(10)−S(3)	120.11(15)
C(1)−C(10)−C(11)	124.10(15)
S(3)−C(10)−C(11)	114.70(14)
C(12)−C(11)−C(10)	94.05(17)
C(13)−C(12)−C(11)	118.2(3)
C(12)−C(13)−S(3)	117.3(3)
C(14)−O(2)−C(17)	107.31(19)
C(14)−O(2)−Nd(1)	127.55(14)
C(17)−O(2)−Nd(1)	124.92(16)
O(2)−C(14)−C(15)	106.1(2)
C(16)−C(15)−C(14)	104.7(3)
C(15)−C(16)−C(17)	99.7(3)
O(2)−C(17)−C(16)	104.9(2)
C(18)#3−O(3)−C(18)	95.3(6)
C(18)#3−O(3)−C(18)#4	95.3(6)
C(18)−O(3)−C(18)#4	95.3(6)
C(19)−C(18)−O(3)	104.6(9)
C(18)−C(19)−C(19)#4	105.4(7)
C(18)−C(19)−C(19)#3	103.6(7)
C(19)#4−C(19)−C(19)#3	59.999(1)

Symmetry transformations used to generate equivalent atoms:
#1 −x+y+1,−x+1,z #2 −y+1,x−y,z #3 −y+2,x−y+1,z
#4 −x+y+1,−x+2,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2390. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nd(1)	9(1)	9(1)	12(1)	0	0	5(1)
S(1)	24(1)	37(1)	28(1)	−7(1)	2(1)	16(1)
S(2)	19(1)	31(1)	74(1)	20(1)	10(1)	15(1)
S(3)	45(1)	49(1)	42(1)	6(1)	−3(1)	19(1)
O(1)	15(1)	13(1)	23(1)	−5(1)	−4(1)	5(1)
C(1)	12(1)	13(1)	19(1)	−3(1)	−2(1)	5(1)
C(2)	13(1)	15(1)	22(1)	−2(1)	−1(1)	7(1)
C(3)	15(1)	29(1)	31(1)	−5(1)	−2(1)	8(1)
C(4)	14(1)	31(1)	45(2)	2(1)	−1(1)	9(1)
C(5)	22(1)	34(1)	38(1)	2(1)	5(1)	16(1)
C(6)	14(1)	15(1)	21(1)	−1(1)	0(1)	7(1)
C(7)	22(1)	16(1)	40(1)	5(1)	7(1)	11(1)
C(8)	32(1)	21(1)	44(2)	9(1)	11(1)	18(1)
C(9)	31(1)	31(1)	40(1)	5(1)	4(1)	23(1)
C(10)	16(1)	16(1)	21(1)	−1(1)	−1(1)	7(1)
C(11)	22(1)	15(1)	9(1)	−2(1)	4(1)	9(1)
C(12)	38(2)	40(2)	34(1)	−9(1)	7(1)	12(1)
C(13)	30(1)	39(1)	31(1)	13(1)	4(1)	18(1)
O(2)	20(1)	24(1)	18(1)	4(1)	5(1)	14(1)
C(14)	26(1)	34(1)	26(1)	13(1)	9(1)	20(1)
C(15)	95(4)	136(6)	62(3)	74(4)	66(3)	100(5)
C(16)	24(1)	37(1)	41(1)	7(1)	9(1)	21(1)
C(17)	33(1)	37(1)	54(2)	16(1)	20(1)	27(1)

Compound 19

Table 1. Crystal data and structure refinement for sh2557.

Identification code	sh2557	
Empirical formula	C55 H59 O7 S9 Sm	
Formula weight	1270.91	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R3	
Unit cell dimensions	a = 13.9401(10) Å	α = 90°.
	b = 13.9401(10) Å	β = 90°.
	c = 24.700(4) Å	γ = 120°.
Volume	4156.8(8) Å^3	
Z	3	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	1.450 mm^{-1}	
F(000)	1953	
Crystal size	0.3 x 0.44 x 0.5 mm^3	
Theta range for data collection	1.88 to 34.27°.	
Index ranges	−20<=h<=22, −21<=k<=21, −17<=l<=39	
Reflections collected	26806	
Independent reflections	5629 [R(int) = 0.0350]	
Completeness to theta = 34.27°	99.9 %	
Absorption correction	Multiscan	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	5629 / 1 / 216	
Goodness−of−fit on F^2	1.433	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1311	
R indices (all data)	R1 = 0.0488, wR2 = 0.1318	
Absolute structure parameter	0.021(13)	
Largest diff. peak and hole	2.826 and −1.752 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2557. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sm	0	0	−2913	13(1)
S(1)	444(1)	3073(1)	−2278(1)	46(1)
S(2)	3545(1)	2457(2)	−2975(1)	38(1)
S(3)	1700(2)	1005(2)	−1358(1)	64(1)
O(1)	1312(3)	1438(3)	−2518(2)	21(1)
O(2)	−1264(3)	−1312(3)	−3671(2)	24(1)
C(1)	2017(3)	2381(3)	−2222(2)	19(1)
C(2)	1768(3)	3298(4)	−2357(2)	20(1)
C(3)	2445(4)	4320(4)	−2585(3)	28(1)
C(4)	1849(6)	4908(5)	−2686(3)	37(1)
C(5)	784(5)	4334(5)	−2540(3)	36(1)
C(6)	3212(4)	2760(4)	−2361(2)	20(1)
C(7)	4185(4)	3364(5)	−2043(2)	28(1)
C(8)	5142(5)	3593(5)	−2338(3)	40(1)
C(9)	4934(5)	3144(6)	−2844(4)	38(1)
C(10)	1880(4)	2172(4)	−1618(2)	22(1)
C(11)	2126(3)	3142(3)	−1148(1)	9(1)
C(12)	1864(7)	2365(7)	−646(3)	48(2)
C(13)	1674(5)	1342(6)	−741(3)	42(2)
C(14)	−2447(5)	−1803(6)	−3682(4)	50(2)
C(15)	−2887(5)	−2907(5)	−3939(3)	41(2)
C(16)	−2032(7)	−2627(10)	−4361(5)	82(4)
C(17)	−955(4)	−1779(5)	−4112(2)	32(1)
O(3)	0	0	2820(4)	48(2)
C(18)	199(17)	696(15)	1927(8)	57(4)
C(19)	360(20)	1020(20)	2463(11)	49(5)
C(20)	990(30)	420(30)	2486(17)	81(10)

Table 3. Bond lengths [Å] and angles [°] for sh2557.

Sm−O(1)#1	2.156(3)	C(8)−C(9)	1.363(11)
Sm−O(1)	2.156(3)	C(10)−C(11)	1.683(6)
Sm−O(1)#2	2.156(3)	C(11)−C(12)	1.565(9)

Sm−O(2)#2	2.594(3)
Sm−O(2)	2.594(3)
Sm−O(2)#1	2.594(3)
S(1)−C(5)	1.703(6)
S(1)−C(2)	1.721(4)
S(2)−C(6)	1.700(5)
S(2)−C(9)	1.708(7)
S(3)−C(13)	1.600(8)
S(3)−C(10)	1.649(5)
O(1)−C(1)	1.391(5)
O(2)−C(14)	1.434(6)
O(2)−C(17)	1.442(6)
C(1)−C(10)	1.512(7)
C(1)−C(6)	1.513(6)
C(1)−C(2)	1.520(6)
C(2)−C(3)	1.377(6)
C(3)−C(4)	1.451(8)
C(4)−C(5)	1.336(9)
C(6)−C(7)	1.424(6)
C(7)−C(8)	1.409(8)
C(12)−C(13)	1.335(11)
C(14)−C(15)	1.484(9)
C(15)−C(16)	1.482(12)
C(16)−C(17)	1.502(10)
O(3)−C(20)#1	1.45(4)
O(3)−C(20)#2	1.45(4)
O(3)−C(20)	1.45(4)
O(3)−C(19)#2	1.53(3)
O(3)−C(19)#1	1.53(3)
O(3)−C(19)	1.53(3)
C(18)−C(19)	1.38(3)
C(18)−C(18)#2	1.50(3)
C(18)−C(18)#1	1.50(3)
C(18)−C(20)#2	1.59(5)
C(18)−C(20)	1.92(5)
C(19)−C(20)#2	0.95(4)
C(19)−C(20)	1.49(4)
C(20)−C(19)#1	0.95(4)
C(20)−C(18)#1	1.59(5)

O(1)#1−Sm−O(1)	101.11(12)
O(1)#1−Sm−O(1)#2	101.11(12)
O(1)−Sm−O(1)#2	101.11(12)
O(1)#1−Sm−O(2)#2	89.58(12)
O(1)−Sm−O(2)#2	92.50(13)
O(1)#2−Sm−O(2)#2	160.62(13)
O(1)#1−Sm−O(2)	92.50(13)
O(1)−Sm−O(2)	160.62(13)
O(1)#2−Sm−O(2)	89.58(12)
O(2)#2−Sm−O(2)	73.70(13)
O(1)#1−Sm−O(2)#1	160.62(13)
O(1)−Sm−O(2)#1	89.58(12)
O(1)#2−Sm−O(2)#1	92.50(13)
O(2)#2−Sm−O(2)#1	73.70(13)
O(2)−Sm−O(2)#1	73.70(13)
C(5)−S(1)−C(2)	92.9(3)
C(6)−S(2)−C(9)	93.8(3)
C(13)−S(3)−C(10)	95.6(3)
C(1)−O(1)−Sm	170.5(3)
C(14)−O(2)−C(17)	107.5(4)
C(14)−O(2)−Sm	124.4(4)
C(17)−O(2)−Sm	127.8(3)
O(1)−C(1)−C(10)	112.0(4)
O(1)−C(1)−C(6)	110.2(4)
C(10)−C(1)−C(6)	107.6(4)
O(1)−C(1)−C(2)	109.2(4)
C(10)−C(1)−C(2)	108.5(4)
C(6)−C(1)−C(2)	109.3(4)
C(3)−C(2)−C(1)	129.3(4)
C(3)−C(2)−S(1)	110.6(3)
C(1)−C(2)−S(1)	119.8(3)
C(2)−C(3)−C(4)	111.4(5)
C(5)−C(4)−C(3)	113.2(5)
C(4)−C(5)−S(1)	111.9(4)
C(7)−C(6)−C(1)	129.6(4)
C(7)−C(6)−S(2)	110.0(4)
C(1)−C(6)−S(2)	120.4(3)
C(8)−C(7)−C(6)	111.2(5)
C(9)−C(8)−C(7)	114.3(5)
C(8)−C(9)−S(2)	110.6(5)
C(1)−C(10)−S(3)	121.1(4)
C(1)−C(10)−C(11)	124.8(4)
S(3)−C(10)−C(11)	113.1(3)
C(12)−C(11)−C(10)	96.2(4)
C(13)−C(12)−C(11)	117.0(6)
C(12)−C(13)−S(3)	117.4(6)
O(2)−C(14)−C(15)	106.5(5)
C(16)−C(15)−C(14)	99.6(6)
C(15)−C(16)−C(17)	105.9(6)
O(2)−C(17)−C(16)	105.0(5)
C(20)#1−O(3)−C(20)#2	91(2)
C(20)#1−O(3)−C(20)	91(2)
C(20)#2−O(3)−C(20)	91(2)
C(20)#1−O(3)−C(19)#2	36.9(17)
C(20)#2−O(3)−C(19)#2	59.7(17)
C(20)−O(3)−C(19)#2	108.9(19)
C(20)#1−O(3)−C(19)#1	59.7(17)
C(20)#2−O(3)−C(19)#1	108.9(19)
C(20)−O(3)−C(19)#1	36.9(17)
C(19)#2−O(3)−C(19)#1	90.2(14)
C(20)#1−O(3)−C(19)	108.9(19)
C(20)#2−O(3)−C(19)	36.9(17)
C(20)−O(3)−C(19)	59.7(17)
C(19)#2−O(3)−C(19)	90.2(14)
C(19)#1−O(3)−C(19)	90.2(14)
C(19)−C(18)−C(18)#2	106.0(13)
C(19)−C(18)−C(18)#1	102.1(14)
C(18)#2−C(18)−C(18)#1	60.001(3)
C(19)−C(18)−C(20)#2	36.4(17)
C(18)#2−C(18)−C(20)#2	76.7(17)
C(18)#1−C(18)−C(20)#2	105.4(16)
C(19)−C(18)−C(20)	50.4(16)
C(18)#2−C(18)−C(20)	91.1(16)
C(18)#1−C(18)−C(20)	53.8(16)
C(20)#2−C(18)−C(20)	72(3)
C(20)#2−C(19)−C(18)	84(4)
C(20)#2−C(19)−C(20)	114(4)
C(18)−C(19)−C(20)	84(2)
C(20)#2−C(19)−O(3)	67(3)
C(18)−C(19)−O(3)	108.5(18)
C(20)−C(19)−O(3)	57.4(19)
C(19)#1−C(20)−O(3)	76(3)
C(19)#1−C(20)−C(19)	125(4)
O(3)−C(20)−C(19)	63.0(19)
C(19)#1−C(20)−C(18)#1	60(3)
O(3)−C(20)−C(18)#1	102(3)
C(19)−C(20)−C(18)#1	93(3)
C(19)#1−C(20)−C(18)	101(4)
O(3)−C(20)−C(18)	88.2(19)
C(19)−C(20)−C(18)	45.7(16)
C(18)#1−C(20)−C(18)	49.5(16)

Symmetry transformations used to generate equivalent atoms:
#1 −x+y,−x,z   #2 −y,x−y,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2557. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sm	12(1)	12(1)	15(1)	0	0	6(1)
S(1)	25(1)	37(1)	81(1)	22(1)	13(1)	20(1)
S(2)	30(1)	48(1)	36(1)	−10(1)	3(1)	19(1)
S(3)	65(1)	66(1)	56(1)	7(1)	−3(1)	28(1)
O(1)	20(1)	15(1)	26(2)	−6(1)	−5(1)	6(1)
O(2)	20(1)	24(2)	23(2)	−7(1)	−2(1)	8(1)
C(1)	16(2)	17(2)	21(2)	−3(1)	−1(1)	7(1)
C(2)	17(2)	19(2)	25(2)	−2(1)	0(1)	9(1)
C(3)	25(2)	16(2)	42(3)	5(2)	7(2)	10(2)
C(4)	44(3)	25(2)	49(4)	10(3)	12(3)	22(2)
C(5)	42(3)	38(3)	43(3)	5(2)	4(3)	31(3)
C(6)	19(2)	16(2)	26(2)	−2(1)	−2(2)	9(1)
C(7)	15(2)	31(2)	34(3)	−6(2)	−4(2)	7(2)
C(8)	20(2)	40(3)	59(4)	−4(3)	−3(2)	15(2)
C(9)	29(3)	41(3)	50(4)	7(3)	7(3)	22(2)
C(10)	21(2)	19(2)	25(2)	−3(2)	−5(2)	9(2)
C(11)	17(1)	10(1)	2(1)	0(1)	5(1)	9(1)
C(12)	49(4)	52(4)	36(3)	−10(3)	7(3)	19(3)
C(13)	37(3)	51(4)	39(3)	22(3)	9(3)	23(3)
C(14)	16(2)	47(3)	72(5)	−34(4)	−1(3)	5(2)
C(15)	22(2)	30(3)	61(4)	−13(3)	−7(2)	4(2)
C(16)	34(4)	101(8)	68(6)	−60(6)	1(4)	1(4)
C(17)	25(2)	32(2)	30(3)	−11(2)	5(2)	8(2)

Compound <u>21</u>

Table 1. Crystal data and structure refinement for sh2608.

Identification code	sh2608	
Empirical formula	C72 H68 K4 O7 S8	
Formula weight	1458.14	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.7740(15) Å	α = 90°.
	b = 24.2098(16) Å	β = 91.553(4)°.
	c = 49.109(3) Å	γ = 90°.
Volume	29444(3) Å^3	
Z	16	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	0.519 mm^{-1}	
F(000)	12160	
Crystal size	0.55 x 0.37 x 0.22 mm^3	
Theta range for data collection	1.18 to 26.49°.	
Index ranges	−30<=h<=30, −25<=k<=30, −55<=l<=61	
Reflections collected	123598	
Independent reflections	30203 [R(int) = 0.0765]	
Completeness to theta = 26.49°	99.1 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8943 and 0.7633	
Refinement method	Full−matrix−block least−squares on F^2	
Data / restraints / parameters	30203 / 4 / 1671	
Goodness−of−fit on F^2	2.076	
Final R indices [I>2sigma(I)]	R1 = 0.1224, wR2 = 0.3011	
R indices (all data)	R1 = 0.2232, wR2 = 0.3291	
Largest diff. peak and hole	1.207 and −1.201 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2608. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
K(1)	2710(1)	5462(1)	1525(1)	53(1)
K(2)	1640(1)	4329(1)	1584(1)	48(1)
K(3)	1556(1)	5395(1)	1017(1)	58(1)

K(4)	2634(1)	4304(1)	1012(1)	43(1)
K(5)	1814(1)	10127(1)	1041(1)	51(1)
K(6)	2942(1)	10213(1)	1554(1)	86(1)
K(7)	1879(1)	9059(1)	1600(1)	64(1)
K(8)	2863(1)	9031(1)	1027(1)	71(1)
S(8)	419(1)	4657(1)	888(1)	61(1)
S(9)	2976(1)	6571(1)	1146(1)	63(1)
S(11)	476(1)	5048(1)	1606(1)	69(1)
S(12)	1246(1)	3195(1)	1255(1)	73(1)
S(13)	2101(1)	7870(1)	888(1)	70(1)
S(14)	4062(1)	10492(1)	1188(1)	65(1)
S(15)	703(1)	8775(1)	1272(1)	73(1)
S(16)	1508(1)	6621(1)	1368(1)	83(1)
S(17)	2478(1)	4104(1)	2150(1)	64(1)
S(20)	3817(2)	4794(2)	1676(1)	162(2)
S(21)	2169(1)	5799(1)	463(1)	116(1)
S(22)	2161(2)	5536(2)	2121(1)	128(1)
S(23)	3210(1)	9737(2)	470(1)	138(2)
S(24)	4112(2)	8976(2)	1329(1)	67(1)
S(25)	3178(1)	9596(1)	2145(1)	100(1)
S(26)	1747(1)	9791(1)	2185(1)	88(1)
S(27)	2598(1)	7885(1)	1612(1)	94(1)
S(28A)	2141(2)	11454(2)	1670(1)	102(1)
S(28C)	2452(3)	11126(3)	1746(2)	26(2)
S(28B)	684(4)	10395(5)	1273(2)	12(3)
O(1)	1629(2)	5440(2)	1561(1)	52(1)
O(2)	2747(2)	4373(2)	1582(1)	43(1)
O(3)	1522(2)	4250(2)	1042(1)	42(1)
O(4)	2650(2)	5427(2)	973(1)	45(1)
O(5)	1872(2)	10203(2)	1602(1)	72(2)
O(6)	2915(2)	10146(2)	1005(1)	52(1)
O(7)	2962(2)	9082(3)	1583(1)	81(2)
O(8)	1756(2)	8994(2)	1060(1)	47(1)
O(9)	3534(4)	6002(4)	1848(2)	130(3)
O(10)	1070(2)	3617(2)	1913(1)	74(2)
O(11)	868(3)	6032(3)	679(1)	94(2)
O(12)	3519(4)	11174(4)	1812(2)	146(3)
O(13)	1273(2)	8411(3)	1930(1)	82(2)
O(14)	3478(4)	8359(4)	622(2)	162(4)
C(1)	1338(3)	5751(3)	1736(1)	39(2)
C(2)	827(3)	5448(3)	1830(1)	42(2)
C(3)	568(3)	5481(3)	2075(2)	44(2)
C(4)	78(3)	5175(3)	2079(2)	55(2)
C(5)	−44(3)	4907(3)	1833(2)	64(2)
C(6)	1143(3)	6294(3)	1593(1)	46(2)
C(7)	671(3)	6586(3)	1646(2)	51(2)
C(8)	623(3)	7081(3)	1492(2)	63(2)
C(9)	1027(4)	7187(3)	1322(2)	65(2)
C(10)	1670(3)	5919(3)	1995(1)	41(2)
C(11)	1593(3)	6385(3)	2162(2)	49(2)
C(12)	1936(4)	6411(4)	2393(2)	71(3)
C(13)	2300(4)	6020(4)	2439(2)	79(3)
C(14A)	2405(7)	5637(8)	2345(4)	68(5)
C(14B)	1280(20)	7060(20)	1170(12)	280(30)
C(14)	1293(3)	3945(3)	828(1)	41(2)
C(15)	798(3)	4230(3)	693(2)	45(2)
C(16)	566(3)	4150(3)	434(2)	52(2)
C(17)	73(3)	4466(3)	402(2)	61(2)
C(18)	−65(3)	4746(4)	630(2)	66(2)
C(19)	1085(3)	3393(3)	934(1)	45(2)
C(20)	738(2)	2984(2)	778(2)	40(2)
C(21)	699(3)	2508(4)	974(2)	70(3)
C(22)	933(3)	2573(3)	1228(2)	68(3)
C(23)	1725(3)	3850(3)	612(1)	43(2)
C(24)	1855(3)	4283(3)	432(1)	46(2)
C(25)	2275(3)	4217(4)	254(2)	71(3)
C(26)	2574(4)	3732(5)	260(2)	83(3)
C(27)	2456(3)	3313(4)	431(2)	72(3)
C(28)	2038(3)	3349(3)	609(2)	46(2)
C(29)	3082(3)	3952(3)	1684(2)	45(2)
C(30)	2873(3)	3706(3)	1948(1)	42(2)
C(31)	2984(3)	3209(3)	2067(2)	56(2)
C(32)	2734(4)	3150(4)	2331(2)	65(2)

C(33)	2449(4)	3604(4)	2399(2)	73(3)
C(34)	3660(3)	4173(3)	1755(2)	50(2)
C(35)	4098(2)	3908(3)	1908(1)	37(2)
C(36)	4437(9)	4174(9)	1931(3)	219(12)
C(37)	4490(4)	4652(8)	1805(3)	170(8)
C(38)	3113(3)	3488(3)	1471(2)	48(2)
C(39)	2665(3)	3111(3)	1420(2)	41(2)
C(40)	2628(4)	2764(4)	1223(2)	72(3)
C(41)	3044(4)	2727(4)	1042(2)	70(3)
C(42)	3478(4)	3076(4)	1065(2)	71(3)
C(43)	3536(3)	3466(4)	1284(2)	62(2)
C(44)	3056(3)	5643(3)	815(2)	46(2)
C(45)	2817(3)	5891(3)	550(2)	54(2)
C(46)	3063(4)	6232(4)	358(2)	97(4)
C(47)	2673(6)	6379(4)	142(2)	106(4)
C(48)	2199(6)	6178(4)	169(2)	113(5)
C(49)	3334(3)	6125(3)	947(2)	58(2)
C(50)	3857(4)	6331(4)	898(2)	90(3)
C(51)	3931(4)	6880(4)	1037(3)	106(4)
C(52)	3492(4)	7044(4)	1179(2)	97(4)
C(53)	3468(3)	5186(3)	745(2)	43(2)
C(54)	3449(4)	4909(4)	501(2)	85(3)
C(55)	3783(5)	4456(4)	459(2)	99(4)
C(56)	4176(3)	4315(3)	657(2)	70(3)
C(57)	4185(4)	4582(4)	891(2)	82(3)
C(58)	3826(3)	5004(4)	942(2)	72(3)
C(59)	1501(3)	10505(4)	1742(2)	59(2)
C(60)	1307(3)	10192(3)	1994(2)	53(2)
C(61)	800(3)	10225(4)	2118(2)	67(2)
C(62)	818(4)	9907(5)	2374(2)	94(4)
C(63)	1307(4)	9659(4)	2431(2)	77(3)
C(64)	990(2)	10641(3)	1558(1)	77(3)
C(65)	784(4)	11172(3)	1530(2)	322(18)
C(66)	342(4)	11270(3)	1356(3)	420(30)
C(67)	107(3)	10836(5)	1211(2)	192(10)
C(68)	313(3)	10305(4)	1239(2)	196(10)
C(69)	755(3)	10207(3)	1413(2)	143(6)
C(70)	1733(3)	11053(3)	1853(2)	60(2)
C(71)	1599(4)	11346(4)	2076(2)	87(3)
C(72)	1926(4)	11865(4)	2106(2)	90(3)
C(73)	2223(5)	11944(5)	1902(2)	110(4)
C(74)	3125(3)	10565(3)	852(1)	43(2)
C(75)	3379(3)	10340(3)	595(2)	49(2)
C(76)	3758(4)	10600(4)	435(2)	86(3)
C(77)	3877(4)	10238(5)	203(2)	95(4)
C(78)	3618(4)	9801(6)	190(2)	109(5)
C(79)	3587(3)	10861(3)	1004(2)	57(2)
C(80)	3745(4)	11405(4)	989(3)	124(5)
C(81)	4266(6)	11507(5)	1136(4)	180(8)
C(82)	4470(4)	11065(4)	1263(2)	101(4)
C(83)	2684(3)	10987(3)	774(2)	51(2)
C(84)	2511(4)	11129(5)	502(2)	109(4)
C(85)	2078(6)	11474(8)	471(3)	185(9)
C(86)	1823(4)	11696(4)	680(2)	96(4)
C(87)	1980(4)	11587(4)	925(2)	75(3)
C(88)	2396(3)	11267(3)	981(2)	57(2)
C(90)	3528(3)	9064(3)	1985(2)	43(2)
C(91)	4004(3)	8961(3)	2132(2)	53(2)
C(92)	4068(4)	9297(4)	2369(2)	69(3)
C(93)	3657(4)	9661(3)	2410(2)	71(3)
C(94)	3797(2)	8599(3)	1573(1)	58(2)
C(95)	4113(2)	8125(2)	1577(1)	65(2)
C(96)	4556(2)	8087(2)	1410(1)	67(2)
C(97)	4682(2)	8524(3)	1239(1)	60(2)
C(97A)	4366(3)	8999(3)	1236(2)	68(6)
C(97B)	3923(3)	9036(3)	1403(2)	98(9)
C(98)	3055(3)	8210(3)	1821(2)	49(2)
C(99)	3164(3)	7893(3)	2049(2)	50(2)
C(100)	2868(3)	7382(3)	2052(2)	63(2)
C(101)	2538(3)	7303(3)	1826(2)	72(3)
C(102)	1430(3)	8792(3)	848(2)	43(2)
C(103)	1678(3)	8287(3)	707(2)	56(2)
C(104)	1559(4)	8093(4)	446(2)	72(3)

C(105)	1842(4)	7576(4)	404(2)	85(3)
C(106)	2155(4)	7400(4)	625(2)	78(3)
C(107)	881(3)	8583(3)	956(2)	49(2)
C(108)	484(3)	8250(3)	817(2)	49(2)
C(109)	29(3)	8180(3)	1004(2)	69(3)
C(110)	106(3)	8445(4)	1249(2)	73(3)
C(111)	1324(3)	9257(3)	642(1)	48(2)
C(112)	853(3)	9606(3)	645(2)	52(2)
C(113)	819(4)	10061(4)	488(2)	93(3)
C(114)	1220(5)	10206(5)	320(2)	113(4)
C(115)	1674(4)	9880(5)	295(2)	90(3)
C(116)	1729(3)	9415(3)	458(2)	55(2)
C(117)	3314(3)	8758(3)	1725(2)	56(2)
C(120)	484(4)	3586(4)	1930(2)	87(3)
C(121)	751(4)	8546(5)	1989(2)	108(4)
C(123)	1391(5)	7875(5)	2047(2)	114(4)
C(124)	884(4)	2891(5)	2208(3)	111(4)
C(125)	4271(6)	6531(6)	1973(3)	160(7)
C(126)	3353(5)	7899(5)	437(3)	112(4)
C(127)	710(7)	5970(6)	400(2)	145(6)
C(128)	658(6)	8273(6)	2267(3)	142(6)
C(129)	371(4)	3067(6)	2069(3)	150(7)
C(140)	1279(4)	3159(6)	2037(4)	178(8)
C(141)	969(6)	7783(7)	2266(3)	173(8)
C(142)	3921(6)	6402(7)	1747(3)	172(7)
C(143)	4184(6)	6156(9)	2190(3)	199(9)
C(145)	278(7)	6317(8)	343(4)	183(8)
C(146)	3663(6)	5871(8)	2134(3)	169(7)
C(147)	326(7)	6763(5)	541(5)	232(12)
C(149)	3791(6)	7886(11)	278(4)	262(14)
C(151)	4229(6)	11460(6)	2120(4)	155(6)
C(152)	4113(6)	11992(8)	1883(5)	201(9)
C(150)	3941(6)	10982(8)	2025(5)	208(9)
C(153)	3636(9)	11792(7)	1816(7)	360(20)
C(154)	4278(5)	8052(7)	440(4)	193(9)
C(155)	4016(7)	8482(13)	584(5)	284(15)
C(156)	591(9)	6504(12)	763(5)	340(20)
C(01)	4790(4)	6020(5)	441(2)	92(3)
C(02)	98(6)	11476(7)	350(3)	149(5)
C(03)	−424(6)	10726(6)	212(3)	143(5)
C(04)	−524(9)	11172(10)	34(5)	105(7)
C(05)	7(13)	11070(13)	−19(6)	148(10)
C(06)	−153(11)	11586(11)	45(6)	124(8)
C(07)	1258(4)	12005(4)	−44(2)	90(3)
C(08)	3928(5)	2801(5)	317(3)	114(4)
C(09)	3629(6)	2294(6)	396(3)	131(5)
C(010)	3854(11)	2493(12)	−78(6)	134(9)
C(011)	3780(5)	11978(5)	54(2)	101(3)
C(012)	1713(11)	12918(11)	−205(6)	123(8)

Table 3. Bond lengths [Å] and angles [°] for sh2608.

K(1)−O(2)	2.654(5)	C(8)−C(9)	1.347(11)
K(1)−O(1)	2.688(5)	C(9)−C(14B)	1.02(5)
K(1)−O(4)	2.714(5)	C(10)−C(11)	1.409(9)
K(1)−O(9)	2.867(9)	C(11)−C(12)	1.402(11)
K(1)−S(20)	3.253(5)	C(12)−C(13)	1.322(12)
K(1)−S(22)	3.262(4)	C(13)−C(14A)	1.070(18)
K(1)−S(9)	3.344(3)	C(14)−C(19)	1.531(10)
K(1)−K(3)	3.748(2)	C(14)−C(15)	1.540(9)
K(1)−K(4)	3.771(2)	C(14)−C(23)	1.545(9)
K(1)−K(2)	3.832(2)	C(15)−C(16)	1.394(10)
K(2)−O(3)	2.673(5)	C(16)−C(17)	1.448(10)
K(2)−O(1)	2.692(5)	C(17)−C(18)	1.358(11)
K(2)−O(2)	2.746(5)	C(19)−C(20)	1.508(9)
K(2)−O(10)	2.773(6)	C(20)−C(21)	1.507(12)
K(2)−S(12)	3.317(3)	C(21)−C(22)	1.373(12)
K(2)−S(11)	3.372(3)	C(23)−C(24)	1.415(10)
K(2)−S(17)	3.469(3)	C(23)−C(28)	1.440(9)
K(2)−K(4)	3.785(2)	C(24)−C(25)	1.385(10)
K(2)−K(3)	3.798(2)	C(25)−C(26)	1.390(12)
K(3)−O(1)	2.676(5)	C(26)−C(27)	1.355(12)
K(3)−O(4)	2.726(5)	C(27)−C(28)	1.374(10)
K(3)−O(3)	2.775(5)	C(29)−C(30)	1.528(10)

K(3)−O(11)	2.809(7)	C(29)−C(38)	1.538(10)
K(3)−S(21)	3.300(4)	C(29)−C(34)	1.560(10)
K(3)−S(8)	3.380(3)	C(30)−C(31)	1.364(9)
K(3)−S(16)	3.435(3)	C(31)−C(32)	1.461(11)
K(3)−K(4)	3.756(2)	C(32)−C(33)	1.355(12)
K(4)−O(4)	2.726(5)	C(34)−C(35)	1.454(10)
K(4)−O(3)	2.766(4)	C(35)−C(36)	1.06(3)
K(4)−O(2)	2.811(5)	C(36)−C(37)	1.32(2)
K(4)−C(23)	3.148(7)	C(38)−C(43)	1.413(10)
K(4)−C(38)	3.202(7)	C(38)−C(39)	1.453(10)
K(4)−C(53)	3.271(7)	C(39)−C(40)	1.284(11)
K(4)−C(43)	3.276(8)	C(40)−C(41)	1.384(12)
K(4)−C(28)	3.361(7)	C(41)−C(42)	1.370(12)
K(4)−C(24)	3.397(7)	C(42)−C(43)	1.433(11)
K(4)−C(58)	3.431(10)	C(44)−C(49)	1.495(10)
K(4)−C(39)	3.516(7)	C(44)−C(45)	1.537(10)
K(4)−C(14)	3.528(7)	C(44)−C(53)	1.550(10)
K(5)−O(6)	2.740(5)	C(45)−C(46)	1.401(12)
K(5)−O(8)	2.750(5)	C(46)−C(47)	1.458(15)
K(5)−O(5)	2.761(6)	C(47)−C(48)	1.280(16)
K(5)−C(111)	3.105(7)	C(49)−C(50)	1.417(11)
K(5)−S(28B)	3.118(12)	C(50)−C(51)	1.501(14)
K(5)−C(88)	3.131(8)	C(51)−C(52)	1.366(13)
K(5)−C(69)	3.241(9)	C(53)−C(58)	1.366(10)
K(5)−C(112)	3.286(8)	C(53)−C(54)	1.373(11)
K(5)−C(83)	3.293(8)	C(54)−C(55)	1.392(12)
K(5)−C(116)	3.345(8)	C(55)−C(56)	1.399(13)
K(5)−C(102)	3.495(7)	C(56)−C(57)	1.316(12)
K(5)−C(64)	3.527(8)	C(57)−C(58)	1.380(12)
K(6)−O(5)	2.668(6)	C(59)−C(70)	1.539(11)
K(6)−O(6)	2.702(5)	C(59)−C(60)	1.541(11)
K(6)−S(28C)	2.704(8)	C(59)−C(64)	1.569(10)
K(6)−O(7)	2.740(7)	C(60)−C(61)	1.411(10)
K(6)−O(12)	2.993(10)	C(61)−C(62)	1.475(13)
K(6)−S(25)	3.302(4)	C(62)−C(63)	1.375(14)
K(6)−S(14)	3.414(3)	C(64)−C(65)	1.3900
K(6)−S(28A)	3.654(5)	C(64)−C(69)	1.3900
K(6)−K(7)	3.850(3)	C(65)−C(66)	1.3900
K(6)−K(8)	3.859(3)	C(66)−C(67)	1.3900
K(7)−O(8)	2.668(5)	C(67)−C(68)	1.3900
K(7)−O(7)	2.687(5)	C(68)−C(69)	1.3900
K(7)−O(13)	2.732(6)	C(70)−C(71)	1.352(12)
K(7)−O(5)	2.770(6)	C(71)−C(72)	1.500(13)
K(7)−S(27)	3.355(4)	C(72)−C(73)	1.272(14)
K(7)−S(15)	3.362(3)	C(74)−C(75)	1.522(10)
K(7)−S(26)	3.396(4)	C(74)−C(79)	1.529(10)
K(7)−K(8)	3.774(3)	C(74)−C(83)	1.538(10)
K(8)−O(6)	2.704(5)	C(75)−C(76)	1.393(11)
K(8)−O(7)	2.738(7)	C(76)−C(77)	1.474(14)
K(8)−O(8)	2.752(5)	C(77)−C(78)	1.238(15)
K(8)−O(14)	3.015(10)	C(79)−C(80)	1.375(12)
K(8)−C(97B)	3.170(9)	C(80)−C(81)	1.483(15)
K(8)−S(23)	3.357(5)	C(81)−C(82)	1.330(15)
K(8)−S(24)	3.399(4)	C(83)−C(88)	1.425(10)
K(8)−S(13)	3.445(3)	C(83)−C(84)	1.434(12)
S(8)−C(15)	1.708(7)	C(84)−C(85)	1.366(13)
S(8)−C(18)	1.736(9)	C(85)−C(86)	1.335(15)
S(9)−C(52)	1.718(9)	C(86)−C(87)	1.280(13)
S(9)−C(49)	1.719(8)	C(87)−C(88)	1.312(12)
S(11)−C(2)	1.688(7)	C(90)−C(91)	1.391(10)
S(11)−C(5)	1.763(9)	C(90)−C(117)	1.553(11)
S(12)−C(19)	1.684(8)	C(91)−C(92)	1.428(11)
S(12)−C(22)	1.696(9)	C(92)−C(93)	1.364(12)
S(13)−C(103)	1.690(8)	C(94)−C(95)	1.3900
S(13)−C(106)	1.731(9)	C(94)−C(97B)	1.3900
S(14)−C(79)	1.717(8)	C(94)−C(117)	1.480(8)
S(14)−C(82)	1.748(10)	C(95)−C(96)	1.3900
S(15)−C(110)	1.683(9)	C(96)−C(97)	1.3900
S(15)−C(107)	1.687(8)	C(97)−C(97A)	1.3900
S(16)−C(14B)	1.55(6)	C(97A)−C(97B)	1.3900
S(16)−C(6)	1.650(7)	C(98)−C(99)	1.381(10)
S(16)−C(9)	1.826(9)	C(98)−C(117)	1.550(10)
S(17)−C(30)	1.712(7)	C(99)−C(100)	1.438(10)

S(17)−C(33)	1.723(9)	C(100)−C(101)	1.374(12)
S(20)−C(34)	1.603(8)	C(102)−C(111)	1.534(10)
S(20)−C(37)	1.801(16)	C(102)−C(103)	1.539(10)
S(21)−C(45)	1.664(9)	C(102)−C(107)	1.557(10)
S(21)−C(48)	1.713(11)	C(103)−C(104)	1.390(11)
S(22)−C(14A)	1.267(19)	C(104)−C(105)	1.451(12)
S(22)−C(10)	1.638(8)	C(105)−C(106)	1.382(13)
S(22)−C(13)	1.976(12)	C(107)−C(108)	1.432(10)
S(23)−C(75)	1.633(8)	C(108)−C(109)	1.483(11)
S(23)−C(78)	1.735(11)	C(109)−C(110)	1.372(12)
S(24)−C(97B)	0.615(7)	C(111)−C(116)	1.420(10)
S(24)−C(97A)	0.791(7)	C(111)−C(112)	1.440(10)
S(24)−C(94)	1.712(7)	C(112)−C(113)	1.347(12)
S(24)−C(97)	1.850(7)	C(113)−C(114)	1.354(14)
S(25)−C(93)	1.743(10)	C(114)−C(115)	1.383(14)
S(25)−C(90)	1.752(8)	C(115)−C(116)	1.386(12)
S(26)−C(63)	1.680(10)	C(120)−C(129)	1.459(14)
S(26)−C(60)	1.718(9)	C(121)−C(128)	1.542(15)
S(27)−C(98)	1.701(8)	C(123)−C(141)	1.536(15)
S(27)−C(101)	1.765(10)	C(124)−C(140)	1.461(14)
S(28A)−S(28C)	1.159(8)	C(124)−C(129)	1.490(14)
S(28A)−C(73)	1.654(10)	C(125)−C(143)	1.419(19)
S(28A)−C(70)	1.676(8)	C(125)−C(142)	1.424(18)
S(28C)−C(70)	1.878(11)	C(126)−C(149)	1.354(17)
S(28C)−C(73)	2.204(14)	C(127)−C(145)	1.382(17)
S(28B)−C(69)	0.840(14)	C(128)−C(141)	1.415(17)
S(28B)−C(68)	0.954(12)	C(143)−C(146)	1.482(19)
S(28B)−C(64)	1.685(12)	C(145)−C(147)	1.46(2)
S(28B)−C(67)	1.804(12)	C(147)−C(156)	1.40(3)
S(28B)−C(65)	2.277(14)	C(149)−C(154)	1.484(18)
O(1)−C(1)	1.361(7)	C(151)−C(150)	1.43(2)
O(2)−C(29)	1.398(8)	C(151)−C(152)	1.75(3)
O(3)−C(14)	1.394(8)	C(152)−C(153)	1.31(3)
O(4)−C(44)	1.388(8)	C(154)−C(155)	1.43(3)
O(5)−C(59)	1.372(9)	C(01)−C(03)#1	1.419(17)
O(6)−C(74)	1.373(8)	C(01)−C(02)#1	1.421(17)
O(7)−C(117)	1.354(9)	C(02)−C(01)#2	1.421(17)
O(8)−C(102)	1.388(8)	C(02)−C(06)	1.63(3)
O(9)−C(142)	1.458(14)	C(02)−C(05)	2.07(3)
O(9)−C(146)	1.464(14)	C(03)−C(04)	1.41(2)
O(10)−C(140)	1.362(11)	C(03)−C(01)#2	1.419(17)
O(10)−C(120)	1.459(11)	C(03)−C(05)	1.79(3)
O(11)−C(156)	1.400(16)	C(04)−C(05)	1.37(3)
O(11)−C(127)	1.421(13)	C(04)−C(06)	1.36(3)
O(12)−C(153)	1.53(2)	C(05)−C(06)	1.35(3)
O(12)−C(150)	1.533(18)	C(07)−C(010)#3	1.39(3)
O(13)−C(121)	1.373(11)	C(07)−C(08)#3	1.482(15)
O(13)−C(123)	1.445(12)	C(08)−C(07)#3	1.482(15)
O(14)−C(155)	1.383(19)	C(08)−C(09)	1.492(17)
O(14)−C(126)	1.466(14)	C(09)−C(012)#3	1.35(3)
C(1)−C(2)	1.546(9)	C(09)−C(011)#4	1.890(18)
C(1)−C(10)	1.553(10)	C(010)−C(07)#3	1.39(3)
C(1)−C(6)	1.561(9)	C(010)−C(011)#4	1.42(3)
C(2)−C(3)	1.382(9)	C(011)−C(010)#5	1.42(3)
C(3)−C(4)	1.423(10)	C(011)−C(012)#6	1.47(3)
C(4)−C(5)	1.395(11)	C(011)−C(09)#5	1.890(18)
C(6)−C(7)	1.394(10)	C(012)−C(09)#3	1.35(3)
C(7)−C(8)	1.419(10)	C(012)−C(011)#6	1.47(3)

O(2)−K(1)−O(4)	94.30(15)	C(10)−S(22)−C(13)	94.1(4)
O(1)−K(1)−O(4)	92.13(15)	C(14A)−S(22)−K(1)	126.2(9)
O(2)−K(1)−O(9)	111.9(2)	C(10)−S(22)−K(1)	91.0(3)
O(1)−K(1)−O(9)	132.0(2)	C(13)−S(22)−K(1)	132.3(3)
O(4)−K(1)−O(9)	125.9(2)	C(75)−S(23)−C(78)	94.0(5)
O(2)−K(1)−S(20)	56.99(12)	C(75)−S(23)−K(8)	102.5(3)
O(1)−K(1)−S(20)	144.13(14)	C(78)−S(23)−K(8)	149.2(5)
O(4)−K(1)−S(20)	103.57(14)	C(97B)−S(24)−C(97A)	162.5(13)
O(9)−K(1)−S(20)	61.1(2)	C(97B)−S(24)−C(94)	49.2(5)
O(2)−K(1)−S(22)	88.51(13)	C(97A)−S(24)−C(94)	145.9(7)
O(1)−K(1)−S(22)	60.18(14)	C(97B)−S(24)−C(97)	151.2(8)
O(4)−K(1)−S(22)	152.22(14)	C(97A)−S(24)−C(97)	43.7(4)
O(9)−K(1)−S(22)	77.7(2)	C(94)−S(24)−C(97)	102.6(3)
S(20)−K(1)−S(22)	101.11(13)	C(97B)−S(24)−K(8)	63.2(11)

O(2)−K(1)−S(9)	148.20(12)
O(1)−K(1)−S(9)	105.36(12)
O(4)−K(1)−S(9)	58.30(11)
O(9)−K(1)−S(9)	78.07(18)
S(20)−K(1)−S(9)	110.36(9)
S(22)−K(1)−S(9)	123.28(9)
O(2)−K(1)−K(3)	92.89(11)
O(1)−K(1)−K(3)	45.54(11)
O(4)−K(1)−K(3)	46.59(10)
O(9)−K(1)−K(3)	155.14(18)
S(20)−K(1)−K(3)	138.87(11)
S(22)−K(1)−K(3)	105.71(10)
S(9)−K(1)−K(3)	79.78(6)
O(2)−K(1)−K(4)	48.11(11)
O(1)−K(1)−K(4)	89.81(11)
O(4)−K(1)−K(4)	46.25(10)
O(9)−K(1)−K(4)	136.9(2)
S(20)−K(1)−K(4)	78.98(10)
S(22)−K(1)−K(4)	128.69(9)
S(9)−K(1)−K(4)	103.40(6)
K(3)−K(1)−K(4)	59.93(4)
O(2)−K(1)−K(2)	45.76(10)
O(1)−K(1)−K(2)	44.62(10)
O(4)−K(1)−K(2)	91.92(11)
O(9)−K(1)−K(2)	140.28(19)
S(20)−K(1)−K(2)	102.00(8)
S(22)−K(1)−K(2)	70.49(8)
S(9)−K(1)−K(2)	139.84(7)
K(3)−K(1)−K(2)	60.12(5)
K(4)−K(1)−K(2)	59.70(4)
O(3)−K(2)−O(1)	91.66(15)
O(3)−K(2)−O(2)	94.70(14)
O(1)−K(2)−O(2)	88.25(14)
O(3)−K(2)−O(10)	119.47(17)
O(1)−K(2)−O(10)	129.79(17)
O(2)−K(2)−O(10)	123.37(16)
O(3)−K(2)−S(12)	55.60(11)
O(1)−K(2)−S(12)	143.54(14)
O(2)−K(2)−S(12)	108.16(11)
O(10)−K(2)−S(12)	67.78(14)
O(3)−K(2)−S(11)	89.89(11)
O(1)−K(2)−S(11)	58.51(11)
O(2)−K(2)−S(11)	146.59(11)
O(10)−K(2)−S(11)	81.59(13)
S(12)−K(2)−S(11)	101.70(7)
O(3)−K(2)−S(17)	146.43(11)
O(1)−K(2)−S(17)	101.24(13)
O(2)−K(2)−S(17)	55.39(11)
O(10)−K(2)−S(17)	74.82(13)
S(12)−K(2)−S(17)	114.96(7)
S(11)−K(2)−S(17)	123.30(7)
O(3)−K(2)−K(4)	46.92(10)
O(1)−K(2)−K(4)	89.46(11)
O(2)−K(2)−K(4)	47.79(10)
O(10)−K(2)−K(4)	140.72(14)
S(12)−K(2)−K(4)	79.36(6)
S(11)−K(2)−K(4)	127.27(7)
S(17)−K(2)−K(4)	101.83(6)
O(3)−K(2)−K(3)	46.92(10)
O(1)−K(2)−K(3)	44.79(11)
O(2)−K(2)−K(3)	90.35(10)
O(10)−K(2)−K(3)	146.17(13)
S(12)−K(2)−K(3)	101.33(7)
S(11)−K(2)−K(3)	69.05(6)
S(17)−K(2)−K(3)	135.56(7)
K(4)−K(2)−K(3)	59.38(4)
O(3)−K(2)−K(1)	91.91(11)
O(1)−K(2)−K(1)	44.55(11)
O(2)−K(2)−K(1)	43.82(10)
O(10)−K(2)−K(1)	148.46(14)
S(12)−K(2)−K(1)	138.70(7)
S(11)−K(2)−K(1)	103.05(6)
S(17)−K(2)−K(1)	76.83(6)
C(97A)−S(24)−K(8)	118.2(8)
C(94)−S(24)−K(8)	84.2(3)
C(97)−S(24)−K(8)	127.7(3)
C(93)−S(25)−C(90)	93.8(4)
C(93)−S(25)−K(6)	135.6(3)
C(90)−S(25)−K(6)	90.9(3)
C(63)−S(26)−C(60)	94.9(4)
C(63)−S(26)−K(7)	126.1(3)
C(60)−S(26)−K(7)	84.8(3)
C(98)−S(27)−C(101)	94.4(4)
C(98)−S(27)−K(7)	87.8(3)
C(101)−S(27)−K(7)	129.3(3)
S(28C)−S(28A)−C(73)	101.7(7)
S(28C)−S(28A)−C(70)	80.8(5)
C(73)−S(28A)−C(70)	96.5(5)
S(28C)−S(28A)−K(6)	29.3(4)
C(73)−S(28A)−K(6)	129.8(5)
C(70)−S(28A)−K(6)	86.9(3)
S(28A)−S(28C)−C(70)	61.7(5)
S(28A)−S(28C)−C(73)	47.3(5)
C(70)−S(28C)−C(73)	74.5(5)
S(28A)−S(28C)−K(6)	138.5(6)
C(70)−S(28C)−K(6)	117.3(4)
C(73)−S(28C)−K(6)	168.0(5)
C(69)−S(28B)−C(68)	101.4(16)
C(69)−S(28B)−C(64)	55.2(7)
C(68)−S(28B)−C(64)	129.5(12)
C(69)−S(28B)−C(67)	127.4(12)
C(68)−S(28B)−C(67)	49.6(6)
C(64)−S(28B)−C(67)	105.6(7)
C(69)−S(28B)−C(65)	88.6(9)
C(68)−S(28B)−C(65)	112.1(9)
C(64)−S(28B)−C(65)	37.5(3)
C(67)−S(28B)−C(65)	71.3(5)
C(69)−S(28B)−K(5)	90.8(10)
C(68)−S(28B)−K(5)	139.3(10)
C(64)−S(28B)−K(5)	89.3(5)
C(67)−S(28B)−K(5)	141.0(7)
C(65)−S(28B)−K(5)	106.8(5)
C(1)−O(1)−K(3)	128.9(4)
C(1)−O(1)−K(1)	125.1(4)
K(3)−O(1)−K(1)	88.64(14)
C(1)−O(1)−K(2)	122.1(4)
K(3)−O(1)−K(2)	90.07(15)
K(1)−O(1)−K(2)	90.84(15)
C(29)−O(2)−K(1)	141.3(4)
C(29)−O(2)−K(2)	123.7(4)
K(1)−O(2)−K(2)	90.42(14)
C(29)−O(2)−K(4)	110.8(4)
K(1)−O(2)−K(4)	87.24(14)
K(2)−O(2)−K(4)	85.87(13)
C(14)−O(3)−K(2)	145.1(4)
C(14)−O(3)−K(4)	111.7(4)
K(2)−O(3)−K(4)	88.18(13)
C(14)−O(3)−K(3)	120.5(4)
K(2)−O(3)−K(3)	88.36(14)
K(4)−O(3)−K(3)	85.34(13)
C(44)−O(4)−K(1)	121.8(4)
C(44)−O(4)−K(3)	142.3(4)
K(1)−O(4)−K(3)	87.08(14)
C(44)−O(4)−K(4)	115.2(4)
K(1)−O(4)−K(4)	87.77(14)
K(3)−O(4)−K(4)	87.07(14)
C(59)−O(5)−K(6)	136.0(4)
C(59)−O(5)−K(5)	121.1(5)
K(6)−O(5)−K(5)	86.38(15)
C(59)−O(5)−K(7)	122.7(5)
K(6)−O(5)−K(7)	90.1(2)
K(5)−O(5)−K(7)	85.98(15)
C(74)−O(6)−K(6)	120.3(4)
C(74)−O(6)−K(8)	141.1(4)
K(6)−O(6)−K(8)	91.11(16)
C(74)−O(6)−K(5)	116.1(4)

K(4)−K(2)−K(1)	59.35(4)
K(3)−K(2)−K(1)	58.83(4)
O(1)−K(3)−O(4)	92.14(15)
O(1)−K(3)−O(3)	89.81(15)
O(4)−K(3)−O(3)	93.67(14)
O(1)−K(3)−O(11)	126.29(18)
O(4)−K(3)−O(11)	121.75(18)
O(3)−K(3)−O(11)	123.79(18)
O(1)−K(3)−S(21)	142.27(13)
O(4)−K(3)−S(21)	56.28(11)
O(3)−K(3)−S(21)	110.39(12)
O(11)−K(3)−S(21)	68.64(15)
O(1)−K(3)−S(8)	103.98(12)
O(4)−K(3)−S(8)	145.65(12)
O(3)−K(3)−S(8)	56.93(10)
O(11)−K(3)−S(8)	71.97(16)
S(21)−K(3)−S(8)	113.76(8)
O(1)−K(3)−S(16)	57.77(11)
O(4)−K(3)−S(16)	93.61(12)
O(3)−K(3)−S(16)	146.99(12)
O(11)−K(3)−S(16)	78.07(16)
S(21)−K(3)−S(16)	100.37(9)
S(8)−K(3)−S(16)	120.68(7)
O(1)−K(3)−K(1)	45.82(11)
O(4)−K(3)−K(1)	46.33(10)
O(3)−K(3)−K(1)	92.12(10)
O(11)−K(3)−K(1)	144.08(16)
S(21)−K(3)−K(1)	100.14(7)
S(8)−K(3)−K(1)	139.82(7)
S(16)−K(3)−K(1)	70.41(6)
O(1)−K(3)−K(4)	90.34(11)
O(4)−K(3)−K(4)	46.47(10)
O(3)−K(3)−K(4)	47.23(9)
O(11)−K(3)−K(4)	143.37(15)
S(21)−K(3)−K(4)	81.93(7)
S(8)−K(3)−K(4)	102.48(6)
S(16)−K(3)−K(4)	130.17(7)
K(1)−K(3)−K(4)	60.35(4)
O(1)−K(3)−K(2)	45.14(11)
O(4)−K(3)−K(2)	92.47(11)
O(3)−K(3)−K(2)	44.72(10)
O(11)−K(3)−K(2)	145.76(16)
S(21)−K(3)−K(2)	142.04(8)
S(8)−K(3)−K(2)	78.83(6)
S(16)−K(3)−K(2)	102.81(7)
K(1)−K(3)−K(2)	61.04(4)
K(4)−K(3)−K(2)	60.14(4)
O(4)−K(4)−O(3)	93.88(14)
O(4)−K(4)−O(2)	90.58(14)
O(3)−K(4)−O(2)	91.24(14)
O(4)−K(4)−C(23)	108.46(17)
O(3)−K(4)−C(23)	47.19(16)
O(2)−K(4)−C(23)	133.87(17)
O(4)−K(4)−C(38)	131.25(17)
O(3)−K(4)−C(38)	106.50(17)
O(2)−K(4)−C(38)	46.40(16)
C(23)−K(4)−C(38)	118.0(2)
O(4)−K(4)−C(53)	46.38(15)
O(3)−K(4)−C(53)	133.94(16)
O(2)−K(4)−C(53)	108.27(16)
C(23)−K(4)−C(53)	115.30(19)
C(38)−K(4)−C(53)	117.28(19)
O(4)−K(4)−C(43)	129.45(18)
O(3)−K(4)−C(43)	128.18(18)
O(2)−K(4)−C(43)	65.32(17)
C(23)−K(4)−C(43)	120.4(2)
C(38)−K(4)−C(43)	25.16(19)
C(53)−K(4)−C(43)	97.8(2)
O(4)−K(4)−C(28)	130.71(17)
O(3)−K(4)−C(28)	64.98(15)
O(2)−K(4)−C(28)	131.13(16)
C(23)−K(4)−C(28)	25.29(17)
C(38)−K(4)−C(28)	97.95(18)
K(6)−O(6)−K(5)	86.16(15)
K(8)−O(6)−K(5)	86.09(15)
C(117)−O(7)−K(7)	127.0(4)
C(117)−O(7)−K(8)	121.9(5)
K(7)−O(7)−K(8)	88.16(16)
C(117)−O(7)−K(6)	128.0(5)
K(7)−O(7)−K(6)	90.37(19)
K(8)−O(7)−K(6)	89.56(16)
C(102)−O(8)−K(7)	144.4(4)
C(102)−O(8)−K(5)	111.0(4)
K(7)−O(8)−K(5)	88.23(15)
C(102)−O(8)−K(8)	121.9(4)
K(7)−O(8)−K(8)	88.24(14)
K(5)−O(8)−K(8)	84.96(14)
C(142)−O(9)−C(146)	109.9(11)
C(142)−O(9)−K(1)	125.5(8)
C(146)−O(9)−K(1)	124.4(9)
C(140)−O(10)−C(120)	107.4(7)
C(140)−O(10)−K(2)	125.0(6)
C(120)−O(10)−K(2)	126.1(5)
C(156)−O(11)−C(127)	104.2(10)
C(156)−O(11)−K(3)	124.6(9)
C(127)−O(11)−K(3)	131.2(6)
C(153)−O(12)−C(150)	99.3(16)
C(153)−O(12)−K(6)	149.1(15)
C(150)−O(12)−K(6)	111.2(9)
C(121)−O(13)−C(123)	108.1(8)
C(121)−O(13)−K(7)	121.6(6)
C(123)−O(13)−K(7)	130.0(6)
C(155)−O(14)−C(126)	105.5(13)
C(155)−O(14)−K(8)	118.6(12)
C(126)−O(14)−K(8)	135.9(7)
O(1)−C(1)−C(2)	112.3(5)
O(1)−C(1)−C(10)	112.6(6)
C(2)−C(1)−C(10)	107.3(5)
O(1)−C(1)−C(6)	110.4(6)
C(2)−C(1)−C(6)	106.7(5)
C(10)−C(1)−C(6)	107.3(5)
C(3)−C(2)−C(1)	129.6(6)
C(3)−C(2)−S(11)	111.1(5)
C(1)−C(2)−S(11)	119.1(5)
C(2)−C(3)−C(4)	113.3(7)
C(5)−C(4)−C(3)	113.4(7)
C(4)−C(5)−S(11)	108.2(5)
C(7)−C(6)−C(1)	126.6(6)
C(7)−C(6)−S(16)	111.0(5)
C(1)−C(6)−S(16)	122.4(6)
C(6)−C(7)−C(8)	112.9(7)
C(9)−C(8)−C(7)	115.9(8)
C(14B)−C(9)−C(8)	150(3)
C(14B)−C(9)−S(16)	58(3)
C(8)−C(9)−S(16)	105.9(6)
C(11)−C(10)−C(1)	127.6(6)
C(11)−C(10)−S(22)	110.3(6)
C(1)−C(10)−S(22)	122.1(5)
C(12)−C(11)−C(10)	114.7(7)
C(13)−C(12)−C(11)	120.0(8)
C(14A)−C(13)−C(12)	136.1(15)
C(14A)−C(13)−S(22)	35.5(11)
C(12)−C(13)−S(22)	100.9(7)
C(13)−C(14A)−S(22)	115.2(17)
C(9)−C(14B)−S(16)	88(4)
O(3)−C(14)−C(19)	109.8(6)
O(3)−C(14)−C(15)	113.0(5)
C(19)−C(14)−C(15)	105.5(5)
O(3)−C(14)−C(23)	108.9(5)
C(19)−C(14)−C(23)	110.4(5)
C(15)−C(14)−C(23)	109.3(6)
O(3)−C(14)−K(4)	46.8(3)
C(19)−C(14)−K(4)	116.7(4)
C(15)−C(14)−K(4)	137.1(4)
C(23)−C(14)−K(4)	63.1(3)
C(16)−C(15)−C(14)	129.2(6)

C(53)−K(4)−C(28)	119.05(18)	C(16)−C(15)−S(8)	112.2(5)
C(43)−K(4)−C(28)	95.57(19)	C(14)−C(15)−S(8)	118.2(5)
O(4)−K(4)−C(24)	87.99(16)	C(15)−C(16)−C(17)	110.5(7)
O(3)−K(4)−C(24)	60.05(15)	C(18)−C(17)−C(16)	113.8(7)
O(2)−K(4)−C(24)	151.06(16)	C(17)−C(18)−S(8)	110.9(6)
C(23)−K(4)−C(24)	24.60(17)	C(20)−C(19)−C(14)	126.2(6)
C(38)−K(4)−C(24)	140.57(19)	C(20)−C(19)−S(12)	114.1(5)
C(53)−K(4)−C(24)	91.40(18)	C(14)−C(19)−S(12)	119.7(5)
C(43)−K(4)−C(24)	134.2(2)	C(21)−C(20)−C(19)	102.8(6)
C(28)−K(4)−C(24)	42.72(18)	C(22)−C(21)−C(20)	117.4(7)
O(4)−K(4)−C(58)	59.08(17)	C(21)−C(22)−S(12)	110.7(7)
O(3)−K(4)−C(58)	152.92(18)	C(24)−C(23)−C(28)	119.1(6)
O(2)−K(4)−C(58)	90.48(18)	C(24)−C(23)−C(14)	119.4(6)
C(23)−K(4)−C(58)	135.5(2)	C(28)−C(23)−C(14)	121.1(6)
C(38)−K(4)−C(58)	94.1(2)	C(24)−C(23)−K(4)	87.6(4)
C(53)−K(4)−C(58)	23.36(18)	C(28)−C(23)−K(4)	85.6(4)
C(43)−K(4)−C(58)	76.5(2)	C(14)−C(23)−K(4)	90.9(4)
C(28)−K(4)−C(58)	130.24(19)	C(25)−C(24)−C(23)	119.7(7)
C(24)−K(4)−C(58)	113.2(2)	C(25)−C(24)−K(4)	96.4(5)
O(4)−K(4)−C(39)	149.25(17)	C(23)−C(24)−K(4)	67.8(4)
O(3)−K(4)−C(39)	86.39(14)	C(24)−C(25)−C(26)	119.6(8)
O(2)−K(4)−C(39)	58.69(16)	C(27)−C(26)−C(25)	121.5(8)
C(23)−K(4)−C(39)	94.20(18)	C(26)−C(27)−C(28)	121.7(8)
C(38)−K(4)−C(39)	24.41(17)	C(27)−C(28)−C(23)	118.4(7)
C(53)−K(4)−C(39)	139.49(17)	C(27)−C(28)−K(4)	95.2(5)
C(43)−K(4)−C(39)	41.80(18)	C(23)−C(28)−K(4)	69.1(4)
C(28)−K(4)−C(39)	76.88(18)	O(2)−C(29)−C(30)	112.1(6)
C(24)−K(4)−C(39)	117.99(17)	O(2)−C(29)−C(38)	109.3(6)
C(58)−K(4)−C(39)	117.21(18)	C(30)−C(29)−C(38)	108.4(6)
O(4)−K(4)−C(14)	104.08(15)	O(2)−C(29)−C(34)	111.3(6)
O(3)−K(4)−C(14)	21.54(14)	C(30)−C(29)−C(34)	105.9(6)
O(2)−K(4)−C(14)	109.73(15)	C(38)−C(29)−C(34)	109.8(6)
C(23)−K(4)−C(14)	25.97(16)	C(31)−C(30)−C(29)	129.7(7)
C(38)−K(4)−C(14)	110.93(18)	C(31)−C(30)−S(17)	111.0(6)
C(53)−K(4)−C(14)	131.24(18)	C(29)−C(30)−S(17)	119.1(5)
C(43)−K(4)−C(14)	125.38(19)	C(30)−C(31)−C(32)	112.5(7)
C(28)−K(4)−C(14)	44.27(16)	C(33)−C(32)−C(31)	112.1(7)
C(24)−K(4)−C(14)	43.29(16)	C(32)−C(33)−S(17)	111.3(7)
C(58)−K(4)−C(14)	154.6(2)	C(35)−C(34)−C(29)	129.3(6)
C(39)−K(4)−C(14)	87.13(16)	C(35)−C(34)−S(20)	110.9(5)
O(6)−K(5)−O(8)	94.10(14)	C(29)−C(34)−S(20)	119.7(6)
O(6)−K(5)−O(5)	92.26(16)	C(36)−C(35)−C(34)	111.4(11)
O(8)−K(5)−O(5)	91.99(17)	C(35)−C(36)−C(37)	124.8(15)
O(6)−K(5)−C(111)	110.07(18)	C(36)−C(37)−S(20)	103.3(11)
O(8)−K(5)−C(111)	47.42(17)	C(43)−C(38)−C(39)	116.2(7)
O(5)−K(5)−C(111)	133.20(19)	C(43)−C(38)−C(29)	121.4(7)
O(6)−K(5)−S(28B)	157.8(2)	C(39)−C(38)−C(29)	121.5(6)
O(8)−K(5)−S(28B)	98.5(2)	C(43)−C(38)−K(4)	80.3(5)
O(5)−K(5)−S(28B)	69.2(2)	C(39)−C(38)−K(4)	90.0(4)
C(111)−K(5)−S(28B)	91.8(3)	C(29)−C(38)−K(4)	90.1(4)
O(6)−K(5)−C(88)	61.15(18)	C(40)−C(39)−C(38)	125.3(7)
O(8)−K(5)−C(88)	155.13(18)	C(40)−C(39)−K(4)	96.2(5)
O(5)−K(5)−C(88)	91.44(19)	C(38)−C(39)−K(4)	65.6(4)
C(111)−K(5)−C(88)	135.3(2)	C(39)−C(40)−C(41)	119.3(9)
S(28B)−K(5)−C(88)	105.8(3)	C(42)−C(41)−C(40)	120.2(8)
O(6)−K(5)−C(69)	149.16(18)	C(41)−C(42)−C(43)	122.0(8)
O(8)−K(5)−C(69)	89.84(18)	C(38)−C(43)−C(42)	116.9(7)
O(5)−K(5)−C(69)	57.01(18)	C(38)−C(43)−K(4)	74.5(4)
C(111)−K(5)−C(69)	95.00(18)	C(42)−C(43)−K(4)	92.9(5)
S(28B)−K(5)−C(69)	15.0(2)	O(4)−C(44)−C(49)	112.4(6)
C(88)−K(5)−C(69)	112.51(19)	O(4)−C(44)−C(45)	110.7(6)
O(6)−K(5)−C(112)	132.41(18)	C(49)−C(44)−C(45)	103.0(6)
O(8)−K(5)−C(112)	66.32(17)	O(4)−C(44)−C(53)	110.3(6)
O(5)−K(5)−C(112)	129.32(18)	C(49)−C(44)−C(53)	110.7(6)
C(111)−K(5)−C(112)	25.85(18)	C(45)−C(44)−C(53)	109.5(6)
S(28B)−K(5)−C(112)	69.7(2)	C(46)−C(45)−C(44)	129.4(8)
C(88)−K(5)−C(112)	127.6(2)	C(46)−C(45)−S(21)	109.9(7)
C(69)−K(5)−C(112)	76.79(18)	C(44)−C(45)−S(21)	120.6(6)
O(6)−K(5)−C(83)	45.59(16)	C(45)−C(46)−C(47)	109.9(10)
O(8)−K(5)−C(83)	132.78(17)	C(48)−C(47)−C(46)	115.0(10)
O(5)−K(5)−C(83)	109.78(18)	C(47)−C(48)−S(21)	110.5(9)
C(111)−K(5)−C(83)	115.2(2)	C(50)−C(49)−C(44)	127.9(7)
S(28B)−K(5)−C(83)	128.1(3)	C(50)−C(49)−S(9)	111.2(6)

C(88)−K(5)−C(83)	25.48(18)
C(69)−K(5)−C(83)	137.27(19)
C(112)−K(5)−C(83)	118.6(2)
O(6)−K(5)−C(116)	89.55(17)
O(8)−K(5)−C(116)	60.74(17)
O(5)−K(5)−C(116)	152.7(2)
C(111)−K(5)−C(116)	25.08(18)
S(28B)−K(5)−C(116)	112.5(2)
C(88)−K(5)−C(116)	113.0(2)
C(69)−K(5)−C(116)	118.64(18)
C(112)−K(5)−C(116)	42.87(19)
C(83)−K(5)−C(116)	90.7(2)
O(6)−K(5)−C(102)	105.17(15)
O(8)−K(5)−C(102)	21.77(14)
O(5)−K(5)−C(102)	109.78(17)
C(111)−K(5)−C(102)	26.03(17)
S(28B)−K(5)−C(102)	92.9(2)
C(88)−K(5)−C(102)	155.82(19)
C(69)−K(5)−C(102)	89.38(17)
C(112)−K(5)−C(102)	45.27(17)
C(83)−K(5)−C(102)	130.78(18)
C(116)−K(5)−C(102)	43.96(18)
O(6)−K(5)−C(64)	129.65(14)
O(8)−K(5)−C(64)	107.25(16)
O(5)−K(5)−C(64)	43.42(15)
C(111)−K(5)−C(64)	118.04(17)
S(28B)−K(5)−C(64)	28.5(2)
C(88)−K(5)−C(64)	91.99(18)
C(69)−K(5)−C(64)	23.21(6)
C(112)−K(5)−C(64)	97.91(16)
C(83)−K(5)−C(64)	117.46(18)
C(116)−K(5)−C(64)	140.71(16)
C(102)−K(5)−C(64)	111.28(16)
O(5)−K(6)−O(6)	95.21(17)
O(5)−K(6)−S(28C)	61.3(2)
O(6)−K(6)−S(28C)	113.4(2)
O(5)−K(6)−O(7)	90.17(18)
O(6)−K(6)−O(7)	89.54(19)
S(28C)−K(6)−O(7)	143.7(2)
O(5)−K(6)−O(12)	115.7(2)
O(6)−K(6)−O(12)	117.8(2)
S(28C)−K(6)−O(12)	55.3(2)
O(7)−K(6)−O(12)	138.3(2)
O(5)−K(6)−S(25)	94.06(15)
O(6)−K(6)−S(25)	148.17(15)
S(28C)−K(6)−S(25)	97.72(19)
O(7)−K(6)−S(25)	60.03(15)
O(12)−K(6)−S(25)	84.8(2)
O(5)−K(6)−S(14)	150.72(16)
O(6)−K(6)−S(14)	58.98(12)
S(28C)−K(6)−S(14)	113.58(17)
O(7)−K(6)−S(14)	102.22(15)
O(12)−K(6)−S(14)	71.50(19)
S(25)−K(6)−S(14)	115.15(8)
O(5)−K(6)−S(28A)	56.49(14)
O(6)−K(6)−S(28A)	101.93(13)
S(28C)−K(6)−S(28A)	12.13(17)
O(7)−K(6)−S(28A)	145.25(15)
O(12)−K(6)−S(28A)	63.25(19)
S(25)−K(6)−S(28A)	108.56(11)
S(14)−K(6)−S(28A)	111.85(9)
O(5)−K(6)−K(5)	47.86(13)
O(6)−K(6)−K(5)	47.35(11)
S(28C)−K(6)−K(5)	86.83(17)
O(7)−K(6)−K(5)	89.52(12)
O(12)−K(6)−K(5)	132.1(2)
S(25)−K(6)−K(5)	133.04(8)
S(14)−K(6)−K(5)	105.15(7)
S(28A)−K(6)−K(5)	75.51(8)
O(5)−K(6)−K(7)	46.01(13)
O(6)−K(6)−K(7)	90.98(12)
S(28C)−K(6)−K(7)	104.98(17)
O(7)−K(6)−K(7)	44.25(12)
C(44)−C(49)−S(9)	120.0(5)
C(49)−C(50)−C(51)	109.7(8)
C(52)−C(51)−C(50)	113.5(9)
C(51)−C(52)−S(9)	111.0(8)
C(58)−C(53)−C(54)	117.7(7)
C(58)−C(53)−C(44)	119.6(7)
C(54)−C(53)−C(44)	122.2(7)
C(58)−C(53)−K(4)	84.9(5)
C(54)−C(53)−K(4)	91.4(6)
C(44)−C(53)−K(4)	87.1(4)
C(53)−C(54)−C(55)	120.5(8)
C(54)−C(55)−C(56)	119.6(9)
C(57)−C(56)−C(55)	118.7(8)
C(56)−C(57)−C(58)	121.7(9)
C(53)−C(58)−C(57)	121.3(8)
C(53)−C(58)−K(4)	71.7(5)
C(57)−C(58)−K(4)	102.3(7)
O(5)−C(59)−C(70)	112.8(6)
O(5)−C(59)−C(60)	111.5(7)
C(70)−C(59)−C(60)	105.1(6)
O(5)−C(59)−C(64)	111.4(6)
C(70)−C(59)−C(64)	108.1(7)
C(60)−C(59)−C(64)	107.5(6)
C(61)−C(60)−C(59)	128.2(8)
C(61)−C(60)−S(26)	111.0(6)
C(59)−C(60)−S(26)	120.5(6)
C(60)−C(61)−C(62)	109.3(8)
C(63)−C(62)−C(61)	114.1(8)
C(62)−C(63)−S(26)	110.8(7)
C(65)−C(64)−C(69)	120.0
C(65)−C(64)−C(59)	122.7(6)
C(69)−C(64)−C(59)	117.2(6)
C(65)−C(64)−S(28B)	95.0(5)
C(69)−C(64)−S(28B)	29.7(6)
C(59)−C(64)−S(28B)	137.9(7)
C(65)−C(64)−K(5)	118.3(5)
C(69)−C(64)−K(5)	66.8(4)
C(59)−C(64)−K(5)	82.3(4)
S(28B)−C(64)−K(5)	62.1(5)
C(64)−C(65)−C(66)	120.0
C(64)−C(65)−S(28B)	47.5(3)
C(66)−C(65)−S(28B)	74.2(3)
C(65)−C(66)−C(67)	120.0
C(68)−C(67)−C(66)	120.0
C(68)−C(67)−S(28B)	31.5(5)
C(66)−C(67)−S(28B)	92.3(4)
S(28B)−C(68)−C(69)	36.3(9)
S(28B)−C(68)−C(67)	98.9(9)
C(69)−C(68)−C(67)	120.0
S(28B)−C(69)−C(68)	42.3(9)
S(28B)−C(69)−C(64)	95.0(10)
C(68)−C(69)−C(64)	120.0
S(28B)−C(69)−K(5)	74.2(10)
C(68)−C(69)−K(5)	107.5(4)
C(64)−C(69)−K(5)	90.0(4)
C(71)−C(70)−C(59)	129.8(8)
C(71)−C(70)−S(28A)	107.1(7)
C(59)−C(70)−S(28A)	122.3(6)
C(71)−C(70)−S(28C)	115.6(7)
C(59)−C(70)−S(28C)	109.2(6)
S(28A)−C(70)−S(28C)	37.5(3)
C(70)−C(71)−C(72)	112.0(9)
C(73)−C(72)−C(71)	111.8(10)
C(72)−C(73)−S(28A)	111.6(8)
C(72)−C(73)−S(28C)	107.3(8)
S(28A)−C(73)−S(28C)	31.0(3)
O(6)−C(74)−C(75)	111.1(6)
O(6)−C(74)−C(79)	111.6(6)
C(75)−C(74)−C(79)	104.6(6)
O(6)−C(74)−C(83)	110.4(6)
C(75)−C(74)−C(83)	109.9(6)
C(79)−C(74)−C(83)	109.0(6)
C(76)−C(75)−C(74)	127.3(8)

O(12)−K(6)−K(7)	149.2(2)
S(25)−K(6)−K(7)	74.07(7)
S(14)−K(6)−K(7)	137.89(10)
S(28A)−K(6)−K(7)	102.22(8)
K(5)−K(6)−K(7)	59.77(5)
O(5)−K(6)−K(8)	91.17(13)
O(6)−K(6)−K(8)	44.47(11)
S(28C)−K(6)−K(8)	145.52(17)
O(7)−K(6)−K(8)	45.19(14)
O(12)−K(6)−K(8)	151.0(2)
S(25)−K(6)−K(8)	105.02(9)
S(14)−K(6)−K(8)	79.71(7)
S(28A)−K(6)−K(8)	134.12(8)
K(5)−K(6)−K(8)	58.71(5)
K(7)−K(6)−K(8)	58.62(6)
O(8)−K(7)−O(7)	93.27(17)
O(8)−K(7)−O(13)	120.37(19)
O(7)−K(7)−O(13)	126.55(18)
O(8)−K(7)−O(5)	93.57(16)
O(7)−K(7)−O(5)	89.15(18)
O(13)−K(7)−O(5)	124.66(18)
O(8)−K(7)−S(27)	90.74(13)
O(7)−K(7)−S(27)	59.21(14)
O(13)−K(7)−S(27)	78.65(14)
O(5)−K(7)−S(27)	148.28(14)
O(8)−K(7)−S(15)	55.72(11)
O(7)−K(7)−S(15)	147.36(17)
O(13)−K(7)−S(15)	71.59(15)
O(5)−K(7)−S(15)	101.59(14)
S(27)−K(7)−S(15)	106.73(8)
O(8)−K(7)−S(26)	149.38(14)
O(7)−K(7)−S(26)	97.71(17)
O(13)−K(7)−S(26)	74.48(16)
O(5)−K(7)−S(26)	58.29(13)
S(27)−K(7)−S(26)	119.39(9)
S(15)−K(7)−S(26)	114.22(8)
O(8)−K(7)−K(5)	46.78(11)
O(7)−K(7)−K(5)	89.17(12)
O(13)−K(7)−K(5)	144.27(15)
O(5)−K(7)−K(5)	46.91(12)
S(27)−K(7)−K(5)	127.27(8)
S(15)−K(7)−K(5)	76.81(6)
S(26)−K(7)−K(5)	104.72(8)
O(8)−K(7)−K(8)	46.80(10)
O(7)−K(7)−K(8)	46.48(14)
O(13)−K(7)−K(8)	143.88(15)
O(5)−K(7)−K(8)	91.42(12)
S(27)−K(7)−K(8)	69.15(7)
S(15)−K(7)−K(8)	101.96(7)
S(26)−K(7)−K(8)	135.92(8)
K(5)−K(7)−K(8)	59.00(5)
O(8)−K(7)−K(6)	92.53(11)
O(7)−K(7)−K(6)	45.38(14)
O(13)−K(7)−K(6)	147.05(16)
O(5)−K(7)−K(6)	43.87(12)
S(27)−K(7)−K(6)	104.58(7)
S(15)−K(7)−K(6)	134.85(8)
S(26)−K(7)−K(6)	75.68(7)
K(5)−K(7)−K(6)	58.36(5)
K(8)−K(7)−K(6)	60.81(6)
O(6)−K(8)−O(7)	89.55(18)
O(6)−K(8)−O(8)	94.85(15)
O(7)−K(8)−O(8)	90.33(16)
O(6)−K(8)−O(14)	119.1(2)
O(7)−K(8)−O(14)	130.5(3)
O(8)−K(8)−O(14)	122.9(2)
O(6)−K(8)−C(97B)	88.85(17)
O(7)−K(8)−C(97B)	50.86(17)
O(8)−K(8)−C(97B)	141.04(18)
O(14)−K(8)−C(97B)	87.7(3)
O(6)−K(8)−S(23)	56.32(12)
O(7)−K(8)−S(23)	140.52(15)
O(8)−K(8)−S(23)	109.99(13)
C(76)−C(75)−S(23)	111.2(7)
C(74)−C(75)−S(23)	121.6(5)
C(75)−C(76)−C(77)	108.7(10)
C(78)−C(77)−C(76)	115.6(9)
C(77)−C(78)−S(23)	110.5(8)
C(80)−C(79)−C(74)	129.3(8)
C(80)−C(79)−S(14)	109.5(7)
C(74)−C(79)−S(14)	120.5(5)
C(79)−C(80)−C(81)	112.3(9)
C(82)−C(81)−C(80)	114.0(9)
C(81)−C(82)−S(14)	109.4(7)
C(88)−C(83)−C(84)	114.0(7)
C(88)−C(83)−C(74)	120.5(7)
C(84)−C(83)−C(74)	125.5(7)
C(88)−C(83)−K(5)	70.9(4)
C(84)−C(83)−K(5)	109.9(7)
C(74)−C(83)−K(5)	87.2(4)
C(85)−C(84)−C(83)	117.7(9)
C(86)−C(85)−C(84)	123.0(11)
C(87)−C(86)−C(85)	120.2(10)
C(86)−C(87)−C(88)	122.2(9)
C(87)−C(88)−C(83)	122.6(8)
C(87)−C(88)−K(5)	100.3(6)
C(83)−C(88)−K(5)	83.6(4)
C(91)−C(90)−C(117)	127.4(7)
C(91)−C(90)−S(25)	108.7(6)
C(117)−C(90)−S(25)	123.9(5)
C(90)−C(91)−C(92)	113.3(7)
C(93)−C(92)−C(91)	114.9(7)
C(92)−C(93)−S(25)	109.2(6)
C(95)−C(94)−C(97B)	120.0
C(95)−C(94)−C(117)	132.3(5)
C(97B)−C(94)−C(117)	107.7(5)
C(95)−C(94)−S(24)	100.5(2)
C(97B)−C(94)−S(24)	19.6(2)
C(117)−C(94)−S(24)	127.3(5)
C(94)−C(95)−C(96)	120.0
C(97)−C(96)−C(95)	120.0
C(96)−C(97)−C(97A)	120.0
C(96)−C(97)−S(24)	96.9(2)
C(97A)−C(97)−S(24)	23.1(2)
S(24)−C(97A)−C(97B)	7.7(6)
S(24)−C(97A)−C(97)	113.2(5)
C(97B)−C(97A)−C(97)	120.0
S(24)−C(97B)−C(97A)	9.9(8)
S(24)−C(97B)−C(94)	111.2(6)
C(97A)−C(97B)−C(94)	120.0
S(24)−C(97B)−K(8)	106.8(12)
C(97A)−C(97B)−K(8)	108.1(3)
C(94)−C(97B)−K(8)	98.7(3)
C(99)−C(98)−C(117)	130.4(7)
C(99)−C(98)−S(27)	110.1(6)
C(117)−C(98)−S(27)	119.3(6)
C(98)−C(99)−C(100)	113.5(7)
C(101)−C(100)−C(99)	113.9(8)
C(100)−C(101)−S(27)	108.2(6)
O(8)−C(102)−C(111)	108.8(5)
O(8)−C(102)−C(103)	112.7(6)
C(111)−C(102)−C(103)	110.4(6)
O(8)−C(102)−C(107)	110.8(6)
C(111)−C(102)−C(107)	109.1(6)
C(103)−C(102)−C(107)	105.0(6)
O(8)−C(102)−K(5)	47.3(3)
C(111)−C(102)−K(5)	62.7(3)
C(103)−C(102)−K(5)	138.3(4)
C(107)−C(102)−K(5)	116.2(4)
C(104)−C(103)−C(102)	127.4(7)
C(104)−C(103)−S(13)	113.2(6)
C(102)−C(103)−S(13)	119.2(6)
C(103)−C(104)−C(105)	109.4(8)
C(106)−C(105)−C(104)	114.7(8)
C(105)−C(106)−S(13)	109.2(7)
C(108)−C(107)−C(102)	127.9(7)

O(14)−K(8)−S(23)	65.9(2)
C(97B)−K(8)−S(23)	104.25(15)
O(6)−K(8)−S(24)	90.71(14)
O(7)−K(8)−S(24)	60.68(13)
O(8)−K(8)−S(24)	150.46(14)
O(14)−K(8)−S(24)	78.3(2)
C(97B)−K(8)−S(24)	9.98(14)
S(23)−K(8)−S(24)	97.22(10)
O(6)−K(8)−S(13)	146.44(13)
O(7)−K(8)−S(13)	105.56(14)
O(8)−K(8)−S(13)	56.16(11)
O(14)−K(8)−S(13)	73.31(19)
C(97B)−K(8)−S(13)	124.02(13)
S(23)−K(8)−S(13)	113.89(9)
S(24)−K(8)−S(13)	122.84(10)
O(6)−K(8)−K(5)	47.36(11)
O(7)−K(8)−K(5)	89.58(14)
O(8)−K(8)−K(5)	47.49(11)
O(14)−K(8)−K(5)	139.8(2)
C(97B)−K(8)−K(5)	123.75(13)
S(23)−K(8)−K(5)	81.18(8)
S(24)−K(8)−K(5)	130.44(10)
S(13)−K(8)−K(5)	101.94(6)
O(6)−K(8)−K(7)	92.60(12)
O(7)−K(8)−K(7)	45.36(12)
O(8)−K(8)−K(7)	44.97(10)
O(14)−K(8)−K(7)	148.2(2)
C(97B)−K(8)−K(7)	96.18(14)
S(23)−K(8)−K(7)	141.60(9)
S(24)−K(8)−K(7)	105.89(9)
S(13)−K(8)−K(7)	78.50(6)
K(5)−K(8)−K(7)	60.47(5)
O(6)−K(8)−K(6)	44.42(12)
O(7)−K(8)−K(6)	45.25(14)
O(8)−K(8)−K(6)	91.03(11)
O(14)−K(8)−K(6)	145.6(2)
C(97B)−K(8)−K(6)	65.20(13)
S(23)−K(8)−K(6)	99.20(7)
S(24)−K(8)−K(6)	72.95(9)
S(13)−K(8)−K(6)	139.07(8)
K(5)−K(8)−K(6)	58.73(5)
K(7)−K(8)−K(6)	60.58(5)
C(15)−S(8)−C(18)	92.5(4)
C(15)−S(8)−K(3)	87.5(2)
C(18)−S(8)−K(3)	128.7(3)
C(52)−S(9)−C(49)	94.5(5)
C(52)−S(9)−K(1)	129.8(4)
C(49)−S(9)−K(1)	85.6(3)
C(2)−S(11)−C(5)	94.0(4)
C(2)−S(11)−K(2)	83.8(3)
C(5)−S(11)−K(2)	124.0(3)
C(19)−S(12)−C(22)	94.8(4)
C(19)−S(12)−K(2)	106.2(3)
C(22)−S(12)−K(2)	154.2(3)
C(103)−S(13)−C(106)	93.5(4)
C(103)−S(13)−K(8)	86.8(3)
C(106)−S(13)−K(8)	129.1(3)
C(79)−S(14)−C(82)	94.6(4)
C(79)−S(14)−K(6)	80.0(3)
C(82)−S(14)−K(6)	121.4(4)
C(110)−S(15)−C(107)	93.4(5)
C(110)−S(15)−K(7)	151.3(3)
C(107)−S(15)−K(7)	104.6(3)
C(14B)−S(16)−C(6)	124(2)
C(14B)−S(16)−C(9)	34(2)
C(6)−S(16)−C(9)	94.3(4)
C(14B)−S(16)−K(3)	108(2)
C(6)−S(16)−K(3)	87.1(3)
C(9)−S(16)−K(3)	128.2(3)
C(30)−S(17)−C(33)	93.1(4)
C(30)−S(17)−K(2)	87.8(2)
C(33)−S(17)−K(2)	130.1(3)
C(34)−S(20)−C(37)	87.9(7)
C(108)−C(107)−S(15)	113.6(6)
C(102)−C(107)−S(15)	118.4(5)
C(107)−C(108)−C(109)	106.9(7)
C(110)−C(109)−C(108)	113.7(7)
C(109)−C(110)−S(15)	112.3(7)
C(116)−C(111)−C(112)	115.8(7)
C(116)−C(111)−C(102)	120.4(7)
C(112)−C(111)−C(102)	123.2(7)
C(116)−C(111)−K(5)	87.0(4)
C(112)−C(111)−K(5)	84.1(4)
C(102)−C(111)−K(5)	91.3(4)
C(113)−C(112)−C(111)	120.8(8)
C(113)−C(112)−K(5)	93.3(6)
C(111)−C(112)−K(5)	70.1(4)
C(112)−C(113)−C(114)	121.7(10)
C(113)−C(114)−C(115)	121.2(10)
C(114)−C(115)−C(116)	118.7(9)
C(115)−C(116)−C(111)	121.6(8)
C(115)−C(116)−K(5)	94.5(6)
C(111)−C(116)−K(5)	68.0(4)
O(7)−C(117)−C(94)	114.1(6)
O(7)−C(117)−C(98)	112.7(6)
C(94)−C(117)−C(98)	106.0(6)
O(7)−C(117)−C(90)	110.3(7)
C(94)−C(117)−C(90)	105.9(6)
C(98)−C(117)−C(90)	107.2(6)
C(129)−C(120)−O(10)	106.0(8)
O(13)−C(121)−C(128)	104.5(9)
O(13)−C(123)−C(141)	106.0(9)
C(140)−C(124)−C(129)	100.7(9)
C(143)−C(125)−C(142)	110.0(13)
C(149)−C(126)−O(14)	102.5(11)
C(145)−C(127)−O(11)	108.9(12)
C(141)−C(128)−C(121)	105.0(10)
C(120)−C(129)−C(124)	106.7(9)
O(10)−C(140)−C(124)	111.4(9)
C(128)−C(141)−C(123)	105.3(11)
C(125)−C(142)−O(9)	105.9(13)
C(125)−C(143)−C(146)	107.9(13)
C(127)−C(145)−C(147)	105.4(13)
O(9)−C(146)−C(143)	104.1(13)
C(156)−C(147)−C(145)	102.4(12)
C(126)−C(149)−C(154)	109.8(14)
C(150)−C(151)−C(152)	107.9(16)
C(153)−C(152)−C(151)	91.5(18)
C(151)−C(150)−O(12)	107.6(16)
C(152)−C(153)−O(12)	122.4(17)
C(155)−C(154)−C(149)	95.1(13)
O(14)−C(155)−C(154)	111(2)
C(147)−C(156)−O(11)	111.1(15)
C(03)#1−C(01)−C(02)#1	109.6(12)
C(01)#2−C(02)−C(06)	102.7(15)
C(01)#2−C(02)−C(05)	81.8(12)
C(06)−C(02)−C(05)	40.6(12)
C(04)−C(03)−C(01)#2	99.3(14)
C(04)−C(03)−C(05)	49.1(13)
C(01)#2−C(03)−C(05)	93.0(14)
C(03)−C(04)−C(05)	80.0(19)
C(03)−C(04)−C(06)	116(2)
C(05)−C(04)−C(06)	59.1(18)
C(06)−C(05)−C(04)	60(2)
C(06)−C(05)−C(03)	96(2)
C(04)−C(05)−C(03)	50.8(15)
C(06)−C(05)−C(02)	51.9(16)
C(04)−C(05)−C(02)	80.2(19)
C(03)−C(05)−C(02)	73.6(13)
C(05)−C(06)−C(04)	60.8(19)
C(05)−C(06)−C(02)	88(2)
C(04)−C(06)−C(02)	99(2)
C(010)#3−C(07)−C(08)#3	93.0(15)
C(07)#3−C(08)−C(09)	110.4(11)
C(012)#3−C(09)−C(08)	116.1(17)
C(012)#3−C(09)−C(011)#4	50.5(12)

C(34)−S(20)−K(1)	108.2(3)	C(08)−C(09)−C(011)#4	89.5(10)
C(37)−S(20)−K(1)	160.4(6)	C(07)#3−C(010)−C(011)#4	123(2)
C(45)−S(21)−C(48)	94.6(6)	C(010)#5−C(011)−C(012)#6	101.5(17)
C(45)−S(21)−K(3)	107.0(3)	C(010)#5−C(011)−C(09)#5	94.7(14)
C(48)−S(21)−K(3)	152.1(5)	C(012)#6−C(011)−C(09)#5	45.2(11)
C(14A)−S(22)−C(10)	123.3(10)	C(09)#3−C(012)−C(011)#6	84.3(17)
C(14A)−S(22)−C(13)	29.3(9)		

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,y−1/2,z #2 x−1/2,y+1/2,z #3 −x+1/2,−y+3/2,−z
#4 x,y−1,z #5 x,y+1,z #6 −x+1/2,−y+5/2,−z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2608. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K(1)	60(1)	49(1)	49(1)	−4(1)	11(1)	−6(1)
K(2)	51(1)	45(1)	47(1)	−6(1)	12(1)	0(1)
K(3)	54(1)	65(1)	54(1)	−12(1)	2(1)	9(1)
K(4)	39(1)	50(1)	40(1)	−5(1)	1(1)	1(1)
K(5)	48(1)	56(1)	48(1)	−7(1)	−8(1)	6(1)
K(6)	51(1)	140(2)	65(1)	45(1)	−14(1)	−34(1)
K(7)	51(1)	87(1)	52(1)	16(1)	−4(1)	−14(1)
K(8)	52(1)	66(1)	93(2)	14(1)	−13(1)	3(1)
S(8)	58(1)	67(1)	57(1)	−12(1)	−2(1)	17(1)
S(9)	62(1)	55(1)	72(2)	−13(1)	9(1)	0(1)
S(11)	75(2)	62(1)	68(2)	−7(1)	5(1)	−1(1)
S(12)	74(2)	74(2)	72(2)	2(1)	6(1)	−10(1)
S(13)	59(1)	85(2)	68(2)	−5(1)	−1(1)	22(1)
S(14)	59(1)	64(1)	71(2)	6(1)	−3(1)	4(1)
S(15)	58(1)	89(2)	73(2)	0(1)	8(1)	−10(1)
S(16)	75(2)	101(2)	75(2)	7(2)	13(1)	−3(1)
S(17)	93(2)	50(1)	51(1)	0(1)	20(1)	3(1)
S(20)	133(3)	152(3)	197(4)	68(3)	−64(3)	−74(3)
S(21)	119(2)	98(2)	127(3)	65(2)	−72(2)	−53(2)
S(22)	141(3)	106(3)	138(3)	7(2)	34(3)	8(2)
S(23)	110(2)	151(3)	158(3)	−111(3)	85(2)	−66(2)
S(24)	62(2)	80(3)	60(3)	16(2)	20(2)	0(2)
S(25)	71(2)	105(2)	124(3)	29(2)	13(2)	5(2)
S(26)	64(2)	124(2)	75(2)	1(2)	3(1)	−8(2)
S(27)	72(2)	144(3)	67(2)	2(2)	−3(1)	−15(2)
S(28A)	105(3)	115(3)	89(3)	−40(2)	34(2)	−53(2)
O(1)	59(3)	44(3)	53(3)	−11(3)	21(3)	6(2)
O(2)	46(3)	37(3)	44(3)	4(2)	−1(2)	−3(2)
O(3)	40(3)	47(3)	38(3)	−10(2)	0(2)	−1(2)
O(4)	39(3)	52(3)	45(3)	5(2)	3(2)	0(2)
O(5)	65(4)	92(4)	61(4)	−34(3)	27(3)	−34(3)
O(6)	58(3)	44(3)	55(3)	3(3)	14(3)	0(2)
O(7)	47(3)	101(5)	92(5)	59(4)	−29(3)	−13(3)
O(8)	43(3)	55(3)	42(3)	2(2)	−8(2)	−5(2)
O(9)	140(7)	131(7)	117(7)	10(6)	−29(6)	−8(6)
O(10)	64(4)	77(4)	81(4)	20(3)	−2(3)	−13(3)
O(11)	85(5)	103(5)	94(5)	−6(4)	9(4)	22(4)
O(12)	119(7)	149(8)	169(9)	−14(7)	−5(6)	7(6)
O(13)	71(4)	86(5)	90(5)	23(4)	31(4)	5(3)
O(14)	113(7)	141(8)	234(12)	−28(8)	63(8)	−13(6)
C(1)	46(4)	36(4)	33(4)	−5(3)	7(3)	5(3)
C(2)	53(4)	33(4)	39(4)	5(3)	2(4)	−7(3)
C(3)	43(4)	38(4)	52(5)	8(4)	14(4)	−3(3)
C(4)	49(5)	54(5)	62(6)	12(4)	10(4)	0(4)
C(5)	54(5)	46(5)	93(7)	12(5)	−5(5)	−14(4)
C(6)	71(5)	30(4)	35(4)	3(3)	−4(4)	−10(4)
C(7)	63(5)	38(4)	53(5)	2(4)	1(4)	10(4)
C(8)	67(6)	58(5)	65(6)	13(5)	0(5)	7(4)
C(9)	75(6)	51(5)	69(6)	6(5)	11(5)	3(4)
C(10)	42(4)	43(4)	39(4)	5(4)	4(3)	0(3)
C(11)	63(5)	47(5)	38(5)	−7(4)	3(4)	−14(4)
C(12)	92(7)	60(6)	61(6)	−13(5)	4(5)	−23(5)
C(13)	82(7)	65(6)	90(8)	19(6)	−10(6)	−12(5)
C(14)	45(4)	39(4)	41(5)	−10(4)	0(3)	1(3)
C(15)	38(4)	46(4)	52(5)	−2(4)	−1(4)	3(3)

C(16)	36(4)	68(5)	50(5)	−5(4)	−10(4)	15(4)
C(17)	51(5)	70(6)	63(6)	−9(5)	−4(4)	11(4)
C(18)	56(5)	76(6)	65(6)	−5(5)	−4(4)	9(4)
C(19)	39(4)	55(5)	42(5)	−6(4)	11(3)	6(3)
C(20)	34(4)	21(3)	65(5)	−15(3)	27(3)	−3(3)
C(21)	51(5)	79(6)	81(7)	−35(6)	16(5)	−3(4)
C(22)	62(5)	49(5)	94(7)	−6(5)	32(5)	4(4)
C(23)	39(4)	57(5)	34(4)	−13(4)	−6(3)	4(3)
C(24)	44(4)	59(5)	34(4)	−3(4)	3(3)	−11(4)
C(25)	63(6)	96(7)	55(6)	0(5)	13(5)	0(5)
C(26)	63(6)	124(9)	64(7)	−11(6)	9(5)	16(6)
C(27)	59(5)	97(7)	61(6)	1(5)	25(5)	14(5)
C(28)	38(4)	58(5)	41(5)	−10(4)	−1(3)	7(3)
C(29)	46(4)	45(4)	44(5)	−2(4)	−3(4)	−4(3)
C(30)	53(4)	44(4)	27(4)	−1(3)	−5(3)	−1(3)
C(31)	74(6)	45(5)	48(5)	5(4)	−3(4)	6(4)
C(32)	84(6)	65(6)	46(5)	11(5)	−4(5)	1(5)
C(33)	112(8)	60(6)	47(5)	−1(5)	14(5)	−10(5)
C(34)	46(4)	54(5)	51(5)	−14(4)	2(4)	−7(4)
C(35)	23(3)	57(5)	30(4)	0(4)	−15(3)	−15(3)
C(36)	330(30)	260(20)	66(10)	−51(12)	−35(13)	240(20)
C(37)	55(7)	270(20)	186(16)	−110(14)	29(8)	−102(10)
C(38)	55(5)	47(5)	40(5)	−4(4)	−8(4)	10(4)
C(39)	31(4)	43(4)	50(5)	13(4)	−2(3)	1(3)
C(40)	78(6)	66(6)	71(7)	1(5)	−7(5)	11(5)
C(41)	74(6)	72(6)	65(6)	−12(5)	−4(5)	14(5)
C(42)	71(6)	88(7)	53(6)	−10(5)	9(5)	18(5)
C(43)	52(5)	78(6)	56(6)	−9(5)	−3(4)	4(4)
C(44)	47(4)	49(5)	42(5)	1(4)	6(4)	4(4)
C(45)	72(5)	38(4)	51(5)	−1(4)	14(4)	12(4)
C(46)	113(8)	96(8)	86(8)	37(7)	51(7)	49(7)
C(47)	178(13)	73(8)	66(7)	12(6)	14(8)	68(8)
C(48)	211(14)	45(6)	78(8)	14(5)	−66(9)	2(8)
C(49)	49(5)	59(5)	65(6)	−18(4)	13(4)	−1(4)
C(50)	88(7)	78(7)	106(9)	−7(6)	18(6)	−23(6)
C(51)	77(7)	85(8)	156(12)	−30(8)	24(7)	−27(6)
C(52)	87(7)	72(7)	132(10)	−24(7)	21(7)	−27(6)
C(53)	47(4)	42(4)	40(5)	1(4)	7(4)	0(3)
C(54)	118(8)	58(6)	77(7)	−14(5)	−19(6)	48(6)
C(55)	146(10)	83(7)	66(7)	−20(6)	−12(7)	41(7)
C(56)	61(5)	55(6)	94(8)	13(5)	4(5)	8(4)
C(57)	77(7)	95(8)	73(7)	−2(6)	−6(6)	21(6)
C(58)	60(5)	94(7)	62(6)	−8(5)	−1(5)	29(5)
C(59)	49(5)	80(6)	49(5)	−17(5)	9(4)	−19(4)
C(60)	58(5)	64(5)	38(5)	−12(4)	7(4)	−10(4)
C(61)	58(5)	85(6)	59(6)	−10(5)	15(4)	−16(5)
C(62)	89(7)	133(10)	63(7)	−1(7)	43(6)	−38(7)
C(63)	86(7)	93(7)	51(6)	5(5)	−10(5)	−11(6)
C(64)	59(5)	127(9)	46(6)	13(6)	−5(4)	−47(6)
C(65)	350(30)	152(14)	440(30)	209(18)	−360(30)	−173(16)
C(66)	450(40)	230(20)	550(50)	270(30)	−390(40)	−280(30)
C(67)	84(10)	300(20)	194(17)	174(18)	−30(10)	−46(12)
C(68)	48(7)	400(30)	145(14)	−163(17)	−12(8)	46(11)
C(69)	48(6)	199(13)	180(13)	−147(12)	−46(7)	34(7)
C(70)	64(5)	68(6)	47(5)	−7(4)	−6(4)	−21(4)
C(71)	93(7)	58(6)	108(9)	−29(6)	−4(6)	6(5)
C(72)	102(8)	60(6)	105(9)	−2(6)	−25(7)	11(6)
C(73)	158(12)	103(9)	70(8)	−12(7)	3(7)	−60(8)
C(74)	46(4)	46(4)	36(4)	−2(4)	3(3)	6(3)
C(75)	43(4)	62(5)	42(5)	11(4)	5(4)	11(4)
C(76)	92(7)	94(7)	74(7)	35(6)	37(6)	49(6)
C(77)	67(7)	165(11)	54(6)	37(7)	17(5)	66(7)
C(78)	52(6)	195(14)	81(8)	−71(9)	17(5)	−5(7)
C(79)	62(5)	45(5)	62(6)	5(4)	−5(4)	0(4)
C(80)	92(8)	59(7)	218(15)	29(8)	−75(9)	−2(6)
C(81)	133(11)	64(8)	340(20)	10(11)	−127(14)	−31(8)
C(82)	85(7)	81(7)	133(10)	0(7)	−60(7)	2(6)
C(83)	45(4)	53(5)	55(5)	1(4)	6(4)	15(4)
C(84)	87(7)	175(11)	63(7)	−41(7)	−20(5)	101(8)
C(85)	174(14)	300(20)	82(9)	−37(11)	−35(9)	175(15)
C(86)	97(8)	102(8)	89(8)	−16(7)	−6(7)	43(6)
C(87)	78(7)	67(6)	81(7)	−6(6)	17(6)	−13(5)
C(88)	82(6)	36(4)	56(5)	−5(4)	24(5)	19(4)

C(90)	44(4)	42(4)	42(5)	8(4)	3(3)	−11(3)
C(91)	45(4)	63(5)	51(5)	10(4)	−6(4)	−6(4)
C(92)	67(6)	79(6)	61(6)	15(5)	−21(5)	−25(5)
C(93)	121(8)	52(5)	39(5)	−4(4)	15(5)	−29(5)
C(94)	40(4)	94(7)	40(5)	10(5)	4(4)	−23(4)
C(95)	52(5)	97(7)	48(5)	−14(5)	11(4)	−15(5)
C(96)	46(5)	87(7)	70(6)	−19(5)	8(4)	−6(5)
C(97)	58(5)	65(6)	58(6)	−8(5)	6(4)	−3(4)
C(98)	31(4)	63(5)	54(5)	4(4)	9(3)	−6(3)
C(99)	50(4)	43(5)	57(5)	9(4)	18(4)	1(4)
C(100)	67(6)	53(5)	71(6)	8(5)	26(5)	−1(4)
C(101)	60(5)	61(6)	96(8)	−13(5)	25(5)	−15(4)
C(102)	39(4)	49(4)	42(5)	−3(4)	−5(3)	0(3)
C(103)	48(5)	55(5)	65(6)	−5(4)	7(4)	−1(4)
C(104)	85(6)	61(6)	71(7)	−28(5)	8(5)	11(5)
C(105)	102(8)	85(7)	69(7)	−19(6)	−3(6)	20(6)
C(106)	75(6)	77(6)	84(7)	−17(6)	8(5)	15(5)
C(107)	41(4)	53(5)	52(5)	5(4)	−3(4)	4(4)
C(108)	30(4)	43(4)	75(6)	14(4)	−9(4)	−1(3)
C(109)	40(5)	62(6)	103(8)	17(5)	−14(5)	−1(4)
C(110)	46(5)	78(6)	95(8)	19(6)	0(5)	5(4)
C(111)	55(5)	55(5)	31(4)	−6(4)	−8(4)	−5(4)
C(112)	44(4)	61(5)	50(5)	3(4)	−8(4)	5(4)
C(113)	95(8)	101(8)	82(8)	28(7)	−9(6)	20(6)
C(114)	110(9)	140(11)	91(9)	55(8)	8(7)	30(8)
C(115)	101(8)	107(8)	63(7)	29(6)	10(6)	2(7)
C(116)	58(5)	67(6)	41(5)	−2(4)	0(4)	−6(4)
C(117)	41(4)	74(6)	54(5)	28(5)	4(4)	−6(4)
C(120)	80(7)	80(7)	100(8)	26(6)	−10(6)	3(5)
C(121)	91(8)	148(11)	87(8)	33(8)	26(7)	36(7)
C(123)	107(9)	131(10)	104(9)	60(8)	24(7)	29(8)
C(124)	73(7)	96(8)	166(12)	69(8)	24(7)	9(6)
C(125)	173(15)	130(11)	171(15)	31(11)	−95(13)	−46(10)
C(126)	97(9)	118(10)	120(11)	−3(8)	−17(8)	−16(7)
C(127)	201(15)	168(13)	66(8)	−3(8)	−17(9)	94(12)
C(128)	172(13)	131(11)	129(11)	28(9)	97(10)	10(10)
C(129)	65(7)	173(13)	213(15)	138(12)	−3(8)	−19(8)
C(140)	54(6)	161(12)	320(20)	184(14)	21(9)	21(7)
C(141)	168(14)	185(15)	172(14)	97(12)	112(12)	90(12)
C(142)	155(14)	204(17)	156(14)	36(13)	−8(11)	−111(13)
C(143)	126(12)	350(30)	114(12)	70(15)	−34(10)	−106(15)
C(145)	159(14)	199(17)	188(17)	34(14)	−64(13)	77(13)
C(146)	122(11)	300(20)	83(10)	47(12)	−44(9)	−1(13)
C(147)	193(16)	60(8)	430(30)	−86(13)	−167(19)	61(9)
C(149)	73(9)	500(40)	220(20)	−220(20)	40(11)	−58(15)
C(151)	143(13)	112(11)	215(18)	−30(12)	63(13)	18(10)
C(152)	95(11)	201(18)	310(30)	−53(18)	−6(14)	41(12)
C(150)	112(12)	203(18)	300(30)	−32(18)	−95(15)	39(12)
C(153)	220(20)	115(13)	760(60)	230(20)	280(30)	84(14)
C(154)	63(8)	185(15)	330(30)	−153(16)	−8(11)	24(9)
C(155)	105(14)	490(40)	260(30)	−130(30)	6(15)	−20(20)
C(156)	260(20)	480(40)	260(20)	−230(30)	−177(19)	310(30)

Compound 23

Table 1. Crystal data and structure refinement for sh2595.

Identification code	sh2595	
Empirical formula	C61 H65 Nd O7 S6	
Formula weight	1246.73	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R3	
Unit cell dimensions	a = 14.1347(5) Å	α = 90°.
	b = 14.1347(5) Å	β = 90°.
	c = 24.8973(9) Å	γ = 120°.
Volume	4307.8(3) Å^3	
Z	3	
Density (calculated)	1.442 Mg/m^3	
Absorption coefficient	1.174 mm^{-1}	
F(000)	1929	

Crystal size	0.44 x 0.3 x 0.25 mm^3
Theta range for data collection	1.85 to 28.31°.
Index ranges	−18<=h<=18, −18<=k<=18, −33<=l<=33
Reflections collected	33002
Independent reflections	4775 [R(int) = 0.0378]
Completeness to theta = 28.31°	99.9 %
Absorption correction	Multiscan
Refinement method	Full−matrix least−squares on F^2
Data / restraints / parameters	4775 / 9 / 210
Goodness−of−fit on F^2	1.720
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1372
R indices (all data)	R1 = 0.0515, wR2 = 0.1372
Absolute structure parameter	−0.037(19)
Largest diff. peak and hole	2.182 and −1.327 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2595. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nd	6667	3333	432	20(1)
O(1)	5370(3)	3464(3)	23(2)	33(1)
O(2)	7929(3)	3280(4)	1197(2)	37(1)
S(1)	3189(2)	2408(2)	494(1)	63(1)
S(2A)	4547(5)	4364(5)	−1315(2)	67(1)
S(2B)	4927(6)	2608(4)	−1122(3)	59(2)
C(1)	4706(4)	3752(4)	−260(2)	28(1)
C(2)	3514(4)	2948(4)	−122(3)	32(1)
C(3)	2582(5)	2541(6)	−447(3)	47(2)
C(4)	1628(5)	1802(6)	−175(4)	55(2)
C(5)	1790(9)	1644(7)	358(5)	71(3)
C(6)	4831(5)	3671(5)	−866(3)	34(1)
C(7A)	5061(11)	2907(10)	−1146(4)	25
C(7B)	4790(20)	4310(20)	−1316(7)	45
C(8)	5008(7)	3019(9)	−1727(3)	75(3)
C(9)	4801(9)	3834(11)	−1849(4)	97(5)
C(10)	5117(3)	5003(3)	−133(2)	38(1)
C(11)	6221(3)	5773(4)	−174(2)	39(2)
C(12)	6593(3)	6853(4)	−31(3)	270(20)
C(13)	5860(4)	7163(3)	154(3)	73(3)
C(14)	4756(4)	6394(4)	196(3)	56(2)
C(15)	4384(2)	5314(3)	52(2)	48(2)
C(16)	9116(6)	3972(7)	1212(4)	54(2)
C(17)	9530(8)	3371(12)	1509(7)	115(7)
C(18)	8655(9)	2665(15)	1878(6)	105(6)
C(19)	7619(6)	2516(7)	1630(3)	50(2)
O(01)	10000	0	1344(7)	93(4)
C(02)	11000(30)	430(30)	1727(18)	131(12)
C(03)	9670(30)	340(30)	2222(12)	97(8)

Table 3. Bond lengths [Å] and angles [°] for sh2595.

Nd−O(1)	2.184(4)	C(6)−C(7A)	1.454(12)
Nd−O(1)#1	2.185(4)	C(6)−C(7B)	1.459(17)
Nd−O(1)#2	2.185(4)	C(7A)−C(8)	1.462(13)
Nd−O(2)#2	2.635(4)	C(7B)−C(9)	1.491(18)
Nd−O(2)#1	2.635(4)	C(8)−C(9)	1.357(17)
Nd−O(2)	2.636(4)	C(10)−C(11)	1.3900
O(1)−C(1)	1.388(6)	C(10)−C(15)	1.3900
O(2)−C(19)	1.432(8)	C(11)−C(12)	1.3900
O(2)−C(16)	1.459(8)	C(12)−C(13)	1.3900
S(1)−C(2)	1.672(7)	C(13)−C(14)	1.3900
S(1)−C(5)	1.749(12)	C(14)−C(15)	1.3900
S(2A)−C(9)	1.651(13)	C(16)−C(17)	1.452(12)
S(2A)−C(6)	1.663(8)	C(17)−C(18)	1.460(16)
S(2B)−C(8)	1.598(11)	C(18)−C(19)	1.503(12)
S(2B)−C(6)	1.699(8)	O(01)−C(02)#3	1.55(5)
C(1)−C(2)	1.527(7)	O(01)−C(02)#4	1.55(5)
C(1)−C(6)	1.529(8)	O(01)−C(02)	1.55(5)
C(1)−C(10)	1.593(6)	C(02)−C(03)#4	1.30(5)
C(2)−C(3)	1.403(8)	C(03)−C(02)#3	1.30(5)
C(3)−C(4)	1.399(10)	C(03)−C(03)#3	1.41(5)

C(4)−C(5)	1.385(16)	C(03)−C(03)#4	1.41(5)
O(1)−Nd−O(1)#1	99.96(16)	C(7B)−C(6)−C(1)	132.1(9)
O(1)−Nd−O(1)#2	99.96(16)	C(7A)−C(6)−S(2A)	108.9(6)
O(1)#1−Nd−O(1)#2	99.96(16)	C(7B)−C(6)−S(2A)	12.2(11)
O(1)−Nd−O(2)#2	93.24(17)	C(1)−C(6)−S(2A)	123.3(4)
O(1)#1−Nd−O(2)#2	90.37(16)	C(7A)−C(6)−S(2B)	10.1(6)
O(1)#2−Nd−O(2)#2	161.50(15)	C(7B)−C(6)−S(2B)	107.7(9)
O(1)−Nd−O(2)#1	90.36(16)	C(1)−C(6)−S(2B)	120.0(5)
O(1)#1−Nd−O(2)#1	161.50(15)	S(2A)−C(6)−S(2B)	114.7(5)
O(1)#2−Nd−O(2)#1	93.24(17)	C(6)−C(7A)−C(8)	110.6(9)
O(2)#2−Nd−O(2)#1	73.64(16)	C(6)−C(7B)−C(9)	113.0(14)
O(1)−Nd−O(2)	161.50(15)	C(9)−C(8)−C(7A)	111.0(9)
O(1)#1−Nd−O(2)	93.24(17)	C(9)−C(8)−S(2B)	120.8(8)
O(1)#2−Nd−O(2)	90.37(16)	C(7A)−C(8)−S(2B)	13.0(5)
O(2)#2−Nd−O(2)	73.64(16)	C(8)−C(9)−C(7B)	103.9(10)
O(2)#1−Nd−O(2)	73.64(16)	C(8)−C(9)−S(2A)	113.2(7)
C(1)−O(1)−Nd	168.9(4)	C(7B)−C(9)−S(2A)	13.0(10)
C(19)−O(2)−C(16)	107.6(5)	C(11)−C(10)−C(15)	120.0
C(19)−O(2)−Nd	127.5(4)	C(11)−C(10)−C(1)	119.8(3)
C(16)−O(2)−Nd	124.5(4)	C(15)−C(10)−C(1)	120.1(3)
C(2)−S(1)−C(5)	94.1(5)	C(12)−C(11)−C(10)	120.0
C(9)−S(2A)−C(6)	95.9(5)	C(11)−C(12)−C(13)	120.0
C(8)−S(2B)−C(6)	93.2(5)	C(14)−C(13)−C(12)	120.0
O(1)−C(1)−C(2)	108.9(4)	C(15)−C(14)−C(13)	120.0
O(1)−C(1)−C(6)	111.0(5)	C(14)−C(15)−C(10)	120.0
C(2)−C(1)−C(6)	107.0(5)	C(17)−C(16)−O(2)	106.6(7)
O(1)−C(1)−C(10)	107.5(4)	C(16)−C(17)−C(18)	105.6(10)
C(2)−C(1)−C(10)	115.8(4)	C(17)−C(18)−C(19)	105.8(8)
C(6)−C(1)−C(10)	106.7(4)	O(2)−C(19)−C(18)	107.0(7)
C(3)−C(2)−C(1)	129.4(6)	C(02)#3−O(01)−C(02)#4	86(2)
C(3)−C(2)−S(1)	110.8(5)	C(02)#3−O(01)−C(02)	86(2)
C(1)−C(2)−S(1)	119.7(4)	C(02)#4−O(01)−C(02)	86(2)
C(4)−C(3)−C(2)	112.5(7)	C(03)#4−C(02)−O(01)	109(3)
C(5)−C(4)−C(3)	114.2(7)	C(02)#3−C(03)−C(03)#3	108(3)
C(4)−C(5)−S(1)	108.2(6)	C(02)#3−C(03)−C(03)#4	104(3)
C(7A)−C(6)−C(7B)	100.6(10)	C(03)#3−C(03)−C(03)#4	60.002(3)
C(7A)−C(6)−C(1)	127.3(7)		

Symmetry transformations used to generate equivalent atoms:
#1 −y+1,x−y,z #2 −x+y+1,−x+1,z #3 −y+1,x−y−1,z
#4 −x+y+2,−x+1,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2595. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nd	20(1)	20(1)	20(1)	0	0	10(1)
O(1)	32(2)	33(2)	39(2)	−2(2)	−12(2)	20(2)
O(2)	32(2)	46(2)	33(2)	6(2)	−4(2)	21(2)
S(2A)	91(4)	75(2)	52(2)	9(2)	1(2)	55(3)
S(2B)	67(4)	46(3)	66(3)	3(3)	5(3)	29(3)
C(1)	23(2)	29(2)	34(2)	3(2)	−3(2)	15(2)
C(2)	26(2)	26(2)	45(3)	−1(2)	0(2)	13(2)
C(3)	26(3)	58(4)	49(4)	0(3)	−4(2)	14(3)
C(4)	27(3)	49(4)	73(5)	−3(4)	−4(3)	8(3)
C(5)	66(5)	49(4)	92(8)	10(5)	35(5)	25(4)
C(6)	31(3)	37(3)	35(3)	−1(2)	−5(2)	18(2)
C(8)	51(4)	76(6)	64(5)	−31(5)	13(4)	6(4)
C(9)	58(5)	152(13)	57(6)	50(7)	4(4)	33(7)
C(10)	54(3)	35(3)	34(3)	−3(2)	−10(2)	30(3)
C(11)	7(2)	49(3)	45(3)	−13(3)	10(2)	2(2)
C(12)	144(15)	620(60)	167(18)	270(30)	127(15)	270(30)
C(13)	61(5)	68(6)	69(6)	17(5)	−8(4)	17(4)
C(14)	61(5)	40(4)	76(6)	−6(4)	−3(4)	32(4)
C(15)	43(3)	36(3)	72(5)	−6(3)	−9(3)	26(3)
C(16)	36(3)	66(5)	59(4)	18(4)	1(3)	24(3)
C(17)	37(4)	127(11)	157(14)	80(11)	−15(6)	23(5)
C(18)	50(5)	158(13)	88(8)	75(9)	−7(5)	38(7)
C(19)	42(3)	57(4)	46(4)	16(3)	−4(3)	21(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for sh2595.

	x	y	z	U(eq)
H(3)	2596	2744	−812	57
H(4)	931	1440	−342	65
H(5)	1235	1198	608	85
H(7A)	5224	2404	−975	30
H(7B)	4765	4965	−1274	54
H(8)	5106	2581	−1985	90
H(9)	4802	4075	−2205	117
H(11)	6722	5560	−301	47
H(12)	7347	7378	−59	330
H(13)	6114	7901	253	88
H(14)	4255	6606	322	67
H(15)	3629	4788	80	57
H(16A)	9418	4127	843	65
H(16B)	9324	4673	1392	65
H(17A)	10198	3878	1711	138
H(17B)	9705	2930	1263	138
H(18A)	8774	3011	2236	126
H(18B)	8622	1953	1918	126
H(19A)	7168	1760	1495	60
H(19B)	7188	2656	1900	60

Compound 25

Table 1. Crystal data and structure refinement for sh2565.

Identification code	sh2565	
Empirical formula	C82 H78 K4 O7 S3 · 0.5 C4 H8 O	
Formula weight	1464.08	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	P2(1)3	
Unit cell dimensions	a = 24.4943(6) Å	α = 90°.
	b = 24.4943(6) Å	β = 90°.
	c = 24.4943(6) Å	γ = 90°.
Volume	14695.9(6) Å^3	
Z	8	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.384 mm^{-1}	
F(000)	6160	
Crystal size	0.5 x 0.2 x 0.09 mm^3	
Theta range for data collection	1.18 to 28.26°.	
Index ranges	−26<=h<=32, −32<=k<=32, −32<=l<=29	
Reflections collected	83983	
Independent reflections	12157 [R(int) = 0.1092]	
Completeness to theta = 28.26°	100.0 %	
Absorption correction	None	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	12157 / 0 / 589	
Goodness−of−fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1497	
R indices (all data)	R1 = 0.1109, wR2 = 0.1784	
Absolute structure parameter	0.03(5)	
Largest diff. peak and hole	1.010 and −0.516 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2565. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
K(1)	7556(1)	2556(1)	2444(1)	24(1)
K(2)	7578(1)	3768(1)	1490(1)	27(1)
S(1)	6608(1)	7069(1)	349(1)	41(1)
O(1)	8686(1)	2443(1)	2362(1)	23(1)
O(2)	8663(1)	3663(1)	1337(1)	25(1)
O(5)	7151(2)	4735(2)	1094(2)	57(1)

C(1)	8877(2)	1945(2)	2555(2)	24(1)
C(2)	9205(2)	2014(2)	3084(2)	27(1)
C(3)	9522(2)	1645(2)	3367(2)	39(1)
C(4)	9732(2)	1880(3)	3871(2)	49(2)
C(5)	9572(2)	2399(3)	3943(2)	46(1)
C(6)	9260(2)	1661(2)	2142(2)	28(1)
C(7)	9556(2)	1977(2)	1758(2)	32(1)
C(8)	9906(3)	1731(3)	1402(2)	55(2)
C(9)	9993(3)	1179(3)	1408(3)	68(2)
C(10)	9727(3)	860(3)	1772(3)	63(2)
C(11)	9356(2)	1092(2)	2146(2)	41(1)
C(12)	8378(2)	1576(2)	2667(2)	26(1)
C(13)	8190(2)	1440(2)	3191(2)	34(1)
C(14)	7703(2)	1159(2)	3260(3)	48(1)
C(15)	7404(2)	1004(2)	2816(3)	49(1)
C(16)	7585(2)	1123(2)	2296(2)	42(1)
C(17)	8060(2)	1405(2)	2227(2)	32(1)
C(18)	8991(2)	3991(2)	1010(2)	26(2)
C(19)	8697(2)	4121(2)	462(2)	32(1)
C(20)	8354(1)	3663(2)	175(1)	19(1)
C(21)	8144(3)	3863(3)	−313(3)	57(2)
C(22)	8225(4)	4342(4)	−512(4)	92(3)
C(23)	8517(5)	4706(4)	−291(3)	107(4)
C(24)	8739(3)	4622(2)	172(2)	53(2)
C(25)	6594(3)	4907(3)	1047(4)	81(2)
C(26)	6615(4)	5449(4)	785(4)	103(3)
C(27)	7183(4)	5561(3)	640(4)	82(3)
C(28)	7434(4)	5039(4)	706(4)	105(3)
K(3)	6325(1)	8675(1)	1325(1)	25(1)
K(4)	6335(1)	7622(1)	2446(1)	26(1)
O(3)	6275(1)	7537(1)	1349(1)	25(1)
O(4)	7423(1)	7577(1)	2423(1)	24(1)
O(6)	5800(2)	6987(2)	3197(2)	42(1)
S(2)	9158(1)	2619(1)	3427(1)	42(1)
C(29)	5812(2)	7308(2)	1116(2)	23(1)
C(30)	5947(2)	7032(2)	570(2)	26(1)
C(31)	5647(2)	6713(2)	230(2)	37(1)
C(32)	5953(2)	6497(2)	−217(2)	40(1)
C(33)	6481(2)	6652(2)	−202(2)	39(1)
C(34)	5569(2)	6833(2)	1462(2)	27(1)
C(35)	5020(2)	6675(2)	1417(2)	35(1)
C(36)	4831(3)	6209(2)	1688(2)	49(2)
C(37)	5183(3)	5902(2)	2003(2)	57(2)
C(38)	5719(3)	6054(2)	2049(2)	47(1)
C(39)	5916(2)	6522(2)	1777(2)	35(1)
C(40)	5386(2)	7778(2)	1036(2)	26(1)
C(41)	5110(2)	7985(2)	1488(2)	30(1)
C(42)	4785(2)	8446(2)	1450(2)	33(1)
C(43)	4731(2)	8713(2)	951(2)	41(1)
C(44)	5013(2)	8517(2)	498(2)	38(1)
C(45)	5334(2)	8051(2)	539(2)	29(1)
C(46)	7753(2)	7247(2)	2753(2)	23(2)
C(47)	7728(2)	7431(2)	3355(2)	27(1)
C(48)	8723(2)	6856(2)	2583(3)	48(1)
C(49)	9270(3)	6961(3)	2437(3)	72(2)
C(50)	9425(3)	7433(4)	2284(3)	72(2)
C(51)	9118(4)	7820(5)	2281(5)	117(4)
C(52)	8602(1)	7812(2)	2332(2)	21(1)
C(53)	6038(3)	6529(3)	3494(3)	58(2)
C(54)	5578(3)	6204(3)	3697(4)	91(3)
C(55)	5088(3)	6500(3)	3595(4)	89(3)
C(56)	5221(2)	6927(2)	3192(2)	45(1)
O(7)	4627(4)	5373(4)	373(4)	163(6)
C(58)	5219(5)	5300(5)	513(5)	69(3)
C(59)	5442(6)	4954(6)	94(6)	82(4)
C(60)	5207(7)	4793(7)	−207(7)	74(7)

Table 3. Bond lengths [Å] and angles [°] for sh2565.

K(1)−O(1)#1	2.789(3)	K(3)−C(40)	3.258(4)
K(1)−O(1)#2	2.789(3)	K(3)−C(40)#3	3.258(4)
K(1)−O(1)	2.789(3)	K(3)−C(41)#4	3.445(4)
K(1)−C(17)#2	3.124(5)	K(3)−C(41)#3	3.445(4)
K(1)−C(17)#1	3.124(5)	K(3)−C(41)	3.445(4)

K(1)−C(17)	3.124(5)
K(1)−C(12)#2	3.179(4)
K(1)−C(12)	3.179(4)
K(1)−C(12)#1	3.179(4)
K(1)−C(16)#2	3.529(5)
K(1)−C(16)	3.529(5)
K(1)−C(16)#1	3.529(5)
K(2)−O(1)#1	2.625(3)
K(2)−O(2)	2.696(3)
K(2)−O(5)	2.765(4)
K(2)−O(1)#2	2.822(3)
K(2)−C(7)#2	3.223(5)
K(2)−S(2)#1	3.4265(17)
K(2)−K(2)#1	3.7563(16)
K(2)−K(2)#2	3.7563(16)
S(1)−C(30)	1.709(5)
S(1)−C(33)	1.720(5)
S(1)−K(4)#3	3.2875(16)
O(1)−C(1)	1.390(5)
O(1)−K(2)#2	2.625(3)
O(1)−K(2)#1	2.822(3)
O(2)−C(18)	1.390(9)
O(2)−K(2)#2	2.696(3)
O(2)−K(2)#1	2.696(3)
O(5)−C(28)	1.391(9)
O(5)−C(25)	1.433(8)
C(1)−C(2)	1.532(6)
C(1)−C(12)	1.545(6)
C(1)−C(6)	1.545(6)
C(2)−C(3)	1.382(7)
C(2)−S(2)	1.707(5)
C(3)−C(4)	1.456(8)
C(4)−C(5)	1.341(8)
C(5)−S(2)	1.707(6)
C(6)−C(11)	1.413(7)
C(6)−C(7)	1.419(7)
C(7)−C(8)	1.361(7)
C(7)−K(2)#1	3.223(5)
C(8)−C(9)	1.370(9)
C(9)−C(10)	1.353(9)
C(10)−C(11)	1.413(8)
C(12)−C(17)	1.392(6)
C(12)−C(13)	1.404(7)
C(13)−C(14)	1.387(7)
C(14)−C(15)	1.365(8)
C(15)−C(16)	1.381(8)
C(16)−C(17)	1.364(7)
C(18)−C(19)#2	1.556(5)
C(18)−C(19)	1.556(5)
C(18)−C(19)#1	1.556(5)
C(19)−C(24)	1.421(7)
C(19)−C(20)	1.569(7)
C(20)−C(21)	1.391(8)
C(21)−C(22)	1.286(11)
C(22)−C(23)	1.264(13)
C(23)−C(24)	1.275(10)
C(25)−C(26)	1.476(11)
C(26)−C(27)	1.463(13)
C(27)−C(28)	1.429(11)
K(3)−O(3)	2.790(3)
K(3)−O(3)#4	2.790(3)
K(3)−O(3)#3	2.790(3)
K(3)−C(40)#4	3.258(4)
K(3)−C(45)#4	3.454(5)
K(3)−C(45)	3.454(5)
K(3)−C(45)#3	3.454(5)
K(4)−O(4)	2.667(3)
K(4)−O(3)	2.698(3)
K(4)−O(3)#4	2.702(3)
K(4)−O(6)	2.742(4)
K(4)−S(1)#4	3.2873(16)
K(4)−C(39)	3.316(5)
K(4)−C(52)#3	3.520(3)
K(4)−K(4)#4	3.7344(16)
K(4)−K(4)#3	3.7346(16)
O(3)−C(29)	1.387(5)
O(3)−K(4)#3	2.702(3)
O(4)−C(46)	1.400(8)
O(4)−K(4)#4	2.667(3)
O(4)−K(4)#3	2.667(3)
O(6)−C(56)	1.427(7)
O(6)−C(53)	1.459(7)
S(2)−K(2)#2	3.4265(17)
C(29)−C(30)	1.535(6)
C(29)−C(34)	1.558(6)
C(29)−C(40)	1.567(6)
C(30)−C(31)	1.359(7)
C(31)−C(32)	1.427(7)
C(32)−C(33)	1.347(7)
C(34)−C(39)	1.377(7)
C(34)−C(35)	1.404(7)
C(35)−C(36)	1.399(7)
C(36)−C(37)	1.380(10)
C(37)−C(38)	1.371(9)
C(38)−C(39)	1.411(7)
C(40)−C(41)	1.393(6)
C(40)−C(45)	1.394(7)
C(41)−C(42)	1.384(7)
C(42)−C(43)	1.392(7)
C(43)−C(44)	1.391(7)
C(44)−C(45)	1.389(7)
C(46)−C(47)	1.543(5)
C(46)−C(47)#3	1.543(5)
C(46)−C(47)#4	1.543(5)
C(47)−C(48)#3	1.362(7)
C(47)−C(52)#3	1.567(6)
C(48)−C(47)#4	1.361(7)
C(48)−C(49)	1.410(8)
C(49)−C(50)	1.273(10)
C(50)−C(51)	1.211(12)
C(51)−C(52)	1.270(10)
C(52)−C(47)#4	1.567(6)
C(52)−K(4)#4	3.520(3)
C(53)−C(54)	1.467(9)
C(54)−C(55)	1.424(10)
C(55)−C(56)	1.478(8)
O(7)−C(58)#5	1.501(15)
O(7)−C(58)	1.501(15)
O(7)−C(58)#6	1.501(15)
C(58)−C(59)	1.440(19)
C(59)−C(60)	1.014(16)
C(59)−C(59)#5	1.67(3)
C(59)−C(59)#6	1.67(3)
C(60)−C(59)#5	1.014(16)
C(60)−C(59)#6	1.014(16)

O(1)#1−K(1)−O(1)#2	91.95(9)
O(1)#1−K(1)−O(1)	91.95(9)
O(1)#2−K(1)−O(1)	91.95(9)
O(1)#1−K(1)−C(17)#2	86.29(11)
O(1)#2−K(1)−C(17)#2	60.37(10)
O(1)−K(1)−C(17)#2	152.14(11)
O(1)#1−K(1)−C(17)#1	60.37(10)
O(1)#2−K(1)−C(17)#1	152.14(11)
O(1)−K(1)−C(17)#1	86.28(11)
O(3)#3−K(3)−C(40)#3	45.57(10)
C(40)#4−K(3)−C(40)#3	117.98(4)
C(40)−K(3)−C(40)#3	117.98(4)
O(3)−K(3)−C(41)#4	149.01(11)
O(3)#4−K(3)−C(41)#4	57.96(10)
O(3)#3−K(3)−C(41)#4	85.65(10)
C(40)#4−K(3)−C(41)#4	23.78(11)
C(40)−K(3)−C(41)#4	140.43(11)
C(40)#3−K(3)−C(41)#4	94.61(11)

C(17)#2−K(1)−C(17)#1	116.32(6)
O(1)#1−K(1)−C(17)	152.14(11)
O(1)#2−K(1)−C(17)	86.28(11)
O(1)−K(1)−C(17)	60.37(10)
C(17)#2−K(1)−C(17)	116.32(6)
C(17)#1−K(1)−C(17)	116.32(6)
O(1)#1−K(1)−C(12)#2	106.68(10)
O(1)#2−K(1)−C(12)#2	46.31(10)
O(1)−K(1)−C(12)#2	133.37(10)
C(17)#2−K(1)−C(12)#2	25.50(11)
C(17)#1−K(1)−C(12)#2	140.15(12)
C(17)−K(1)−C(12)#2	92.08(11)
O(1)#1−K(1)−C(12)	133.37(10)
O(1)#2−K(1)−C(12)	106.68(10)
O(1)−K(1)−C(12)	46.31(10)
C(17)#2−K(1)−C(12)	140.14(12)
C(17)#1−K(1)−C(12)	92.08(11)
C(17)−K(1)−C(12)	25.50(11)
C(12)#2−K(1)−C(12)	117.20(5)
O(1)#1−K(1)−C(12)#1	46.31(10)
O(1)#2−K(1)−C(12)#1	133.37(10)
O(1)−K(1)−C(12)#1	106.68(10)
C(17)#2−K(1)−C(12)#1	92.09(11)
C(17)#1−K(1)−C(12)#1	25.50(11)
C(17)−K(1)−C(12)#1	140.14(12)
C(12)#2−K(1)−C(12)#1	117.20(5)
C(12)−K(1)−C(12)#1	117.20(5)
O(1)#1−K(1)−C(16)#2	88.35(11)
O(1)#2−K(1)−C(16)#2	82.75(10)
O(1)−K(1)−C(16)#2	174.70(11)
C(17)#2−K(1)−C(16)#2	22.62(12)
C(17)#1−K(1)−C(16)#2	98.45(13)
C(17)−K(1)−C(16)#2	118.89(13)
C(12)#2−K(1)−C(16)#2	41.76(12)
C(12)−K(1)−C(16)#2	135.31(13)
C(12)#1−K(1)−C(16)#2	77.28(12)
O(1)#1−K(1)−C(16)	174.70(11)
O(1)#2−K(1)−C(16)	88.35(11)
O(1)−K(1)−C(16)	82.75(10)
C(17)#2−K(1)−C(16)	98.44(13)
C(17)#1−K(1)−C(16)	118.89(13)
C(17)−K(1)−C(16)	22.62(12)
C(12)#2−K(1)−C(16)	77.27(12)
C(12)−K(1)−C(16)	41.76(12)
C(12)#1−K(1)−C(16)	135.31(13)
C(16)#2−K(1)−C(16)	96.93(13)
O(1)#1−K(1)−C(16)#1	82.75(10)
O(1)#2−K(1)−C(16)#1	174.70(11)
O(1)−K(1)−C(16)#1	88.35(11)
C(17)#2−K(1)−C(16)#1	118.89(13)
C(17)#1−K(1)−C(16)#1	22.62(12)
C(17)−K(1)−C(16)#1	98.44(13)
C(12)#2−K(1)−C(16)#1	135.31(13)
C(12)−K(1)−C(16)#1	77.28(12)
C(12)#1−K(1)−C(16)#1	41.76(12)
C(16)#2−K(1)−C(16)#1	96.94(13)
C(16)−K(1)−C(16)#1	96.93(13)
O(1)#1−K(2)−O(2)	94.37(9)
O(1)#1−K(2)−O(5)	115.90(12)
O(2)−K(2)−O(5)	113.95(12)
O(1)#1−K(2)−O(1)#2	94.76(12)
O(2)−K(2)−O(1)#2	90.02(8)
O(5)−K(2)−O(1)#2	137.93(12)
O(1)#1−K(2)−C(7)#2	141.81(11)
O(2)−K(2)−C(7)#2	107.52(10)
O(5)−K(2)−C(7)#2	83.70(13)
O(1)#2−K(2)−C(7)#2	55.45(10)
O(1)#1−K(2)−S(2)#1	55.07(7)
O(2)−K(2)−S(2)#1	145.46(5)
O(5)−K(2)−S(2)#1	73.34(10)
O(1)#2−K(2)−S(2)#1	106.65(7)
C(7)#2−K(2)−S(2)#1	106.83(10)
O(1)#1−K(2)−K(2)#1	94.26(6)
O(3)−K(3)−C(41)#3	85.65(10)
O(3)#4−K(3)−C(41)#3	149.01(11)
O(3)#3−K(3)−C(41)#3	57.96(10)
C(40)#4−K(3)−C(41)#3	140.43(11)
C(40)−K(3)−C(41)#3	94.61(11)
C(40)#3−K(3)−C(41)#3	23.78(11)
C(41)#4−K(3)−C(41)#3	117.84(4)
O(3)−K(3)−C(41)	57.96(10)
O(3)#4−K(3)−C(41)	85.65(10)
O(3)#3−K(3)−C(41)	149.01(11)
C(40)#4−K(3)−C(41)	94.61(11)
C(40)−K(3)−C(41)	23.78(11)
C(40)#3−K(3)−C(41)	140.43(11)
C(41)#4−K(3)−C(41)	117.84(4)
C(41)#3−K(3)−C(41)	117.84(4)
O(3)−K(3)−C(45)#4	131.92(10)
O(3)#4−K(3)−C(45)#4	62.56(10)
O(3)#3−K(3)−C(45)#4	126.22(10)
C(40)#4−K(3)−C(45)#4	23.75(11)
C(40)−K(3)−C(45)#4	100.20(11)
C(40)#3−K(3)−C(45)#4	122.36(12)
C(41)#4−K(3)−C(45)#4	40.58(11)
C(41)#3−K(3)−C(45)#4	137.47(12)
C(41)−K(3)−C(45)#4	79.19(11)
O(3)−K(3)−C(45)	62.56(10)
O(3)#4−K(3)−C(45)	126.22(10)
O(3)#3−K(3)−C(45)	131.92(10)
C(40)#4−K(3)−C(45)	122.36(12)
C(40)−K(3)−C(45)	23.75(11)
C(40)#3−K(3)−C(45)	100.20(11)
C(41)#4−K(3)−C(45)	137.46(12)
C(41)#3−K(3)−C(45)	79.19(11)
C(41)−K(3)−C(45)	40.58(11)
C(45)#4−K(3)−C(45)	99.55(10)
O(3)−K(3)−C(45)#3	126.22(10)
O(3)#4−K(3)−C(45)#3	131.92(10)
O(3)#3−K(3)−C(45)#3	62.56(10)
C(40)#4−K(3)−C(45)#3	100.20(11)
C(40)−K(3)−C(45)#3	122.35(12)
C(40)#3−K(3)−C(45)#3	23.75(11)
C(41)#4−K(3)−C(45)#3	79.19(11)
C(41)#3−K(3)−C(45)#3	40.59(11)
C(41)−K(3)−C(45)#3	137.46(12)
C(45)#4−K(3)−C(45)#3	99.55(10)
C(45)−K(3)−C(45)#3	99.55(10)
O(4)−K(4)−O(3)	91.78(8)
O(4)−K(4)−O(3)#4	91.69(9)
O(3)−K(4)−O(3)#4	95.33(12)
O(4)−K(4)−O(6)	117.89(12)
O(3)−K(4)−O(6)	126.71(10)
O(3)#4−K(4)−O(6)	124.26(11)
O(4)−K(4)−S(1)#4	139.96(4)
O(3)−K(4)−S(1)#4	111.33(7)
O(3)#4−K(4)−S(1)#4	55.26(7)
O(6)−K(4)−S(1)#4	74.43(9)
O(4)−K(4)−C(39)	105.40(10)
O(3)−K(4)−C(39)	55.17(10)
O(3)#4−K(4)−C(39)	145.46(11)
O(6)−K(4)−C(39)	73.87(12)
S(1)#4−K(4)−C(39)	114.64(10)
O(4)−K(4)−C(52)#3	54.94(8)
O(3)−K(4)−C(52)#3	146.71(9)
O(3)#4−K(4)−C(52)#3	87.07(9)
O(6)−K(4)−C(52)#3	76.22(11)
S(1)#4−K(4)−C(52)#3	97.29(7)
C(39)−K(4)−C(52)#3	127.35(11)
O(4)−K(4)−K(4)#4	45.57(6)
O(3)−K(4)−K(4)#4	92.77(6)
O(3)#4−K(4)−K(4)#4	46.21(7)
O(6)−K(4)−K(4)#4	139.99(8)
S(1)#4−K(4)−K(4)#4	99.16(4)
C(39)−K(4)−K(4)#4	139.40(10)
C(52)#3−K(4)−K(4)#4	65.31(8)

O(2)−K(2)−K(2)#1	45.84(6)
O(5)−K(2)−K(2)#1	146.64(10)
O(1)#2−K(2)−K(2)#1	44.26(6)
C(7)#2−K(2)−K(2)#1	80.40(9)
S(2)#1−K(2)−K(2)#1	139.50(3)
O(1)#1−K(2)−K(2)#2	48.62(7)
O(2)−K(2)−K(2)#2	45.84(6)
O(5)−K(2)−K(2)#2	130.66(10)
O(1)#2−K(2)−K(2)#2	91.05(6)
C(7)#2−K(2)−K(2)#2	140.35(9)
S(2)#1−K(2)−K(2)#2	102.58(4)
K(2)#1−K(2)−K(2)#2	59.999(1)
O(1)#1−K(2)−K(1)	47.53(6)
O(2)−K(2)−K(1)	91.43(8)
O(5)−K(2)−K(1)	152.23(10)
O(1)#2−K(2)−K(1)	47.28(6)
C(7)#2−K(2)−K(1)	99.84(9)
S(2)#1−K(2)−K(1)	79.33(3)
K(2)#1−K(2)−K(1)	60.205(16)
K(2)#2−K(2)−K(1)	60.204(16)
C(30)−S(1)−C(33)	92.6(2)
C(30)−S(1)−K(4)#3	109.22(16)
C(33)−S(1)−K(4)#3	153.5(2)
C(1)−O(1)−K(2)#2	146.0(2)
C(1)−O(1)−K(1)	113.4(2)
K(2)#2−O(1)−K(1)	88.50(9)
C(1)−O(1)−K(2)#1	119.2(2)
K(2)#2−O(1)−K(2)#1	87.11(9)
K(1)−O(1)−K(2)#1	84.69(8)
C(18)−O(2)−K(2)	126.45(8)
C(18)−O(2)−K(2)#2	126.45(8)
K(2)−O(2)−K(2)#2	88.32(12)
C(18)−O(2)−K(2)#1	126.45(8)
K(2)−O(2)−K(2)#1	88.32(12)
K(2)#2−O(2)−K(2)#1	88.31(12)
C(28)−O(5)−C(25)	105.3(5)
C(28)−O(5)−K(2)	120.6(5)
C(25)−O(5)−K(2)	129.8(4)
O(1)−C(1)−C(2)	111.5(3)
O(1)−C(1)−C(12)	107.9(3)
C(2)−C(1)−C(12)	109.4(4)
O(1)−C(1)−C(6)	112.1(4)
C(2)−C(1)−C(6)	106.5(3)
C(12)−C(1)−C(6)	109.5(3)
C(3)−C(2)−C(1)	130.3(4)
C(3)−C(2)−S(2)	111.0(4)
C(1)−C(2)−S(2)	118.6(3)
C(2)−C(3)−C(4)	111.4(5)
C(5)−C(4)−C(3)	112.6(5)
C(4)−C(5)−S(2)	112.0(4)
C(11)−C(6)−C(7)	117.3(4)
C(11)−C(6)−C(1)	122.6(4)
C(7)−C(6)−C(1)	120.0(4)
C(8)−C(7)−C(6)	120.3(5)
C(8)−C(7)−K(2)#1	116.5(4)
C(6)−C(7)−K(2)#1	96.2(3)
C(7)−C(8)−C(9)	121.9(6)
C(10)−C(9)−C(8)	120.2(6)
C(9)−C(10)−C(11)	120.3(6)
C(10)−C(11)−C(6)	120.0(5)
C(17)−C(12)−C(13)	116.9(4)
C(17)−C(12)−C(1)	118.8(4)
C(13)−C(12)−C(1)	124.0(4)
C(17)−C(12)−K(1)	75.0(2)
C(13)−C(12)−K(1)	97.4(3)
C(1)−C(12)−K(1)	91.7(2)
C(14)−C(13)−C(12)	120.7(5)
C(15)−C(14)−C(13)	120.1(5)
C(14)−C(15)−C(16)	120.3(5)
C(17)−C(16)−C(15)	119.7(5)
C(17)−C(16)−K(1)	61.7(3)
C(15)−C(16)−K(1)	96.2(3)
C(16)−C(17)−C(12)	122.3(5)
O(4)−K(4)−K(4)#3	45.57(6)
O(3)−K(4)−K(4)#3	46.30(7)
O(3)#4−K(4)−K(4)#3	92.70(6)
O(6)−K(4)−K(4)#3	142.18(9)
S(1)#4−K(4)−K(4)#3	142.33(3)
C(39)−K(4)−K(4)#3	79.40(10)
C(52)#3−K(4)−K(4)#3	100.47(6)
K(4)#4−K(4)−K(4)#3	60.0
O(4)−K(4)−K(3)	91.16(8)
O(3)−K(4)−K(3)	47.68(6)
O(3)#4−K(4)−K(3)	47.68(6)
O(6)−K(4)−K(3)	150.92(8)
S(1)#4−K(4)−K(3)	82.29(3)
C(39)−K(4)−K(3)	101.20(9)
C(52)#3−K(4)−K(3)	124.67(8)
K(4)#4−K(4)−K(3)	60.286(16)
K(4)#3−K(4)−K(3)	60.288(16)
C(29)−O(3)−K(4)	119.0(2)
C(29)−O(3)−K(4)#3	144.8(2)
K(4)−O(3)−K(4)#3	87.49(9)
C(29)−O(3)−K(3)	115.6(2)
K(4)−O(3)−K(3)	86.67(9)
K(4)#3−O(3)−K(3)	86.59(8)
C(46)−O(4)−K(4)	126.07(8)
C(46)−O(4)−K(4)#4	126.07(8)
K(4)−O(4)−K(4)#4	88.86(12)
C(46)−O(4)−K(4)#3	126.07(8)
K(4)−O(4)−K(4)#3	88.86(12)
K(4)#4−O(4)−K(4)#3	88.86(12)
C(56)−O(6)−C(53)	108.8(4)
C(56)−O(6)−K(4)	121.8(3)
C(53)−O(6)−K(4)	125.5(3)
C(5)−S(2)−C(2)	93.0(3)
C(5)−S(2)−K(2)#2	154.0(2)
C(2)−S(2)−K(2)#2	102.50(16)
O(3)−C(29)−C(30)	111.2(3)
O(3)−C(29)−C(34)	113.1(3)
C(30)−C(29)−C(34)	103.1(3)
O(3)−C(29)−C(40)	107.3(3)
C(30)−C(29)−C(40)	110.9(3)
C(34)−C(29)−C(40)	111.3(4)
C(31)−C(30)−C(29)	132.2(4)
C(31)−C(30)−S(1)	110.3(4)
C(29)−C(30)−S(1)	117.2(3)
C(30)−C(31)−C(32)	113.6(5)
C(33)−C(32)−C(31)	112.2(5)
C(32)−C(33)−S(1)	111.3(4)
C(39)−C(34)−C(35)	118.9(4)
C(39)−C(34)−C(29)	118.8(4)
C(35)−C(34)−C(29)	121.9(4)
C(36)−C(35)−C(34)	120.2(5)
C(37)−C(36)−C(35)	120.3(6)
C(38)−C(37)−C(36)	119.8(5)
C(37)−C(38)−C(39)	120.5(6)
C(34)−C(39)−C(38)	120.2(5)
C(34)−C(39)−K(4)	91.1(3)
C(38)−C(39)−K(4)	122.3(3)
C(41)−C(40)−C(45)	118.3(4)
C(41)−C(40)−C(29)	119.4(4)
C(45)−C(40)−C(29)	121.6(4)
C(41)−C(40)−K(3)	85.6(3)
C(45)−C(40)−K(3)	86.0(3)
C(29)−C(40)−K(3)	89.9(2)
C(42)−C(41)−C(40)	121.5(5)
C(42)−C(41)−K(3)	95.1(3)
C(40)−C(41)−K(3)	70.6(2)
C(41)−C(42)−C(43)	119.8(5)
C(44)−C(43)−C(42)	119.4(5)
C(45)−C(44)−C(43)	120.4(5)
C(44)−C(45)−C(40)	120.7(4)
C(44)−C(45)−K(3)	94.3(3)
C(40)−C(45)−K(3)	70.2(3)
O(4)−C(46)−C(47)	111.1(3)

C(16)−C(17)−K(1)	95.7(3)
C(12)−C(17)−K(1)	79.5(3)
O(2)−C(18)−C(19)#2	110.5(3)
O(2)−C(18)−C(19)	110.5(3)
C(19)#2−C(18)−C(19)	108.5(3)
O(2)−C(18)−C(19)#1	110.5(3)
C(19)#2−C(18)−C(19)#1	108.5(3)
C(19)−C(18)−C(19)#1	108.5(3)
C(24)−C(19)−C(18)	125.0(5)
C(24)−C(19)−C(20)	115.7(4)
C(18)−C(19)−C(20)	119.2(4)
C(21)−C(20)−C(19)	109.3(4)
C(22)−C(21)−C(20)	126.1(7)
C(23)−C(22)−C(21)	124.7(9)
C(22)−C(23)−C(24)	120.6(9)
C(23)−C(24)−C(19)	123.5(7)
O(5)−C(25)−C(26)	105.4(6)
C(27)−C(26)−C(25)	108.0(7)
C(28)−C(27)−C(26)	102.3(7)
O(5)−C(28)−C(27)	110.0(8)
O(3)−K(3)−O(3)#4	91.35(9)
O(3)−K(3)−O(3)#3	91.35(9)
O(3)#4−K(3)−O(3)#3	91.35(9)
O(3)−K(3)−C(40)#4	132.91(10)
O(3)#4−K(3)−C(40)#4	45.57(10)
O(3)#3−K(3)−C(40)#4	105.17(10)
O(3)−K(3)−C(40)	45.57(10)
O(3)#4−K(3)−C(40)	105.17(10)
O(3)#3−K(3)−C(40)	132.91(10)
C(40)#4−K(3)−C(40)	117.98(4)
O(3)−K(3)−C(40)#3	105.17(10)
O(3)#4−K(3)−C(40)#3	132.91(10)
O(4)−C(46)−C(47)#3	111.1(3)
C(47)−C(46)−C(47)#3	107.8(3)
O(4)−C(46)−C(47)#4	111.1(3)
C(47)−C(46)−C(47)#4	107.8(3)
C(47)#3−C(46)−C(47)#4	107.8(3)
C(48)#3−C(47)−C(46)	126.6(4)
C(48)#3−C(47)−C(52)#3	112.7(4)
C(46)−C(47)−C(52)#3	120.7(4)
C(47)#4−C(48)−C(49)	119.2(5)
C(50)−C(49)−C(48)	121.5(7)
C(51)−C(50)−C(49)	121.9(8)
C(50)−C(51)−C(52)	127.4(9)
C(51)−C(52)−C(47)#4	115.7(5)
C(51)−C(52)−K(4)#4	142.7(5)
C(47)#4−C(52)−K(4)#4	100.3(2)
O(6)−C(53)−C(54)	106.3(5)
C(55)−C(54)−C(53)	108.2(6)
C(54)−C(55)−C(56)	107.0(6)
O(6)−C(56)−C(55)	106.6(5)
C(58)#5−O(7)−C(58)	97.6(10)
C(58)#5−O(7)−C(58)#6	97.6(10)
C(58)−O(7)−C(58)#6	97.6(10)
C(59)−C(58)−O(7)	106.0(12)
C(60)−C(59)−C(58)	122(2)
C(60)−C(59)−C(59)#5	34.7(9)
C(58)−C(59)−C(59)#5	102.6(8)
C(60)−C(59)−C(59)#6	34.7(9)
C(58)−C(59)−C(59)#6	101.0(9)
C(59)#5−C(59)−C(59)#6	60.002(2)
C(59)#5−C(60)−C(59)	110.6(18)
C(59)#5−C(60)−C(59)#6	110.6(18)
C(59)−C(60)−C(59)#6	110.6(18)

Symmetry transformations used to generate equivalent atoms:
#1 −z+1,x−1/2,−y+1/2 #2 y+1/2,−z+1/2,−x+1 #3 −y+3/2,−z+1,x−1/2
#4 z+1/2,−x+3/2,−y+1 #5 −y+1,z+1/2,−x+1/2 #6 −z+1/2,−x+1,y−1/2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2565. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2 a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K(1)	24(1)	24(1)	24(1)	−1(1)	−1(1)	1(1)
K(2)	25(1)	28(1)	28(1)	6(1)	−1(1)	0(1)
S(1)	33(1)	47(1)	43(1)	−16(1)	14(1)	−7(1)
O(1)	24(1)	20(1)	25(1)	−1(1)	0(1)	2(1)
O(2)	25(1)	25(1)	25(1)	6(1)	6(1)	−6(1)
O(5)	53(2)	47(2)	69(3)	26(2)	0(2)	3(2)
C(1)	26(2)	21(2)	25(2)	−3(2)	−2(2)	2(2)
C(2)	23(2)	30(2)	28(2)	−2(2)	5(2)	3(2)
C(3)	32(3)	46(3)	38(3)	7(2)	−8(2)	8(2)
C(4)	36(3)	71(4)	39(3)	11(3)	−7(2)	11(3)
C(5)	40(3)	70(4)	29(3)	−14(3)	−6(2)	−3(3)
C(6)	23(2)	28(2)	33(2)	−6(2)	−5(2)	2(2)
C(7)	30(2)	34(3)	32(2)	−3(2)	6(2)	8(2)
C(8)	59(4)	60(4)	45(3)	8(3)	19(3)	7(3)
C(9)	72(5)	62(4)	69(4)	−14(4)	38(4)	3(4)
C(10)	59(4)	40(3)	88(5)	−24(3)	13(4)	9(3)
C(11)	40(3)	29(3)	53(3)	−7(2)	7(3)	6(2)
C(12)	25(2)	18(2)	35(2)	0(2)	0(2)	5(2)
C(13)	32(2)	32(2)	38(3)	−1(2)	7(2)	−3(2)
C(14)	42(3)	42(3)	58(4)	5(3)	17(3)	−10(2)
C(15)	37(3)	32(3)	76(4)	4(3)	3(3)	−11(2)
C(16)	36(3)	27(2)	61(4)	−3(2)	−16(3)	−2(2)
C(17)	32(2)	24(2)	40(3)	4(2)	−10(2)	−3(2)
C(18)	26(2)	26(2)	26(2)	1(2)	1(2)	−1(2)
C(19)	33(2)	36(2)	26(2)	6(2)	7(2)	9(2)
C(20)	7(2)	47(2)	2(1)	12(2)	−2(1)	2(2)
C(21)	47(3)	75(5)	50(4)	−18(3)	−7(3)	6(3)
C(22)	118(8)	88(6)	71(6)	6(5)	2(5)	42(6)
C(23)	211(13)	70(5)	41(4)	2(4)	−7(6)	29(7)
C(24)	97(5)	33(3)	30(3)	5(2)	−3(3)	10(3)

C(25)	52(4)	85(5)	105(6)	40(5)	0(4)	3(4)
C(26)	123(8)	115(7)	70(5)	24(5)	23(5)	77(7)
C(27)	117(7)	48(4)	80(5)	14(4)	−15(5)	−8(4)
C(28)	76(5)	111(7)	129(8)	67(6)	6(6)	−3(5)
K(3)	25(1)	25(1)	25(1)	0(1)	0(1)	0(1)
K(4)	25(1)	24(1)	28(1)	3(1)	1(1)	−1(1)
O(3)	20(1)	27(2)	28(2)	0(1)	−3(1)	0(1)
O(4)	24(1)	24(1)	24(1)	4(1)	−4(1)	4(1)
O(6)	43(2)	42(2)	39(2)	13(2)	−3(2)	−10(2)
S(2)	43(1)	43(1)	41(1)	−10(1)	−13(1)	10(1)
C(29)	24(2)	24(2)	21(2)	−3(2)	−3(2)	−1(2)
C(30)	24(2)	32(2)	23(2)	0(2)	1(2)	4(2)
C(31)	30(2)	44(3)	36(3)	−13(2)	−3(2)	3(2)
C(32)	46(3)	49(3)	24(2)	−7(2)	−6(2)	3(3)
C(33)	47(3)	41(3)	30(2)	−3(2)	11(2)	3(2)
C(34)	36(2)	25(2)	21(2)	−3(2)	6(2)	−8(2)
C(35)	40(3)	27(2)	38(3)	−6(2)	13(2)	−6(2)
C(36)	59(4)	41(3)	46(3)	−14(3)	27(3)	−26(3)
C(37)	102(5)	27(3)	43(3)	−3(3)	30(4)	−17(3)
C(38)	80(4)	23(2)	38(3)	4(2)	1(3)	1(3)
C(39)	50(3)	23(2)	33(3)	−4(2)	1(2)	1(2)
C(40)	17(2)	30(2)	29(2)	−9(2)	−1(2)	0(2)
C(41)	26(2)	30(2)	35(2)	−2(2)	4(2)	−1(2)
C(42)	25(2)	33(2)	40(3)	−5(2)	4(2)	1(2)
C(43)	33(3)	32(3)	56(3)	−3(2)	−6(2)	8(2)
C(44)	38(3)	40(3)	35(3)	4(2)	−8(2)	3(2)
C(45)	25(2)	32(2)	31(2)	−2(2)	−2(2)	−2(2)
C(46)	23(2)	23(2)	23(2)	4(2)	−4(2)	4(2)
C(47)	32(2)	23(2)	25(2)	8(2)	−2(2)	3(2)
C(48)	29(3)	34(3)	81(4)	−6(3)	11(3)	2(2)
C(49)	41(3)	72(5)	103(6)	−18(5)	11(4)	11(3)
C(50)	75(5)	77(5)	64(4)	1(4)	17(4)	−17(4)
C(51)	82(6)	101(7)	167(11)	60(8)	3(7)	−29(6)
C(52)	0(2)	21(2)	43(2)	29(2)	6(2)	8(1)
C(53)	62(4)	61(4)	49(3)	20(3)	−11(3)	0(3)
C(54)	80(5)	71(5)	123(7)	58(5)	17(5)	8(4)
C(55)	54(4)	84(5)	129(7)	70(5)	−1(5)	−10(4)
C(56)	41(3)	42(3)	52(3)	10(3)	−1(3)	−3(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for sh2565.

	x	y	z	U(eq)
H(3)	9595	1283	3249	47
H(4)	9956	1687	4122	58
H(5)	9677	2618	4245	56
H(7)	9510	2362	1748	39
H(8)	10094	1949	1143	66
H(9)	10241	1020	1156	82
H(10)	9791	477	1776	75
H(11)	9170	866	2401	49
H(13)	8399	1541	3501	41
H(14)	7577	1075	3617	57
H(15)	7070	813	2865	58
H(16)	7380	1009	1987	50
H(17)	8179	1487	1867	38
H(20)	8298	3305	313	22
H(21)	7920	3623	−520	69
H(22)	8052	4430	−848	111
H(23)	8572	5044	−472	129
H(24)	8944	4910	332	64
H(25A)	6422	4932	1412	97
H(25B)	6383	4647	821	97
H(26A)	6384	5452	454	123
H(26B)	6478	5732	1039	123
H(27A)	7214	5692	259	98
H(27B)	7347	5835	888	98
H(28A)	7434	4843	353	126
H(28B)	7818	5086	824	126
H(31)	5270	6640	284	44
H(32)	5802	6271	−494	48
H(33)	6748	6544	−461	47

H(35)	4776	6886	1201	42
H(36)	4459	6104	1655	58
H(37)	5053	5586	2187	69
H(38)	5961	5841	2266	56
H(39)	6288	6624	1812	42
H(41)	5146	7806	1830	37
H(42)	4600	8579	1763	40
H(43)	4503	9025	920	49
H(44)	4986	8704	159	45
H(45)	5519	7918	226	35
H(48)	8613	6499	2689	58
H(49)	9530	6673	2453	86
H(50)	9792	7483	2169	87
H(51)	9281	8168	2234	140
H(52)	8380	8115	2234	26
H(53A)	6264	6661	3801	69
H(53B)	6270	6307	3249	69
H(54A)	5566	5847	3508	109
H(54B)	5620	6137	4093	109
H(55A)	4951	6667	3937	107
H(55B)	4802	6253	3450	107
H(56A)	5094	6818	2824	54
H(56B)	5042	7276	3291	54

Compound 26

Table 1. Crystal data and structure refinement for sh2579.

Identification code	sh2579	
Empirical formula	C66 H63 O5 S3 Y	
Formula weight	1121.25	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.6782(18) Å	α = 90°.
	b = 13.7601(16) Å	β = 94.496(6)°.
	c = 27.649(3) Å	γ = 90°.
Volume	5567.2(11) Å^3	
Z	4	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	1.211 mm^{-1}	
F(000)	2344	
Crystal size	0.56 x 0.4 x 0.23 mm^3	
Theta range for data collection	1.39 to 26.78°.	
Index ranges	−18<=h<=18, −17<=k<=17, −29<=l<=35	
Reflections collected	56064	
Independent reflections	11862 [R(int) = 0.1223]	
Completeness to theta = 26.78°	99.7 %	
Absorption correction	Multiscan	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	11862 / 0 / 633	
Goodness−of−fit on F^2	2.530	
Final R indices [I>2sigma(I)]	R1 = 0.1496, wR2 = 0.3516	
R indices (all data)	R1 = 0.2070, wR2 = 0.3647	
Largest diff. peak and hole	1.829 and −2.047 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2579. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(001)	7365(1)	4880(1)	1557(1)	15(1)
S(1)	7646(3)	6352(3)	2789(2)	68(1)
S(2)	7624(4)	6257(4)	331(2)	111(2)
S(3)	7500(3)	3700(3)	3063(2)	59(1)
O(1)	7331(5)	6341(5)	1786(2)	24(2)
O(2)	7295(5)	4499(5)	837(2)	24(2)
O(3)	7557(5)	3709(5)	2041(2)	22(2)
O(4)	5803(4)	4840(5)	1666(2)	23(2)

O(5)	8948(4)	5034(5)	1611(2)	18(2)
C(1)	7462(7)	7306(7)	1915(4)	23(2)
C(2)	6607(8)	7902(7)	1761(3)	25(2)
C(3)	5689(6)	7427(6)	1668(3)	16(2)
C(4)	5001(9)	8043(10)	1547(5)	50(4)
C(5)	5040(10)	8981(10)	1534(5)	54(4)
C(6)	5832(9)	9444(10)	1594(5)	48(4)
C(7)	6624(8)	8917(8)	1716(5)	43(3)
C(8)	8294(7)	7704(7)	1689(4)	26(3)
C(9)	8236(8)	7957(7)	1193(4)	34(3)
C(10)	9002(9)	8228(9)	965(4)	40(3)
C(11)	9842(9)	8250(8)	1222(6)	51(4)
C(12)	9917(8)	8011(8)	1723(5)	35(3)
C(13)	9190(9)	7754(7)	1955(5)	40(3)
C(14)	7587(7)	7362(8)	2467(4)	30(3)
C(15)	7679(7)	8192(7)	2780(4)	29(3)
C(16)	7834(9)	7969(15)	3269(5)	73(6)
C(17)	7812(10)	6870(20)	3358(6)	109(9)
C(18)	7428(8)	4297(8)	335(3)	27(3)
C(19)	6648(8)	3636(8)	135(4)	31(3)
C(20)	5687(7)	3922(7)	161(3)	17(2)
C(21)	5021(10)	3413(11)	−49(5)	56(4)
C(22)	5175(9)	2572(10)	−264(5)	45(3)
C(23)	6027(10)	2232(10)	−293(5)	58(4)
C(24)	6809(8)	2782(9)	−92(4)	41(3)
C(25)	8383(4)	3844(5)	325(3)	29(3)
C(26)	8692(5)	3181(5)	681(2)	9(2)
C(27)	9522(6)	2709(6)	648(3)	113(8)
C(28)	10044(5)	2900(8)	261(4)	119(9)
C(29)	9735(6)	3562(7)	−95(3)	89(6)
C(30)	8905(6)	4034(5)	−62(2)	43(3)
C(31)	7340(8)	5271(8)	57(4)	30(3)
C(32)	7072(7)	5386(6)	−462(3)	19(2)
C(33)	7076(10)	6439(19)	−590(6)	115(9)
C(34)	7413(9)	7025(9)	−97(8)	86(7)
C(35)	7412(7)	2752(7)	2169(4)	19(2)
C(36)	6493(8)	2426(7)	1939(4)	26(3)
C(37)	6377(8)	2395(7)	1408(4)	27(3)
C(38)	5546(9)	2161(8)	1196(5)	47(4)
C(39)	4767(10)	1996(9)	1445(6)	51(4)
C(40)	4884(9)	2042(8)	1932(5)	45(3)
C(41)	5731(7)	2251(8)	2188(4)	31(3)
C(42)	8209(7)	2098(7)	2000(3)	22(2)
C(43)	9135(6)	2453(6)	1984(3)	3(2)
C(44)	9738(12)	1905(15)	1854(6)	77(6)
C(45)	9635(10)	964(12)	1754(5)	57(4)
C(46)	8824(9)	537(9)	1774(5)	43(3)
C(47)	8057(8)	1108(8)	1897(4)	33(3)
C(48)	7477(6)	2682(7)	2726(3)	17(2)
C(49)	7509(7)	1850(8)	3018(4)	25(2)
C(50)	7570(8)	2034(10)	3510(4)	38(3)
C(51)	7573(8)	3114(14)	3607(5)	69(6)
C(52)	4985(8)	4861(10)	1337(4)	41(3)
C(53)	4265(8)	5090(10)	1604(4)	46(4)
C(54)	4477(8)	4758(11)	2123(4)	49(4)
C(55)	5504(7)	4861(8)	2170(4)	29(2)
C(56)	9493(8)	5152(9)	2082(4)	35(3)
C(57)	10477(9)	5074(13)	1969(6)	69(5)
C(58)	10415(8)	4994(11)	1476(5)	65(5)
C(59)	9568(8)	5372(9)	1252(4)	40(3)
C(60)	2101(17)	5230(16)	4854(9)	109(7)
C(61)	2813(16)	5175(15)	4522(8)	102(7)
C(62)	3618(15)	4728(15)	4734(8)	99(6)
C(63)	3732(16)	4499(15)	5208(8)	103(7)
C(64)	2987(18)	4595(16)	5515(8)	111(7)
C(65)	2250(20)	4933(18)	5340(10)	135(9)
C(66A)	1340(30)	5080(30)	5456(17)	115(15)
C(66B)	1210(30)	5580(30)	4682(13)	85(11)

Table 3. Bond lengths [Å] and angles [°] for sh2579.

Y(001)−O(2)	2.051(6)	C(22)−C(23)	1.344(19)
Y(001)−O(3)	2.102(6)	C(23)−C(24)	1.448(17)
Y(001)−O(1)	2.110(6)	C(25)−C(26)	1.3900

Y(001)−O(5)	2.326(6)
Y(001)−O(4)	2.336(6)
S(1)−C(14)	1.649(12)
S(1)−C(17)	1.73(2)
S(2)−C(31)	1.594(12)
S(2)−C(34)	1.600(17)
S(3)−C(48)	1.681(10)
S(3)−C(51)	1.703(17)
O(1)−C(1)	1.384(11)
O(2)−C(18)	1.445(12)
O(3)−C(35)	1.383(11)
O(4)−C(52)	1.449(12)
O(4)−C(55)	1.495(12)
O(5)−C(59)	1.475(12)
O(5)−C(56)	1.482(11)
C(1)−C(8)	1.516(15)
C(1)−C(14)	1.524(15)
C(1)−C(2)	1.532(15)
C(2)−C(7)	1.403(15)
C(2)−C(3)	1.501(14)
C(3)−C(4)	1.341(15)
C(4)−C(5)	1.292(18)
C(5)−C(6)	1.324(18)
C(6)−C(7)	1.389(16)
C(8)−C(9)	1.413(15)
C(8)−C(13)	1.456(16)
C(9)−C(10)	1.383(16)
C(10)−C(11)	1.375(17)
C(11)−C(12)	1.419(18)
C(12)−C(13)	1.335(16)
C(14)−C(15)	1.433(14)
C(15)−C(16)	1.388(18)
C(16)−C(17)	1.53(3)
C(18)−C(19)	1.531(15)
C(18)−C(25)	1.536(12)
C(18)−C(31)	1.546(15)
C(19)−C(24)	1.361(16)
C(19)−C(20)	1.472(15)
C(20)−C(21)	1.302(17)
C(21)−C(22)	1.329(18)
C(25)−C(30)	1.3900
C(26)−C(27)	1.3900
C(27)−C(28)	1.3900
C(28)−C(29)	1.3900
C(29)−C(30)	1.3900
C(31)−C(32)	1.464(14)
C(32)−C(33)	1.49(2)
C(33)−C(34)	1.63(3)
C(35)−C(36)	1.514(14)
C(35)−C(48)	1.537(14)
C(35)−C(42)	1.576(14)
C(36)−C(41)	1.381(15)
C(36)−C(37)	1.463(15)
C(37)−C(38)	1.349(16)
C(38)−C(39)	1.398(19)
C(39)−C(40)	1.346(18)
C(40)−C(41)	1.411(16)
C(42)−C(47)	1.406(14)
C(42)−C(43)	1.449(13)
C(43)−C(44)	1.24(2)
C(44)−C(45)	1.33(2)
C(45)−C(46)	1.333(18)
C(46)−C(47)	1.434(16)
C(48)−C(49)	1.398(14)
C(49)−C(50)	1.380(15)
C(50)−C(51)	1.51(2)
C(52)−C(53)	1.373(17)
C(53)−C(54)	1.514(15)
C(54)−C(55)	1.509(16)
C(56)−C(57)	1.506(18)
C(57)−C(58)	1.364(19)
C(58)−C(59)	1.441(16)
C(60)−C(65)	1.40(3)
C(60)−C(61)	1.45(3)
C(60)−C(66B)	1.44(4)
C(61)−C(62)	1.42(3)
C(62)−C(63)	1.34(3)
C(63)−C(64)	1.44(3)
C(64)−C(65)	1.24(3)
C(65)−C(66A)	1.41(5)

O(2)−Y(001)−O(3)	114.6(3)
O(2)−Y(001)−O(1)	122.3(3)
O(3)−Y(001)−O(1)	123.0(3)
O(2)−Y(001)−O(5)	93.5(2)
O(3)−Y(001)−O(5)	86.8(2)
O(1)−Y(001)−O(5)	86.6(2)
O(2)−Y(001)−O(4)	98.3(3)
O(3)−Y(001)−O(4)	89.0(3)
O(1)−Y(001)−O(4)	86.4(2)
O(5)−Y(001)−O(4)	168.2(2)
C(14)−S(1)−C(17)	98.0(9)
C(31)−S(2)−C(34)	100.4(8)
C(48)−S(3)−C(51)	95.2(7)
C(1)−O(1)−Y(001)	170.2(7)
C(18)−O(2)−Y(001)	168.8(6)
C(35)−O(3)−Y(001)	151.3(6)
C(52)−O(4)−C(55)	107.2(8)
C(52)−O(4)−Y(001)	133.8(6)
C(55)−O(4)−Y(001)	118.9(5)
C(59)−O(5)−C(56)	103.8(8)
C(59)−O(5)−Y(001)	130.6(6)
C(56)−O(5)−Y(001)	122.3(6)
O(1)−C(1)−C(8)	109.9(8)
O(1)−C(1)−C(14)	108.1(8)
C(8)−C(1)−C(14)	110.9(8)
O(1)−C(1)−C(2)	110.3(8)
C(8)−C(1)−C(2)	111.1(8)
C(14)−C(1)−C(2)	106.5(8)
C(7)−C(2)−C(3)	116.1(10)
C(7)−C(2)−C(1)	122.6(10)
C(3)−C(2)−C(1)	121.3(8)
C(4)−C(3)−C(2)	114.6(10)
C(19)−C(24)−C(23)	117.9(12)
C(26)−C(25)−C(30)	120.0
C(26)−C(25)−C(18)	120.1(6)
C(30)−C(25)−C(18)	119.7(6)
C(25)−C(26)−C(27)	120.0
C(26)−C(27)−C(28)	120.0
C(29)−C(28)−C(27)	120.0
C(30)−C(29)−C(28)	120.0
C(29)−C(30)−C(25)	120.0
C(32)−C(31)−C(18)	125.9(9)
C(32)−C(31)−S(2)	114.5(8)
C(18)−C(31)−S(2)	119.5(8)
C(31)−C(32)−C(33)	109.4(11)
C(32)−C(33)−C(34)	106.8(10)
S(2)−C(34)−C(33)	108.8(11)
O(3)−C(35)−C(36)	108.9(8)
O(3)−C(35)−C(48)	108.5(8)
C(36)−C(35)−C(48)	112.7(8)
O(3)−C(35)−C(42)	109.6(8)
C(36)−C(35)−C(42)	111.2(8)
C(48)−C(35)−C(42)	105.8(7)
C(41)−C(36)−C(37)	117.4(10)
C(41)−C(36)−C(35)	124.8(9)
C(37)−C(36)−C(35)	117.5(10)
C(38)−C(37)−C(36)	118.2(11)
C(37)−C(38)−C(39)	124.9(13)
C(40)−C(39)−C(38)	116.0(13)
C(39)−C(40)−C(41)	123.4(13)
C(36)−C(41)−C(40)	120.0(11)
C(47)−C(42)−C(43)	117.0(9)
C(47)−C(42)−C(35)	120.3(10)
C(43)−C(42)−C(35)	122.4(8)

C(5)−C(4)−C(3)	127.2(13)	C(44)−C(43)−C(42)	119.8(11)
C(4)−C(5)−C(6)	121.2(15)	C(43)−C(44)−C(45)	125.7(15)
C(5)−C(6)−C(7)	119.3(14)	C(46)−C(45)−C(44)	120.4(16)
C(6)−C(7)−C(2)	121.4(12)	C(45)−C(46)−C(47)	119.3(13)
C(9)−C(8)−C(13)	117.5(11)	C(42)−C(47)−C(46)	117.7(11)
C(9)−C(8)−C(1)	120.0(9)	C(49)−C(48)−C(35)	128.7(9)
C(13)−C(8)−C(1)	122.3(10)	C(49)−C(48)−S(3)	111.4(7)
C(10)−C(9)−C(8)	121.3(11)	C(35)−C(48)−S(3)	119.9(7)
C(11)−C(10)−C(9)	120.0(12)	C(50)−C(49)−C(48)	114.6(10)
C(10)−C(11)−C(12)	119.8(13)	C(49)−C(50)−C(51)	110.7(10)
C(13)−C(12)−C(11)	121.7(12)	C(50)−C(51)−S(3)	108.1(8)
C(12)−C(13)−C(8)	119.7(12)	C(53)−C(52)−O(4)	107.5(9)
C(15)−C(14)−C(1)	130.0(10)	C(52)−C(53)−C(54)	109.3(10)
C(15)−C(14)−S(1)	110.3(8)	C(55)−C(54)−C(53)	100.5(9)
C(1)−C(14)−S(1)	119.7(8)	O(4)−C(55)−C(54)	106.4(8)
C(16)−C(15)−C(14)	114.3(12)	O(5)−C(56)−C(57)	105.7(9)
C(15)−C(16)−C(17)	111.9(13)	C(58)−C(57)−C(56)	102.9(11)
C(16)−C(17)−S(1)	105.4(9)	C(57)−C(58)−C(59)	112.9(11)
O(2)−C(18)−C(19)	107.9(9)	C(58)−C(59)−O(5)	98.9(10)
O(2)−C(18)−C(25)	106.7(7)	C(65)−C(60)−C(61)	122(2)
C(19)−C(18)−C(25)	114.2(9)	C(65)−C(60)−C(66B)	119(3)
O(2)−C(18)−C(31)	107.4(8)	C(61)−C(60)−C(66B)	119(2)
C(19)−C(18)−C(31)	107.7(8)	C(62)−C(61)−C(60)	112(2)
C(25)−C(18)−C(31)	112.6(8)	C(63)−C(62)−C(61)	123(2)
C(24)−C(19)−C(20)	117.0(10)	C(62)−C(63)−C(64)	121(2)
C(24)−C(19)−C(18)	121.8(11)	C(65)−C(64)−C(63)	119(2)
C(20)−C(19)−C(18)	121.1(9)	C(64)−C(65)−C(60)	123(3)
C(21)−C(20)−C(19)	121.6(10)	C(64)−C(65)−C(66A)	141(3)
C(20)−C(21)−C(22)	121.3(14)	C(60)−C(65)−C(66A)	96(3)
C(21)−C(22)−C(23)	121.4(14)		
C(22)−C(23)−C(24)	120.6(13)		

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2579. The anisotropic displacement factor exponent takes the form: $-2p^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(001)	15(1)	10(1)	19(1)	0(1)	1(1)	−1(1)
S(1)	57(3)	69(3)	77(3)	20(2)	8(2)	3(2)
S(2)	117(5)	68(3)	147(5)	4(3)	6(4)	−9(3)
S(3)	59(3)	50(2)	68(3)	6(2)	9(2)	1(2)
O(1)	23(4)	23(4)	26(4)	−4(3)	−6(3)	−5(3)
O(2)	27(4)	31(4)	15(4)	−2(3)	3(3)	0(3)
O(3)	22(4)	21(4)	22(4)	5(3)	−2(3)	−4(3)
O(4)	4(3)	37(4)	27(4)	−18(3)	−1(3)	2(3)
O(5)	9(3)	32(4)	12(3)	−9(3)	7(2)	−8(3)
C(1)	19(6)	17(5)	33(6)	−8(4)	1(5)	−2(4)
C(2)	39(7)	23(5)	15(5)	−3(4)	18(5)	−1(5)
C(3)	8(5)	12(4)	26(6)	0(4)	−15(4)	6(4)
C(4)	23(7)	64(10)	60(9)	−12(7)	−11(6)	−3(7)
C(5)	42(9)	54(9)	68(10)	−22(8)	15(7)	−5(7)
C(6)	33(8)	56(8)	55(9)	−4(7)	−4(7)	26(7)
C(7)	25(7)	29(6)	74(10)	−15(6)	−2(6)	−5(5)
C(8)	22(6)	28(6)	27(6)	−6(5)	−4(5)	−5(5)
C(9)	35(7)	23(6)	43(7)	−1(5)	−1(6)	−4(5)
C(10)	46(9)	43(7)	33(7)	−7(6)	8(6)	−10(6)
C(11)	38(9)	22(6)	95(12)	4(7)	9(8)	1(6)
C(12)	21(7)	29(6)	52(8)	−15(6)	−8(6)	−2(5)
C(13)	43(8)	19(6)	59(9)	−11(6)	13(7)	2(5)
C(14)	18(6)	51(7)	21(6)	−7(5)	6(5)	−8(5)
C(15)	24(6)	16(5)	47(8)	−14(5)	9(5)	−2(5)
C(16)	31(8)	169(19)	21(8)	−34(10)	6(6)	12(10)
C(17)	23(9)	260(30)	44(10)	86(14)	−5(7)	−10(12)
C(18)	33(7)	37(6)	10(5)	2(4)	−3(5)	−5(5)
C(19)	40(8)	26(6)	25(6)	−1(5)	−2(5)	−4(5)
C(20)	27(6)	13(5)	13(5)	−8(4)	5(4)	1(4)
C(21)	56(10)	69(10)	43(8)	−7(7)	0(7)	18(8)
C(22)	38(8)	54(8)	44(8)	12(7)	0(6)	−9(7)
C(23)	55(10)	42(8)	75(11)	−21(7)	−9(8)	−10(7)
C(24)	23(7)	56(8)	44(8)	−10(6)	6(6)	6(6)
C(25)	22(6)	38(6)	26(6)	−1(5)	−2(5)	−9(5)
C(26)	1(4)	15(4)	13(5)	4(4)	4(4)	9(4)

C(27)	160(20)	138(19)	39(11)	7(11)	−25(12)	−11(17)
C(28)	89(17)	99(16)	160(20)	33(16)	−60(16)	−25(13)
C(29)	54(12)	64(11)	153(18)	29(12)	43(11)	24(9)
C(30)	26(7)	37(7)	65(9)	0(6)	−5(6)	17(6)
C(31)	32(7)	33(6)	26(6)	0(5)	2(5)	1(5)
C(32)	26(6)	13(5)	18(5)	−1(4)	−10(4)	1(4)
C(33)	23(9)	260(30)	61(11)	97(15)	5(8)	36(13)
C(34)	24(8)	25(7)	210(20)	41(10)	34(11)	−6(6)
C(35)	15(6)	18(5)	24(6)	5(4)	4(4)	1(4)
C(36)	30(7)	20(5)	26(6)	2(4)	−8(5)	4(5)
C(37)	29(7)	17(5)	35(7)	2(5)	5(5)	−8(5)
C(38)	50(9)	33(7)	55(9)	0(6)	−10(7)	−14(6)
C(39)	49(9)	29(7)	73(11)	4(7)	−18(8)	2(6)
C(40)	34(8)	32(7)	70(10)	16(7)	12(7)	−9(6)
C(41)	22(7)	30(6)	40(7)	−3(5)	1(5)	0(5)
C(42)	29(6)	27(5)	8(5)	5(4)	−7(4)	10(5)
C(43)	1(4)	0(4)	7(4)	−8(3)	0(3)	−4(3)
C(44)	61(12)	116(16)	52(10)	29(10)	−2(9)	−40(12)
C(45)	38(9)	87(12)	45(9)	8(8)	1(7)	−9(8)
C(46)	37(8)	31(6)	60(9)	−3(6)	−2(7)	14(6)
C(47)	25(7)	36(6)	37(7)	−2(5)	3(5)	−12(5)
C(48)	1(5)	27(5)	23(6)	−1(4)	2(4)	−3(4)
C(49)	11(6)	42(6)	23(6)	−4(5)	6(4)	−1(5)
C(50)	26(7)	62(8)	24(7)	27(6)	3(5)	−2(6)
C(51)	18(7)	165(18)	26(7)	−55(9)	6(5)	1(9)
C(52)	35(7)	60(8)	27(6)	2(6)	−10(5)	6(7)
C(53)	21(6)	79(10)	34(7)	25(7)	−17(5)	−42(7)
C(54)	30(7)	82(10)	36(7)	−2(7)	9(6)	3(7)
C(55)	25(6)	37(6)	27(6)	4(5)	8(5)	10(5)
C(56)	28(7)	39(6)	36(7)	−8(6)	−14(5)	6(6)
C(57)	27(8)	112(14)	65(10)	−9(10)	−7(7)	4(9)
C(58)	17(7)	100(12)	75(10)	−71(9)	−24(6)	35(7)
C(59)	29(7)	58(8)	35(7)	1(6)	14(6)	−4(6)

Compound 27

Table 1. Crystal data and structure refinement for sh2620.

Identification code	sh2620	
Empirical formula	C68 H57 N2 O3 S3 Y	
Formula weight	1135.25	
Temperature	146(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 12.6757(4) Å	α = 97.748(2)°.
	b = 14.0423(4) Å	β = 95.195(2)°.
	c = 18.1640(8) Å	γ = 116.5880(10)°.
Volume	2822.97(17) Å^3	
Z	2	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	1.194 mm^{-1}	
F(000)	1180	
Crystal size	0.52 x 0.33 x 0.12 mm^3	
Theta range for data collection	1.15 to 29.05°.	
Index ranges	−17<=h<=17, −19<=k<=19, −24<=l<=24	
Reflections collected	64544	
Independent reflections	14865 [R(int) = 0.0383]	
Completeness to theta = 29.05°	98.5 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8739 and 0.5751	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	14865 / 1 / 673	
Goodness−of−fit on F^2	2.401	
Final R indices [I>2sigma(I)]	R1 = 0.0865, wR2 = 0.2458	
R indices (all data)	R1 = 0.1098, wR2 = 0.2536	
Largest diff. peak and hole	2.440 and −1.952 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2620. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	7711(1)	8053(1)	7125(1)	19(1)
S(1)	10163(2)	11553(2)	7626(1)	76(1)
S(2)	9381(2)	6134(2)	7526(2)	110(1)
S(3)	6154(2)	5039(2)	7253(1)	89(1)
N(1)	7412(3)	8401(3)	5843(2)	28(1)
N(2)	8207(3)	7776(3)	8423(2)	30(1)
O(1)	7927(3)	9575(2)	7608(2)	27(1)
O(2)	9153(3)	7843(2)	6815(2)	29(1)
O(3)	5953(3)	6820(2)	6963(2)	25(1)
C(1)	7776(4)	10496(3)	7815(2)	24(1)
C(2)	9005(4)	11514(4)	7985(3)	28(1)
C(3)	9316(5)	12484(4)	8441(3)	38(1)
C(4)	10496(5)	13303(4)	8491(3)	41(1)
C(5)	11184(6)	12961(6)	8071(4)	63(2)
C(6)	6927(4)	10561(4)	7175(2)	27(1)
C(7)	7088(4)	11533(4)	6955(3)	31(1)
C(8)	6274(6)	11505(5)	6388(3)	50(2)
C(9)	5339(6)	10580(6)	6034(4)	55(2)
C(10)	5158(6)	9643(6)	6228(4)	58(2)
C(11)	5853(4)	9565(3)	6770(2)	26(1)
C(12)	7225(4)	10442(3)	8543(2)	28(1)
C(13)	6559(4)	10979(4)	8734(3)	31(1)
C(14)	6233(5)	10974(4)	9443(3)	40(1)
C(15)	6545(5)	10479(5)	9946(4)	51(2)
C(16)	7131(5)	9936(5)	9783(3)	53(2)
C(17)	7499(3)	9919(3)	9131(2)	8(1)
C(18)	10147(4)	7710(4)	6654(3)	30(1)
C(19)	9942(4)	6563(4)	6744(3)	37(1)
C(20)	10218(5)	5893(4)	6274(4)	48(1)
C(21A)	9854(11)	4894(10)	6660(7)	58(3)
C(21B)	10081(10)	4883(9)	6283(7)	25(2)
C(22B)	9561(11)	4464(10)	6887(7)	30(2)
C(23)	9339(6)	4995(5)	7346(4)	68(2)
C(24)	11281(4)	8602(4)	7186(3)	35(1)
C(25)	12261(5)	8470(4)	7432(3)	40(1)
C(26)	13267(5)	9376(5)	7865(4)	51(2)
C(27)	13255(7)	10337(6)	8037(4)	68(2)
C(28)	12344(8)	10483(7)	7873(5)	83(2)
C(29)	11442(3)	9748(2)	7408(2)	7(1)
C(30)	10305(5)	7801(4)	5827(3)	34(1)
C(31)	11454(5)	8227(4)	5590(3)	39(1)
C(32)	11520(8)	8211(5)	4851(4)	64(2)
C(33)	10548(8)	7832(6)	4330(4)	68(2)
C(34)	9463(7)	7434(6)	4515(4)	65(2)
C(35)	9287(5)	7400(4)	5242(3)	40(1)
C(36)	4781(4)	6018(3)	6941(2)	22(1)
C(37)	4831(4)	4971(4)	7078(2)	27(1)
C(38)	3827(4)	3919(3)	7107(2)	20(1)
C(39)	4425(11)	3175(6)	7277(3)	114(4)
C(40)	5751(7)	3849(5)	7343(3)	57(2)
C(41)	4051(4)	5816(3)	6162(2)	24(1)
C(42)	3962(5)	5054(4)	5561(3)	36(1)
C(43)	3418(5)	4968(4)	4836(3)	48(2)
C(44)	2949(5)	5638(5)	4718(3)	44(1)
C(45)	3005(5)	6371(5)	5272(3)	45(1)
C(46)	3522(4)	6532(4)	6014(2)	31(1)
C(47)	4205(4)	6384(3)	7560(2)	23(1)
C(48)	4961(3)	7427(3)	8129(2)	9(1)
C(49)	4308(6)	7668(5)	8629(3)	46(1)
C(50)	3171(6)	7078(5)	8645(4)	52(2)
C(51)	2528(6)	6176(5)	8160(3)	49(1)
C(52)	2957(4)	5797(3)	7638(2)	21(1)
C(53)	8310(5)	9190(4)	5619(3)	36(1)
C(54)	8263(5)	9408(4)	4898(3)	40(1)
C(55)	7217(5)	8772(5)	4391(3)	44(1)
C(56)	6279(5)	7952(4)	4610(3)	39(1)
C(57)	6407(4)	7785(4)	5338(2)	30(1)
C(58)	9324(5)	8414(5)	8767(3)	51(2)

C(59)	9716(6)	8533(7)	9524(4)	79(3)
C(60)	8921(7)	7914(6)	9945(3)	69(2)
C(61)	7763(6)	7216(6)	9598(3)	60(2)
C(62)	7435(5)	7170(4)	8845(3)	38(1)
C(63)	5468(6)	4604(5)	516(4)	59(2)
C(64)	5312(6)	5437(5)	757(4)	56(2)
C(65)	4863(6)	5892(6)	272(4)	62(2)
C(66)	4816(14)	6799(12)	542(9)	72(4)
C(67A)	8577(15)	4156(12)	−149(8)	60(3)
C(68A)	9698(13)	4178(9)	330(7)	55(3)
C(69A)	10758(15)	5154(13)	342(9)	68(4)
C(70A)	11890(40)	5050(40)	800(20)	92(11)
C(69B)	11292(19)	5036(16)	551(11)	75(5)
C(68B)	10280(20)	4184(17)	517(12)	49(5)
C(67B)	9155(15)	4128(10)	70(8)	58(3)
C(68C)	7980(60)	4490(50)	−780(30)	121(19)

Table 3. Bond lengths [Å] and angles [°] for sh2620.

O(3)−Y(1)−O(1)	113.77(12)
O(3)−Y(1)−O(2)	124.76(12)
O(1)−Y(1)−O(2)	121.43(12)
O(3)−Y(1)−N(1)	91.35(12)
O(1)−Y(1)−N(1)	91.05(12)
O(2)−Y(1)−N(1)	86.27(12)
O(3)−Y(1)−N(2)	93.29(12)
O(1)−Y(1)−N(2)	88.76(12)
O(2)−Y(1)−N(2)	89.58(13)
N(1)−Y(1)−N(2)	175.02(12)
C(2)−S(1)−C(5)	95.5(3)
C(23)−S(2)−C(19)	96.0(4)
C(40)−S(3)−C(37)	98.4(3)
C(53)−N(1)−C(57)	117.6(4)
C(53)−N(1)−Y(1)	119.1(3)
C(57)−N(1)−Y(1)	123.2(3)
C(58)−N(2)−C(62)	116.5(4)
C(58)−N(2)−Y(1)	115.3(3)
C(62)−N(2)−Y(1)	127.4(3)
C(1)−O(1)−Y(1)	164.9(3)
C(18)−O(2)−Y(1)	176.4(3)
C(36)−O(3)−Y(1)	173.5(3)
O(1)−C(1)−C(2)	109.4(3)
O(1)−C(1)−C(12)	110.3(3)
C(2)−C(1)−C(12)	107.3(3)
O(1)−C(1)−C(6)	109.7(3)
C(2)−C(1)−C(6)	111.2(4)
C(12)−C(1)−C(6)	108.8(4)
C(3)−C(2)−C(1)	127.4(4)
C(3)−C(2)−S(1)	110.0(4)
C(1)−C(2)−S(1)	122.6(3)
C(2)−C(3)−C(4)	116.6(5)
C(5)−C(4)−C(3)	113.2(5)
C(4)−C(5)−S(1)	104.7(4)
C(7)−C(6)−C(11)	116.0(4)
C(7)−C(6)−C(1)	124.0(4)
C(11)−C(6)−C(1)	120.0(4)
C(8)−C(7)−C(6)	119.5(5)
C(9)−C(8)−C(7)	121.7(6)
C(8)−C(9)−C(10)	120.5(6)
C(11)−C(10)−C(9)	123.7(6)
C(10)−C(11)−C(6)	118.7(5)
C(13)−C(12)−C(17)	115.1(4)
C(13)−C(12)−C(1)	123.4(4)
C(17)−C(12)−C(1)	121.0(4)
C(14)−C(13)−C(12)	117.9(5)
C(15)−C(14)−C(13)	122.2(5)
C(16)−C(15)−C(14)	122.0(6)
C(15)−C(16)−C(17)	119.7(6)
C(16)−C(17)−C(12)	122.8(4)
O(2)−C(18)−C(24)	109.1(4)
O(2)−C(18)−C(19)	109.6(4)
C(24)−C(18)−C(19)	111.3(4)
O(2)−C(18)−C(30)	110.4(4)
C(24)−C(18)−C(30)	109.1(4)
C(69B)#2−C(67A)−C(68C)	34(2)
C(67B)−C(67A)−C(68A)	4.8(13)
C(69A)#2−C(67A)−C(68A)	84.6(15)
C(69B)#2−C(67A)−C(68A)	121.2(15)
C(68C)−C(67A)−C(68A)	153(3)
C(67B)−C(67A)−C(70A)#2	143(2)
C(69A)#2−C(67A)−C(70A)#2	58.3(17)
C(69B)#2−C(67A)−C(70A)#2	21.5(15)
C(68C)−C(67A)−C(70A)#2	15(3)
C(68A)−C(67A)−C(70A)#2	142.7(17)
C(67B)−C(68A)−C(68B)	168(3)
C(67B)−C(68A)−C(69A)	112.5(18)
C(68B)−C(68A)−C(69A)	66(2)
C(67B)−C(68A)−C(67A)	5.2(14)
C(68B)−C(68A)−C(67A)	173(2)
C(69A)−C(68A)−C(67A)	111.1(12)
C(67B)−C(68A)−C(69B)	138.6(19)
C(68B)−C(68A)−C(69B)	39.2(19)
C(69A)−C(68A)−C(69B)	27.0(9)
C(67A)−C(68A)−C(69B)	137.7(12)
C(67B)−C(68A)−C(69A)#2	36.9(14)
C(68B)−C(68A)−C(69A)#2	139(2)
C(69A)−C(68A)−C(69A)#2	75.7(12)
C(67A)−C(68A)−C(69A)#2	36.2(7)
C(69B)−C(68A)−C(69A)#2	101.7(12)
C(69B)−C(69A)−C(67A)#2	91(2)
C(69B)−C(69A)−C(67B)#2	130(3)
C(67A)#2−C(69A)−C(67B)#2	38.7(11)
C(69B)−C(69A)−C(68B)	70(2)
C(67A)#2−C(69A)−C(68B)	156(2)
C(67B)#2−C(69A)−C(68B)	155.2(19)
C(69B)−C(69A)−C(68A)	102(2)
C(67A)#2−C(69A)−C(68A)	160.1(19)
C(67B)#2−C(69A)−C(68A)	125.0(16)
C(68B)−C(69A)−C(68A)	32.9(10)
C(69B)−C(69A)−C(68C)#2	27(3)
C(67A)#2−C(69A)−C(68C)#2	70(2)
C(67B)#2−C(69A)−C(68C)#2	108(3)
C(68B)−C(69A)−C(68C)#2	95(3)
C(68A)−C(69A)−C(68C)#2	127(3)
C(69B)−C(69A)−C(70A)	6(2)
C(67A)#2−C(69A)−C(70A)	88(2)
C(67B)#2−C(69A)−C(70A)	127(2)
C(68B)−C(69A)−C(70A)	74(2)
C(68A)−C(69A)−C(70A)	107(2)
C(68C)#2−C(69A)−C(70A)	21(2)
C(69B)−C(69A)−C(68A)#2	149(2)
C(67A)#2−C(69A)−C(68A)#2	59.2(13)
C(67B)#2−C(69A)−C(68A)#2	20.7(8)
C(68B)−C(69A)−C(68A)#2	135.7(16)
C(68A)−C(69A)−C(68A)#2	104.3(12)
C(68C)#2−C(69A)−C(68A)#2	128(3)
C(70A)−C(69A)−C(68A)#2	146.6(18)
C(69B)−C(69A)−C(67B)	124(2)
C(67A)#2−C(69A)−C(67B)	139.6(18)

C(19)−C(18)−C(30)	107.3(4)
C(20)−C(19)−C(18)	125.8(5)
C(20)−C(19)−S(2)	117.9(4)
C(18)−C(19)−S(2)	116.3(4)
C(21B)−C(20)−C(19)	131.9(8)
C(21B)−C(20)−C(21A)	29.6(6)
C(19)−C(20)−C(21A)	102.4(7)
C(23)−C(21A)−C(20)	113.4(9)
C(20)−C(21B)−C(22B)	112.8(10)
C(23)−C(22B)−C(21B)	120.8(12)
C(22B)−C(23)−C(21A)	30.3(7)
C(22B)−C(23)−S(2)	140.4(9)
C(21A)−C(23)−S(2)	110.3(6)
C(25)−C(24)−C(29)	114.9(4)
C(25)−C(24)−C(18)	124.0(5)
C(29)−C(24)−C(18)	120.9(4)
C(24)−C(25)−C(26)	117.8(5)
C(27)−C(26)−C(25)	120.2(6)
C(28)−C(27)−C(26)	124.5(8)
C(29)−C(28)−C(27)	119.3(9)
C(28)−C(29)−C(24)	121.9(5)
C(35)−C(30)−C(31)	116.0(5)
C(35)−C(30)−C(18)	120.8(4)
C(31)−C(30)−C(18)	123.0(5)
C(32)−C(31)−C(30)	119.9(6)
C(33)−C(32)−C(31)	121.7(7)
C(34)−C(33)−C(32)	121.2(7)
C(33)−C(34)−C(35)	122.2(7)
C(34)−C(35)−C(30)	119.0(6)
O(3)−C(36)−C(41)	108.5(3)
O(3)−C(36)−C(47)	110.5(3)
C(41)−C(36)−C(47)	109.7(3)
O(3)−C(36)−C(37)	108.0(3)
C(41)−C(36)−C(37)	110.5(3)
C(47)−C(36)−C(37)	109.5(3)
C(38)−C(37)−C(36)	127.8(4)
C(38)−C(37)−S(3)	114.8(3)
C(36)−C(37)−S(3)	117.3(3)
C(37)−C(38)−C(39)	105.0(5)
C(40)−C(39)−C(38)	107.4(5)
C(39)−C(40)−S(3)	114.4(5)
C(42)−C(41)−C(46)	117.4(4)
C(42)−C(41)−C(36)	122.7(4)
C(46)−C(41)−C(36)	119.6(4)
C(41)−C(42)−C(43)	122.0(5)
C(44)−C(43)−C(42)	119.1(5)
C(45)−C(44)−C(43)	121.2(5)
C(44)−C(45)−C(46)	124.9(5)
C(45)−C(46)−C(41)	115.4(4)
C(52)−C(47)−C(48)	116.1(3)
C(52)−C(47)−C(36)	124.5(4)
C(48)−C(47)−C(36)	119.4(3)
C(49)−C(48)−C(47)	112.7(4)
C(50)−C(49)−C(48)	126.1(6)
C(51)−C(50)−C(49)	121.0(6)
C(50)−C(51)−C(52)	123.3(6)
C(51)−C(52)−C(47)	120.8(4)
N(1)−C(53)−C(54)	123.7(5)
C(55)−C(54)−C(53)	117.7(5)
C(56)−C(55)−C(54)	119.5(5)
C(55)−C(56)−C(57)	119.0(5)
N(1)−C(57)−C(56)	122.5(5)
N(2)−C(58)−C(59)	124.1(5)
C(60)−C(59)−C(58)	118.6(6)
C(61)−C(60)−C(59)	118.7(5)
C(60)−C(61)−C(62)	119.0(6)
N(2)−C(62)−C(61)	123.0(5)
C(64)−C(63)−C(65)#1	120.2(7)
C(63)−C(64)−C(65)	121.7(7)
C(66)−C(65)−C(64)	119.0(9)
C(66)−C(65)−C(63)#1	122.9(9)
C(64)−C(65)−C(63)#1	118.0(6)
C(67B)−C(67A)−C(69A)#2	85(2)
C(67B)#2−C(69A)−C(67B)	102.6(13)
C(68B)−C(69A)−C(67B)	55.0(12)
C(68A)−C(69A)−C(67B)	22.5(7)
C(68C)#2−C(69A)−C(67B)	150(3)
C(70A)−C(69A)−C(67B)	128.9(19)
C(68A)#2−C(69A)−C(67B)	81.9(9)
C(69B)−C(69A)−C(69A)#2	158(3)
C(67A)#2−C(69A)−C(69A)#2	101.3(18)
C(67B)#2−C(69A)−C(69A)#2	63.6(12)
C(68B)−C(69A)−C(69A)#2	93.4(16)
C(68A)−C(69A)−C(69A)#2	61.5(10)
C(68C)#2−C(69A)−C(69A)#2	171(3)
C(70A)−C(69A)−C(69A)#2	164(2)
C(68A)#2−C(69A)−C(69A)#2	42.9(8)
C(67B)−C(69A)−C(69A)#2	39.0(7)
C(68C)#2−C(70A)−C(69B)	74(8)
C(68C)#2−C(70A)−C(69A)	69(9)
C(69B)−C(70A)−C(69A)	6(2)
C(68C)#2−C(70A)−C(68B)	111(10)
C(69B)−C(70A)−C(68B)	40(3)
C(69A)−C(70A)−C(68B)	44.2(15)
C(68C)#2−C(70A)−C(67A)#2	41(8)
C(69B)−C(70A)−C(67A)#2	37(3)
C(69A)−C(70A)−C(67A)#2	33.8(11)
C(68B)−C(70A)−C(67A)#2	77.2(19)
C(69A)−C(69B)−C(70A)	169(5)
C(69A)−C(69B)−C(68C)#2	128(6)
C(70A)−C(69B)−C(68C)#2	41(5)
C(69A)−C(69B)−C(68B)	73(2)
C(70A)−C(69B)−C(68B)	116(4)
C(68C)#2−C(69B)−C(68B)	152(5)
C(69A)−C(69B)−C(67A)#2	51.7(19)
C(70A)−C(69B)−C(67A)#2	121(4)
C(68C)#2−C(69B)−C(67A)#2	83(5)
C(68B)−C(69B)−C(67A)#2	123(2)
C(69A)−C(69B)−C(68A)	50.5(18)
C(70A)−C(69B)−C(68A)	138(4)
C(68C)#2−C(69B)−C(68A)	164(4)
C(68B)−C(69B)−C(68A)	22.5(11)
C(67A)#2−C(69B)−C(68A)	101.1(16)
C(69A)−C(69B)−C(67B)#2	30.9(17)
C(70A)−C(69B)−C(67B)#2	142(4)
C(68C)#2−C(69B)−C(67B)#2	103(5)
C(68B)−C(69B)−C(67B)#2	102.5(18)
C(67A)#2−C(69B)−C(67B)#2	20.9(8)
C(68A)−C(69B)−C(67B)#2	80.3(11)
C(68A)−C(68B)−C(69B)	118(3)
C(68A)−C(68B)−C(69A)	81(2)
C(69B)−C(68B)−C(69A)	37.4(11)
C(68A)−C(68B)−C(67B)	5.8(15)
C(69B)−C(68B)−C(67B)	117.8(19)
C(69A)−C(68B)−C(67B)	80.6(15)
C(68A)−C(68B)−C(70A)	143(3)
C(69B)−C(68B)−C(70A)	24.5(17)
C(69A)−C(68B)−C(70A)	61.7(18)
C(67B)−C(68B)−C(70A)	142(2)
C(68A)−C(67B)−C(67A)	170(3)
C(68A)−C(67B)−C(69A)#2	122(2)
C(67A)−C(67B)−C(69A)#2	56.2(16)
C(68A)−C(67B)−C(68B)	5.9(15)
C(67A)−C(67B)−C(68B)	175(2)
C(69A)#2−C(67B)−C(68B)	120.9(15)
C(68A)−C(67B)−C(69A)	45.0(14)
C(67A)−C(67B)−C(69A)	131.6(18)
C(69A)#2−C(67B)−C(69A)	77.4(13)
C(68B)−C(67B)−C(69A)	44.4(10)
C(68A)−C(67B)−C(69B)#2	140.4(19)
C(67A)−C(67B)−C(69B)#2	37.1(15)
C(69A)#2−C(67B)−C(69B)#2	19.2(10)
C(68B)−C(67B)−C(69B)#2	139.7(12)
C(69A)−C(67B)−C(69B)#2	95.5(12)
C(70A)#2−C(68C)−C(69B)#2	65(8)
C(70A)#2−C(68C)−C(67A)	124(10)

C(67B)−C(67A)−C(69B)#2	122(2)	C(69B)#2−C(68C)−C(67A)	63(5)
C(69A)#2−C(67A)−C(69B)#2	37.1(11)	C(70A)#2−C(68C)−C(69A)#2	90(9)
C(67B)−C(67A)−C(68C)	152(3)	C(69B)#2−C(68C)−C(69A)#2	25(3)
C(69A)#2−C(67A)−C(68C)	69(3)	C(67A)−C(68C)−C(69A)#2	41.1(19)

Symmetry transformations used to generate equivalent atoms:
#1 −x+1,−y+1,−z   #2 −x+2,−y+1,−z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2620. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	20(1)	22(1)	17(1)	4(1)	2(1)	10(1)
S(1)	74(1)	72(1)	87(1)	9(1)	33(1)	37(1)
S(2)	93(2)	78(2)	183(3)	66(2)	41(2)	46(1)
S(3)	111(2)	90(2)	84(2)	13(1)	13(1)	64(1)
N(1)	30(2)	34(2)	22(2)	8(2)	6(2)	17(2)
N(2)	30(2)	36(2)	25(2)	10(2)	1(2)	16(2)
O(1)	37(2)	27(2)	23(2)	5(1)	8(1)	20(1)
O(2)	24(2)	34(2)	34(2)	12(1)	10(1)	17(1)
O(3)	19(1)	28(2)	23(2)	6(1)	3(1)	6(1)
C(1)	26(2)	23(2)	21(2)	0(2)	7(2)	11(2)
C(2)	26(2)	28(2)	31(2)	11(2)	8(2)	12(2)
C(3)	35(3)	34(2)	39(3)	4(2)	13(2)	9(2)
C(4)	44(3)	27(2)	34(3)	1(2)	6(2)	3(2)
C(5)	38(3)	94(5)	68(4)	54(4)	21(3)	26(3)
C(6)	30(2)	31(2)	23(2)	3(2)	7(2)	18(2)
C(7)	38(3)	34(2)	26(2)	6(2)	5(2)	21(2)
C(8)	70(4)	68(4)	38(3)	15(3)	10(3)	52(4)
C(9)	58(4)	74(4)	44(3)	0(3)	5(3)	45(4)
C(10)	48(4)	72(4)	52(4)	−2(3)	−2(3)	32(3)
C(11)	28(2)	28(2)	27(2)	0(2)	4(2)	19(2)
C(12)	25(2)	22(2)	26(2)	−2(2)	6(2)	3(2)
C(13)	24(2)	33(2)	30(2)	0(2)	8(2)	10(2)
C(14)	35(3)	41(3)	39(3)	−1(2)	13(2)	14(2)
C(15)	41(3)	49(3)	45(3)	3(3)	2(3)	9(3)
C(16)	48(3)	64(4)	28(3)	2(3)	7(2)	10(3)
C(17)	4(1)	11(1)	4(1)	0(1)	−3(1)	0(1)
C(18)	27(2)	30(2)	41(3)	14(2)	11(2)	17(2)
C(19)	22(2)	35(3)	60(3)	21(2)	8(2)	14(2)
C(20)	40(3)	30(3)	72(4)	6(3)	−2(3)	19(2)
C(23)	53(4)	43(3)	89(5)	39(4)	−6(4)	3(3)
C(24)	28(2)	41(3)	41(3)	23(2)	13(2)	14(2)
C(25)	32(3)	41(3)	49(3)	16(2)	3(2)	18(2)
C(26)	37(3)	45(3)	67(4)	21(3)	−2(3)	15(3)
C(27)	72(5)	52(4)	82(5)	24(4)	28(4)	24(4)
C(30)	41(3)	30(2)	41(3)	10(2)	16(2)	24(2)
C(31)	41(3)	43(3)	46(3)	13(2)	13(2)	28(2)
C(32)	88(5)	56(4)	67(5)	23(3)	47(4)	41(4)
C(33)	110(7)	73(5)	48(4)	12(3)	30(4)	64(5)
C(34)	88(5)	69(4)	43(3)	−15(3)	−3(4)	51(4)
C(35)	46(3)	36(3)	46(3)	0(2)	14(2)	27(2)
C(36)	21(2)	24(2)	19(2)	4(2)	2(2)	8(2)
C(37)	35(2)	31(2)	18(2)	6(2)	3(2)	18(2)
C(38)	23(2)	20(2)	12(2)	1(1)	9(2)	5(2)
C(39)	226(11)	44(4)	13(3)	3(3)	41(5)	10(5)
C(40)	91(5)	61(4)	37(3)	−5(3)	−13(3)	60(4)
C(41)	21(2)	26(2)	20(2)	5(2)	3(2)	6(2)
C(42)	48(3)	28(2)	25(2)	5(2)	1(2)	13(2)
C(43)	61(4)	41(3)	23(2)	0(2)	−4(2)	11(3)
C(44)	34(3)	59(3)	28(3)	10(2)	−4(2)	13(3)
C(45)	36(3)	66(4)	42(3)	22(3)	2(2)	30(3)
C(46)	23(2)	45(3)	15(2)	3(2)	3(2)	8(2)
C(47)	24(2)	26(2)	16(2)	4(2)	0(2)	10(2)
C(48)	13(2)	10(1)	8(2)	1(1)	4(1)	8(1)
C(49)	68(4)	55(3)	28(3)	2(2)	4(3)	44(3)
C(50)	55(4)	54(4)	55(4)	25(3)	16(3)	26(3)
C(51)	46(3)	67(4)	47(3)	27(3)	17(3)	31(3)
C(52)	18(2)	18(2)	21(2)	1(2)	−4(2)	6(2)
C(53)	36(3)	38(3)	29(2)	12(2)	3(2)	12(2)
C(54)	46(3)	40(3)	34(3)	14(2)	11(2)	18(2)

C(55)	64(4)	54(3)	23(2)	17(2)	8(2)	31(3)
C(56)	43(3)	46(3)	26(2)	8(2)	3(2)	19(2)
C(57)	34(3)	36(2)	23(2)	6(2)	5(2)	19(2)
C(58)	30(3)	59(4)	41(3)	17(3)	−2(2)	−1(3)
C(59)	38(4)	105(6)	53(4)	23(4)	−20(3)	1(4)
C(60)	68(5)	91(5)	30(3)	21(3)	−12(3)	24(4)
C(61)	54(4)	91(5)	35(3)	34(3)	11(3)	27(4)
C(62)	34(3)	46(3)	33(3)	17(2)	6(2)	16(2)

Compound 28

Table 1. Crystal data and structure refinement for sh2591.

Identification code	sh2591	
Empirical formula	C67 H71 Nd O7 S3	
Formula weight	1228.66	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = 14.6024(7) Å	α = 90°.
	b = 14.6024(7) Å	β = 90°.
	c = 15.8933(9) Å	γ = 120°.
Volume	2934.9(3) Å^3	
Z	2	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	1.045 mm^{-1}	
F(000)	1274	
Crystal size	0.31 x 0.28 x 0.18 mm^3	
Theta range for data collection	1.61 to 27.18°.	
Index ranges	−18<=h<=18, −18<=k<=18, −20<=l<=20	
Reflections collected	59099	
Independent reflections	4365 [R(int) = 0.0546]	
Completeness to theta = 27.18°	100.0 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8374 and 0.7383	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	4365 / 1 / 174	
Goodness−of−fit on F^2	2.049	
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1646	
R indices (all data)	R1 = 0.0636, wR2 = 0.1687	
Absolute structure parameter	0.03(4)	
Largest diff. peak and hole	1.012 and −0.755 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2591. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nd(1)	6667	3333	2510(1)	31(1)
O(1)	7055(4)	4824(3)	3112(3)	43(1)
C(1)	7206(5)	5720(4)	3549(4)	36(1)
C(2)	6246(4)	5899(4)	3405(4)	48(2)
C(3)	5326(4)	5068(4)	3068(6)	115(6)
C(4)	4446(4)	5180(6)	2939(8)	142(8)
C(5)	4485(4)	6124(6)	3145(9)	142(8)
C(6)	5404(5)	6955(4)	3482(8)	111(6)
C(7)	6285(4)	6843(4)	3612(5)	72(3)
S(1)	7441(5)	6389(6)	5227(4)	87(1)
C(8)	7369(10)	5631(7)	4485(5)	76(3)
C(9)	7670(9)	4891(10)	4789(7)	83(3)
C(10)	7893(17)	4997(17)	5663(12)	71(4)
C(11A)	7310(40)	5700(30)	6130(30)	130(11)
C(11B)	7850(20)	5712(19)	6035(15)	79(5)
C(12)	7670(20)	6260(20)	5868(16)	82(5)
S(2)	8250(6)	7324(6)	2347(5)	108(2)
C(13)	8220(7)	6657(5)	3186(6)	51(2)
C(14)	9288(9)	7003(10)	3454(8)	81(3)
C(15)	10114(9)	7938(10)	2851(8)	84(3)
C(16)	9850(17)	8237(17)	2337(13)	74(5)

C(17)	9180(20)	8060(20)	2126(16)	94(7)
O(2)	8069(5)	4425(5)	1373(3)	59(1)
C(18)	8530(12)	4091(12)	726(9)	103(4)
C(19A)	9610(20)	4990(20)	590(16)	100(6)
C(19B)	9044(18)	5109(18)	56(13)	71(5)
C(20)	9229(15)	5873(15)	565(12)	107(5)
C(21)	8563(19)	5550(20)	1304(14)	125(6)
C(22)	0	0	730(20)	139(11)
C(23)	480(40)	1130(40)	−120(30)	144(13)
C(24)	790(30)	200(30)	−500(20)	106(9)
C(25)	290(30)	760(30)	470(30)	116(10)

Table 3. Bond lengths [Å] and angles [°] for sh2591.

Nd(1)−O(1)#1	2.178(4)	C(14)−C(15)	1.609(17)
Nd(1)−O(1)	2.178(4)	C(15)−C(16)	1.08(2)
Nd(1)−O(1)#2	2.178(4)	C(15)−C(17)	1.85(3)
Nd(1)−O(2)	2.595(6)	O(2)−C(21)	1.43(3)
Nd(1)−O(2)#2	2.595(6)	O(2)−C(18)	1.440(15)
Nd(1)−O(2)#1	2.595(6)	C(18)−C(19A)	1.48(3)
O(1)−C(1)	1.397(7)	C(18)−C(19B)	1.67(3)
C(1)−C(8)	1.522(11)	C(19A)−C(19B)	1.26(3)
C(1)−C(13)	1.540(10)	C(19A)−C(20)	1.64(3)
C(1)−C(2)	1.567(7)	C(19B)−C(20)	1.29(3)
C(2)−C(3)	1.3900	C(20)−C(21)	1.45(3)
C(2)−C(7)	1.3900	C(22)−C(25)	1.05(4)
C(3)−C(4)	1.3900	C(22)−C(25)#3	1.05(4)
C(4)−C(5)	1.3900	C(22)−C(25)#4	1.05(4)
C(5)−C(6)	1.3900	C(22)−C(23)	1.97(5)
C(6)−C(7)	1.3900	C(22)−C(23)#3	1.97(5)
S(1)−C(12)	1.12(3)	C(22)−C(23)#4	1.97(5)
S(1)−C(8)	1.584(11)	C(23)−C(25)	1.05(5)
S(1)−C(11A)	1.71(4)	C(23)−C(24)#3	1.08(5)
S(1)−C(11B)	1.89(3)	C(23)−C(24)	1.73(6)
C(8)−C(9)	1.439(15)	C(24)−C(23)#4	1.08(5)
C(9)−C(10)	1.42(2)	C(24)−C(25)#4	1.65(4)
C(10)−C(11A)	1.79(5)	C(24)−C(24)#4	1.80(6)
C(11B)−C(12)	0.98(3)	C(24)−C(24)#3	1.80(6)
S(2)−C(17)	1.29(3)	C(24)−C(25)	2.03(5)
S(2)−C(13)	1.638(13)	C(25)−C(24)#3	1.65(4)
S(2)−C(16)	2.03(2)	C(25)−C(25)#4	1.67(7)
C(13)−C(14)	1.442(15)	C(25)−C(25)#3	1.67(7)

O(1)#1−Nd(1)−O(1)	102.15(15)	C(19B)−C(19A)−C(18)	74.8(18)
O(1)#1−Nd(1)−O(1)#2	102.14(15)	C(19B)−C(19A)−C(20)	50.8(16)
O(1)−Nd(1)−O(1)#2	102.15(15)	C(18)−C(19A)−C(20)	93.9(17)
O(1)#1−Nd(1)−O(2)	161.84(18)	C(19A)−C(19B)−C(20)	80.3(19)
O(1)−Nd(1)−O(2)	87.76(18)	C(19A)−C(19B)−C(18)	58.6(16)
O(1)#2−Nd(1)−O(2)	90.38(18)	C(20)−C(19B)−C(18)	100.1(16)
O(1)#1−Nd(1)−O(2)#2	90.38(18)	C(19B)−C(20)−C(21)	114(2)
O(1)−Nd(1)−O(2)#2	161.84(18)	C(19B)−C(20)−C(19A)	49.0(14)
O(1)#2−Nd(1)−O(2)#2	87.77(18)	C(21)−C(20)−C(19A)	99.2(17)
O(2)−Nd(1)−O(2)#2	76.9(2)	O(2)−C(21)−C(20)	108.0(17)
O(1)#1−Nd(1)−O(2)#1	87.77(19)	C(25)−C(22)−C(25)#3	105(4)
O(1)−Nd(1)−O(2)#1	90.38(18)	C(25)−C(22)−C(25)#4	105(4)
O(1)#2−Nd(1)−O(2)#1	161.84(18)	C(25)#3−C(22)−C(25)#4	105(4)
O(2)−Nd(1)−O(2)#1	76.9(2)	C(25)−C(22)−C(23)	20(3)
O(2)#2−Nd(1)−O(2)#1	76.9(2)	C(25)#3−C(22)−C(23)	95(4)
C(1)−O(1)−Nd(1)	173.9(4)	C(25)#4−C(22)−C(23)	92(3)
O(1)−C(1)−C(8)	111.4(5)	C(25)−C(22)−C(23)#3	92(3)
O(1)−C(1)−C(13)	106.1(5)	C(25)#3−C(22)−C(23)#3	20(3)
C(8)−C(1)−C(13)	108.7(7)	C(25)#4−C(22)−C(23)#3	95(4)
O(1)−C(1)−C(2)	110.4(5)	C(23)−C(22)−C(23)#3	78(2)
C(8)−C(1)−C(2)	110.3(7)	C(25)−C(22)−C(23)#4	95(4)
C(13)−C(1)−C(2)	109.9(5)	C(25)#3−C(22)−C(23)#4	92(3)
C(3)−C(2)−C(7)	120.0	C(25)#4−C(22)−C(23)#4	20(3)
C(3)−C(2)−C(1)	117.6(4)	C(23)−C(22)−C(23)#4	78(2)
C(7)−C(2)−C(1)	122.4(4)	C(23)#3−C(22)−C(23)#4	78(2)
C(2)−C(3)−C(4)	120.0	C(25)−C(23)−C(24)#3	102(5)
C(5)−C(4)−C(3)	120.0	C(25)−C(23)−C(24)	91(4)
C(4)−C(5)−C(6)	120.0	C(24)#3−C(23)−C(24)	76(4)
C(7)−C(6)−C(5)	120.0	C(25)−C(23)−C(22)	20(3)
C(6)−C(7)−C(2)	120.0	C(24)#3−C(23)−C(22)	88(3)
C(12)−S(1)−C(8)	118.4(15)	C(24)−C(23)−C(22)	73(2)

C(12)−S(1)−C(11A)	24(2)	C(23)#4−C(24)−C(25)#4	38(3)
C(8)−S(1)−C(11A)	105.4(15)	C(23)#4−C(24)−C(23)	122(5)
C(12)−S(1)−C(11B)	24.4(15)	C(25)#4−C(24)−C(23)	84(3)
C(8)−S(1)−C(11B)	94.0(9)	C(23)#4−C(24)−C(24)#4	69(4)
C(11A)−S(1)−C(11B)	24.9(15)	C(25)#4−C(24)−C(24)#4	72(2)
C(9)−C(8)−C(1)	120.8(8)	C(23)−C(24)−C(24)#4	90(2)
C(9)−C(8)−S(1)	109.5(7)	C(23)#4−C(24)−C(24)#3	118(3)
C(1)−C(8)−S(1)	128.9(7)	C(25)#4−C(24)−C(24)#3	92(2)
C(10)−C(9)−C(8)	112.8(12)	C(23)−C(24)−C(24)#3	36(2)
C(9)−C(10)−C(11A)	108.8(18)	C(24)#4−C(24)−C(24)#3	59.999(3)
S(1)−C(11A)−C(10)	92(2)	C(23)#4−C(24)−C(25)	91(4)
C(12)−C(11B)−S(1)	28.1(17)	C(25)#4−C(24)−C(25)	53(2)
C(11B)−C(12)−S(1)	128(3)	C(23)−C(24)−C(25)	30.9(18)
C(17)−S(2)−C(13)	114.7(14)	C(24)#4−C(24)−C(25)	80.6(17)
C(17)−S(2)−C(16)	20.3(14)	C(24)#3−C(24)−C(25)	50.5(16)
C(13)−S(2)−C(16)	94.4(8)	C(22)−C(25)−C(23)	139(6)
C(14)−C(13)−C(1)	126.3(9)	C(22)−C(25)−C(24)#3	107(4)
C(14)−C(13)−S(2)	109.2(8)	C(23)−C(25)−C(24)#3	40(3)
C(1)−C(13)−S(2)	124.1(7)	C(22)−C(25)−C(25)#4	37.4(18)
C(13)−C(14)−C(15)	110.0(11)	C(23)−C(25)−C(25)#4	110(4)
C(16)−C(15)−C(14)	121.6(16)	C(24)#3−C(25)−C(25)#4	97(2)
C(16)−C(15)−C(17)	21.5(15)	C(22)−C(25)−C(25)#3	37.4(18)
C(14)−C(15)−C(17)	100.1(11)	C(23)−C(25)−C(25)#3	115(4)
S(2)−C(17)−C(15)	105.9(17)	C(24)#3−C(25)−C(25)#3	76(2)
C(21)−O(2)−C(18)	106.3(12)	C(25)#4−C(25)−C(25)#3	59.999(4)
C(21)−O(2)−Nd(1)	123.3(10)	C(22)−C(25)−C(24)	85(4)
C(18)−O(2)−Nd(1)	130.4(7)	C(23)−C(25)−C(24)	58(3)
O(2)−C(18)−C(19A)	106.1(14)	C(24)#3−C(25)−C(24)	57(2)
O(2)−C(18)−C(19B)	103.4(12)	C(25)#4−C(25)−C(24)	51.7(18)
C(19A)−C(18)−C(19B)	46.6(13)	C(25)#3−C(25)−C(24)	83.6(18)

Symmetry transformations used to generate equivalent atoms:
#1 −y+1,x−y,z #2 −x+y+1,−x+1,z #3 −y,x−y,z
#4 −x+y,−x,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2591. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nd(1)	27(1)	27(1)	37(1)	0	0	14(1)
O(1)	48(2)	24(2)	53(2)	−2(2)	−4(2)	16(2)
C(1)	43(3)	20(2)	48(3)	−10(2)	−9(3)	18(2)
C(2)	34(3)	43(3)	68(4)	5(3)	10(3)	20(3)
C(3)	26(3)	84(7)	222(15)	−86(9)	0(6)	17(4)
C(4)	35(5)	75(7)	310(30)	−11(10)	20(8)	24(5)
C(5)	63(7)	56(7)	310(20)	3(10)	29(10)	30(6)
C(6)	64(6)	68(6)	227(18)	23(9)	23(9)	54(6)
C(7)	51(5)	33(4)	122(9)	3(4)	−3(5)	13(3)
C(8)	119(9)	42(4)	55(4)	−7(3)	−13(5)	32(5)
C(9)	70(6)	89(7)	95(8)	−11(6)	−19(5)	44(6)
C(13)	45(4)	31(3)	76(5)	−12(3)	8(4)	17(3)
C(14)	63(6)	79(6)	100(8)	−16(6)	7(5)	34(5)

Compound 29

Table 1. Crystal data and structure refinement for sh2605.

Identification code	sh2605	
Empirical formula	C67 H71 O7 S3 Sm	
Formula weight	1234.77	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = 14.5682(4) Å	α = 90°.
	b = 14.5682(4) Å	β = 90°.
	c = 15.7803(13) Å	γ = 120°.
Volume	2900.4(3) $Å^3$	
Z	2	
Density (calculated)	1.414 Mg/m^3	

Absorption coefficient	1.175 mm^{-1}
F(000)	1278
Crystal size	0.50 x 0.37 x 0.06 mm^{3}
Theta range for data collection	1.61 to 26.41°.
Index ranges	−18<=h<=17, −17<=k<=18, −19<=l<=19
Reflections collected	16454
Independent reflections	3955 [R(int) = 0.0397]
Completeness to theta = 26.41°	100.0 %
Absorption correction	Multiscan
Max. and min. transmission	0.9328 and 0.5895
Refinement method	Full−matrix least−squares on F^{2}
Data / restraints / parameters	3955 / 1 / 209
Goodness−of−fit on F^{2}	1.375
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1275
R indices (all data)	R1 = 0.0560, wR2 = 0.1318
Absolute structure parameter	−0.06(3)
Largest diff. peak and hole	0.916 and −0.416 e.Å^{-3}

Table 2. Atomic coordinates (x 10^{4}) and equivalent isotropic displacement parameters (Å^{2}x 10^{3}) for sh2605. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sm(1)	3333	6667	2502(1)	25(1)
O(1)	2919(4)	5176(3)	3101(3)	35(1)
S(1)	2535(5)	3584(4)	5228(3)	79(2)
S(2)	1752(5)	2664(5)	2342(6)	98(2)
C(1)	2770(6)	4274(5)	3530(5)	34(2)
C(2)	2599(8)	4369(6)	4478(6)	64(2)
C(3)	2273(7)	5081(8)	4782(7)	72(3)
C(4A)	2168(12)	5042(12)	5660(10)	71(3)
C(5A)	2400(20)	4250(20)	6076(18)	103(8)
C(4B)	2140(30)	4530(30)	6100(20)	59(7)
C(5B)	2340(20)	3760(20)	5917(16)	60(5)
C(6)	1758(6)	3325(5)	3170(6)	45(2)
C(7)	675(7)	2978(8)	3443(7)	67(2)
C(8)	−120(9)	2089(8)	2851(6)	71(2)
C(9A)	178(12)	1808(12)	2270(10)	75(4)
C(9B)	910(20)	2020(20)	2060(16)	45(5)
C(10)	3734(6)	4122(6)	3416(5)	44(2)
C(11)	4705(6)	4935(8)	3058(10)	96(5)
C(12)	5531(9)	4875(9)	3046(13)	127(7)
C(13)	5435(8)	3863(9)	3164(13)	122(6)
C(14)	4594(8)	3054(8)	3483(10)	86(4)
C(15)	3727(7)	3136(6)	3627(7)	59(2)
O(2)	1949(4)	5595(4)	1377(3)	48(1)
C(17)	794(12)	4143(12)	552(10)	77(4)
C(16A)	1465(15)	4436(15)	1310(12)	63(5)
C(18A)	340(17)	5048(17)	576(13)	88(5)
C(19A)	1399(13)	6037(13)	875(11)	65(4)
C(16B)	1040(30)	4590(30)	1450(20)	58(7)
C(18B)	992(18)	4934(18)	43(14)	62(5)
C(19B)	1655(16)	5928(16)	595(13)	46(4)
O(01)	9930(20)	9368(19)	−629(16)	130(8)
C(01)	10000	10000	770(20)	139(10)
C(02)	10643(17)	9693(17)	−1(16)	75(5)
C(03)	9680(20)	9240(20)	412(17)	84(6)

Table 3. Bond lengths [Å] and angles [°] for sh2605.

Sm(1)−O(1)	2.160(4)	C(13)−C(14)	1.304(18)
Sm(1)−O(1)#1	2.160(4)	C(14)−C(15)	1.347(14)
Sm(1)−O(1)#2	2.160(4)	O(2)−C(16B)	1.40(4)
Sm(1)−O(2)#1	2.552(5)	O(2)−C(19B)	1.47(2)
Sm(1)−O(2)#2	2.552(5)	O(2)−C(16A)	1.47(2)
Sm(1)−O(2)	2.552(5)	O(2)−C(19A)	1.483(18)
O(1)−C(1)	1.395(8)	C(17)−C(18B)	1.31(3)
S(1)−C(5B)	1.18(3)	C(17)−C(16A)	1.47(2)
S(1)−C(2)	1.616(10)	C(17)−C(16B)	1.53(3)
S(1)−C(5A)	1.72(3)	C(17)−C(18A)	1.75(2)
S(1)−C(4B)	2.22(3)	C(18A)−C(19A)	1.57(3)
S(2)−C(9B)	1.19(3)	C(18B)−C(19B)	1.55(3)

S(2)−C(6)	1.621(11)	O(01)−C(02)	1.34(3)
S(2)−C(9A)	1.991(16)	O(01)−O(01)#3	1.51(4)
C(1)−C(2)	1.533(12)	O(01)−O(01)#4	1.51(4)
C(1)−C(6)	1.539(10)	O(01)−C(02)#4	1.61(4)
C(1)−C(10)	1.539(11)	O(01)−C(03)	1.67(3)
C(2)−C(3)	1.423(13)	C(01)−C(03)#3	1.12(3)
C(3)−C(4A)	1.393(18)	C(01)−C(03)#4	1.12(3)
C(4A)−C(5A)	1.51(3)	C(01)−C(03)	1.12(3)
C(4B)−C(5B)	1.33(5)	C(01)−C(02)#3	1.73(4)
C(6)−C(7)	1.461(12)	C(01)−C(02)#4	1.73(4)
C(7)−C(8)	1.546(15)	C(01)−C(02)	1.73(4)
C(8)−C(9A)	1.172(18)	C(02)−C(03)#3	1.21(3)
C(8)−C(9B)	2.00(3)	C(02)−C(03)	1.38(4)
C(10)−C(11)	1.431(12)	C(02)−O(01)#3	1.61(4)
C(10)−C(15)	1.468(10)	C(03)−C(02)#4	1.21(3)
C(11)−C(12)	1.248(14)	C(03)−C(03)#3	1.68(5)
C(12)−C(13)	1.421(15)	C(03)−C(03)#4	1.68(5)

O(1)−Sm(1)−O(1)#1	102.28(15)	C(16A)−O(2)−Sm(1)	122.0(8)
O(1)−Sm(1)−O(1)#2	102.28(15)	C(19A)−O(2)−Sm(1)	122.6(7)
O(1)#1−Sm(1)−O(1)#2	102.28(15)	C(18B)−C(17)−C(16A)	114.9(17)
O(1)−Sm(1)−O(2)#1	90.76(17)	C(18B)−C(17)−C(16B)	107.0(19)
O(1)#1−Sm(1)−O(2)#1	87.22(17)	C(16A)−C(17)−C(16B)	30.3(13)
O(1)#2−Sm(1)−O(2)#1	161.66(18)	C(18B)−C(17)−C(18A)	49.5(13)
O(1)−Sm(1)−O(2)#2	161.66(18)	C(16A)−C(17)−C(18A)	102.2(13)
O(1)#1−Sm(1)−O(2)#2	90.76(17)	C(16B)−C(17)−C(18A)	75.9(15)
O(1)#2−Sm(1)−O(2)#2	87.22(17)	O(2)−C(16A)−C(17)	105.0(13)
O(2)#1−Sm(1)−O(2)#2	76.89(19)	C(19A)−C(18A)−C(17)	97.5(14)
O(1)−Sm(1)−O(2)	87.21(17)	O(2)−C(19A)−C(18A)	105.0(13)
O(1)#1−Sm(1)−O(2)	161.66(18)	O(2)−C(16B)−C(17)	105(2)
O(1)#2−Sm(1)−O(2)	90.76(17)	C(17)−C(18B)−C(19B)	103.7(18)
O(2)#1−Sm(1)−O(2)	76.89(19)	O(2)−C(19B)−C(18B)	108.2(15)
O(2)#2−Sm(1)−O(2)	76.89(19)	C(02)−O(01)−O(01)#3	69(2)
C(1)−O(1)−Sm(1)	173.3(5)	C(02)−O(01)−O(01)#4	107.9(15)
C(5B)−S(1)−C(2)	117.3(14)	O(01)#3−O(01)−O(01)#4	60.000(5)
C(5B)−S(1)−C(5A)	19.4(16)	C(02)−O(01)−C(02)#4	91(2)
C(2)−S(1)−C(5A)	99.0(10)	O(01)#3−O(01)−C(02)#4	95.1(14)
C(5B)−S(1)−C(4B)	29.7(15)	O(01)#4−O(01)−C(02)#4	50.6(15)
C(2)−S(1)−C(4B)	87.6(10)	C(02)−O(01)−C(03)	53.2(16)
C(5A)−S(1)−C(4B)	13.9(12)	O(01)#3−O(01)−C(03)	96.6(13)
C(9B)−S(2)−C(6)	117.9(13)	O(01)#4−O(01)−C(03)	85.9(13)
C(9B)−S(2)−C(9A)	23.3(13)	C(02)#4−O(01)−C(03)	43.0(14)
C(6)−S(2)−C(9A)	94.6(6)	C(03)#3−C(01)−C(03)#4	97(3)
O(1)−C(1)−C(2)	110.1(6)	C(03)#3−C(01)−C(03)	97(3)
O(1)−C(1)−C(6)	107.2(6)	C(03)#4−C(01)−C(03)	97(3)
C(2)−C(1)−C(6)	108.4(7)	C(03)#3−C(01)−C(02)#3	53(2)
O(1)−C(1)−C(10)	110.8(6)	C(03)#4−C(01)−C(02)#3	44.0(18)
C(2)−C(1)−C(10)	109.1(7)	C(03)−C(01)−C(02)#3	104(3)
C(6)−C(1)−C(10)	111.1(6)	C(03)#3−C(01)−C(02)#4	104(3)
C(3)−C(2)−C(1)	121.5(8)	C(03)#4−C(01)−C(02)#4	53(2)
C(3)−C(2)−S(1)	110.3(7)	C(03)−C(01)−C(02)#4	44.0(18)
C(1)−C(2)−S(1)	127.2(6)	C(02)#3−C(01)−C(02)#4	75.7(18)
C(4A)−C(3)−C(2)	112.1(11)	C(03)#3−C(01)−C(02)	44.0(18)
C(3)−C(4A)−C(5A)	113.6(15)	C(03)#4−C(01)−C(02)	104(3)
C(4A)−C(5A)−S(1)	102.9(17)	C(03)−C(01)−C(02)	53(2)
C(5B)−C(4B)−S(1)	26.2(12)	C(02)#3−C(01)−C(02)	75.7(18)
S(1)−C(5B)−C(4B)	124(2)	C(02)#4−C(01)−C(02)	75.7(18)
C(7)−C(6)−C(1)	125.8(8)	C(03)#3−C(02)−O(01)	117(3)
C(7)−C(6)−S(2)	110.3(7)	C(03)#3−C(02)−C(03)	80(3)
C(1)−C(6)−S(2)	123.4(6)	O(01)−C(02)−C(03)	75.9(18)
C(6)−C(7)−C(8)	109.8(9)	C(03)#3−C(02)−O(01)#3	71(2)
C(9A)−C(8)−C(7)	120.8(12)	O(01)−C(02)−O(01)#3	61(2)
C(9A)−C(8)−C(9B)	22.1(11)	C(03)−C(02)−O(01)#3	105(2)
C(7)−C(8)−C(9B)	98.7(10)	C(03)#3−C(02)−C(01)	40.2(17)
C(8)−C(9A)−S(2)	104.4(12)	O(01)−C(02)−C(01)	100.8(17)
S(2)−C(9B)−C(8)	103.2(16)	C(03)−C(02)−C(01)	40.4(14)
C(11)−C(10)−C(15)	114.8(7)	O(01)#3−C(02)−C(01)	90.6(16)
C(11)−C(10)−C(1)	121.6(7)	C(01)−C(03)−C(02)#4	96(3)
C(15)−C(10)−C(1)	123.6(7)	C(01)−C(03)−C(02)	87(2)
C(12)−C(11)−C(10)	122.5(9)	C(02)#4−C(03)−C(02)	110(3)
C(11)−C(12)−C(13)	118.2(10)	C(01)−C(03)−C(03)#3	41.7(15)
C(14)−C(13)−C(12)	123.3(11)	C(02)#4−C(03)−C(03)#3	103.6(19)
C(13)−C(14)−C(15)	118.9(10)	C(02)−C(03)−C(03)#3	45.3(18)

C(14)−C(15)−C(10)	120.1(9)	C(01)−C(03)−C(03)#4	41.7(15)
C(16B)−O(2)−C(19B)	97.9(15)	C(02)#4−C(03)−C(03)#4	54(2)
C(16B)−O(2)−C(16A)	31.6(14)	C(02)−C(03)−C(03)#4	96.2(17)
C(19B)−O(2)−C(16A)	105.5(11)	C(03)#3−C(03)−C(03)#4	59.999(1)
C(16B)−O(2)−C(19A)	93.9(15)	C(01)−C(03)−O(01)	115(3)
C(19B)−O(2)−C(19A)	25.3(8)	C(02)#4−C(03)−O(01)	66(2)
C(16A)−O(2)−C(19A)	114.0(10)	C(02)−C(03)−O(01)	51.0(16)
C(16B)−O(2)−Sm(1)	128.6(13)	C(03)#3−C(03)−O(01)	80.9(13)
C(19B)−O(2)−Sm(1)	131.0(8)	C(03)#4−C(03)−O(01)	90.7(12)

Symmetry transformations used to generate equivalent atoms:
#1 −y+1,x−y+1,z #2 −x+y,−x+1,z #3 −y+2,x−y+1,z
#4 −x+y+1,−x+2,z

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for sh2605. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sm(1)	22(1)	22(1)	32(1)	0	0	11(1)
O(1)	37(2)	19(2)	47(2)	2(2)	6(2)	12(2)
S(1)	110(4)	47(2)	69(3)	12(2)	7(3)	32(3)
S(2)	64(3)	64(3)	172(7)	−25(4)	−2(4)	38(3)
C(1)	38(4)	14(3)	46(4)	5(3)	1(3)	11(3)
C(2)	87(7)	30(4)	65(5)	10(3)	20(4)	22(4)
C(3)	63(6)	67(6)	74(6)	5(5)	26(5)	24(5)
C(6)	32(3)	26(3)	74(5)	12(3)	−2(3)	12(3)
C(7)	61(6)	71(5)	76(6)	23(5)	4(4)	37(5)
C(10)	33(3)	42(4)	61(4)	−8(3)	−7(3)	21(3)
C(11)	20(3)	58(5)	204(13)	63(7)	−2(5)	16(4)
C(12)	48(6)	48(6)	280(20)	19(8)	−10(8)	18(5)
C(13)	38(5)	66(7)	270(20)	1(9)	−15(8)	30(5)
C(14)	62(6)	44(5)	162(12)	−11(6)	−17(7)	34(5)
C(15)	51(4)	22(3)	100(7)	−6(3)	−5(4)	13(3)
O(2)	48(3)	46(3)	40(3)	−6(2)	−13(2)	15(2)

Compound 31

Table 1. Crystal data and structure refinement for sh2656.

Identification code	sh2656	
Empirical formula	C80 H76 K4 O6 S4	
Formula weight	1418.05	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.6467(9) Å	α = 90°.
	b = 14.2193(9) Å	β = 94.105(3)°.
	c = 42.900(2) Å	γ = 90°.
Volume	14387.5(13) $Å^3$	
Z	8	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.416 mm^{-1}	
F(000)	5952	
Crystal size	0.42 x 0.40 x 0.29 mm^3	
Theta range for data collection	1.67 to 26.44°.	
Index ranges	−27<=h<=29, −17<=k<=17, −53<=l<=53	
Reflections collected	117135	
Independent reflections	14786 [R(int) = 0.0406]	
Completeness to theta = 26.44°	99.7 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8880 and 0.8432	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	14786 / 13 / 874	
Goodness−of−fit on F^2	1.228	
Final R indices [I>2sigma(I)]	R1 = 0.1107, wR2 = 0.2368	
R indices (all data)	R1 = 0.1201, wR2 = 0.2415	
Largest diff. peak and hole	1.386 and −1.718 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2656. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
K(1)	746(1)	2996(1)	833(1)	26(1)
K(2)	387(1)	1630(1)	1542(1)	31(1)
K(3)	1377(1)	3521(1)	1631(1)	29(1)
K(4)	1736(1)	1256(1)	1153(1)	32(1)
O(1)	287(2)	3409(3)	1408(1)	27(1)
O(2)	1844(2)	3145(3)	1054(1)	25(1)
O(3)	1467(2)	1698(3)	1719(1)	35(1)
O(4)	608(2)	1212(3)	974(1)	32(1)
O(5)	−269(3)	416(6)	1803(2)	92(3)
O(6)	2267(2)	−367(3)	981(1)	44(1)
S(1)	−823(1)	2801(1)	1536(1)	41(1)
S(2)	2877(1)	2268(1)	879(1)	35(1)
S(4)	1358(1)	850(1)	410(1)	41(1)
C(1)	−64(2)	4190(4)	1378(1)	27(1)
C(2)	−677(2)	3946(4)	1446(1)	28(1)
C(3)	−1153(3)	4484(6)	1461(2)	45(2)
C(4)	−1636(3)	3956(7)	1540(2)	53(2)
C(5)	−1527(3)	3037(6)	1587(2)	48(2)
C(6)	−1919(3)	2274(7)	1679(2)	67(3)
C(7)	107(2)	4963(4)	1620(1)	28(1)
C(8)	329(3)	4693(5)	1918(1)	33(1)
C(9)	456(3)	5346(6)	2152(2)	48(2)
C(10)	371(4)	6288(6)	2092(2)	55(2)
C(11)	159(4)	6563(6)	1802(2)	58(2)
C(12)	22(3)	5931(5)	1569(2)	40(2)
C(13)	−38(2)	4550(4)	1040(1)	27(1)
C(14)	439(3)	5056(4)	962(1)	30(1)
C(15)	554(3)	5222(5)	656(2)	41(2)
C(16)	186(3)	4877(7)	421(2)	60(2)
C(17)	−292(3)	4397(7)	489(2)	56(2)
C(18)	−408(3)	4220(5)	799(2)	37(2)
C(19)	2219(2)	3850(4)	986(1)	24(1)
C(20)	2822(3)	3454(5)	953(1)	31(1)
C(21)	3602(3)	2330(5)	847(2)	37(2)
C(22)	3942(3)	1488(6)	779(2)	54(2)
C(23)	3785(3)	3248(6)	890(2)	41(2)
C(24)	3338(3)	3875(5)	949(2)	37(2)
C(25)	2054(2)	4316(4)	665(1)	26(1)
C(26)	1762(2)	3750(4)	432(1)	22(1)
C(27)	1606(3)	4163(5)	142(1)	36(2)
C(28)	1740(3)	5074(6)	74(2)	43(2)
C(29)	2047(3)	5593(6)	297(2)	42(2)
C(30)	2208(3)	5222(4)	587(1)	30(1)
C(31)	2238(2)	4553(4)	1259(1)	26(1)
C(32)	2570(2)	4382(4)	1536(1)	29(1)
C(33)	2489(3)	4890(5)	1805(1)	38(2)
C(34)	2078(3)	5570(6)	1812(2)	45(2)
C(35)	1762(3)	5778(5)	1537(2)	43(2)
C(36)	1846(2)	5284(4)	1266(1)	27(1)
C(37)	1744(3)	1459(5)	2001(2)	40(2)
C(38)	1574(3)	2166(6)	2252(2)	46(2)
S(3A)	929(2)	2141(3)	2314(1)	50
C(39A)	1007(8)	3090(11)	2573(4)	52(4)
C(40A)	621(12)	3490(20)	2715(7)	91(9)
C(39B)	1043(6)	2132(11)	2385(3)	50
C(40B)	797(5)	2756(10)	2576(3)	42(3)
C(41B)	1161(5)	3515(8)	2676(3)	38(3)
C(41)	1679(4)	3571(7)	2575(2)	75(3)
C(42)	1895(3)	2890(6)	2375(2)	55(2)
C(43)	1609(3)	447(7)	2093(2)	52(2)
C(44A)	1496(19)	−280(30)	1840(10)	123(18)
C(45A)	1438(8)	−1247(11)	1885(4)	55(5)
C(46A)	1482(7)	−1570(14)	2197(4)	46(4)
S(3B)	1560(3)	−279(4)	1840(1)	36(1)
C(45B)	1516(6)	−1189(12)	2101(6)	44(5)
C(46B)	1502(9)	−2171(12)	2001(5)	69(5)
C(47)	1552(4)	−903(6)	2417(2)	52(2)
C(48)	1609(3)	71(5)	2389(2)	51(2)

C(49)	2399(3)	1517(6)	1987(2)	46(2)
C(50)	2648(3)	1936(5)	1743(2)	38(2)
C(51)	3240(3)	1951(5)	1745(2)	38(2)
C(52)	3568(4)	1564(6)	1994(2)	61(2)
C(53)	3322(7)	1175(8)	2236(3)	121(6)
C(54)	2820(2)	1083(4)	2213(1)	15(1)
C(55)	369(3)	722(4)	719(2)	36(2)
C(56)	650(3)	1043(4)	429(2)	37(2)
C(57)	1397(3)	1494(6)	64(2)	46(2)
C(58)	1921(4)	1579(6)	−82(2)	59(2)
C(59)	879(3)	1848(5)	−27(2)	40(2)
C(60)	455(3)	1599(5)	184(2)	41(2)
C(61)	−282(3)	946(5)	659(2)	41(2)
C(62)	−489(3)	1646(4)	818(1)	28(1)
C(63)	−1115(3)	1881(7)	756(2)	58(2)
C(64)	−1438(3)	1430(6)	529(2)	52(2)
C(65)	−1174(3)	721(5)	366(2)	48(2)
C(66)	−617(3)	469(5)	424(2)	43(2)
C(67)	432(3)	−344(5)	768(2)	42(2)
C(68)	492(3)	−984(5)	527(2)	51(2)
C(69)	531(4)	−1948(6)	591(2)	55(2)
C(70)	513(4)	−2285(5)	890(2)	59(2)
C(71)	443(4)	−1647(6)	1129(2)	58(2)
C(72)	409(3)	−689(5)	1068(2)	44(2)
C(73)	−770(4)	−9(7)	1672(3)	80(3)
C(74)	−770(4)	−980(7)	1781(3)	79(3)
C(75)	−312(5)	−1002(7)	2047(3)	89(4)
C(76)	−146(6)	−36(9)	2086(2)	97(4)
C(77)	1992(4)	−1244(6)	1027(2)	55(2)
C(78)	2254(5)	−1958(7)	822(2)	75(3)
C(79)	2468(5)	−1352(6)	563(2)	79(3)
C(80)	2648(4)	−481(6)	743(2)	57(2)

Table 3. Bond lengths [Å] and angles [°] for sh2656.

K(1)−O(4)	2.633(4)
K(1)−O(2)	2.709(4)
K(1)−O(1)	2.826(4)
K(1)−C(13)	3.057(6)
K(1)−C(14)	3.077(6)
K(1)−C(18)	3.231(7)
K(1)−C(26)	3.238(5)
K(1)−C(56)	3.272(6)
K(1)−C(15)	3.279(7)
K(1)−C(55)	3.379(6)
K(1)−C(17)	3.413(8)
K(1)−C(16)	3.421(9)
K(2)−O(4)	2.598(4)
K(2)−O(1)	2.601(4)
K(2)−O(3)	2.613(4)
K(2)−O(5)	2.623(6)
K(2)−S(1)	3.310(2)
K(2)−S(3A)	3.542(4)
K(2)−K(3)	3.5673(18)
K(2)−K(4)	3.7435(19)
K(3)−O(3)	2.626(5)
K(3)−O(1)	2.689(4)
K(3)−O(2)	2.833(4)
K(3)−C(31)	3.053(5)
K(3)−C(32)	3.129(6)
K(3)−C(36)	3.196(6)
K(3)−C(38)	3.295(6)
K(3)−C(8)	3.297(7)
K(3)−C(33)	3.314(6)
K(3)−C(35)	3.368(8)
K(3)−C(34)	3.414(7)
K(3)−C(37)	3.418(7)
K(4)−O(3)	2.631(5)
K(4)−O(4)	2.723(4)
K(4)−O(2)	2.733(4)
K(4)−O(6)	2.752(5)
K(4)−S(4)	3.297(2)
K(4)−S(2)	3.343(2)
K(4)−C(50)	3.347(7)
C(19)−C(31)	1.536(8)
C(19)−C(20)	1.548(8)
C(19)−C(25)	1.555(8)
C(20)−C(24)	1.359(9)
C(21)−C(23)	1.383(10)
C(21)−C(22)	1.483(10)
C(23)−C(24)	1.419(10)
C(25)−C(30)	1.384(8)
C(25)−C(26)	1.423(8)
C(26)−C(27)	1.400(8)
C(27)−C(28)	1.371(10)
C(28)−C(29)	1.375(10)
C(29)−C(30)	1.381(9)
C(31)−C(36)	1.395(8)
C(31)−C(32)	1.398(8)
C(32)−C(33)	1.386(9)
C(33)−C(34)	1.373(10)
C(34)−C(35)	1.383(10)
C(35)−C(36)	1.385(9)
C(37)−C(43)	1.532(10)
C(37)−C(38)	1.547(11)
C(37)−C(49)	1.557(9)
C(38)−C(42)	1.363(10)
C(38)−C(39B)	1.415(14)
C(38)−S(3A)	1.568(8)
S(3A)−C(39A)	1.751(14)
C(39A)−C(40A)	1.27(3)
C(39A)−C(41)	1.73(2)
C(39B)−C(40B)	1.368(15)
C(40B)−C(41B)	1.427(14)
C(41B)−C(41)	1.331(12)
C(41)−C(42)	1.414(10)
C(43)−C(48)	1.377(10)
C(43)−S(3B)	1.497(12)
C(43)−C(44A)	1.51(4)
C(44A)−C(45A)	1.40(4)
C(45A)−C(46A)	1.41(2)
C(46A)−C(47)	1.34(2)
S(3B)−C(45B)	1.72(2)

K(4)−S(3B)	3.718(7)	C(45B)−C(47)	1.41(2)
O(1)−C(1)	1.387(7)	C(45B)−C(46B)	1.46(2)
O(2)−C(19)	1.383(6)	C(47)−C(48)	1.397(10)
O(3)−C(37)	1.378(7)	C(49)−C(50)	1.372(9)
O(4)−C(55)	1.381(7)	C(49)−C(54)	1.475(8)
O(5)−C(76)	1.388(12)	C(50)−C(51)	1.401(9)
O(5)−C(73)	1.410(11)	C(51)−C(52)	1.391(11)
O(6)−C(80)	1.416(9)	C(52)−C(53)	1.343(16)
O(6)−C(77)	1.427(9)	C(53)−C(54)	1.193(17)
S(1)−C(2)	1.713(6)	C(55)−C(56)	1.525(9)
S(1)−C(5)	1.727(7)	C(55)−C(67)	1.537(9)
S(2)−C(20)	1.723(7)	C(55)−C(61)	1.575(10)
S(2)−C(21)	1.732(7)	C(56)−C(60)	1.368(9)
S(4)−C(56)	1.704(7)	C(57)−C(59)	1.357(10)
S(4)−C(57)	1.752(8)	C(57)−C(58)	1.435(11)
C(1)−C(2)	1.537(8)	C(59)−C(60)	1.441(10)
C(1)−C(7)	1.545(8)	C(61)−C(62)	1.320(10)
C(1)−C(13)	1.544(8)	C(61)−C(66)	1.411(9)
C(2)−C(3)	1.367(9)	C(62)−C(63)	1.524(10)
C(3)−C(4)	1.429(10)	C(63)−C(64)	1.354(11)
C(4)−C(5)	1.345(12)	C(64)−C(65)	1.399(11)
C(5)−C(6)	1.498(11)	C(65)−C(66)	1.370(11)
C(7)−C(8)	1.398(8)	C(67)−C(72)	1.380(9)
C(7)−C(12)	1.405(9)	C(67)−C(68)	1.392(10)
C(8)−C(9)	1.384(9)	C(68)−C(69)	1.399(11)
C(9)−C(10)	1.376(11)	C(69)−C(70)	1.376(12)
C(10)−C(11)	1.363(12)	C(70)−C(71)	1.387(12)
C(11)−C(12)	1.365(10)	C(71)−C(72)	1.389(10)
C(13)−C(18)	1.389(8)	C(73)−C(74)	1.458(13)
C(13)−C(14)	1.401(8)	C(74)−C(75)	1.515(13)
C(14)−C(15)	1.376(9)	C(75)−C(76)	1.436(14)
C(15)−C(16)	1.376(11)	C(77)−C(78)	1.504(12)
C(16)−C(17)	1.371(11)	C(78)−C(79)	1.519(12)
C(17)−C(18)	1.398(10)	C(79)−C(80)	1.506(12)

O(4)−K(1)−O(2)	97.24(13)	K(4)−O(2)−K(3)	90.21(12)
O(4)−K(1)−O(1)	86.50(13)	C(37)−O(3)−K(2)	129.8(4)
O(2)−K(1)−O(1)	95.57(12)	C(37)−O(3)−K(3)	113.5(4)
O(4)−K(1)−C(13)	122.85(16)	K(2)−O(3)−K(3)	85.82(14)
O(2)−K(1)−C(13)	115.33(14)	C(37)−O(3)−K(4)	128.4(4)
O(1)−K(1)−C(13)	46.93(13)	K(2)−O(3)−K(4)	91.09(14)
O(4)−K(1)−C(14)	147.31(15)	K(3)−O(3)−K(4)	97.22(14)
O(2)−K(1)−C(14)	95.44(15)	C(55)−O(4)−K(2)	139.3(4)
O(1)−K(1)−C(14)	62.32(14)	C(55)−O(4)−K(1)	110.8(3)
C(13)−K(1)−C(14)	26.40(16)	K(2)−O(4)−K(1)	91.77(14)
O(4)−K(1)−C(18)	114.33(17)	C(55)−O(4)−K(4)	124.9(4)
O(2)−K(1)−C(18)	139.39(16)	K(2)−O(4)−K(4)	89.39(12)
O(1)−K(1)−C(18)	63.38(14)	K(1)−O(4)−K(4)	84.71(12)
C(13)−K(1)−C(18)	25.33(16)	C(76)−O(5)−C(73)	105.4(7)
C(14)−K(1)−C(18)	44.47(17)	C(76)−O(5)−K(2)	125.8(6)
O(4)−K(1)−C(26)	123.34(15)	C(73)−O(5)−K(2)	128.2(6)
O(2)−K(1)−C(26)	55.29(12)	C(80)−O(6)−C(77)	108.6(6)
O(1)−K(1)−C(26)	137.83(13)	C(80)−O(6)−K(4)	127.9(4)
C(13)−K(1)−C(26)	113.81(16)	C(77)−O(6)−K(4)	118.3(4)
C(14)−K(1)−C(26)	88.46(15)	C(2)−S(1)−C(5)	93.3(4)
C(18)−K(1)−C(26)	116.98(17)	C(2)−S(1)−K(2)	106.9(2)
O(4)−K(1)−C(56)	45.52(14)	C(5)−S(1)−K(2)	159.6(3)
O(2)−K(1)−C(56)	106.24(16)	C(20)−S(2)−C(21)	93.0(3)
O(1)−K(1)−C(56)	128.52(15)	C(20)−S(2)−K(4)	106.5(2)
C(13)−K(1)−C(56)	138.35(17)	C(21)−S(2)−K(4)	151.3(2)
C(14)−K(1)−C(56)	153.45(17)	C(56)−S(4)−C(57)	93.8(3)
C(18)−K(1)−C(56)	114.02(18)	C(56)−S(4)−K(4)	97.3(2)
C(26)−K(1)−C(56)	91.42(16)	C(57)−S(4)−K(4)	134.5(2)
O(4)−K(1)−C(15)	164.96(17)	O(1)−C(1)−C(2)	111.6(5)
O(2)−K(1)−C(15)	96.82(16)	O(1)−C(1)−C(7)	112.5(5)
O(1)−K(1)−C(15)	86.85(15)	C(2)−C(1)−C(7)	103.9(5)
C(13)−K(1)−C(15)	44.96(16)	O(1)−C(1)−C(13)	106.6(4)
C(14)−K(1)−C(15)	24.74(16)	C(2)−C(1)−C(13)	110.7(5)
C(18)−K(1)−C(15)	50.71(18)	C(7)−C(1)−C(13)	111.6(5)
C(26)−K(1)−C(15)	69.70(16)	C(3)−C(2)−C(1)	132.3(6)
C(56)−K(1)−C(15)	133.90(17)	C(3)−C(2)−S(1)	109.9(5)
O(4)−K(1)−C(55)	22.47(13)	C(1)−C(2)−S(1)	117.8(4)
O(2)−K(1)−C(55)	111.21(15)	C(2)−C(3)−C(4)	113.1(7)

O(1)−K(1)−C(55)	102.18(15)
C(13)−K(1)−C(55)	125.05(17)
C(14)−K(1)−C(55)	150.87(17)
C(18)−K(1)−C(55)	107.20(18)
C(26)−K(1)−C(55)	116.00(16)
C(56)−K(1)−C(55)	26.45(16)
C(15)−K(1)−C(55)	149.26(17)
O(4)−K(1)−C(17)	124.38(19)
O(2)−K(1)−C(17)	138.37(18)
O(1)−K(1)−C(17)	86.95(15)
C(13)−K(1)−C(17)	43.27(17)
C(14)−K(1)−C(17)	49.52(19)
C(18)−K(1)−C(17)	24.10(17)
C(26)−K(1)−C(17)	96.59(17)
C(56)−K(1)−C(17)	104.23(19)
C(15)−K(1)−C(17)	41.7(2)
C(55)−K(1)−C(17)	108.8(2)
O(4)−K(1)−C(16)	145.35(18)
O(2)−K(1)−C(16)	116.45(17)
O(1)−K(1)−C(16)	97.46(17)
C(13)−K(1)−C(16)	50.57(18)
C(14)−K(1)−C(16)	42.34(19)
C(18)−K(1)−C(16)	42.34(18)
C(26)−K(1)−C(16)	74.94(17)
C(56)−K(1)−C(16)	112.3(2)
C(15)−K(1)−C(16)	23.57(19)
C(55)−K(1)−C(16)	125.83(19)
C(17)−K(1)−C(16)	23.15(19)
O(4)−K(2)−O(1)	92.11(13)
O(4)−K(2)−O(3)	91.31(14)
O(1)−K(2)−O(3)	95.74(14)
O(4)−K(2)−O(5)	114.5(2)
O(1)−K(2)−O(5)	133.4(2)
O(3)−K(2)−O(5)	119.7(2)
O(4)−K(2)−S(1)	109.88(11)
O(1)−K(2)−S(1)	56.20(9)
O(3)−K(2)−S(1)	144.10(12)
O(5)−K(2)−S(1)	78.3(2)
O(4)−K(2)−S(3A)	147.23(13)
O(1)−K(2)−S(3A)	91.63(12)
O(3)−K(2)−S(3A)	55.92(12)
O(5)−K(2)−S(3A)	85.47(18)
S(1)−K(2)−S(3A)	99.15(9)
O(4)−K(2)−K(3)	95.65(10)
O(1)−K(2)−K(3)	48.65(9)
O(3)−K(2)−K(3)	47.24(10)
O(5)−K(2)−K(3)	148.57(17)
S(1)−K(2)−K(3)	100.47(5)
S(3A)−K(2)−K(3)	63.54(8)
O(4)−K(2)−K(4)	46.67(10)
O(1)−K(2)−K(4)	96.13(9)
O(3)−K(2)−K(4)	44.64(10)
O(5)−K(2)−K(4)	130.2(2)
S(1)−K(2)−K(4)	146.33(6)
S(3A)−K(2)−K(4)	100.56(8)
K(3)−K(2)−K(4)	65.24(4)
O(4)−K(2)−K(1)	44.49(10)
O(1)−K(2)−K(1)	48.75(9)
O(3)−K(2)−K(1)	86.77(9)
O(5)−K(2)−K(1)	149.34(16)
S(1)−K(2)−K(1)	88.78(5)
S(3A)−K(2)−K(1)	124.32(9)
K(3)−K(2)−K(1)	60.82(3)
K(4)−K(2)−K(1)	57.54(3)
O(3)−K(3)−O(1)	93.36(13)
O(3)−K(3)−O(2)	84.62(13)
O(1)−K(3)−O(2)	95.87(12)
O(3)−K(3)−C(31)	119.93(16)
O(1)−K(3)−C(31)	120.08(14)
O(2)−K(3)−C(31)	46.92(13)
O(3)−K(3)−C(32)	109.88(16)
O(1)−K(3)−C(32)	145.81(15)
O(2)−K(3)−C(32)	63.13(13)
C(5)−C(4)−C(3)	113.5(7)
C(4)−C(5)−C(6)	128.9(7)
C(4)−C(5)−S(1)	110.2(6)
C(6)−C(5)−S(1)	120.9(7)
C(8)−C(7)−C(12)	116.8(6)
C(8)−C(7)−C(1)	118.7(6)
C(12)−C(7)−C(1)	124.4(6)
C(9)−C(8)−C(7)	121.7(7)
C(9)−C(8)−K(3)	118.7(5)
C(7)−C(8)−K(3)	92.3(4)
C(10)−C(9)−C(8)	119.7(7)
C(11)−C(10)−C(9)	119.3(7)
C(10)−C(11)−C(12)	122.0(8)
C(11)−C(12)−C(7)	120.5(7)
C(18)−C(13)−C(14)	118.0(6)
C(18)−C(13)−C(1)	121.6(6)
C(14)−C(13)−C(1)	118.9(5)
C(18)−C(13)−K(1)	84.3(4)
C(14)−C(13)−K(1)	77.6(3)
C(1)−C(13)−K(1)	95.7(3)
C(15)−C(14)−C(13)	122.3(6)
C(15)−C(14)−K(1)	85.9(4)
C(13)−C(14)−K(1)	76.0(3)
C(16)−C(15)−C(14)	118.8(7)
C(16)−C(15)−K(1)	84.0(5)
C(14)−C(15)−K(1)	69.4(4)
C(17)−C(16)−C(15)	120.5(7)
C(17)−C(16)−K(1)	78.1(5)
C(15)−C(16)−K(1)	72.4(5)
C(16)−C(17)−C(18)	120.9(7)
C(16)−C(17)−K(1)	78.7(5)
C(18)−C(17)−K(1)	70.6(4)
C(13)−C(18)−C(17)	119.5(7)
C(13)−C(18)−K(1)	70.3(3)
C(17)−C(18)−K(1)	85.3(4)
O(2)−C(19)−C(31)	107.2(4)
O(2)−C(19)−C(20)	111.4(5)
C(31)−C(19)−C(20)	109.2(4)
O(2)−C(19)−C(25)	111.8(4)
C(31)−C(19)−C(25)	112.9(5)
C(20)−C(19)−C(25)	104.4(4)
C(24)−C(20)−C(19)	132.4(6)
C(24)−C(20)−S(2)	110.5(5)
C(19)−C(20)−S(2)	117.0(4)
C(23)−C(21)−C(22)	128.2(7)
C(23)−C(21)−S(2)	109.9(5)
C(22)−C(21)−S(2)	121.8(6)
C(21)−C(23)−C(24)	112.7(6)
C(20)−C(24)−C(23)	114.0(6)
C(30)−C(25)−C(26)	118.7(5)
C(30)−C(25)−C(19)	123.8(5)
C(26)−C(25)−C(19)	117.4(5)
C(27)−C(26)−C(25)	118.0(6)
C(27)−C(26)−K(1)	116.9(4)
C(25)−C(26)−K(1)	98.9(3)
C(28)−C(27)−C(26)	122.4(6)
C(27)−C(28)−C(29)	118.5(6)
C(28)−C(29)−C(30)	121.3(7)
C(29)−C(30)−C(25)	120.8(6)
C(36)−C(31)−C(32)	116.3(5)
C(36)−C(31)−C(19)	121.3(5)
C(32)−C(31)−C(19)	121.2(6)
C(36)−C(31)−K(3)	82.9(3)
C(32)−C(31)−K(3)	80.0(3)
C(19)−C(31)−K(3)	95.8(3)
C(33)−C(32)−C(31)	121.0(6)
C(33)−C(32)−K(3)	85.2(4)
C(31)−C(32)−K(3)	73.9(3)
C(34)−C(33)−C(32)	121.7(6)
C(34)−C(33)−K(3)	82.3(4)
C(32)−C(33)−K(3)	70.2(3)
C(33)−C(34)−C(35)	118.2(6)
C(33)−C(34)−K(3)	74.2(4)

C(31)−K(3)−C(32)	26.10(15)
O(3)−K(3)−C(36)	144.79(15)
O(1)−K(3)−C(36)	103.31(14)
O(2)−K(3)−C(36)	63.22(13)
C(31)−K(3)−C(36)	25.67(15)
C(32)−K(3)−C(36)	44.04(16)
O(3)−K(3)−C(38)	45.64(17)
O(1)−K(3)−C(38)	109.26(15)
O(2)−K(3)−C(38)	123.66(16)
C(31)−K(3)−C(38)	129.99(17)
C(32)−K(3)−C(38)	104.90(16)
C(36)−K(3)−C(38)	145.15(17)
O(3)−K(3)−C(8)	120.05(16)
O(1)−K(3)−C(8)	55.66(14)
O(2)−K(3)−C(8)	140.58(14)
C(31)−K(3)−C(8)	120.01(17)
C(32)−K(3)−C(8)	124.04(17)
C(36)−K(3)−C(8)	94.78(16)
C(38)−K(3)−C(8)	93.48(17)
O(3)−K(3)−C(33)	119.48(17)
O(1)−K(3)−C(33)	147.16(16)
O(2)−K(3)−C(33)	87.39(14)
C(31)−K(3)−C(33)	44.51(15)
C(32)−K(3)−C(33)	24.63(15)
C(36)−K(3)−C(33)	49.59(16)
C(38)−K(3)−C(33)	95.56(17)
C(8)−K(3)−C(33)	102.99(17)
O(3)−K(3)−C(35)	159.70(17)
O(1)−K(3)−C(35)	105.93(16)
O(2)−K(3)−C(35)	87.12(14)
C(31)−K(3)−C(35)	44.22(16)
C(32)−K(3)−C(35)	50.03(17)
C(36)−K(3)−C(35)	24.18(15)
C(38)−K(3)−C(35)	129.07(18)
C(8)−K(3)−C(35)	77.29(17)
C(33)−K(3)−C(35)	41.44(18)
O(3)−K(3)−C(34)	140.92(17)
O(1)−K(3)−C(34)	124.70(17)
O(2)−K(3)−C(34)	98.42(14)
C(31)−K(3)−C(34)	51.51(16)
C(32)−K(3)−C(34)	42.94(17)
C(36)−K(3)−C(34)	42.45(16)
C(38)−K(3)−C(34)	106.05(18)
C(8)−K(3)−C(34)	81.35(17)
C(33)−K(3)−C(34)	23.49(18)
C(35)−K(3)−C(34)	23.53(17)
O(3)−K(3)−C(37)	21.69(15)
O(1)−K(3)−C(37)	108.65(14)
O(2)−K(3)−C(37)	98.14(15)
C(31)−K(3)−C(37)	119.88(16)
C(32)−K(3)−C(37)	101.21(16)
C(36)−K(3)−C(37)	144.56(16)
C(38)−K(3)−C(37)	26.56(18)
C(8)−K(3)−C(37)	115.67(17)
C(33)−K(3)−C(37)	103.16(17)
C(35)−K(3)−C(37)	144.21(18)
C(34)−K(3)−C(37)	121.53(18)
O(3)−K(4)−O(4)	88.20(13)
O(3)−K(4)−O(2)	86.55(13)
O(4)−K(4)−O(2)	94.56(13)
O(3)−K(4)−O(6)	126.36(15)
O(4)−K(4)−O(6)	111.18(15)
O(2)−K(4)−O(6)	137.11(14)
O(3)−K(4)−S(4)	150.08(11)
O(4)−K(4)−S(4)	62.03(9)
O(2)−K(4)−S(4)	92.52(9)
O(6)−K(4)−S(4)	72.05(11)
O(3)−K(4)−S(2)	118.48(11)
O(4)−K(4)−S(2)	135.16(10)
O(2)−K(4)−S(2)	55.67(9)
O(6)−K(4)−S(2)	82.64(11)
S(4)−K(4)−S(2)	84.56(5)
O(3)−K(4)−C(50)	54.44(15)
C(35)−C(34)−K(3)	76.4(4)
C(34)−C(35)−C(36)	120.3(7)
C(34)−C(35)−K(3)	80.1(5)
C(36)−C(35)−K(3)	70.9(4)
C(35)−C(36)−C(31)	122.3(6)
C(35)−C(36)−K(3)	84.9(4)
C(31)−C(36)−K(3)	71.4(3)
O(3)−C(37)−C(43)	111.3(6)
O(3)−C(37)−C(38)	108.7(6)
C(43)−C(37)−C(38)	111.2(6)
O(3)−C(37)−C(49)	111.4(5)
C(43)−C(37)−C(49)	106.7(6)
C(38)−C(37)−C(49)	107.6(6)
O(3)−C(37)−K(3)	44.8(3)
C(43)−C(37)−K(3)	151.0(4)
C(38)−C(37)−K(3)	72.3(3)
C(49)−C(37)−K(3)	99.0(4)
C(42)−C(38)−C(39B)	110.8(9)
C(42)−C(38)−C(37)	126.5(6)
C(39B)−C(38)−C(37)	122.7(8)
C(42)−C(38)−S(3A)	118.3(6)
C(39B)−C(38)−S(3A)	13.9(6)
C(37)−C(38)−S(3A)	114.1(5)
C(42)−C(38)−K(3)	85.0(5)
C(39B)−C(38)−K(3)	105.5(7)
C(37)−C(38)−K(3)	81.2(3)
S(3A)−C(38)−K(3)	93.9(3)
C(38)−S(3A)−C(39A)	91.8(7)
C(38)−S(3A)−K(2)	97.9(3)
C(39A)−S(3A)−K(2)	140.1(6)
C(38)−S(3A)−K(3)	61.4(3)
C(39A)−S(3A)−K(3)	94.0(6)
K(2)−S(3A)−K(3)	58.56(7)
C(40A)−C(39A)−C(41)	120.9(18)
C(40A)−C(39A)−S(3A)	127.2(19)
C(41)−C(39A)−S(3A)	111.2(9)
C(40B)−C(39B)−C(38)	130.3(13)
C(39B)−C(40B)−C(41B)	113.4(12)
C(41)−C(41B)−C(40B)	119.8(11)
C(41B)−C(41)−C(42)	122.6(10)
C(41B)−C(41)−C(39A)	27.2(7)
C(42)−C(41)−C(39A)	95.7(8)
C(38)−C(42)−C(41)	122.5(8)
C(38)−C(42)−K(3)	71.8(4)
C(41)−C(42)−K(3)	105.3(5)
C(48)−C(43)−S(3B)	113.3(7)
C(48)−C(43)−C(44A)	112.8(16)
S(3B)−C(43)−C(44A)	5.7(19)
C(48)−C(43)−C(37)	128.1(8)
S(3B)−C(43)−C(37)	117.8(6)
C(44A)−C(43)−C(37)	118.9(15)
C(45A)−C(44A)−C(43)	126(3)
C(44A)−C(45A)−C(46A)	117(2)
C(47)−C(46A)−C(45A)	115.8(16)
C(43)−S(3B)−C(45B)	93.1(8)
C(43)−S(3B)−K(4)	99.4(4)
C(45B)−S(3B)−K(4)	166.9(7)
C(47)−C(45B)−C(46B)	123.7(18)
C(47)−C(45B)−S(3B)	113.9(11)
C(46B)−C(45B)−S(3B)	122.1(18)
C(46A)−C(47)−C(48)	130.5(11)
C(46A)−C(47)−C(45B)	28.8(7)
C(48)−C(47)−C(45B)	101.7(9)
C(43)−C(48)−C(47)	118.0(8)
C(50)−C(49)−C(54)	112.3(6)
C(50)−C(49)−C(37)	122.3(6)
C(54)−C(49)−C(37)	125.2(5)
C(49)−C(50)−C(51)	119.0(7)
C(49)−C(50)−K(4)	99.4(4)
C(51)−C(50)−K(4)	126.7(4)
C(52)−C(51)−C(50)	120.0(7)
C(53)−C(52)−C(51)	120.6(10)
C(54)−C(53)−C(52)	117.8(10)

O(4)−K(4)−C(50)	141.68(15)	C(53)−C(54)−C(49)	128.9(7)
O(2)−K(4)−C(50)	76.77(15)	O(4)−C(55)−C(56)	108.5(5)
O(6)−K(4)−C(50)	99.41(17)	O(4)−C(55)−C(67)	111.0(5)
S(4)−K(4)−C(50)	153.70(12)	C(56)−C(55)−C(67)	111.3(6)
S(2)−K(4)−C(50)	69.51(11)	O(4)−C(55)−C(61)	111.7(6)
O(3)−K(4)−K(1)	89.63(10)	C(56)−C(55)−C(61)	106.5(5)
O(4)−K(4)−K(1)	46.58(9)	C(67)−C(55)−C(61)	107.8(5)
O(2)−K(4)−K(1)	48.17(8)	O(4)−C(55)−K(1)	46.8(3)
O(6)−K(4)−K(1)	140.24(12)	C(56)−C(55)−K(1)	72.9(3)
S(4)−K(4)−K(1)	68.22(5)	C(67)−C(55)−K(1)	154.4(4)
S(2)−K(4)−K(1)	95.11(5)	C(61)−C(55)−K(1)	94.3(4)
C(50)−K(4)−K(1)	117.04(13)	C(60)−C(56)−C(55)	131.1(7)
O(3)−K(4)−S(3B)	50.15(12)	C(60)−C(56)−S(4)	109.6(5)
O(4)−K(4)−S(3B)	92.67(13)	C(55)−C(56)−S(4)	118.5(5)
O(2)−K(4)−S(3B)	135.80(11)	C(60)−C(56)−K(1)	85.6(4)
O(6)−K(4)−S(3B)	78.44(13)	C(55)−C(56)−K(1)	80.7(3)
S(4)−K(4)−S(3B)	128.74(9)	S(4)−C(56)−K(1)	97.5(3)
S(2)−K(4)−S(3B)	132.17(11)	C(59)−C(57)−C(58)	129.3(8)
C(50)−K(4)−S(3B)	70.88(14)	C(59)−C(57)−S(4)	109.8(6)
K(1)−K(4)−S(3B)	126.67(10)	C(58)−C(57)−S(4)	120.9(6)
O(3)−K(4)−K(2)	44.27(10)	C(57)−C(59)−C(60)	112.4(7)
O(4)−K(4)−K(2)	43.94(9)	C(56)−C(60)−C(59)	114.4(7)
O(2)−K(4)−K(2)	91.23(9)	C(56)−C(60)−K(1)	71.1(4)
O(6)−K(4)−K(2)	131.16(12)	C(59)−C(60)−K(1)	105.0(4)
S(4)−K(4)−K(2)	105.94(5)	C(62)−C(61)−C(66)	121.5(7)
S(2)−K(4)−K(2)	146.13(6)	C(62)−C(61)−C(55)	117.4(6)
C(50)−K(4)−K(2)	98.34(12)	C(66)−C(61)−C(55)	120.8(7)
K(1)−K(4)−K(2)	61.40(4)	C(61)−C(62)−C(63)	117.7(6)
S(3B)−K(4)−K(2)	65.28(10)	C(61)−C(62)−K(1)	94.8(4)
O(3)−K(4)−K(3)	41.35(10)	C(63)−C(62)−K(1)	133.2(4)
O(4)−K(4)−K(3)	85.53(10)	C(64)−C(63)−C(62)	120.9(8)
O(2)−K(4)−K(3)	45.91(8)	C(63)−C(64)−C(65)	116.8(8)
O(6)−K(4)−K(3)	160.64(12)	C(66)−C(65)−C(64)	123.8(7)
S(4)−K(4)−K(3)	126.27(5)	C(65)−C(66)−C(61)	119.1(7)
S(2)−K(4)−K(3)	92.34(5)	C(72)−C(67)−C(68)	118.2(7)
C(50)−K(4)−K(3)	61.45(13)	C(72)−C(67)−C(55)	117.8(6)
K(1)−K(4)−K(3)	58.64(3)	C(68)−C(67)−C(55)	123.9(7)
S(3B)−K(4)−K(3)	91.50(8)	C(67)−C(68)−C(69)	120.3(8)
K(2)−K(4)−K(3)	55.22(3)	C(70)−C(69)−C(68)	121.1(8)
C(1)−O(1)−K(2)	147.5(3)	C(69)−C(70)−C(71)	118.5(7)
C(1)−O(1)−K(3)	122.5(3)	C(70)−C(71)−C(72)	120.6(8)
K(2)−O(1)−K(3)	84.79(12)	C(67)−C(72)−C(71)	121.3(7)
C(1)−O(1)−K(1)	110.6(3)	O(5)−C(73)−C(74)	107.4(8)
K(2)−O(1)−K(1)	87.47(12)	C(73)−C(74)−C(75)	104.1(8)
K(3)−O(1)−K(1)	84.52(11)	C(76)−C(75)−C(74)	104.1(9)
C(19)−O(2)−K(1)	126.6(3)	O(5)−C(76)−C(75)	107.6(9)
C(19)−O(2)−K(4)	144.4(3)	O(6)−C(77)−C(78)	107.4(7)
K(1)−O(2)−K(4)	83.09(11)	C(77)−C(78)−C(79)	102.5(7)
C(19)−O(2)−K(3)	110.1(3)	C(80)−C(79)−C(78)	100.9(7)
K(1)−O(2)−K(3)	84.03(11)	O(6)−C(80)−C(79)	107.0(7)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2656. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K(1)	24(1)	27(1)	28(1)	−1(1)	0(1)	−3(1)
K(2)	30(1)	30(1)	34(1)	6(1)	2(1)	−7(1)
K(3)	25(1)	32(1)	29(1)	3(1)	0(1)	−8(1)
K(4)	32(1)	28(1)	34(1)	−2(1)	−1(1)	−1(1)
O(1)	27(2)	25(2)	28(2)	2(2)	3(2)	−3(2)
O(2)	24(2)	23(2)	27(2)	0(2)	2(2)	−6(2)
O(3)	37(2)	38(3)	30(2)	17(2)	−3(2)	−5(2)
O(4)	42(2)	28(2)	25(2)	−1(2)	−5(2)	−12(2)
O(5)	98(5)	100(6)	76(5)	32(4)	−8(4)	−63(5)
O(6)	52(3)	35(3)	46(3)	−5(2)	5(2)	0(2)
S(1)	31(1)	42(1)	53(1)	−2(1)	12(1)	−9(1)
S(2)	32(1)	39(1)	34(1)	5(1)	5(1)	0(1)
S(4)	38(1)	47(1)	39(1)	−3(1)	4(1)	−2(1)
C(1)	23(3)	32(3)	26(3)	0(2)	2(2)	−2(2)
C(2)	27(3)	34(3)	25(3)	4(2)	4(2)	−2(2)
C(3)	27(3)	64(5)	45(4)	18(4)	4(3)	4(3)

C(4)	24(3)	90(7)	45(4)	18(4)	6(3)	2(4)
C(5)	26(3)	75(6)	43(4)	4(4)	4(3)	−10(4)
C(6)	37(4)	79(7)	85(7)	2(5)	14(4)	−22(4)
C(7)	24(3)	34(3)	28(3)	0(2)	5(2)	−3(2)
C(8)	31(3)	38(4)	30(3)	3(3)	−3(2)	0(3)
C(9)	49(4)	56(5)	36(4)	−7(3)	−7(3)	3(4)
C(10)	70(6)	47(5)	50(5)	−22(4)	10(4)	−2(4)
C(11)	84(6)	41(4)	50(5)	−7(4)	19(4)	6(4)
C(12)	48(4)	33(4)	40(4)	2(3)	9(3)	14(3)
C(13)	27(3)	28(3)	25(3)	0(2)	−1(2)	6(2)
C(14)	32(3)	26(3)	32(3)	6(2)	5(2)	2(2)
C(15)	39(4)	46(4)	38(4)	13(3)	9(3)	9(3)
C(16)	50(5)	100(7)	31(4)	17(4)	4(3)	−2(5)
C(17)	40(4)	94(7)	31(4)	−1(4)	−10(3)	5(4)
C(18)	29(3)	50(4)	32(3)	3(3)	−4(3)	4(3)
C(19)	19(3)	29(3)	24(3)	−4(2)	1(2)	−6(2)
C(20)	28(3)	39(3)	25(3)	−1(3)	1(2)	−2(3)
C(21)	38(4)	43(4)	29(3)	3(3)	4(3)	9(3)
C(22)	47(4)	64(5)	51(4)	10(4)	9(3)	10(4)
C(23)	24(3)	62(5)	36(3)	3(3)	3(3)	−1(3)
C(24)	28(3)	44(4)	39(3)	−5(3)	0(3)	−6(3)
C(25)	19(3)	35(3)	25(3)	0(2)	7(2)	−2(2)
C(26)	16(2)	36(3)	16(2)	1(2)	2(2)	−4(2)
C(27)	32(3)	51(4)	25(3)	−5(3)	1(2)	2(3)
C(28)	35(4)	66(5)	28(3)	7(3)	6(3)	−1(3)
C(29)	39(4)	55(5)	32(3)	6(3)	5(3)	−6(3)
C(30)	30(3)	37(3)	23(3)	−3(2)	3(2)	−8(3)
C(31)	28(3)	28(3)	23(3)	2(2)	3(2)	−14(2)
C(32)	23(3)	34(3)	30(3)	1(3)	1(2)	−11(2)
C(33)	33(3)	55(4)	26(3)	−6(3)	−2(2)	−12(3)
C(34)	46(4)	54(5)	34(4)	−16(3)	5(3)	−12(3)
C(35)	41(4)	49(4)	40(4)	−8(3)	7(3)	−1(3)
C(36)	28(3)	28(3)	24(3)	0(2)	0(2)	−3(2)
C(37)	31(3)	49(4)	40(4)	26(3)	1(3)	−6(3)
C(38)	42(4)	66(5)	28(3)	24(3)	−7(3)	−2(4)
C(41)	85(7)	101(8)	40(4)	10(5)	19(4)	30(6)
C(42)	55(5)	75(6)	37(4)	1(4)	14(3)	−6(4)
C(43)	26(3)	77(6)	52(5)	35(4)	−9(3)	−12(4)
C(44A)	140(40)	120(30)	110(30)	90(20)	−10(20)	−10(20)
C(45A)	96(14)	29(8)	38(9)	9(7)	−5(9)	−24(8)
C(46A)	52(10)	26(9)	57(11)	22(9)	−12(7)	−11(8)
S(3B)	50(3)	29(3)	31(2)	−10(2)	9(2)	−13(2)
C(45B)	34(8)	14(8)	85(16)	30(9)	11(8)	−3(6)
C(46B)	81(13)	33(9)	95(15)	−4(10)	26(11)	−11(9)
C(47)	63(5)	47(5)	44(4)	14(4)	−2(4)	−16(4)
C(48)	59(5)	46(4)	43(4)	25(3)	−24(3)	−24(4)
C(49)	32(4)	53(5)	52(4)	16(4)	5(3)	−8(3)
C(50)	36(3)	41(4)	36(3)	4(3)	4(3)	−12(3)
C(51)	35(3)	40(4)	39(4)	−4(3)	2(3)	−4(3)
C(52)	77(6)	42(5)	62(5)	−6(4)	−7(4)	8(4)
C(53)	225(17)	62(7)	70(7)	24(6)	−40(9)	8(9)
C(54)	0(2)	25(3)	16(2)	22(2)	−17(2)	−8(2)
C(55)	52(4)	21(3)	34(3)	−1(3)	−5(3)	−5(3)
C(56)	54(4)	26(3)	29(3)	−8(3)	−5(3)	−7(3)
C(57)	52(4)	47(4)	40(4)	−16(3)	4(3)	−6(3)
C(58)	77(6)	54(5)	45(4)	−9(4)	14(4)	−20(4)
C(59)	45(4)	42(4)	33(3)	−4(3)	−5(3)	−4(3)
C(60)	57(4)	36(4)	30(3)	−2(3)	−4(3)	−8(3)
C(61)	46(4)	35(4)	41(4)	12(3)	−12(3)	−23(3)
C(62)	37(3)	17(3)	28(3)	−13(2)	−13(2)	−7(2)
C(63)	39(4)	65(6)	68(5)	−11(4)	4(4)	−3(4)
C(64)	38(4)	52(5)	66(5)	−6(4)	−4(4)	−8(3)
C(65)	46(4)	44(4)	54(4)	−16(4)	3(3)	−9(3)
C(66)	54(4)	32(4)	42(4)	−11(3)	−6(3)	−13(3)
C(67)	47(4)	30(3)	45(4)	−1(3)	−11(3)	−16(3)
C(68)	65(5)	36(4)	49(4)	−6(3)	−10(4)	−19(4)
C(69)	62(5)	36(4)	67(5)	−6(4)	−8(4)	−11(4)
C(70)	61(5)	22(3)	92(7)	9(4)	−8(5)	−11(3)
C(71)	68(5)	40(4)	67(5)	16(4)	0(4)	−20(4)
C(72)	64(5)	33(4)	34(3)	8(3)	2(3)	−13(3)
C(73)	58(6)	69(6)	109(8)	22(6)	−10(5)	−28(5)
C(74)	72(6)	68(6)	93(7)	15(6)	−26(5)	−29(5)
C(75)	95(8)	53(6)	112(9)	4(6)	−46(7)	−3(5)

C(76)	124(10)	98(9)	66(6)	26(6)	−8(6)	−64(8)
C(77)	59(5)	50(5)	56(5)	−5(4)	11(4)	−7(4)
C(78)	114(9)	47(5)	66(6)	−2(4)	22(6)	−12(5)
C(79)	139(10)	46(5)	55(5)	−5(4)	34(6)	12(6)
C(80)	69(6)	50(5)	53(5)	7(4)	18(4)	15(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for sh2656.

	x	y	z	U(eq)
H(3)	−1161	5142	1422	54
H(4)	−2000	4227	1557	63
H(6A)	−2297	2537	1700	100
H(6B)	−1775	2001	1879	100
H(6C)	−1942	1783	1518	100
H(8)	394	4045	1960	40
H(9)	600	5144	2353	57
H(10)	460	6742	2250	67
H(11)	105	7215	1761	69
H(12)	−132	6147	1371	48
H(14)	693	5293	1125	36
H(15)	880	5569	609	49
H(16)	265	4973	209	72
H(17)	−548	4180	323	67
H(18)	−738	3877	843	45
H(22A)	4342	1664	776	81
H(22B)	3808	1231	575	81
H(22C)	3900	1012	941	81
H(23)	4169	3438	882	49
H(24)	3393	4530	981	44
H(26)	1676	3111	471	27
H(27)	1400	3797	−13	43
H(28)	1622	5341	−124	51
H(29)	2152	6220	250	50
H(30)	2426	5592	736	36
H(32)	2855	3911	1540	35
H(33)	2724	4764	1989	46
H(34)	2012	5888	2001	54
H(35)	1485	6263	1534	52
H(36)	1630	5449	1079	32
H(40A)	766	4086	2806	136
H(40B)	504	3082	2883	136
H(40C)	294	3620	2568	136
H(39B)	823	1588	2332	60
H(40D)	421	2690	2637	50
H(41B)	1034	3980	2814	46
H(41)	1846	4109	2676	90
H(42)	2278	2940	2324	66
H(44A)	1462	−55	1631	148
H(45A)	1371	−1666	1714	66
H(46A)	1464	−2219	2248	55
H(46A)	1752	−2255	1831	103
H(46B)	1113	−2343	1928	103
H(46C)	1630	−2574	2177	103
H(47)	1566	−1129	2626	62
H(48)	1646	462	2569	61
H(50)	2421	2212	1575	45
H(51)	3418	2226	1575	45
H(52)	3970	1575	1994	73
H(53)	3542	979	2418	146
H(54)	2669	674	2362	17
H(58A)	2036	961	−156	88
H(58B)	2215	1821	70	88
H(58C)	1872	2014	−259	88
H(59)	803	2219	−210	48
H(60)	73	1803	155	49
H(62)	−255	1991	966	33
H(63)	−1282	2350	877	69
H(64)	−1826	1588	483	63
H(65)	−1394	395	207	58
H(66)	−459	−21	307	52
H(68)	506	−766	319	61
H(69)	570	−2377	424	66

H(70)	547	−2939	933	71
H(71)	419	−1867	1337	70
H(72)	368	−262	1235	53
H(73A)	−781	9	1441	96
H(73B)	−1106	328	1740	96
H(74A)	−680	−1419	1613	95
H(74B)	−1143	−1151	1856	95
H(75A)	−461	−1253	2240	107
H(75B)	12	−1395	1992	107
H(76A)	−356	261	2251	116
H(76B)	265	7	2148	116
H(77A)	1581	−1189	969	66
H(77B)	2046	−1436	1249	66
H(78A)	1969	−2419	738	90
H(78B)	2569	−2297	937	90
H(79A)	2791	−1651	467	94
H(79B)	2164	−1216	399	94
H(80A)	3041	−550	837	68
H(80B)	2632	74	603	68

Compound 33

Table 1. Crystal data and structure refinement for sh2667.

Identification code	sh2667	
Empirical formula	C69 H69 O5 S3 Y	
Formula weight	1163.33	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.687(4) Å	α = 90°.
	b = 14.686(3) Å	β = 93.56(3)°.
	c = 28.052(6) Å	γ = 90°.
Volume	7684(3) Å^3	
Z	4	
Density (calculated)	1.006 Mg/m^3	
Absorption coefficient	0.880 mm^{-1}	
F(000)	2440	
Crystal size	0.61 x 0.46 x 0.32 mm^3	
Theta range for data collection	2.33 to 28.32°.	
Index ranges	−24<=h<=24, −19<=k<=19, −36<=l<=37	
Reflections collected	68245	
Independent reflections	18377 [R(int) = 0.1499]	
Completeness to theta = 28.32°	95.9 %	
Absorption correction	None	
Max. and min. transmission	0.7661 and 0.6160	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	18377 / 2 / 703	
Goodness−of−fit on F^2	1.546	
Final R indices [I>2sigma(I)]	R1 = 0.1110, wR2 = 0.2847	
R indices (all data)	R1 = 0.2374, wR2 = 0.3113	
Largest diff. peak and hole	1.070 and −0.656 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2667. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	3606(1)	7914(1)	8687(1)	38(1)
S(1)	5595(2)	7721(2)	8146(1)	70(1)
S(2)	5614(2)	7567(2)	9498(2)	111(1)
S(3)	2191(2)	9253(2)	7872(1)	93(1)
O(1)	4121(3)	8012(4)	8045(2)	48(1)
O(2)	4128(3)	7785(4)	9361(2)	52(2)
O(3)	2502(3)	8085(4)	8667(2)	56(2)
O(4)	3839(3)	9498(4)	8770(2)	51(2)
O(5)	3618(3)	6316(3)	8627(2)	49(2)
C(1)	4339(5)	7821(6)	7585(3)	48(2)
C(2)	5155(5)	7758(5)	7603(3)	48(2)

C(3)	5639(5)	7761(5)	7255(3)	54(2)
C(4)	6379(7)	7714(6)	7421(5)	84(4)
C(5)	6443(6)	7696(6)	7922(5)	79(3)
C(6)	7125(6)	7639(9)	8219(5)	114(5)
C(7)	4127(5)	8591(6)	7229(3)	50(2)
C(8)	4043(5)	9471(5)	7392(3)	59(3)
C(9)	3882(6)	10178(7)	7075(4)	75(3)
C(10)	3816(6)	10025(7)	6593(4)	72(3)
C(11)	3919(6)	9166(7)	6432(4)	76(3)
C(12)	4071(5)	8465(6)	6736(3)	54(2)
C(13)	3960(5)	6939(5)	7419(3)	50(2)
C(14)	4356(6)	6109(6)	7370(3)	60(3)
C(15)	3971(6)	5323(6)	7248(3)	65(3)
C(16)	3193(7)	5343(7)	7169(4)	72(3)
C(17)	2828(6)	6121(8)	7215(4)	84(3)
C(18)	3236(4)	6889(5)	7360(3)	41(2)
C(19)	4291(5)	7537(6)	9847(3)	50(2)
C(20)	5101(5)	7451(6)	9939(3)	56(2)
C(21)	5487(6)	7308(6)	10365(3)	63(3)
C(22)	6239(7)	7300(7)	10350(5)	87(4)
C(23)	6413(7)	7455(10)	9794(12)	178(13)
C(24)	7024(18)	7509(14)	9784(14)	320(20)
C(25)	4035(5)	8297(6)	10169(3)	53(2)
C(26)	3781(5)	8134(6)	10615(3)	62(3)
C(27)	3568(6)	8861(8)	10906(4)	76(3)
C(28)	3613(6)	9746(8)	10741(5)	78(3)
C(29)	3860(7)	9917(7)	10308(4)	86(4)
C(30)	4053(5)	9214(5)	10030(3)	45(2)
C(31)	3830(3)	6630(3)	9929(2)	79(4)
C(32)	3088(3)	6620(3)	9853(2)	20(2)
C(33)	2707(3)	5827(4)	9930(3)	350(30)
C(34)	3068(4)	5043(3)	10084(3)	144(7)
C(35)	3810(4)	5052(3)	10160(2)	75(3)
C(36)	4191(3)	5846(4)	10083(2)	60(3)
C(37)	1758(5)	8266(6)	8637(4)	57(2)
C(38)	1572(6)	8992(7)	8260(4)	68(3)
C(39)	982(5)	9509(8)	8182(5)	75(3)
C(40)	983(8)	10079(12)	7795(5)	166(9)
C(41)	1680(8)	10056(8)	7588(5)	112(5)
C(42)	1964(10)	10619(14)	7154(7)	192(9)
C(43)	1514(5)	8604(6)	9123(4)	59(3)
C(44)	771(6)	8687(8)	9202(5)	85(4)
C(45)	574(8)	9022(10)	9648(6)	114(5)
C(46)	1082(8)	9282(12)	9987(6)	123(6)
C(47)	1776(7)	9181(10)	9895(5)	103(4)
C(48)	2024(6)	8877(7)	9471(4)	64(3)
C(49)	1364(5)	7353(7)	8488(5)	70(3)
C(50)	1216(6)	6698(8)	8841(6)	98(4)
C(51)	938(9)	5890(11)	8744(8)	135(7)
C(52)	765(9)	5695(12)	8288(11)	155(10)
C(53)	905(9)	6304(11)	7906(7)	138(7)
C(54)	3361(6)	10259(6)	8845(4)	67(3)
C(55)	1195(6)	7165(9)	8010(5)	97(4)
C(56)	3732(7)	11041(7)	8618(4)	90(4)
C(57)	4536(7)	10841(6)	8750(5)	86(4)
C(58)	4577(5)	9831(6)	8742(4)	57(2)
C(59)	4291(5)	5822(6)	8690(4)	65(3)
C(60)	4131(7)	4871(7)	8701(6)	105(5)
C(61)	3386(8)	4787(7)	8594(6)	113(5)
C(62)	3032(5)	5697(6)	8559(4)	72(3)
C(63)	973(12)	2150(17)	1421(9)	84(6)
C(64)	1525(15)	1060(20)	1007(10)	102(8)
C(65)	1435(15)	682(19)	1379(11)	107(8)
C(66)	1193(15)	820(20)	1797(11)	111(9)
C(67)	869(15)	1760(20)	1797(11)	112(9)
C(68)	1253(16)	1930(20)	1036(12)	123(10)
C(69)	1688(13)	3342(16)	3830(10)	82(7)
C(70)	1489(12)	1937(15)	4171(8)	78(6)
C(71)	1520(15)	3119(18)	4173(11)	102(8)
C(72)	1673(13)	1561(16)	3806(9)	88(7)
C(73)	223(19)	7550(20)	1694(12)	141(12)
C(74)	1874(14)	2185(19)	3382(10)	105(8)
C(75)	1854(14)	3057(19)	3520(10)	99(8)

C(76)	2118(15)	6995(19)	1176(10)	109(8)
C(77)	1382(18)	6800(20)	1677(12)	115(10)
C(78)	1550(30)	7260(40)	1378(19)	110(15)
C(79)	1163(18)	7850(20)	1142(12)	139(11)
C(80)	820(20)	6950(30)	1681(14)	127(13)

Table 3. Bond lengths [Å] and angles [°] for sh2667.

Y(1)−O(3)	2.075(6)	C(31)−C(32)	1.3900
Y(1)−O(2)	2.082(6)	C(31)−C(36)	1.3900
Y(1)−O(1)	2.098(5)	C(32)−C(33)	1.3900
Y(1)−O(5)	2.352(5)	C(33)−C(34)	1.3900
Y(1)−O(4)	2.376(5)	C(34)−C(35)	1.3900
S(1)−C(2)	1.686(9)	C(35)−C(36)	1.3900
S(1)−C(5)	1.741(12)	C(37)−C(38)	1.526(13)
S(2)−C(20)	1.621(10)	C(37)−C(43)	1.546(13)
S(2)−C(23)	1.67(2)	C(37)−C(49)	1.573(13)
S(3)−C(38)	1.682(10)	C(38)−C(39)	1.346(13)
S(3)−C(41)	1.686(13)	C(39)−C(40)	1.371(9)
O(1)−C(1)	1.407(9)	C(40)−C(41)	1.459(9)
O(2)−C(19)	1.425(10)	C(41)−C(42)	1.593(19)
O(3)−C(37)	1.414(10)	C(43)−C(48)	1.381(13)
O(4)−C(54)	1.455(10)	C(43)−C(44)	1.423(13)
O(4)−C(58)	1.470(10)	C(44)−C(45)	1.416(17)
O(5)−C(62)	1.428(10)	C(45)−C(46)	1.356(18)
O(5)−C(59)	1.453(10)	C(46)−C(47)	1.345(17)
C(1)−C(2)	1.526(12)	C(47)−C(48)	1.377(14)
C(1)−C(13)	1.535(11)	C(49)−C(55)	1.386(15)
C(1)−C(7)	1.543(12)	C(49)−C(50)	1.419(15)
C(2)−C(3)	1.372(11)	C(50)−C(51)	1.318(18)
C(3)−C(4)	1.432(15)	C(51)−C(52)	1.33(3)
C(4)−C(5)	1.404(16)	C(52)−C(53)	1.43(3)
C(5)−C(6)	1.482(16)	C(53)−C(55)	1.400(18)
C(7)−C(8)	1.382(11)	C(54)−C(56)	1.502(14)
C(7)−C(12)	1.393(12)	C(56)−C(57)	1.553(16)
C(8)−C(9)	1.388(13)	C(57)−C(58)	1.486(12)
C(9)−C(10)	1.369(14)	C(59)−C(60)	1.429(13)
C(10)−C(11)	1.358(13)	C(60)−C(61)	1.411(16)
C(11)−C(12)	1.356(12)	C(61)−C(62)	1.492(15)
C(13)−C(18)	1.355(11)	C(63)−C(67)	1.23(3)
C(13)−C(14)	1.437(12)	C(63)−C(68)	1.27(3)
C(14)−C(15)	1.392(12)	C(64)−C(65)	1.20(3)
C(15)−C(16)	1.458(14)	C(64)−C(68)	1.38(4)
C(16)−C(17)	1.340(14)	C(65)−C(66)	1.30(3)
C(17)−C(18)	1.407(12)	C(66)−C(67)	1.51(4)
C(19)−C(20)	1.527(13)	C(69)−C(75)	1.03(3)
C(19)−C(25)	1.533(11)	C(69)−C(71)	1.08(3)
C(19)−C(31)	1.611(10)	C(70)−C(72)	1.23(3)
C(20)−C(21)	1.373(12)	C(70)−C(71)	1.74(3)
C(21)−C(22)	1.408(15)	C(71)−C(75)	1.97(4)
C(22)−C(23)	1.63(3)	C(72)−C(74)	1.57(3)
C(23)−C(24)	1.15(3)	C(73)−C(80)	1.42(5)
C(25)−C(26)	1.385(12)	C(74)−C(75)	1.34(3)
C(25)−C(30)	1.402(11)	C(76)−C(78)	1.29(5)
C(26)−C(27)	1.417(12)	C(77)−C(80)	1.07(4)
C(27)−C(28)	1.384(14)	C(77)−C(78)	1.14(5)
C(28)−C(29)	1.348(15)	C(78)−C(79)	1.29(5)
C(29)−C(30)	1.357(13)	C(78)−C(80)	1.72(6)

O(3)−Y(1)−O(2)	116.4(2)	C(29)−C(30)−C(25)	124.0(9)
O(3)−Y(1)−O(1)	118.5(2)	C(32)−C(31)−C(36)	120.0
O(2)−Y(1)−O(1)	124.8(2)	C(32)−C(31)−C(19)	121.6(5)
O(3)−Y(1)−O(5)	97.7(2)	C(36)−C(31)−C(19)	118.4(5)
O(2)−Y(1)−O(5)	88.2(2)	C(33)−C(32)−C(31)	120.0
O(1)−Y(1)−O(5)	90.0(2)	C(34)−C(33)−C(32)	120.0
O(3)−Y(1)−O(4)	93.4(2)	C(35)−C(34)−C(33)	120.0
O(2)−Y(1)−O(4)	85.8(2)	C(34)−C(35)−C(36)	120.0
O(1)−Y(1)−O(4)	85.7(2)	C(35)−C(36)−C(31)	120.0
O(5)−Y(1)−O(4)	168.8(2)	O(3)−C(37)−C(38)	110.7(8)
C(2)−S(1)−C(5)	94.5(6)	O(3)−C(37)−C(43)	110.6(8)
C(20)−S(2)−C(23)	99.3(10)	C(38)−C(37)−C(43)	108.6(8)
C(38)−S(3)−C(41)	94.1(6)	O(3)−C(37)−C(49)	107.3(7)
C(1)−O(1)−Y(1)	161.6(5)	C(38)−C(37)−C(49)	109.2(8)
C(19)−O(2)−Y(1)	162.2(5)	C(43)−C(37)−C(49)	110.4(8)

C(37)−O(3)−Y(1)	175.7(6)	C(39)−C(38)−C(37)	131.0(10)
C(54)−O(4)−C(58)	109.8(6)	C(39)−C(38)−S(3)	110.8(8)
C(54)−O(4)−Y(1)	131.0(5)	C(37)−C(38)−S(3)	118.1(8)
C(58)−O(4)−Y(1)	119.2(4)	C(38)−C(39)−C(40)	115.7(12)
C(62)−O(5)−C(59)	110.5(7)	C(39)−C(40)−C(41)	110.2(12)
C(62)−O(5)−Y(1)	129.3(6)	C(40)−C(41)−C(42)	129.8(13)
C(59)−O(5)−Y(1)	120.1(5)	C(40)−C(41)−S(3)	108.9(9)
O(1)−C(1)−C(2)	109.1(7)	C(42)−C(41)−S(3)	121.3(12)
O(1)−C(1)−C(13)	107.0(6)	C(48)−C(43)−C(44)	120.2(10)
C(2)−C(1)−C(13)	113.6(7)	C(48)−C(43)−C(37)	119.2(8)
O(1)−C(1)−C(7)	111.7(7)	C(44)−C(43)−C(37)	120.5(9)
C(2)−C(1)−C(7)	106.4(6)	C(45)−C(44)−C(43)	118.5(12)
C(13)−C(1)−C(7)	109.1(7)	C(46)−C(45)−C(44)	120.5(13)
C(3)−C(2)−C(1)	132.6(8)	C(47)−C(46)−C(45)	118.4(14)
C(3)−C(2)−S(1)	109.8(7)	C(46)−C(47)−C(48)	125.6(13)
C(1)−C(2)−S(1)	117.5(6)	C(47)−C(48)−C(43)	116.7(10)
C(2)−C(3)−C(4)	115.7(10)	C(55)−C(49)−C(50)	119.8(11)
C(5)−C(4)−C(3)	110.3(10)	C(55)−C(49)−C(37)	120.1(10)
C(4)−C(5)−C(6)	125.6(12)	C(50)−C(49)−C(37)	120.0(11)
C(4)−C(5)−S(1)	109.8(9)	C(51)−C(50)−C(49)	123.8(16)
C(6)−C(5)−S(1)	124.6(11)	C(50)−C(51)−C(52)	118(2)
C(8)−C(7)−C(12)	116.6(8)	C(51)−C(52)−C(53)	122.6(18)
C(8)−C(7)−C(1)	120.1(8)	C(55)−C(53)−C(52)	119.7(17)
C(12)−C(7)−C(1)	123.0(7)	O(4)−C(54)−C(56)	102.8(8)
C(7)−C(8)−C(9)	120.9(9)	C(49)−C(55)−C(53)	116.4(14)
C(10)−C(9)−C(8)	120.8(9)	C(54)−C(56)−C(57)	102.7(9)
C(11)−C(10)−C(9)	118.4(10)	C(58)−C(57)−C(56)	103.6(8)
C(12)−C(11)−C(10)	121.6(10)	O(4)−C(58)−C(57)	106.4(8)
C(11)−C(12)−C(7)	121.6(9)	C(60)−C(59)−O(5)	108.1(8)
C(18)−C(13)−C(14)	117.3(8)	C(61)−C(60)−C(59)	106.6(10)
C(18)−C(13)−C(1)	121.4(7)	C(60)−C(61)−C(62)	111.3(10)
C(14)−C(13)−C(1)	120.9(8)	O(5)−C(62)−C(61)	103.2(9)
C(15)−C(14)−C(13)	117.7(10)	C(67)−C(63)−C(68)	135(3)
C(14)−C(15)−C(16)	121.1(9)	C(65)−C(64)−C(68)	108(3)
C(17)−C(16)−C(15)	120.7(10)	C(64)−C(65)−C(66)	142(3)
C(16)−C(17)−C(18)	116.2(11)	C(65)−C(66)−C(67)	107(3)
C(13)−C(18)−C(17)	126.6(8)	C(63)−C(67)−C(66)	110(3)
O(2)−C(19)−C(20)	109.5(7)	C(63)−C(68)−C(64)	117(3)
O(2)−C(19)−C(25)	108.8(7)	C(75)−C(69)−C(71)	138(3)
C(20)−C(19)−C(25)	107.7(7)	C(72)−C(70)−C(71)	116(2)
O(2)−C(19)−C(31)	105.3(6)	C(69)−C(71)−C(70)	108(3)
C(20)−C(19)−C(31)	116.2(7)	C(69)−C(71)−C(75)	20.3(17)
C(25)−C(19)−C(31)	109.2(7)	C(70)−C(71)−C(75)	87.9(16)
C(21)−C(20)−C(19)	128.5(9)	C(70)−C(72)−C(74)	117(2)
C(21)−C(20)−S(2)	112.2(8)	C(75)−C(74)−C(72)	109(2)
C(19)−C(20)−S(2)	119.3(7)	C(69)−C(75)−C(74)	130(3)
C(20)−C(21)−C(22)	116.5(11)	C(69)−C(75)−C(71)	21.4(19)
C(21)−C(22)−C(23)	106.7(11)	C(74)−C(75)−C(71)	109(2)
C(24)−C(23)−C(22)	107(3)	C(80)−C(77)−C(78)	102(5)
C(24)−C(23)−S(2)	147(4)	C(77)−C(78)−C(76)	115(5)
C(22)−C(23)−S(2)	105.4(9)	C(77)−C(78)−C(79)	127(5)
C(26)−C(25)−C(30)	115.7(8)	C(76)−C(78)−C(79)	115(5)
C(26)−C(25)−C(19)	122.9(8)	C(77)−C(78)−C(80)	38(3)
C(30)−C(25)−C(19)	121.4(8)	C(76)−C(78)−C(80)	147(5)
C(25)−C(26)−C(27)	120.9(9)	C(79)−C(78)−C(80)	89(4)
C(28)−C(27)−C(26)	119.3(10)	C(77)−C(80)−C(73)	154(5)
C(29)−C(28)−C(27)	120.6(10)	C(77)−C(80)−C(78)	41(3)
C(28)−C(29)−C(30)	119.5(10)	C(73)−C(80)−C(78)	120(4)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2667. The anisotropic displacement factor exponent takes the form: $-2p^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	40(1)	35(1)	38(1)	−2(1)	−1(1)	−1(1)
S(1)	69(2)	66(2)	73(2)	−5(1)	−10(1)	−1(1)
S(2)	108(3)	94(2)	130(3)	10(2)	9(3)	−7(2)
S(3)	83(2)	96(2)	99(2)	19(2)	2(2)	9(2)
O(1)	63(4)	41(3)	42(3)	−2(3)	9(3)	1(3)
O(2)	71(4)	42(3)	42(3)	−1(3)	−1(3)	3(3)
O(3)	49(3)	58(4)	61(4)	5(3)	1(3)	3(3)
O(4)	50(4)	39(3)	63(4)	−1(3)	−4(3)	4(3)

O(5)	56(4)	37(3)	54(4)	−1(3)	1(3)	−4(3)
C(1)	63(5)	40(5)	41(5)	−7(4)	15(4)	−4(4)
C(2)	59(5)	33(5)	52(5)	0(4)	5(5)	−3(4)
C(3)	54(6)	47(5)	61(6)	−5(4)	9(5)	−5(4)
C(4)	100(10)	44(6)	110(10)	−1(6)	25(8)	−8(6)
C(5)	60(7)	41(6)	136(12)	4(6)	−11(7)	−3(5)
C(6)	76(9)	94(10)	169(15)	8(9)	−8(9)	−14(7)
C(7)	58(6)	40(5)	52(6)	2(4)	12(5)	−1(4)
C(8)	88(7)	31(5)	55(6)	−2(4)	−6(5)	4(5)
C(9)	108(9)	42(5)	77(8)	−1(5)	10(7)	2(6)
C(10)	87(8)	61(7)	69(8)	15(6)	9(7)	0(6)
C(11)	114(9)	60(7)	55(7)	2(5)	3(7)	−14(6)
C(12)	78(7)	51(5)	33(5)	5(4)	−1(5)	1(5)
C(13)	75(6)	37(5)	38(5)	−6(4)	15(5)	−3(4)
C(14)	78(7)	50(6)	52(6)	1(5)	2(5)	−14(5)
C(15)	92(8)	40(5)	64(7)	−4(5)	17(6)	−2(5)
C(16)	94(9)	52(6)	69(7)	−3(5)	7(7)	0(6)
C(17)	71(8)	86(9)	93(9)	−11(7)	7(7)	−18(7)
C(18)	41(5)	27(4)	55(5)	−12(3)	3(4)	−9(3)
C(19)	70(6)	42(4)	37(5)	−5(4)	−13(5)	2(4)
C(20)	73(7)	44(5)	49(6)	−11(4)	−6(5)	7(5)
C(21)	79(7)	55(6)	51(6)	−15(4)	−24(5)	19(5)
C(22)	77(8)	60(8)	121(11)	−25(7)	−21(8)	11(6)
C(23)	44(8)	62(8)	430(40)	−67(15)	68(15)	−19(7)
C(24)	320(40)	74(13)	570(60)	30(20)	−100(40)	20(20)
C(25)	69(6)	46(5)	44(6)	−9(4)	−3(5)	−2(4)
C(26)	89(7)	48(6)	49(6)	−11(4)	2(5)	−2(5)
C(27)	92(8)	82(8)	55(7)	−16(6)	6(6)	−3(6)
C(28)	82(8)	65(7)	84(9)	−22(6)	−13(7)	13(6)
C(29)	133(11)	51(6)	71(8)	−7(6)	−14(8)	1(7)
C(30)	74(6)	26(4)	32(5)	1(3)	−8(4)	4(4)
C(31)	178(13)	25(5)	36(5)	2(4)	20(7)	17(6)
C(32)	5(3)	9(3)	43(5)	8(3)	−12(3)	−9(2)
C(33)	270(30)	690(60)	75(13)	−150(30)	−85(16)	320(40)
C(34)	191(19)	149(15)	92(12)	−36(10)	4(13)	33(14)
C(35)	87(8)	66(7)	74(8)	−12(6)	22(7)	−11(6)
C(36)	84(7)	53(6)	45(6)	−5(5)	−1(5)	−1(5)
C(37)	38(5)	60(6)	73(7)	−3(5)	−5(5)	3(4)
C(38)	80(8)	58(6)	67(7)	6(5)	5(6)	2(5)
C(39)	43(6)	94(8)	86(9)	33(7)	−4(6)	39(6)
C(40)	84(12)	230(20)	180(20)	−76(17)	−23(13)	50(13)
C(41)	175(15)	78(8)	76(9)	34(7)	−40(10)	−11(9)
C(42)	180(19)	210(20)	180(19)	106(17)	−19(15)	24(15)
C(43)	49(6)	58(6)	70(7)	1(5)	2(5)	13(5)
C(44)	58(7)	92(9)	105(10)	−20(7)	7(7)	11(6)
C(45)	77(10)	131(12)	137(14)	−7(10)	38(10)	23(9)
C(46)	86(11)	178(16)	105(12)	−45(11)	8(9)	27(11)
C(47)	87(10)	132(12)	89(10)	−17(9)	−8(8)	21(8)
C(48)	57(6)	78(7)	58(7)	−17(5)	−2(6)	14(5)
C(49)	40(5)	60(7)	110(10)	−5(6)	−4(6)	5(4)
C(50)	88(9)	59(7)	151(13)	17(8)	32(9)	0(7)
C(51)	112(13)	75(11)	220(20)	−3(12)	−1(14)	−26(9)
C(52)	88(12)	71(11)	300(30)	−45(16)	9(16)	−13(9)
C(53)	121(13)	102(12)	187(19)	−74(13)	−18(12)	−22(10)
C(54)	73(7)	35(5)	95(8)	−2(5)	21(6)	15(5)
C(55)	96(9)	84(9)	108(10)	−39(8)	−12(8)	−17(7)
C(56)	123(11)	47(6)	95(9)	−7(6)	−17(8)	0(7)
C(57)	97(9)	43(6)	121(10)	−13(6)	16(8)	−20(6)
C(58)	50(6)	49(5)	70(7)	−10(5)	−3(5)	−12(4)
C(59)	62(7)	47(6)	88(8)	−8(5)	7(6)	6(5)
C(60)	83(9)	41(6)	187(15)	−4(7)	−11(10)	5(6)
C(61)	128(13)	42(6)	173(15)	−1(8)	35(11)	−16(7)
C(62)	68(7)	51(6)	96(9)	−1(6)	−14(6)	−21(5)

Compound 34

Table 1. Crystal data and structure refinement for sh2703.

Identification code	sh2703
Empirical formula	C71 H63 N2 O3 S3 Y
Formula weight	1177.32
Temperature	150(2) K
Wavelength	0.71073 Å

Crystal system	Triclinic	
Space group	P−1	
Unit cell dimensions	a = 12.6267(13) Å	α = 97.844(5)°.
	b = 14.4783(16) Å	β = 95.208(5)°.
	c = 18.2701(19) Å	γ = 113.654(5)°.
Volume	2991.5(5) Å^3	
Z	2	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	1.129 mm^{-1}	
F(000)	1228	
Crystal size	0.77 x 0.28 x 0.27 mm^3	
Theta range for data collection	1.14 to 27.93°.	
Index ranges	−16<=h<=15, −18<=k<=19, −23<=l<=21	
Reflections collected	50050	
Independent reflections	13931 [R(int) = 0.0363]	
Completeness to theta = 27.93°	97.2 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.7533 and 0.4760	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	13931 / 0 / 682	
Goodness−of−fit on F^2	2.086	
Final R indices [I>2sigma(I)]	R1 = 0.0779, wR2 = 0.2188	
R indices (all data)	R1 = 0.1038, wR2 = 0.2267	
Largest diff. peak and hole	1.607 and −1.728 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2703. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	7674(1)	8011(1)	7133(1)	24(1)
S(1)	5810(2)	9517(2)	7015(1)	83(1)
S(2)	11356(1)	9470(1)	7123(1)	54(1)
S(3)	6113(1)	5087(1)	7220(1)	48(1)
N(1)	7314(3)	8421(3)	5878(2)	36(1)
N(2)	8248(3)	7685(3)	8394(2)	36(1)
O(1)	8060(3)	9511(2)	7648(2)	37(1)
O(2)	8987(2)	7641(2)	6757(2)	32(1)
O(3)	5960(2)	6914(2)	7043(2)	30(1)
C(1)	7929(4)	10418(3)	7870(3)	36(1)
C(2)	7099(4)	10500(4)	7247(3)	39(1)
C(3)	7299(5)	11258(5)	6844(3)	55(1)
C(4)	6359(7)	11066(6)	6267(4)	81(2)
C(5)	5332(6)	10023(7)	6298(4)	101(3)
C(6)	4353(11)	9627(10)	5839(6)	157(5)
C(7)	7415(4)	10385(3)	8614(3)	40(1)
C(8)	7706(3)	9826(2)	9156(2)	8(1)
C(9)	7246(6)	9859(6)	9840(3)	76(2)
C(10)	6626(6)	10356(6)	9991(5)	83(2)
C(11)	6361(5)	10852(5)	9508(3)	60(2)
C(12)	6718(4)	10880(4)	8811(3)	47(1)
C(13)	9125(4)	11370(4)	8027(2)	35(1)
C(14)	9244(3)	12390(2)	8361(2)	19(1)
C(15)	10335(6)	13220(5)	8444(3)	76(2)
C(16)	11279(7)	13103(6)	8276(4)	80(2)
C(17)	11183(6)	12161(5)	7988(4)	71(2)
C(18)	10120(5)	11293(4)	7861(3)	53(1)
C(19)	9869(4)	7442(3)	6473(2)	31(1)
C(20)	11050(4)	8203(3)	6930(2)	35(1)
C(21)	11981(4)	8056(4)	7235(3)	42(1)
C(22)	12925(5)	8953(4)	7629(4)	57(2)
C(23)	12756(5)	9809(5)	7628(4)	61(2)
C(24)	13533(7)	10893(5)	7967(6)	122(4)
C(25)	9754(4)	6352(3)	6561(3)	34(1)
C(26)	9319(3)	5956(3)	7173(2)	23(1)
C(27)	9281(5)	5003(4)	7281(3)	51(1)
C(28)	9691(5)	4468(4)	6806(3)	50(1)
C(29)	10137(4)	4859(4)	6198(3)	45(1)
C(30)	10169(4)	5796(4)	6072(3)	39(1)
C(31)	9812(4)	7519(4)	5644(3)	39(1)

C(32)	8740(4)	7091(4)	5160(3)	46(1)
C(33)	8583(9)	7079(7)	4439(4)	91(3)
C(34)	9573(10)	7589(6)	4125(4)	91(3)
C(35)	10697(9)	8040(5)	4560(4)	82(2)
C(36)	10812(6)	8004(4)	5321(3)	56(1)
C(37)	4802(4)	6198(3)	7012(2)	31(1)
C(38)	4825(4)	5177(3)	7128(2)	35(1)
C(39)	3928(5)	4252(4)	7149(3)	44(1)
C(40)	4275(5)	3454(4)	7232(3)	48(1)
C(41)	5462(5)	3781(4)	7289(3)	53(1)
C(42)	6172(6)	3193(6)	7387(5)	81(2)
C(43)	4236(4)	6554(3)	7635(2)	31(1)
C(44)	4877(4)	7440(3)	8176(2)	32(1)
C(45)	4354(4)	7752(4)	8738(3)	40(1)
C(46)	3190(5)	7197(4)	8783(3)	49(1)
C(47)	2546(4)	6323(4)	8246(3)	47(1)
C(48)	3037(3)	6005(3)	7688(2)	28(1)
C(49)	4110(4)	6060(4)	6231(2)	38(1)
C(50)	3612(3)	6722(4)	6077(2)	31(1)
C(51)	3067(5)	6672(6)	5375(3)	65(2)
C(52)	3055(5)	5986(6)	4804(4)	72(2)
C(53)	3565(7)	5336(5)	4920(3)	84(2)
C(54)	4081(6)	5369(4)	5623(3)	60(2)
C(55)	8169(5)	9174(4)	5649(3)	51(1)
C(56)	8073(6)	9352(4)	4920(3)	63(2)
C(57)	7106(6)	8750(5)	4425(3)	59(2)
C(58)	6225(6)	7987(5)	4650(3)	63(2)
C(59)	6362(5)	7838(4)	5381(3)	48(1)
C(60)	7521(4)	7224(4)	8844(3)	40(1)
C(61)	7889(5)	7279(5)	9605(3)	60(2)
C(62)	9037(6)	7798(6)	9883(4)	80(2)
C(63)	9817(7)	8273(6)	9432(4)	80(2)
C(64)	9368(5)	8191(4)	8677(3)	54(1)
C(65)	5346(6)	4504(5)	489(4)	70(2)
C(66)	5111(6)	4122(5)	−285(4)	70(2)
C(67)	5224(6)	5356(5)	760(4)	70(2)
C(68)	5201(14)	3238(12)	−588(9)	86(4)
C(69)	9689(12)	4228(9)	295(7)	91(3)
C(70)	8405(14)	4842(12)	−660(8)	78(4)
C(71)	8317(17)	4186(15)	−318(11)	101(5)
C(72)	10648(17)	5107(17)	241(11)	101(5)
C(73)	9100(20)	4243(16)	−6(12)	96(5)
C(74)	10710(20)	4432(17)	660(11)	116(6)

Table 3. Bond lengths [Å] and angles [°] for sh2703.

Y(1)−O(2)	2.080(3)	C(34)−C(35)	1.408(12)
Y(1)−O(3)	2.083(3)	C(35)−C(36)	1.394(8)
Y(1)−O(1)	2.086(3)	C(37)−C(38)	1.533(6)
Y(1)−N(1)	2.492(4)	C(37)−C(43)	1.534(6)
Y(1)−N(2)	2.515(4)	C(37)−C(49)	1.547(6)
S(1)−C(2)	1.645(5)	C(39)−C(40)	1.411(7)
S(1)−C(5)	1.757(10)	C(40)−C(41)	1.367(8)
S(2)−C(20)	1.694(5)	C(41)−C(42)	1.478(8)
S(2)−C(23)	1.761(6)	C(43)−C(44)	1.398(6)
S(3)−C(38)	1.679(5)	C(43)−C(48)	1.419(6)
S(3)−C(41)	1.762(6)	C(44)−C(45)	1.389(6)
N(1)−C(59)	1.327(6)	C(45)−C(46)	1.381(7)
N(1)−C(55)	1.339(6)	C(46)−C(47)	1.383(7)
N(2)−C(64)	1.318(7)	C(47)−C(48)	1.361(6)
N(2)−C(60)	1.327(6)	C(49)−C(54)	1.378(7)
O(1)−C(1)	1.399(5)	C(49)−C(50)	1.385(7)
O(2)−C(19)	1.384(5)	C(50)−C(51)	1.378(7)
O(3)−C(37)	1.403(5)	C(51)−C(52)	1.334(9)
C(1)−C(2)	1.525(7)	C(52)−C(53)	1.364(10)
C(1)−C(13)	1.551(6)	C(53)−C(54)	1.372(8)
C(1)−C(7)	1.557(6)	C(55)−C(56)	1.393(8)
C(2)−C(3)	1.357(7)	C(56)−C(57)	1.342(9)
C(3)−C(4)	1.423(9)	C(57)−C(58)	1.359(8)
C(4)−C(5)	1.559(12)	C(58)−C(59)	1.388(7)
C(5)−C(6)	1.293(12)	C(60)−C(61)	1.407(8)
C(7)−C(12)	1.384(7)	C(61)−C(62)	1.346(9)
C(7)−C(8)	1.471(6)	C(62)−C(63)	1.371(10)
C(8)−C(9)	1.427(6)	C(63)−C(64)	1.414(9)

C(9)−C(10)	1.281(10)	C(65)−C(67)	1.339(9)
C(10)−C(11)	1.311(10)	C(65)−C(66)	1.403(9)
C(11)−C(12)	1.388(8)	C(66)−C(67)#1	1.368(9)
C(13)−C(18)	1.362(7)	C(66)−C(68)	1.377(16)
C(13)−C(14)	1.461(5)	C(67)−C(66)#1	1.368(9)
C(14)−C(15)	1.396(7)	C(69)−C(73)	0.90(2)
C(15)−C(16)	1.327(10)	C(69)−C(74)	1.29(2)
C(16)−C(17)	1.346(10)	C(69)−C(72)	1.38(2)
C(17)−C(18)	1.395(8)	C(69)−C(72)#2	1.61(2)
C(19)−C(20)	1.530(6)	C(69)−C(71)	1.95(2)
C(19)−C(31)	1.531(6)	C(70)−C(71)	1.18(2)
C(19)−C(25)	1.557(6)	C(70)−C(74)#2	1.19(2)
C(20)−C(21)	1.360(6)	C(70)−C(72)#2	1.33(2)
C(21)−C(22)	1.405(7)	C(70)−C(73)	1.91(3)
C(22)−C(23)	1.339(8)	C(71)−C(73)	1.06(2)
C(23)−C(24)	1.483(9)	C(71)−C(72)#2	1.28(3)
C(25)−C(26)	1.384(6)	C(72)−C(73)#2	1.03(2)
C(25)−C(30)	1.395(6)	C(72)−C(71)#2	1.28(3)
C(26)−C(27)	1.402(6)	C(72)−C(70)#2	1.33(2)
C(27)−C(28)	1.357(8)	C(72)−C(74)	1.34(3)
C(28)−C(29)	1.380(7)	C(72)−C(69)#2	1.61(2)
C(29)−C(30)	1.392(7)	C(72)−C(72)#2	1.68(4)
C(31)−C(32)	1.399(7)	C(72)−C(73)	1.82(3)
C(31)−C(36)	1.404(7)	C(73)−C(72)#2	1.03(2)
C(32)−C(33)	1.310(9)	C(74)−C(70)#2	1.19(2)
C(33)−C(34)	1.394(12)		
C(38)−C(39)	1.373(6)		

O(2)−Y(1)−O(3)	122.14(11)	C(42)−C(41)−S(3)	121.5(5)
O(2)−Y(1)−O(1)	120.19(12)	C(44)−C(43)−C(48)	116.8(4)
O(3)−Y(1)−O(1)	117.65(12)	C(44)−C(43)−C(37)	121.5(4)
O(2)−Y(1)−N(1)	87.62(12)	C(48)−C(43)−C(37)	121.8(4)
O(3)−Y(1)−N(1)	93.26(12)	C(45)−C(44)−C(43)	120.9(4)
O(1)−Y(1)−N(1)	90.73(12)	C(46)−C(45)−C(44)	121.3(5)
O(2)−Y(1)−N(2)	88.22(12)	C(47)−C(46)−C(45)	118.2(5)
O(3)−Y(1)−N(2)	92.13(12)	C(48)−C(47)−C(46)	121.6(5)
O(1)−Y(1)−N(2)	88.11(12)	C(47)−C(48)−C(43)	121.3(4)
N(1)−Y(1)−N(2)	174.39(12)	C(54)−C(49)−C(50)	115.4(4)
C(2)−S(1)−C(5)	93.9(3)	C(54)−C(49)−C(37)	122.6(5)
C(20)−S(2)−C(23)	93.6(3)	C(50)−C(49)−C(37)	121.5(4)
C(38)−S(3)−C(41)	93.2(3)	C(51)−C(50)−C(49)	123.2(5)
C(59)−N(1)−C(55)	117.3(4)	C(52)−C(51)−C(50)	119.1(6)
C(59)−N(1)−Y(1)	122.6(3)	C(51)−C(52)−C(53)	120.0(6)
C(55)−N(1)−Y(1)	119.5(3)	C(52)−C(53)−C(54)	120.8(7)
C(64)−N(2)−C(60)	117.6(4)	C(53)−C(54)−C(49)	121.4(6)
C(64)−N(2)−Y(1)	115.0(3)	N(1)−C(55)−C(56)	122.0(5)
C(60)−N(2)−Y(1)	126.1(3)	C(57)−C(56)−C(55)	119.8(6)
C(1)−O(1)−Y(1)	160.3(3)	C(56)−C(57)−C(58)	119.0(5)
C(19)−O(2)−Y(1)	176.0(3)	C(57)−C(58)−C(59)	119.1(6)
C(37)−O(3)−Y(1)	177.5(3)	N(1)−C(59)−C(58)	122.8(5)
O(1)−C(1)−C(2)	107.6(4)	N(2)−C(60)−C(61)	123.0(5)
O(1)−C(1)−C(13)	111.5(3)	C(62)−C(61)−C(60)	118.4(6)
C(2)−C(1)−C(13)	110.9(4)	C(61)−C(62)−C(63)	120.2(7)
O(1)−C(1)−C(7)	109.7(4)	C(62)−C(63)−C(64)	117.6(7)
C(2)−C(1)−C(7)	110.5(4)	N(2)−C(64)−C(63)	123.1(6)
C(13)−C(1)−C(7)	106.6(4)	C(67)−C(65)−C(66)	120.6(7)
C(3)−C(2)−C(1)	128.6(5)	C(67)#1−C(66)−C(68)	118.3(9)
C(3)−C(2)−S(1)	116.0(4)	C(67)#1−C(66)−C(65)	119.1(7)
C(1)−C(2)−S(1)	115.4(4)	C(68)−C(66)−C(65)	122.6(9)
C(2)−C(3)−C(4)	114.3(6)	C(65)−C(67)−C(66)#1	120.3(7)
C(3)−C(4)−C(5)	108.5(6)	C(73)−C(69)−C(74)	164(2)
C(6)−C(5)−C(4)	123.5(11)	C(73)−C(69)−C(72)	104.0(18)
C(6)−C(5)−S(1)	129.3(10)	C(74)−C(69)−C(72)	60.0(13)
C(4)−C(5)−S(1)	107.2(4)	C(73)−C(69)−C(72)#2	36.3(15)
C(12)−C(7)−C(8)	117.1(4)	C(74)−C(69)−C(72)#2	127.7(16)
C(12)−C(7)−C(1)	123.7(5)	C(72)−C(69)−C(72)#2	67.7(13)
C(8)−C(7)−C(1)	119.2(4)	C(73)−C(69)−C(71)	4.6(17)
C(9)−C(8)−C(7)	116.3(5)	C(74)−C(69)−C(71)	168.3(14)
C(10)−C(9)−C(8)	123.0(8)	C(72)−C(69)−C(71)	108.3(13)
C(9)−C(10)−C(11)	120.8(8)	C(72)#2−C(69)−C(71)	40.6(9)
C(10)−C(11)−C(12)	123.6(7)	C(71)−C(70)−C(74)#2	125(2)
C(7)−C(12)−C(11)	119.1(6)	C(71)−C(70)−C(72)#2	60.8(15)
C(18)−C(13)−C(14)	116.7(4)	C(74)#2−C(70)−C(72)#2	64.0(15)

C(18)−C(13)−C(1)	121.4(4)
C(14)−C(13)−C(1)	122.0(4)
C(15)−C(14)−C(13)	118.7(5)
C(16)−C(15)−C(14)	122.2(7)
C(15)−C(16)−C(17)	119.4(7)
C(16)−C(17)−C(18)	122.3(7)
C(13)−C(18)−C(17)	120.6(5)
O(2)−C(19)−C(20)	108.9(3)
O(2)−C(19)−C(31)	109.7(3)
C(20)−C(19)−C(31)	111.5(4)
O(2)−C(19)−C(25)	110.9(3)
C(20)−C(19)−C(25)	106.3(3)
C(31)−C(19)−C(25)	109.5(3)
C(21)−C(20)−C(19)	131.1(4)
C(21)−C(20)−S(2)	109.2(4)
C(19)−C(20)−S(2)	119.7(3)
C(20)−C(21)−C(22)	114.7(5)
C(23)−C(22)−C(21)	114.0(5)
C(22)−C(23)−C(24)	130.5(6)
C(22)−C(23)−S(2)	108.5(4)
C(24)−C(23)−S(2)	121.1(5)
C(26)−C(25)−C(30)	118.7(4)
C(26)−C(25)−C(19)	119.5(4)
C(30)−C(25)−C(19)	121.7(4)
C(25)−C(26)−C(27)	119.8(4)
C(28)−C(27)−C(26)	121.3(5)
C(27)−C(28)−C(29)	119.4(5)
C(28)−C(29)−C(30)	120.4(5)
C(29)−C(30)−C(25)	120.4(5)
C(32)−C(31)−C(36)	116.0(5)
C(32)−C(31)−C(19)	121.0(4)
C(36)−C(31)−C(19)	122.9(5)
C(33)−C(32)−C(31)	126.7(7)
C(32)−C(33)−C(34)	117.1(7)
C(33)−C(34)−C(35)	120.8(7)
C(36)−C(35)−C(34)	119.3(7)
C(35)−C(36)−C(31)	119.9(6)
O(3)−C(37)−C(38)	108.1(4)
O(3)−C(37)−C(43)	110.8(3)
C(38)−C(37)−C(43)	108.5(3)
O(3)−C(37)−C(49)	108.4(3)
C(38)−C(37)−C(49)	109.9(4)
C(43)−C(37)−C(49)	111.0(4)
C(39)−C(38)−C(37)	130.6(4)
C(39)−C(38)−S(3)	110.4(4)
C(37)−C(38)−S(3)	119.0(3)
C(38)−C(39)−C(40)	114.9(5)
C(41)−C(40)−C(39)	111.9(5)
C(40)−C(41)−C(42)	128.9(6)
C(40)−C(41)−S(3)	109.7(4)
C(71)−C(70)−C(73)	29.7(11)
C(74)#2−C(70)−C(73)	95.1(15)
C(72)#2−C(70)−C(73)	31.1(11)
C(73)−C(71)−C(70)	117(2)
C(73)−C(71)−C(72)#2	51.4(15)
C(70)−C(71)−C(72)#2	65.4(15)
C(73)−C(71)−C(69)	3.8(14)
C(70)−C(71)−C(69)	120.4(16)
C(72)#2−C(71)−C(69)	55.0(14)
C(73)#2−C(72)−C(71)#2	53.5(18)
C(73)#2−C(72)−C(70)#2	107(2)
C(71)#2−C(72)−C(70)#2	53.8(13)
C(73)#2−C(72)−C(74)	160(3)
C(71)#2−C(72)−C(74)	106.8(19)
C(70)#2−C(72)−C(74)	52.9(13)
C(73)#2−C(72)−C(69)	143(2)
C(71)#2−C(72)−C(69)	163(2)
C(70)#2−C(72)−C(69)	109.5(18)
C(74)−C(72)−C(69)	56.5(13)
C(73)#2−C(72)−C(69)#2	30.9(15)
C(71)#2−C(72)−C(69)#2	84.4(17)
C(70)#2−C(72)−C(69)#2	138(2)
C(74)−C(72)−C(69)#2	169(2)
C(69)−C(72)−C(69)#2	112.3(14)
C(73)#2−C(72)−C(72)#2	81(2)
C(71)#2−C(72)−C(72)#2	134(3)
C(70)#2−C(72)−C(72)#2	172(3)
C(74)−C(72)−C(72)#2	119(2)
C(69)−C(72)−C(72)#2	62.5(14)
C(69)#2−C(72)−C(72)#2	49.8(11)
C(73)#2−C(72)−C(73)	115(2)
C(71)#2−C(72)−C(73)	168(2)
C(70)#2−C(72)−C(73)	138(2)
C(74)−C(72)−C(73)	85.0(18)
C(69)−C(72)−C(73)	28.5(9)
C(69)#2−C(72)−C(73)	83.8(11)
C(72)#2−C(72)−C(73)	34.0(10)
C(69)−C(73)−C(72)#2	113(3)
C(69)−C(73)−C(71)	172(3)
C(72)#2−C(73)−C(71)	75(2)
C(69)−C(73)−C(72)	47.5(13)
C(72)#2−C(73)−C(72)	65(2)
C(71)−C(73)−C(72)	140(3)
C(69)−C(73)−C(70)	154(2)
C(72)#2−C(73)−C(70)	41.7(16)
C(71)−C(73)−C(70)	33.5(14)
C(72)−C(73)−C(70)	106.9(16)
C(70)#2−C(74)−C(69)	126(2)
C(70)#2−C(74)−C(72)	63.0(15)
C(69)−C(74)−C(72)	63.4(14)

Symmetry transformations used to generate equivalent atoms:
#1 −x+1,−y+1,−z #2 −x+2,−y+1,−z

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for sh2703. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	24(1)	26(1)	25(1)	4(1)	5(1)	14(1)
S(1)	64(1)	83(1)	96(1)	8(1)	−5(1)	30(1)
S(2)	44(1)	33(1)	84(1)	12(1)	0(1)	17(1)
S(3)	42(1)	44(1)	57(1)	6(1)	6(1)	19(1)
N(1)	45(2)	41(2)	31(2)	11(2)	10(2)	26(2)
N(2)	38(2)	34(2)	34(2)	6(2)	0(2)	16(2)
O(1)	46(2)	31(2)	43(2)	2(1)	13(1)	24(2)
O(2)	27(2)	30(2)	44(2)	6(1)	10(1)	17(1)
O(3)	24(1)	32(2)	32(2)	6(1)	4(1)	10(1)
C(1)	38(2)	33(2)	44(3)	4(2)	16(2)	21(2)
C(2)	46(3)	38(3)	42(3)	1(2)	14(2)	26(2)
C(3)	57(3)	57(4)	49(3)	12(3)	1(3)	22(3)
C(4)	90(5)	90(5)	73(4)	3(4)	−2(4)	55(5)

C(5)	50(4)	149(7)	86(5)	−77(5)	−35(3)	63(5)
C(6)	194(12)	222(14)	105(8)	4(8)	27(8)	145(12)
C(7)	34(2)	28(2)	51(3)	−3(2)	14(2)	8(2)
C(8)	15(2)	4(1)	0(1)	−1(1)	3(1)	−2(1)
C(9)	82(5)	71(4)	40(3)	3(3)	23(3)	−4(4)
C(10)	68(5)	66(5)	89(6)	−8(4)	16(4)	7(4)
C(11)	49(3)	61(4)	59(4)	−3(3)	20(3)	13(3)
C(12)	49(3)	43(3)	49(3)	−2(2)	18(2)	19(2)
C(13)	38(2)	40(3)	31(2)	6(2)	9(2)	19(2)
C(14)	16(2)	6(2)	29(2)	−2(1)	9(1)	0(1)
C(15)	72(5)	62(4)	51(4)	3(3)	3(3)	−13(3)
C(16)	69(5)	76(5)	71(4)	13(4)	−1(4)	10(4)
C(17)	54(4)	59(4)	100(5)	24(4)	20(3)	19(3)
C(18)	40(3)	40(3)	85(4)	10(3)	24(3)	19(2)
C(19)	30(2)	29(2)	39(2)	7(2)	11(2)	18(2)
C(20)	34(2)	38(3)	37(2)	11(2)	15(2)	16(2)
C(21)	33(2)	45(3)	56(3)	11(2)	5(2)	23(2)
C(22)	40(3)	53(3)	83(4)	24(3)	2(3)	23(3)
C(23)	46(3)	51(3)	80(4)	16(3)	−2(3)	15(3)
C(24)	70(5)	53(4)	209(10)	34(5)	−50(6)	4(4)
C(25)	28(2)	31(2)	47(3)	7(2)	3(2)	17(2)
C(26)	22(2)	23(2)	29(2)	10(2)	10(2)	13(2)
C(27)	57(3)	44(3)	56(3)	21(3)	10(3)	22(3)
C(28)	55(3)	38(3)	58(3)	15(2)	5(3)	20(3)
C(29)	52(3)	39(3)	48(3)	6(2)	7(2)	24(2)
C(30)	44(3)	36(3)	46(3)	12(2)	13(2)	24(2)
C(31)	57(3)	34(2)	40(3)	6(2)	11(2)	33(2)
C(32)	44(3)	59(3)	41(3)	−16(2)	−6(2)	37(3)
C(33)	130(7)	112(7)	58(4)	−22(4)	−20(4)	96(6)
C(34)	188(10)	62(5)	50(4)	4(3)	1(5)	85(6)
C(35)	154(8)	43(3)	52(4)	18(3)	41(5)	36(4)
C(36)	75(4)	42(3)	50(3)	12(2)	25(3)	20(3)
C(37)	30(2)	29(2)	28(2)	5(2)	3(2)	6(2)
C(38)	40(2)	36(2)	25(2)	4(2)	6(2)	13(2)
C(39)	45(3)	35(3)	43(3)	4(2)	12(2)	8(2)
C(40)	57(3)	34(3)	51(3)	9(2)	17(3)	16(2)
C(41)	73(4)	55(3)	44(3)	4(2)	10(3)	42(3)
C(42)	82(5)	71(5)	108(6)	26(4)	33(4)	45(4)
C(43)	33(2)	32(2)	29(2)	8(2)	6(2)	14(2)
C(44)	30(2)	36(2)	30(2)	4(2)	2(2)	14(2)
C(45)	44(3)	43(3)	35(2)	1(2)	6(2)	22(2)
C(46)	52(3)	62(3)	47(3)	15(3)	19(2)	32(3)
C(47)	35(3)	55(3)	52(3)	11(3)	14(2)	18(2)
C(48)	19(2)	34(2)	29(2)	3(2)	3(2)	9(2)
C(49)	30(2)	41(3)	31(2)	7(2)	4(2)	2(2)
C(50)	21(2)	51(3)	26(2)	10(2)	2(2)	19(2)
C(51)	42(3)	102(5)	59(4)	37(4)	8(3)	32(3)
C(52)	48(3)	91(5)	47(3)	22(4)	−2(3)	0(3)
C(53)	133(7)	64(4)	29(3)	7(3)	−5(3)	18(5)
C(54)	99(5)	47(3)	28(2)	3(2)	−3(3)	29(3)
C(55)	71(4)	39(3)	39(3)	8(2)	10(3)	17(3)
C(56)	100(5)	44(3)	54(3)	24(3)	34(4)	31(3)
C(57)	96(5)	70(4)	32(3)	22(3)	16(3)	52(4)
C(58)	64(4)	98(5)	39(3)	29(3)	10(3)	41(4)
C(59)	42(3)	69(4)	37(3)	19(2)	6(2)	26(3)
C(60)	41(3)	44(3)	35(2)	13(2)	1(2)	17(2)

Compound 38

Table 1. Crystal data and structure refinement for sh2737.

Identification code	sh2737	
Empirical formula	C53 H49 O5 S6 Y x 0.5 C7 H8	
Formula weight	1093.26	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.598(3) Å	α = 90°.
	b = 16.935(3) Å	β = 102.22(3)°.
	c = 23.892(5) Å	γ = 90°.
Volume	5377.2(19) Å^3	
Z	4	

Density (calculated)	1.350 Mg/m^3
Absorption coefficient	1.364 mm^{-1}
F(000)	2268
Crystal size	0.40 x 0.35 x 0.23 mm^3
Theta range for data collection	2.39 to 28.19°.
Index ranges	−17<=h<=17, −22<=k<=22, −31<=l<=31
Reflections collected	55056
Independent reflections	12833 [R(int) = 0.1099]
Completeness to theta = 28.19°	97.1 %
Absorption correction	Multiscan
Max. and min. transmission	0.7444 and 0.6114
Refinement method	Full−matrix least−squares on F^2
Data / restraints / parameters	12833 / 0 / 578
Goodness−of−fit on F^2	1.138
Final R indices [I>2sigma(I)]	R1 = 0.0737, wR2 = 0.1701
R indices (all data)	R1 = 0.1420, wR2 = 0.1894
Largest diff. peak and hole	1.086 and −0.771 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2737. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	4096(1)	7526(1)	1074(1)	27(1)
S(1)	−333(1)	8191(2)	−360(1)	95(1)
S(2)	2815(1)	10988(1)	557(1)	53(1)
S(3A)	423(3)	7184(2)	2032(2)	80(1)
S(3B)	3564(6)	4412(6)	2028(4)	83(2)
S(4)	5179(2)	8208(1)	3419(1)	73(1)
S(5)	6084(2)	7009(2)	−719(1)	93(1)
S(6A)	8470(3)	8890(2)	1554(2)	79(1)
S(6B)	6440(4)	4956(4)	1842(3)	61(2)
S(6BB)	7611(8)	5055(7)	1809(5)	26(2)
S(6C)	8350(20)	8546(19)	2076(13)	82(8)
O(1)	3238(2)	8186(2)	411(2)	40(1)
O(2)	3481(2)	6973(2)	1715(1)	39(1)
O(3)	5587(2)	7294(2)	1065(2)	37(1)
O(4)	3572(2)	6404(2)	460(2)	43(1)
O(5)	4395(2)	8685(2)	1636(2)	42(1)
C(1)	2664(4)	8705(3)	17(2)	36(1)
C(2)	1546(4)	8517(3)	−19(2)	40(1)
C(3)	825(4)	8434(4)	−510(3)	60(2)
C(4)	119(5)	8211(4)	366(4)	81(2)
C(5)	1134(5)	8395(4)	484(3)	62(2)
C(6)	2898(4)	9549(3)	220(2)	35(1)
C(7)	2236(4)	10109(3)	321(2)	42(1)
C(8)	3965(4)	10608(4)	513(3)	53(2)
C(9)	3906(4)	9841(3)	335(2)	44(1)
C(10)	2917(3)	8605(3)	−592(2)	37(1)
C(11)	3344(4)	7915(4)	−751(2)	44(1)
C(12)	3572(4)	7857(4)	−1312(3)	49(1)
C(13)	3382(4)	8433(5)	−1672(3)	66(2)
C(14)	2945(5)	9110(5)	−1548(3)	70(2)
C(15)	2713(5)	9205(4)	−1006(2)	56(2)
C(16)	3368(4)	6767(3)	2271(2)	37(1)
C(17)	2290(4)	6946(3)	2345(2)	38(1)
C(18)	1508(4)	7092(4)	1869(3)	53(2)
C(27B)	457(13)	7092(12)	2465(10)	57(5)
C(28B)	959(12)	7003(10)	2887(8)	28(5)
C(19)	679(5)	7143(4)	2770(3)	26(1)
C(20)	1953(4)	6922(4)	2873(3)	54(2)
C(21)	4169(4)	7218(3)	2697(2)	39(1)
C(22)	4043(4)	7833(4)	3049(3)	52(1)
C(23)	5839(4)	7550(4)	3111(3)	64(2)
C(24)	5218(4)	7055(4)	2738(3)	55(2)
C(25)	3529(3)	5869(2)	2380(2)	41(1)
C(26)	3396(4)	5367(3)	1909(2)	61(2)
C(27A)	3498(5)	4556(3)	1990(3)	300(20)
C(28A)	3733(5)	4247(2)	2542(3)	93(4)
C(29)	3867(4)	4750(3)	3012(2)	92(3)
C(30)	3765(3)	5561(3)	2931(2)	64(2)

C(31)	6558(3)	7054(3)	1021(2)	31(1)
C(32)	6614(3)	6972(3)	378(2)	36(1)
C(33)	5849(4)	7187(4)	−60(2)	55(2)
C(34)	7212(4)	6653(4)	−507(3)	60(2)
C(35)	7428(5)	6684(5)	153(3)	79(2)
C(36)	7315(2)	7694(2)	1331(1)	34(1)
C(37)	7740(3)	8241(3)	1018(2)	51(1)
C(44B)	8382(5)	8821(3)	1301(3)	52(2)
C(43B)	8598(5)	8855(4)	1895(3)	52(2)
C(38)	8172(4)	8308(3)	2208(2)	60(2)
C(39)	7531(3)	7728(3)	1926(1)	48(1)
C(40)	6822(3)	6237(2)	1329(2)	42(1)
C(41)	6108(3)	5789(3)	1525(2)	59(2)
C(42)	6375(5)	5068(3)	1792(3)	174(9)
C(43A)	7358(5)	4794(3)	1862(3)	52(2)
C(44A)	8072(4)	5242(3)	1666(3)	52(2)
C(45)	7805(3)	5963(3)	1400(2)	73(2)
C(46)	2506(4)	6286(4)	226(3)	59(2)
C(47)	2453(5)	5746(6)	−282(5)	116(4)
C(48)	3501(5)	5472(6)	−264(4)	114(4)
C(49)	4089(4)	5731(4)	282(3)	58(2)
C(50)	3541(4)	9105(3)	1788(2)	43(1)
C(51)	3988(5)	9737(4)	2205(3)	58(2)
C(52)	4969(5)	9922(4)	2031(3)	67(2)
C(53)	5298(4)	9140(4)	1830(3)	57(2)
C(54)	227(7)	4328(6)	154(5)	99(3)
C(55)	515(11)	5266(10)	946(7)	129(5)
C(56)	−84(11)	4184(9)	−403(7)	128(5)
C(57)	340(12)	4856(11)	548(8)	145(5)

Table 3. Bond lengths [Å] and angles [°] for sh2737.

Y(1)−O(3)	2.070(3)	C(14)−C(15)	1.406(8)
Y(1)−O(1)	2.083(3)	C(16)−C(21)	1.529(7)
Y(1)−O(2)	2.112(3)	C(16)−C(17)	1.542(6)
Y(1)−O(5)	2.364(3)	C(16)−C(25)	1.549(6)
Y(1)−O(4)	2.414(3)	C(17)−C(18)	1.406(8)
S(1)−C(4)	1.715(9)	C(17)−C(20)	1.431(7)
S(1)−C(3)	1.737(6)	C(27B)−C(28B)	1.10(3)
S(2)−C(8)	1.714(6)	C(28B)−C(20)	1.366(17)
S(2)−C(7)	1.722(6)	C(19)−C(20)	1.738(9)
S(3A)−C(18)	1.610(7)	C(21)−C(22)	1.371(8)
S(3A)−C(19)	1.727(8)	C(21)−C(24)	1.435(7)
S(3B)−C(26)	1.649(11)	C(23)−C(24)	1.374(9)
S(4)−C(23)	1.694(7)	C(25)−C(26)	1.3900
S(4)−C(22)	1.730(6)	C(25)−C(30)	1.3900
S(5)−C(34)	1.626(6)	C(26)−C(27A)	1.3900
S(5)−C(33)	1.700(6)	C(27A)−C(28A)	1.3900
S(6A)−C(44B)	0.602(6)	C(28A)−C(29)	1.3900
S(6A)−C(43B)	0.801(6)	C(29)−C(30)	1.3900
S(6A)−C(37)	1.814(6)	C(31)−C(32)	1.561(7)
S(6A)−C(38)	1.962(6)	C(31)−C(36)	1.569(6)
S(6B)−S(6BB)	1.620(12)	C(31)−C(40)	1.573(6)
S(6B)−C(41)	1.620(9)	C(32)−C(33)	1.359(7)
S(6BB)−C(42)	1.673(11)	C(32)−C(35)	1.415(7)
S(6BB)−C(45)	1.871(12)	C(34)−C(35)	1.543(9)
S(6C)−C(38)	0.59(3)	C(36)−C(37)	1.3900
S(6C)−C(43B)	0.80(3)	C(36)−C(39)	1.3900
S(6C)−C(39)	1.76(3)	C(37)−C(44B)	1.3900
S(6C)−C(44B)	1.92(3)	C(44B)−C(43B)	1.3900
O(1)−C(1)	1.398(6)	C(43B)−C(38)	1.3900
O(2)−C(16)	1.414(6)	C(38)−C(39)	1.3900
O(3)−C(31)	1.406(5)	C(40)−C(41)	1.3900
O(4)−C(49)	1.450(6)	C(40)−C(45)	1.3900
O(4)−C(46)	1.453(6)	C(41)−C(42)	1.3900
O(5)−C(53)	1.441(6)	C(42)−C(43A)	1.3900
O(5)−C(50)	1.471(6)	C(43A)−C(44A)	1.3900
C(1)−C(6)	1.522(7)	C(44A)−C(45)	1.3900
C(1)−C(2)	1.537(7)	C(46)−C(47)	1.510(10)
C(1)−C(10)	1.575(7)	C(47)−C(48)	1.491(9)
C(2)−C(3)	1.367(8)	C(48)−C(49)	1.445(10)
C(2)−C(5)	1.444(8)	C(50)−C(51)	1.500(8)
C(4)−C(5)	1.384(9)	C(51)−C(52)	1.511(9)
C(6)−C(7)	1.363(7)	C(52)−C(53)	1.508(9)

C(6)−C(9)	1.428(7)
C(8)−C(9)	1.364(8)
C(10)−C(11)	1.393(7)
C(10)−C(15)	1.404(8)
C(11)−C(12)	1.441(8)
C(12)−C(13)	1.290(9)
C(13)−C(14)	1.353(10)
C(54)−C(57)	1.284(19)
C(54)−C(56)	1.332(16)
C(55)−C(57)	1.16(2)
C(55)−C(56)#1	1.60(2)
C(56)−C(55)#1	1.60(2)
C(56)−C(57)#1	1.68(2)
C(57)−C(56)#1	1.68(2)

O(3)−Y(1)−O(1)	119.03(13)
O(3)−Y(1)−O(2)	117.60(13)
O(1)−Y(1)−O(2)	123.05(13)
O(3)−Y(1)−O(5)	96.48(12)
O(1)−Y(1)−O(5)	89.30(13)
O(2)−Y(1)−O(5)	90.16(13)
O(3)−Y(1)−O(4)	90.45(12)
O(1)−Y(1)−O(4)	85.08(14)
O(2)−Y(1)−O(4)	88.89(13)
O(5)−Y(1)−O(4)	172.61(11)
C(4)−S(1)−C(3)	93.3(3)
C(8)−S(2)−C(7)	90.9(3)
C(18)−S(3A)−C(19)	104.3(4)
C(23)−S(4)−C(22)	91.9(3)
C(34)−S(5)−C(33)	97.3(3)
C(44B)−S(6A)−C(43B)	164.4(13)
C(44B)−S(6A)−C(37)	38.0(4)
C(43B)−S(6A)−C(37)	129.9(5)
C(44B)−S(6A)−C(38)	132.2(6)
C(43B)−S(6A)−C(38)	35.5(3)
C(37)−S(6A)−C(38)	94.8(2)
S(6BB)−S(6B)−C(41)	93.8(6)
S(6B)−S(6BB)−C(42)	7.9(3)
S(6B)−S(6BB)−C(45)	111.1(7)
C(42)−S(6BB)−C(45)	103.2(6)
C(38)−S(6C)−C(43B)	177(6)
C(38)−S(6C)−C(39)	43(2)
C(43B)−S(6C)−C(39)	137(3)
C(38)−S(6C)−C(44B)	141(4)
C(43B)−S(6C)−C(44B)	38.7(16)
C(39)−S(6C)−C(44B)	97.9(14)
C(1)−O(1)−Y(1)	172.7(3)
C(16)−O(2)−Y(1)	158.3(3)
C(31)−O(3)−Y(1)	173.1(3)
C(49)−O(4)−C(46)	106.5(4)
C(49)−O(4)−Y(1)	134.3(3)
C(46)−O(4)−Y(1)	119.0(3)
C(53)−O(5)−C(50)	109.0(4)
C(53)−O(5)−Y(1)	131.2(3)
C(50)−O(5)−Y(1)	119.5(3)
O(1)−C(1)−C(6)	109.0(4)
O(1)−C(1)−C(2)	108.3(4)
C(6)−C(1)−C(2)	110.5(4)
O(1)−C(1)−C(10)	110.7(4)
C(6)−C(1)−C(10)	108.8(4)
C(2)−C(1)−C(10)	109.4(4)
C(3)−C(2)−C(5)	111.4(5)
C(3)−C(2)−C(1)	126.3(5)
C(5)−C(2)−C(1)	122.4(5)
C(2)−C(3)−S(1)	111.4(5)
C(5)−C(4)−S(1)	109.7(5)
C(4)−C(5)−C(2)	114.2(6)
C(7)−C(6)−C(9)	111.6(5)
C(7)−C(6)−C(1)	127.4(5)
C(9)−C(6)−C(1)	121.0(4)
C(6)−C(7)−S(2)	112.7(4)
C(9)−C(8)−S(2)	112.5(4)
C(8)−C(9)−C(6)	112.4(5)
C(11)−C(10)−C(15)	116.5(5)
C(11)−C(10)−C(1)	121.8(5)
C(15)−C(10)−C(1)	121.7(5)
C(10)−C(11)−C(12)	119.7(6)
C(13)−C(12)−C(11)	121.1(6)
C(12)−C(13)−C(14)	122.0(6)
C(13)−C(14)−C(15)	119.6(7)
C(24)−C(21)−C(16)	120.5(5)
C(21)−C(22)−S(4)	112.2(4)
C(24)−C(23)−S(4)	111.9(4)
C(23)−C(24)−C(21)	113.1(6)
C(26)−C(25)−C(30)	120.0
C(26)−C(25)−C(16)	118.4(3)
C(30)−C(25)−C(16)	121.6(3)
C(27A)−C(26)−C(25)	120.0
C(27A)−C(26)−S(3B)	2.6(4)
C(25)−C(26)−S(3B)	118.1(4)
C(26)−C(27A)−C(28A)	120.0
C(29)−C(28A)−C(27A)	120.0
C(28A)−C(29)−C(30)	120.0
C(29)−C(30)−C(25)	120.0
O(3)−C(31)−C(32)	110.0(4)
O(3)−C(31)−C(36)	107.3(4)
C(32)−C(31)−C(36)	111.2(3)
O(3)−C(31)−C(40)	110.2(3)
C(32)−C(31)−C(40)	109.1(4)
C(36)−C(31)−C(40)	109.0(3)
C(33)−C(32)−C(35)	109.5(5)
C(33)−C(32)−C(31)	122.9(4)
C(35)−C(32)−C(31)	127.6(5)
C(32)−C(33)−S(5)	113.7(4)
C(35)−C(34)−S(5)	105.6(4)
C(32)−C(35)−C(34)	113.9(5)
C(37)−C(36)−C(39)	120.0
C(37)−C(36)−C(31)	120.9(3)
C(39)−C(36)−C(31)	119.1(3)
C(44B)−C(37)−C(36)	120.0
C(44B)−C(37)−S(6A)	15.47(19)
C(36)−C(37)−S(6A)	104.64(19)
S(6A)−C(44B)−C(37)	126.5(5)
S(6A)−C(44B)−C(43B)	8.9(7)
C(37)−C(44B)−C(43B)	120.0
S(6A)−C(44B)−S(6C)	28.3(10)
C(37)−C(44B)−S(6C)	98.9(9)
C(43B)−C(44B)−S(6C)	21.1(9)
S(6C)−C(43B)−S(6A)	125(2)
S(6C)−C(43B)−C(38)	1(3)
S(6A)−C(43B)−C(38)	124.9(4)
S(6C)−C(43B)−C(44B)	120(2)
S(6A)−C(43B)−C(44B)	6.7(6)
C(38)−C(43B)−C(44B)	120.0
S(6C)−C(38)−C(43B)	1(4)
S(6C)−C(38)−C(39)	120(3)
C(43B)−C(38)−C(39)	120.0
S(6C)−C(38)−S(6A)	20(3)
C(43B)−C(38)−S(6A)	19.54(16)
C(39)−C(38)−S(6A)	100.53(16)
C(38)−C(39)−C(36)	120.0
C(38)−C(39)−S(6C)	16.8(10)
C(36)−C(39)−S(6C)	103.2(10)
C(41)−C(40)−C(45)	120.0
C(41)−C(40)−C(31)	122.0(3)
C(45)−C(40)−C(31)	118.0(3)
C(40)−C(41)−C(42)	120.0
C(40)−C(41)−S(6B)	119.1(3)
C(42)−C(41)−S(6B)	1.1(4)
C(43A)−C(42)−C(41)	120.0
C(43A)−C(42)−S(6BB)	19.6(4)
C(41)−C(42)−S(6BB)	100.8(4)
C(44A)−C(43A)−C(42)	120.0
C(45)−C(44A)−C(43A)	120.0
C(44A)−C(45)−C(40)	120.0

C(10)−C(15)−C(14)	121.1(6)	C(44A)−C(45)−S(6BB)	24.5(3)
O(2)−C(16)−C(21)	107.4(4)	C(40)−C(45)−S(6BB)	95.7(3)
O(2)−C(16)−C(17)	110.7(4)	O(4)−C(46)−C(47)	105.5(5)
C(21)−C(16)−C(17)	112.7(4)	C(48)−C(47)−C(46)	106.4(6)
O(2)−C(16)−C(25)	111.1(4)	C(49)−C(48)−C(47)	106.0(6)
C(21)−C(16)−C(25)	108.8(4)	C(48)−C(49)−O(4)	107.1(5)
C(17)−C(16)−C(25)	106.1(4)	O(5)−C(50)−C(51)	106.2(4)
C(18)−C(17)−C(20)	112.9(5)	C(50)−C(51)−C(52)	102.9(5)
C(18)−C(17)−C(16)	121.1(5)	C(53)−C(52)−C(51)	104.1(5)
C(20)−C(17)−C(16)	125.8(5)	O(5)−C(53)−C(52)	106.3(5)
C(17)−C(18)−S(3A)	113.4(5)	C(57)−C(54)−C(56)	145.4(14)
C(27B)−C(28B)−C(20)	114.5(17)	C(57)−C(55)−C(56)#1	73.1(13)
S(3A)−C(19)−C(20)	97.6(3)	C(54)−C(56)−C(55)#1	133.4(14)
C(28B)−C(20)−C(17)	121.5(9)	C(54)−C(56)−C(57)#1	92.2(12)
C(28B)−C(20)−C(19)	11.5(8)	C(55)#1−C(56)−C(57)#1	41.3(8)
C(17)−C(20)−C(19)	111.4(5)	C(55)−C(57)−C(54)	172(2)
C(22)−C(21)−C(24)	110.8(5)	C(55)−C(57)−C(56)#1	65.7(13)
C(22)−C(21)−C(16)	128.5(5)	C(54)−C(57)−C(56)#1	122.4(15)

Symmetry transformations used to generate equivalent atoms:
#1 −x,−y+1,−z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2737. The anisotropic displacement factor exponent takes the form: −2□^{2}[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	25(1)	27(1)	29(1)	0(1)	8(1)	2(1)
S(1)	44(1)	114(2)	127(2)	−29(2)	17(1)	−5(1)
S(2)	68(1)	40(1)	52(1)	−4(1)	11(1)	3(1)
S(4)	78(1)	70(1)	59(1)	−6(1)	−9(1)	−12(1)
S(5)	89(1)	131(2)	55(1)	−4(1)	5(1)	−11(1)
O(1)	45(2)	37(2)	36(2)	4(2)	3(2)	8(2)
O(2)	43(2)	44(2)	31(2)	6(2)	10(2)	−8(2)
O(3)	24(1)	43(2)	46(2)	0(2)	8(1)	4(1)
O(4)	39(2)	35(2)	55(2)	−16(2)	10(2)	−3(2)
O(5)	37(2)	33(2)	54(2)	−10(2)	9(2)	−2(2)
C(1)	37(3)	38(3)	32(3)	6(2)	4(2)	6(2)
C(2)	38(3)	33(3)	49(3)	−2(2)	10(2)	4(2)
C(3)	37(3)	81(5)	59(4)	−10(4)	7(3)	3(3)
C(4)	70(4)	76(5)	116(7)	−3(5)	66(5)	−6(4)
C(5)	61(4)	70(4)	61(4)	−1(4)	27(3)	−8(3)
C(6)	43(3)	35(3)	26(2)	5(2)	8(2)	2(2)
C(7)	44(3)	39(3)	43(3)	2(3)	8(2)	3(2)
C(8)	56(3)	50(4)	49(3)	2(3)	5(3)	−10(3)
C(9)	45(3)	45(3)	43(3)	1(3)	10(2)	0(2)
C(10)	31(2)	43(3)	40(3)	−2(2)	9(2)	2(2)
C(11)	32(2)	54(3)	42(3)	−8(3)	0(2)	9(2)
C(12)	31(3)	65(4)	48(3)	−25(3)	5(2)	4(3)
C(13)	43(3)	104(6)	57(4)	−22(4)	24(3)	−21(4)
C(14)	83(5)	88(6)	39(3)	6(4)	15(3)	−11(4)
C(15)	79(4)	54(4)	37(3)	8(3)	17(3)	9(3)
C(16)	40(3)	34(3)	38(3)	2(2)	15(2)	−1(2)
C(17)	35(2)	33(3)	49(3)	5(2)	16(2)	0(2)
C(18)	46(3)	52(4)	57(4)	−3(3)	1(3)	0(3)
C(19)	20(3)	31(3)	31(4)	5(3)	14(3)	−1(3)
C(20)	56(3)	58(4)	56(4)	8(3)	30(3)	−2(3)
C(21)	43(3)	43(3)	32(3)	8(2)	7(2)	1(2)
C(22)	58(3)	48(3)	48(3)	2(3)	7(3)	−1(3)
C(23)	46(3)	86(5)	54(3)	9(4)	−4(3)	−3(4)
C(24)	45(3)	68(4)	49(4)	0(3)	7(3)	−2(3)
C(25)	36(3)	35(3)	57(3)	6(3)	19(2)	−1(2)
C(26)	72(4)	40(4)	76(5)	−6(3)	28(4)	−6(3)
C(27A)	180(20)	160(20)	610(70)	−160(30)	180(30)	−52(17)
C(28A)	58(6)	41(5)	183(15)	15(7)	35(7)	13(4)
C(29)	56(4)	73(5)	144(8)	62(6)	14(5)	10(4)
C(30)	55(4)	65(4)	70(4)	34(4)	9(3)	7(3)
C(31)	23(2)	38(3)	29(2)	1(2)	2(2)	4(2)
C(32)	34(2)	39(3)	34(3)	−2(2)	2(2)	1(2)
C(33)	36(3)	86(5)	40(3)	8(3)	3(2)	0(3)
C(34)	56(3)	88(5)	43(3)	−10(3)	27(3)	21(3)
C(35)	61(4)	121(7)	55(4)	−16(4)	9(3)	44(4)

C(36)	25(2)	38(3)	38(3)	−2(2)	4(2)	6(2)
C(37)	38(3)	50(4)	61(4)	9(3)	5(3)	−3(2)
C(38)	61(4)	53(5)	60(5)	−8(4)	2(4)	−4(3)
C(39)	49(3)	55(4)	37(3)	−8(3)	3(2)	1(3)
C(40)	48(3)	39(3)	38(3)	−4(2)	6(2)	−1(2)
C(41)	87(4)	45(4)	41(3)	9(3)	5(3)	−13(3)
C(42)	330(20)	40(6)	99(9)	32(5)	−69(9)	−23(8)
C(45)	73(4)	60(4)	68(4)	−18(4)	−26(3)	35(3)
C(46)	39(3)	57(4)	81(5)	−24(4)	8(3)	−8(3)
C(47)	45(4)	126(8)	166(9)	−101(7)	−1(5)	3(4)
C(48)	65(5)	122(8)	141(8)	−104(7)	−8(5)	13(5)
C(49)	52(3)	42(3)	78(5)	−23(3)	8(3)	8(3)
C(50)	47(3)	39(3)	44(3)	−8(3)	10(2)	7(2)
C(51)	75(4)	43(3)	55(4)	−9(3)	11(3)	8(3)
C(52)	80(5)	46(4)	64(4)	−16(3)	−9(3)	−10(3)
C(53)	40(3)	53(4)	71(4)	−15(3)	−2(3)	−7(3)

Compound <u>43</u>

Table 1. Crystal data and structure refinement for sh2698.

Identification code	sh2698	
Empirical formula	C67 H71 Nd O7 S3	
Formula weight	1228.66	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = 14.5665(6) Å	α = 90°.
	b = 14.5665(6) Å	β = 90°.
	c = 15.9334(7) Å	γ = 120°.
Volume	2927.9(2) Å^3	
Z	2	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	1.048 mm^{-1}	
F(000)	1274	
Crystal size	0.49 x 0.43 x 0.20 mm^3	
Theta range for data collection	1.61 to 38.88°.	
Index ranges	−25<=h<=25, −25<=k<=25, −28<=l<=28	
Reflections collected	142021	
Independent reflections	11239 [R(int) = 0.0313]	
Completeness to theta = 38.88°	99.7 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8178 and 0.6267	
Refinement method	Full−matrix least−squares on F^2	
Data / restraints / parameters	11239 / 1 / 225	
Goodness−of−fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1254	
R indices (all data)	R1 = 0.0521, wR2 = 0.1321	
Absolute structure parameter	0.010(18)	
Largest diff. peak and hole	1.214 and −0.699 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2698. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nd(1)	3333	6667	7496(1)	25(1)
O(1)	2948(2)	5177(1)	8107(1)	37(1)
O(2)	3630(3)	8065(2)	6354(2)	48(1)
C(1)	2812(2)	4275(2)	8522(2)	34(1)
C(2)	2712(5)	4358(3)	9468(3)	72(2)
C(3)	2337(8)	3560(8)	10031(5)	100(3)
C(4)	2610(5)	4135(4)	11088(2)	66(1)
S(1A)	2249(7)	4995(7)	10800(5)	130(2)
C(5A)	2343(5)	5038(5)	9753(4)	48(1)
S(1B)	3665(10)	5468(9)	10782(7)	130(2)
C(5B)	3655(7)	5415(7)	9878(5)	48(1)
C(7)	1764(3)	3331(2)	8181(3)	47(1)
C(8)	797(5)	3176(9)	8436(6)	112(4)

C(9)	−172(5)	2313(15)	8009(12)	206(11)
C(10)	−150(7)	1864(6)	7633(10)	133(6)
C(11)	714(7)	1903(5)	7255(9)	145(5)
C(12)	1723(5)	2670(5)	7585(6)	105(3)
C(13)	3758(2)	4098(2)	8369(2)	43(1)
C(14)	4679(2)	4905(3)	8010(4)	110(3)
C(15)	5553(3)	4774(5)	7895(5)	241(15)
C(16)	5506(3)	3835(5)	8139(5)	115(3)
C(17)	4585(3)	3028(3)	8498(4)	91(2)
C(18)	3711(3)	3159(2)	8613(3)	68(1)
S(1C)	5687(9)	4760(9)	8201(6)	81(2)
S(1D)	5511(6)	4212(6)	7824(4)	61(1)
C(19)	3095(10)	8667(9)	6341(5)	104(3)
C(20)	3353(7)	9249(8)	5552(5)	106(4)
C(21)	4193(17)	9238(15)	5264(12)	307(16)
C(22)	4418(7)	8498(6)	5734(6)	107(3)
C(23)	447(17)	1077(14)	5079(12)	163(5)
C(24)	560(16)	520(17)	4350(14)	181(8)
C(25)	735(19)	470(20)	5444(17)	205(8)

Table 3. Bond lengths [Å] and angles [°] for sh2698.

Nd(1)−O(1)#1	2.1808(18)	C(14)−C(15)	1.3900
Nd(1)−O(1)	2.1808(18)	C(14)−S(1C)	1.614(12)
Nd(1)−O(1)#2	2.1809(17)	C(14)−S(1D)	1.950(7)
Nd(1)−O(2)#2	2.601(2)	C(15)−S(1C)	0.529(13)
Nd(1)−O(2)	2.601(2)	C(15)−S(1D)	0.798(9)
Nd(1)−O(2)#1	2.601(2)	C(15)−C(16)	1.3900
O(1)−C(1)	1.393(3)	C(16)−S(1D)	0.741(8)
O(2)−C(22)	1.402(6)	C(16)−S(1C)	1.240(13)
O(2)−C(19)	1.435(8)	C(16)−C(17)	1.3900
C(1)−C(2)	1.526(5)	C(17)−C(18)	1.3900
C(1)−C(13)	1.543(3)	C(17)−S(1D)	1.903(8)
C(1)−C(7)	1.555(4)	C(17)−S(1C)	2.262(13)
C(2)−C(3)	1.349(7)	S(1C)−S(1D)	0.926(11)
C(2)−C(5A)	1.417(8)	C(19)−C(20)	1.456(9)
C(2)−C(5B)	1.602(10)	C(20)−C(21)	1.314(14)
C(3)−C(4)	1.835(12)	C(21)−C(22)	1.478(12)
C(4)−S(1A)	1.648(10)	C(23)−C(25)	1.29(3)
C(4)−S(1B)	1.840(13)	C(23)−C(25)#3	1.40(3)
S(1A)−C(5A)	1.673(11)	C(23)−C(24)	1.47(3)
S(1B)−C(5B)	1.442(13)	C(23)−C(24)#3	1.87(3)
C(7)−C(12)	1.332(7)	C(24)−C(24)#4	1.36(3)
C(7)−C(8)	1.371(8)	C(24)−C(24)#3	1.36(3)
C(8)−C(9)	1.50(2)	C(24)−C(25)	1.77(3)
C(9)−C(10)	0.90(3)	C(24)−C(23)#4	1.87(3)
C(10)−C(11)	1.371(19)	C(25)−C(23)#4	1.40(3)
C(11)−C(12)	1.429(8)	C(25)−C(25)#4	1.63(4)
C(13)−C(14)	1.3900	C(25)−C(25)#3	1.63(4)
C(13)−C(18)	1.3900		

O(1)#1−Nd(1)−O(1)	101.57(7)	S(1D)−C(16)−C(17)	123.7(7)
O(1)#1−Nd(1)−O(1)#2	101.57(7)	S(1C)−C(16)−C(17)	118.6(6)
O(1)−Nd(1)−O(1)#2	101.57(7)	S(1D)−C(16)−C(15)	26.5(8)
O(1)#1−Nd(1)−O(2)#2	88.06(9)	S(1C)−C(16)−C(15)	22.3(6)
O(1)−Nd(1)−O(2)#2	91.17(9)	C(17)−C(16)−C(15)	120.0
O(1)#2−Nd(1)−O(2)#2	162.02(8)	C(16)−C(17)−C(18)	120.0
O(1)#1−Nd(1)−O(2)	91.17(9)	C(16)−C(17)−S(1D)	18.9(3)
O(1)−Nd(1)−O(2)	162.02(9)	C(18)−C(17)−S(1D)	103.5(2)
O(1)#2−Nd(1)−O(2)	88.05(9)	C(16)−C(17)−S(1C)	28.8(3)
O(2)#2−Nd(1)−O(2)	76.48(10)	C(18)−C(17)−S(1C)	93.6(3)
O(1)#1−Nd(1)−O(2)#1	162.02(9)	S(1D)−C(17)−S(1C)	23.8(3)
O(1)−Nd(1)−O(2)#1	88.06(9)	C(17)−C(18)−C(13)	120.0
O(1)#2−Nd(1)−O(2)#1	91.17(9)	C(15)−S(1C)−S(1D)	59.3(13)
O(2)#2−Nd(1)−O(2)#1	76.48(10)	C(15)−S(1C)−C(16)	95.0(17)
O(2)−Nd(1)−O(2)#1	76.48(10)	S(1D)−S(1C)−C(16)	36.5(7)
C(1)−O(1)−Nd(1)	174.1(2)	C(15)−S(1C)−C(14)	56.1(11)
C(22)−O(2)−C(19)	106.7(4)	S(1D)−S(1C)−C(14)	96.5(9)
C(22)−O(2)−Nd(1)	128.5(3)	C(16)−S(1C)−C(14)	114.5(8)
C(19)−O(2)−Nd(1)	124.1(3)	C(15)−S(1C)−C(17)	99.6(15)
O(1)−C(1)−C(2)	111.6(2)	S(1D)−S(1C)−C(17)	55.9(7)
O(1)−C(1)−C(13)	111.4(2)	C(16)−S(1C)−C(17)	32.7(3)
C(2)−C(1)−C(13)	107.4(3)	C(14)−S(1C)−C(17)	90.1(5)
O(1)−C(1)−C(7)	106.4(2)	C(16)−S(1D)−C(15)	129.1(14)

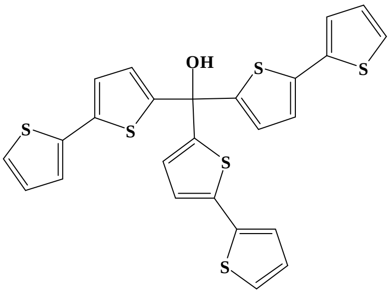
C(2)−C(1)−C(7)	108.9(3)	C(16)−S(1D)−S(1C)	95.4(11)
C(13)−C(1)−C(7)	111.2(2)	C(15)−S(1D)−S(1C)	34.7(9)
C(3)−C(2)−C(5A)	105.0(6)	C(16)−S(1D)−C(17)	37.4(5)
C(3)−C(2)−C(1)	127.0(6)	C(15)−S(1D)−C(17)	120.3(7)
C(5A)−C(2)−C(1)	117.2(4)	S(1C)−S(1D)−C(17)	100.4(8)
C(3)−C(2)−C(5B)	109.9(6)	C(16)−S(1D)−C(14)	120.1(8)
C(5A)−C(2)−C(5B)	68.9(4)	C(15)−S(1D)−C(14)	36.4(4)
C(1)−C(2)−C(5B)	114.1(4)	S(1C)−S(1D)−C(14)	55.3(8)
C(2)−C(3)−C(4)	108.3(7)	C(17)−S(1D)−C(14)	92.4(3)
S(1A)−C(4)−C(3)	90.7(4)	O(2)−C(19)−C(20)	107.9(6)
S(1A)−C(4)−S(1B)	62.6(5)	C(21)−C(20)−C(19)	105.4(7)
C(3)−C(4)−S(1B)	96.6(4)	C(20)−C(21)−C(22)	112.2(5)
C(4)−S(1A)−C(5A)	104.8(6)	O(2)−C(22)−C(21)	104.8(6)
C(2)−C(5A)−S(1A)	110.2(5)	C(25)−C(23)−C(25)#3	75(2)
C(5B)−S(1B)−C(4)	103.2(7)	C(25)−C(23)−C(24)	79.4(18)
S(1B)−C(5B)−C(2)	116.1(7)	C(25)#3−C(23)−C(24)	100.6(19)
C(12)−C(7)−C(8)	114.9(6)	C(25)−C(23)−C(24)#3	95.8(19)
C(12)−C(7)−C(1)	123.9(4)	C(25)#3−C(23)−C(24)#3	63.6(16)
C(8)−C(7)−C(1)	121.1(6)	C(24)−C(23)−C(24)#3	46.4(15)
C(7)−C(8)−C(9)	117.4(12)	C(24)#4−C(24)−C(24)#3	59.998(5)
C(10)−C(9)−C(8)	123.3(11)	C(24)#4−C(24)−C(23)	116.8(12)
C(9)−C(10)−C(11)	128.9(9)	C(24)#3−C(24)−C(23)	82.2(18)
C(10)−C(11)−C(12)	115.7(8)	C(24)#4−C(24)−C(25)	88.7(12)
C(7)−C(12)−C(11)	119.0(7)	C(24)#3−C(24)−C(25)	97.6(11)
C(14)−C(13)−C(18)	120.0	C(23)−C(24)−C(25)	45.6(12)
C(14)−C(13)−C(1)	119.21(19)	C(24)#4−C(24)−C(23)#4	51.4(13)
C(18)−C(13)−C(1)	120.75(19)	C(24)#3−C(24)−C(23)#4	95.6(13)
C(13)−C(14)−C(15)	120.0	C(23)−C(24)−C(23)#4	89.3(18)
C(13)−C(14)−S(1C)	111.6(4)	C(25)−C(24)−C(23)#4	45.2(13)
C(15)−C(14)−S(1C)	18.4(5)	C(23)−C(25)−C(23)#4	123(3)
C(13)−C(14)−S(1D)	102.2(2)	C(23)−C(25)−C(25)#4	108.7(18)
C(15)−C(14)−S(1D)	19.9(3)	C(23)#4−C(25)−C(25)#4	49.5(18)
S(1C)−C(14)−S(1D)	28.2(4)	C(23)−C(25)−C(25)#3	56(2)
S(1C)−C(15)−S(1D)	86.0(14)	C(23)#4−C(25)−C(25)#3	103.1(17)
S(1C)−C(15)−C(16)	62.7(14)	C(25)#4−C(25)−C(25)#3	60.003(4)
S(1D)−C(15)−C(16)	24.4(7)	C(23)−C(25)−C(24)	55.0(15)
S(1C)−C(15)−C(14)	105.4(13)	C(23)#4−C(25)−C(24)	71.2(18)
S(1D)−C(15)−C(14)	123.7(6)	C(25)#4−C(25)−C(24)	88.5(10)
C(16)−C(15)−C(14)	120.0	C(25)#3−C(25)−C(24)	81.1(12)
S(1D)−C(16)−S(1C)	48.1(7)		

Symmetry transformations used to generate equivalent atoms:
#1 −y+1,x−y+1,z #2 −x+y,−x+1,z #3 −y,x−y,z
#4 −x+y,−x,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for sh2698. The anisotropic displacement factor exponent takes the form: −2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nd(1)	23(1)	23(1)	29(1)	0	0	12(1)
O(1)	46(1)	23(1)	41(1)	4(1)	6(1)	17(1)
O(2)	64(1)	41(1)	39(1)	9(1)	−2(1)	26(1)
C(1)	38(1)	21(1)	47(1)	6(1)	8(1)	16(1)
C(2)	137(5)	48(2)	46(2)	16(1)	22(2)	58(3)
C(3)	116(6)	111(5)	78(4)	55(4)	19(4)	60(5)
C(4)	95(3)	67(2)	40(1)	25(2)	11(2)	43(2)
C(7)	34(1)	29(1)	77(2)	9(1)	−1(1)	15(1)
C(8)	46(2)	184(9)	112(6)	65(6)	19(3)	61(4)
C(9)	26(2)	286(18)	261(17)	213(16)	32(5)	44(5)
C(10)	74(5)	53(3)	229(13)	25(4)	−80(7)	0(3)
C(11)	121(6)	58(3)	276(13)	−81(5)	−117(8)	60(4)
C(12)	71(3)	69(3)	199(8)	−79(4)	−76(4)	53(3)
C(13)	34(1)	38(1)	56(2)	−5(1)	−11(1)	17(1)
C(14)	34(2)	119(5)	177(8)	88(6)	17(3)	38(2)
C(15)	52(4)	158(11)	530(40)	143(18)	94(11)	61(6)
C(16)	87(5)	88(5)	185(10)	9(6)	−20(6)	55(4)
C(17)	79(4)	72(3)	148(7)	−30(4)	−42(4)	56(3)
C(18)	64(3)	39(1)	109(4)	−10(2)	−8(3)	31(2)
C(19)	196(9)	124(6)	55(3)	32(3)	29(4)	126(7)
C(20)	176(10)	117(6)	71(4)	53(4)	32(4)	108(7)
C(21)	440(30)	320(20)	360(20)	310(20)	350(20)	340(20)
C(22)	115(5)	79(4)	145(6)	71(4)	79(5)	61(4)

Compounds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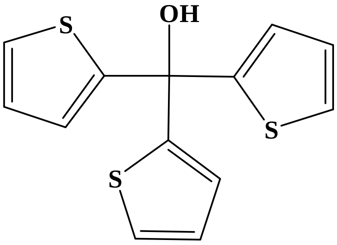
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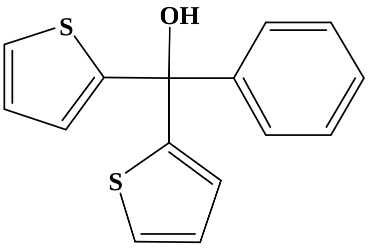
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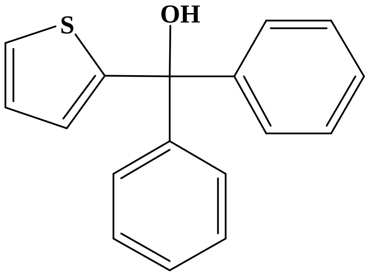
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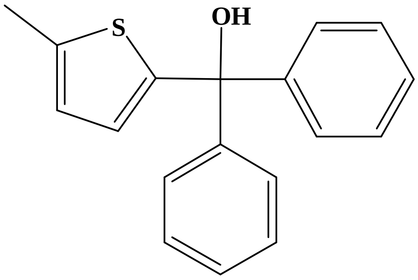
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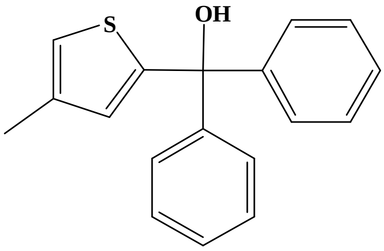
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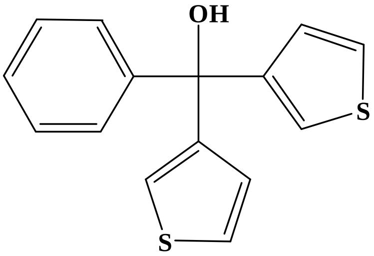
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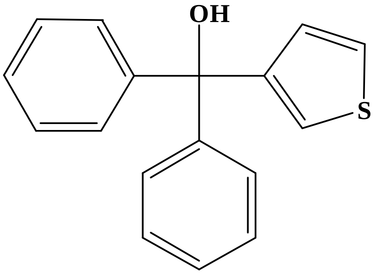
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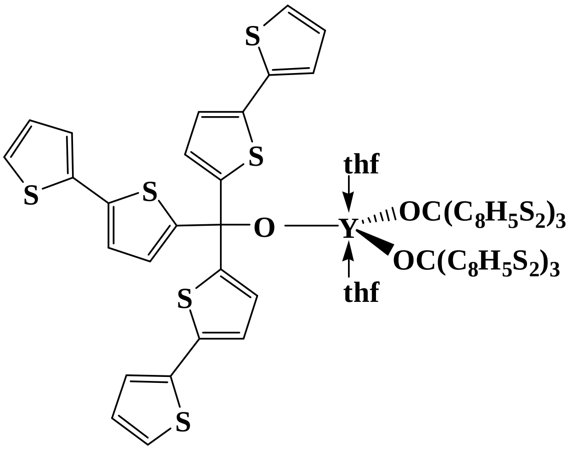
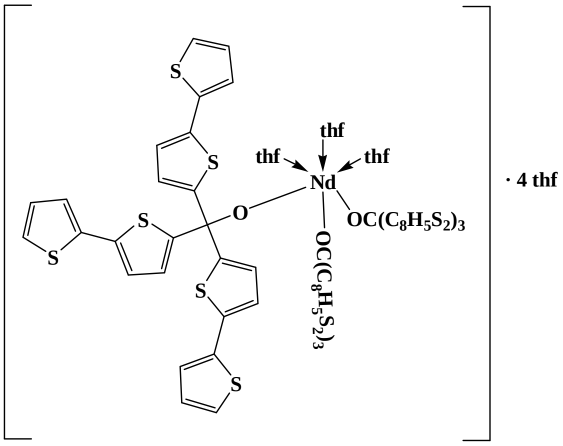
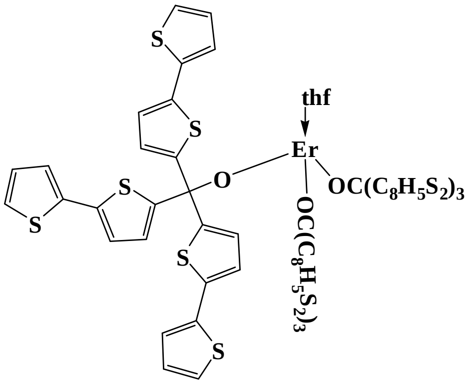

S
S
S
S
S
S
O
Y
thf
thf
OC(C8H5S2)3
OC(C8H5S2)3

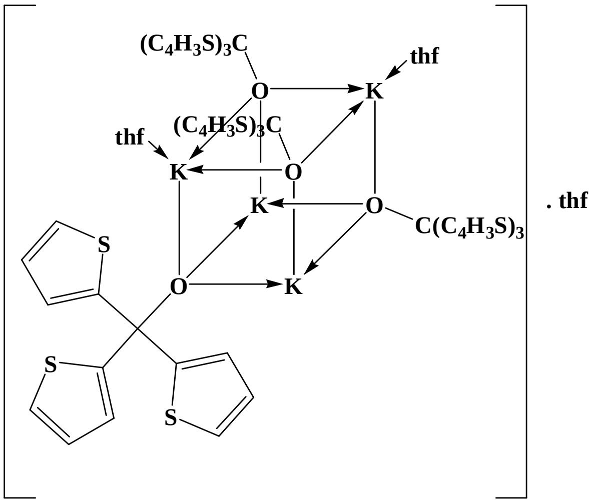
9


S
S
S
S
S
S
O
Nd
thf
thf
thf
OC(C8H5S2)3
OC(C8H5S2)3
· 4 thf

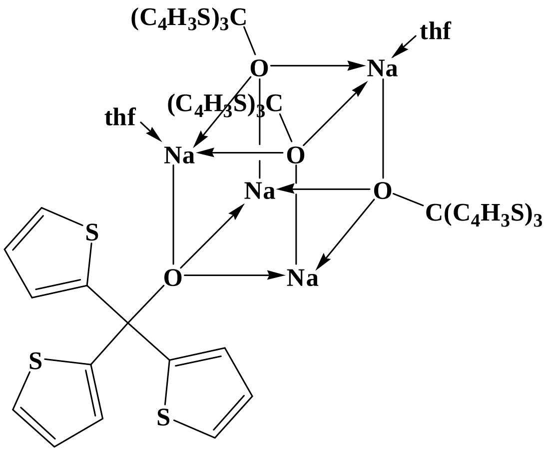
10


S
S
S
S
S
S
O
Er
thf
OC(C8H5S2)3
OC(C8H5S2)3

11


(C4H3S)3C
(C4H3S)3C
C(C4H3S)3
thf
thf
O
O
O
O
K
K
K
K
S
S
S
. thf

12


(C4H3S)3C
(C4H3S)3C
C(C4H3S)3
thf
thf
O
O
O
O
Na
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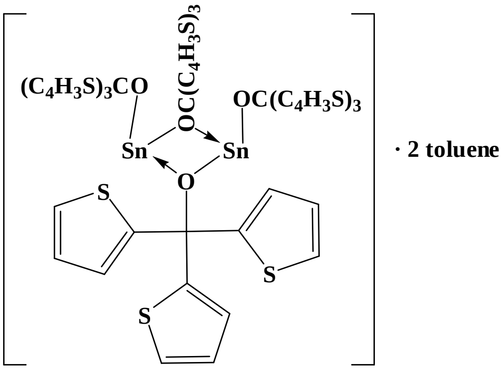
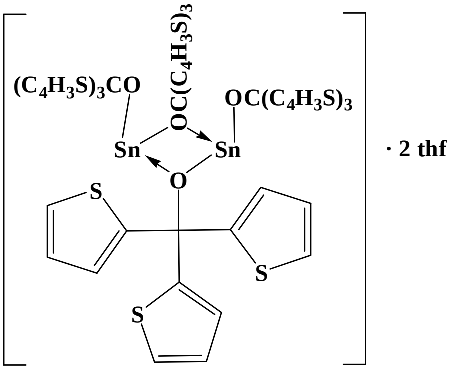
Na
Na
S
S
S

13



14a



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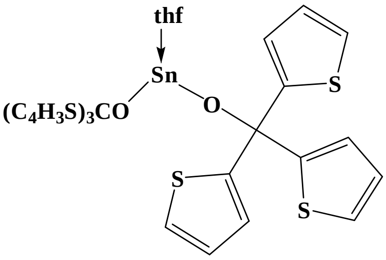

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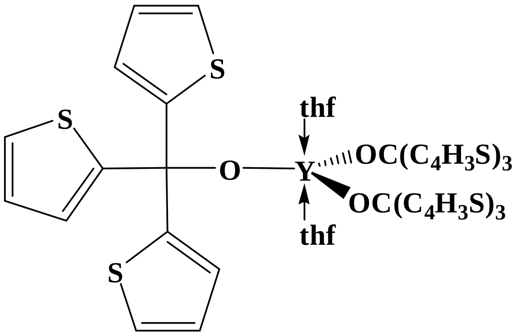
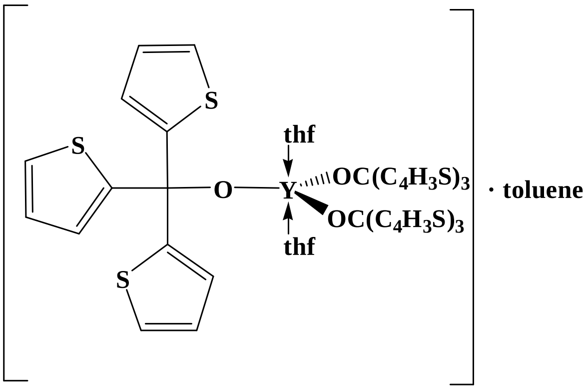
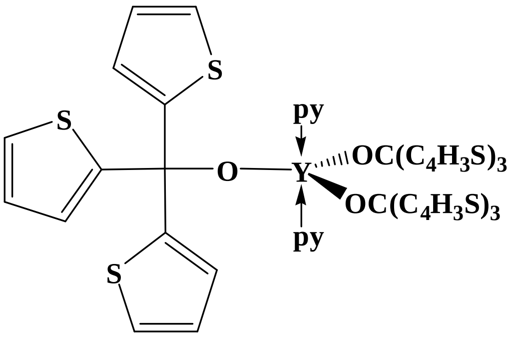


16a



16b



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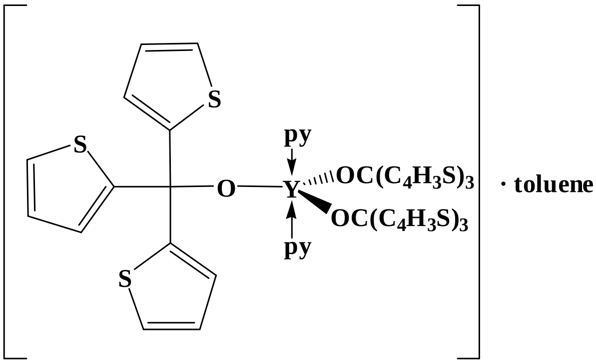

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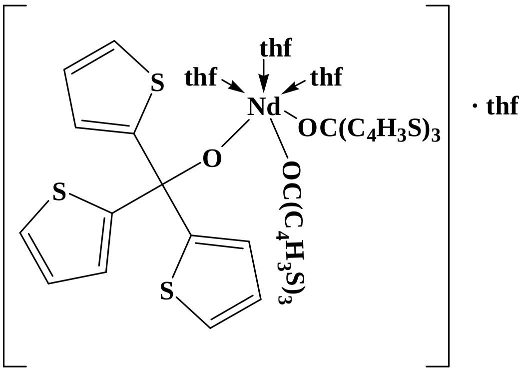

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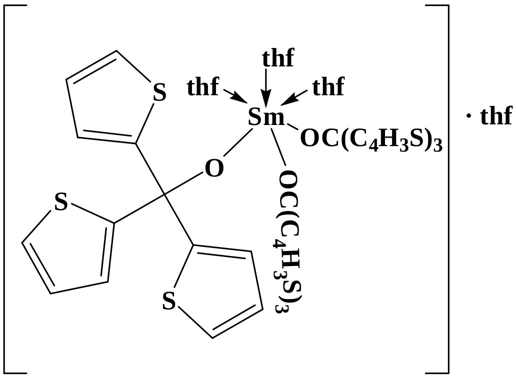

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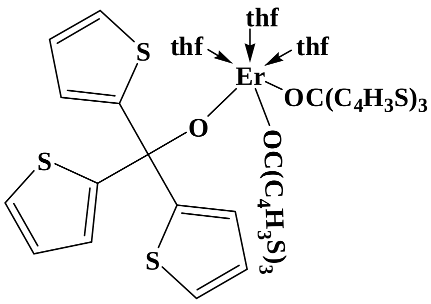

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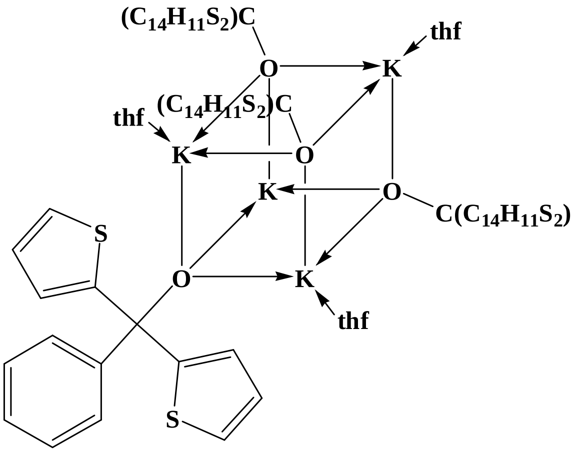

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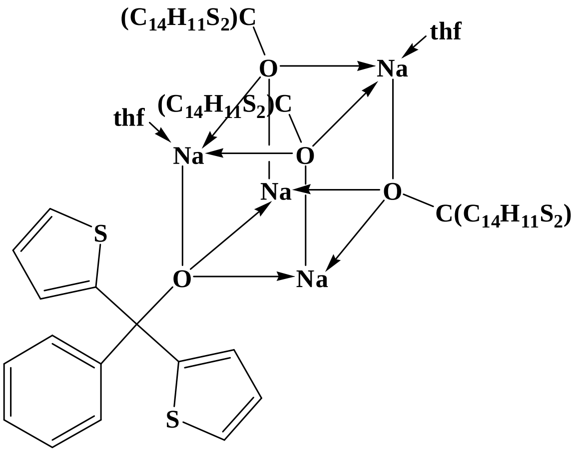

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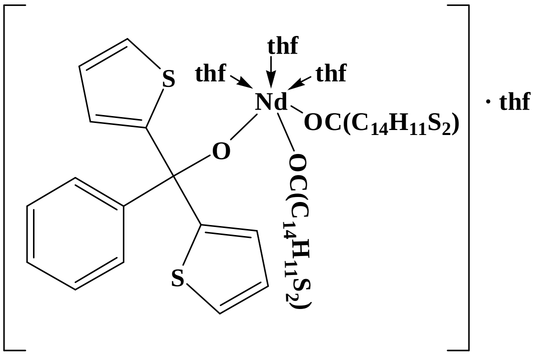

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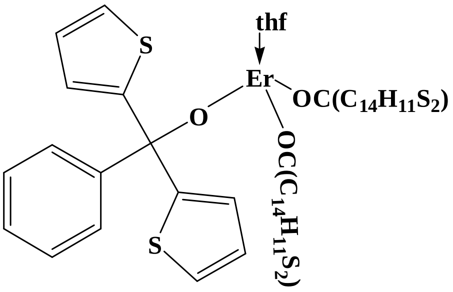

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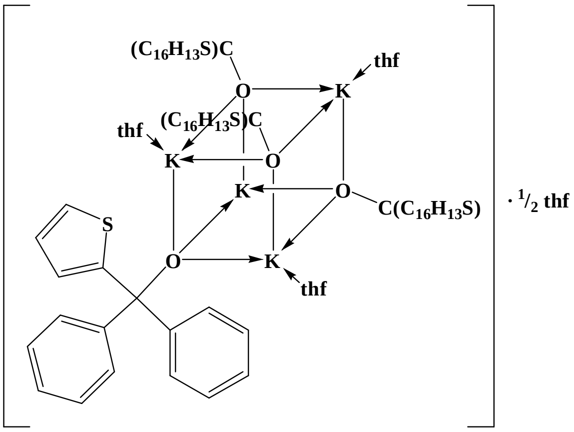

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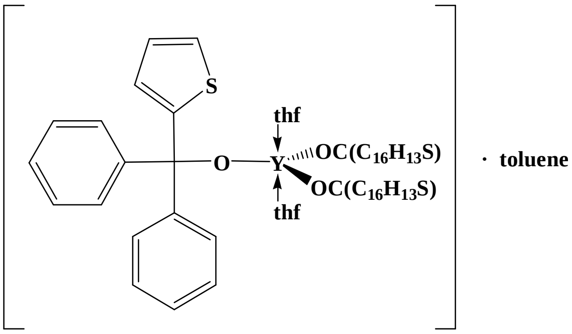

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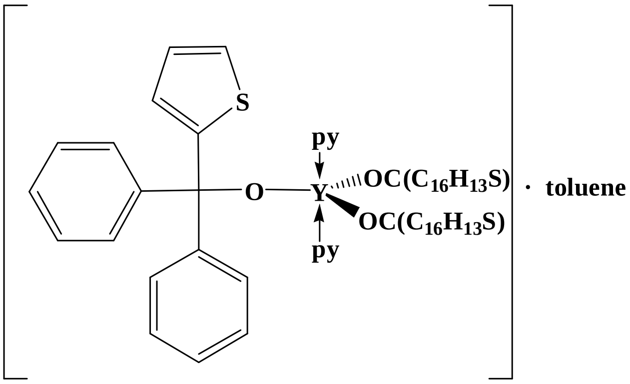

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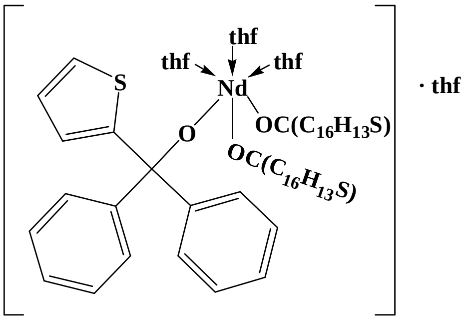

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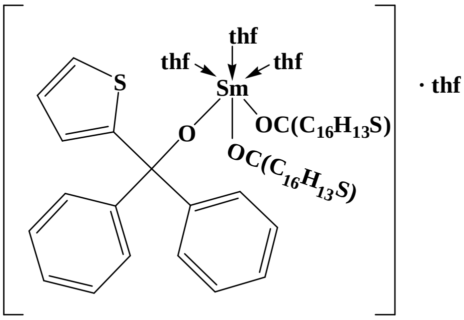

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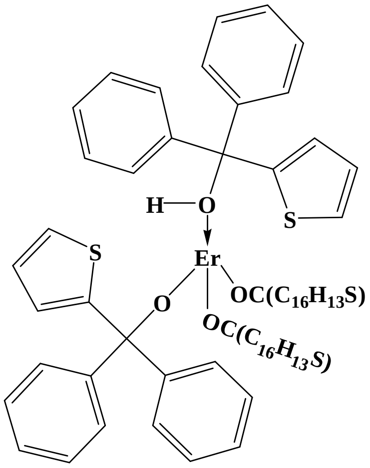

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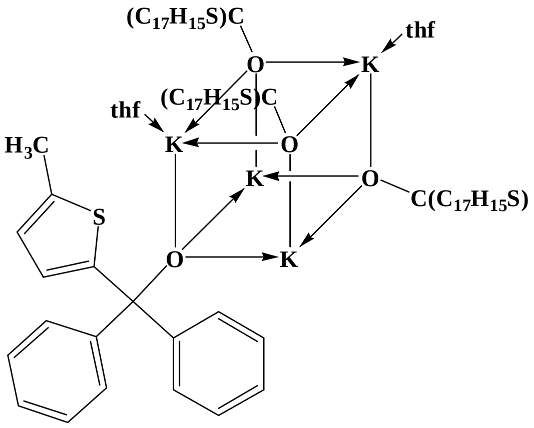
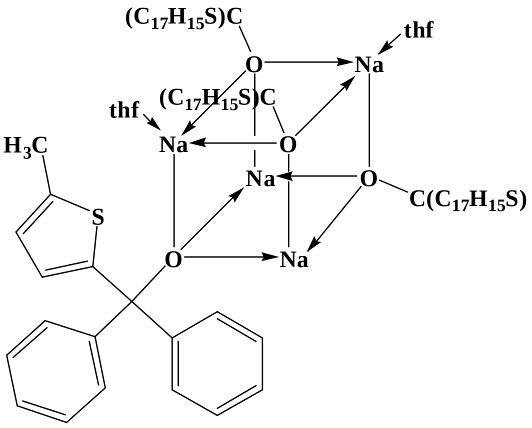
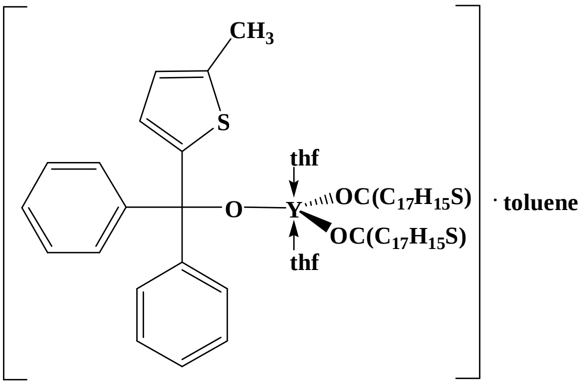

(C17H15S)C
thf
(C17H15S)C
thf
H3C
K
O
S
C(C17H15S)

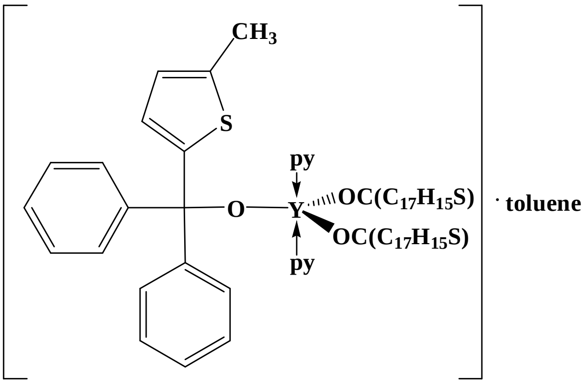
31


(C17H15S)C
thf
(C17H15S)C
thf
H3C
Na
O
S
C(C17H15S)

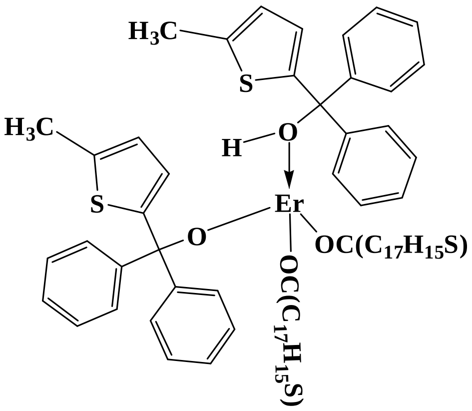
32


CH3
S
thf
O
Y
OC(C17H15S)
OC(C17H15S)
thf
· toluene

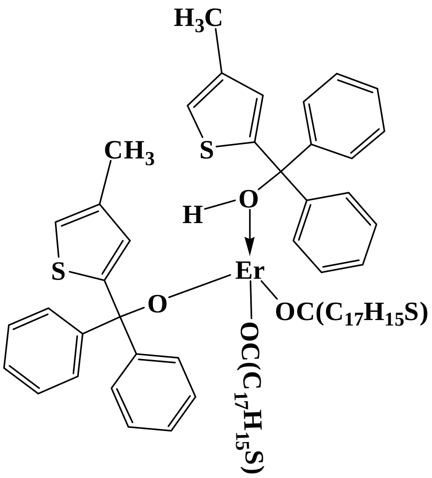
33


CH3
S
py
O
Y
OC(C17H15S)
OC(C17H15S)
py
· toluene

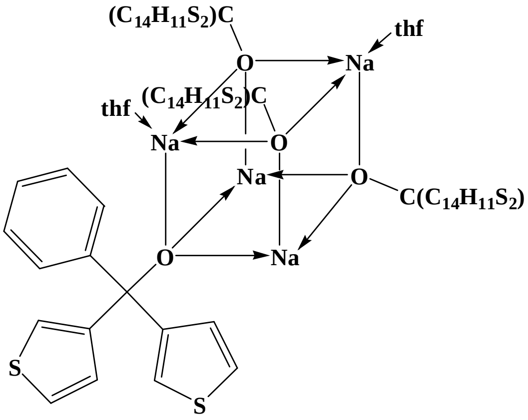
34


H3C
S
H3C
H
O
S
Er
O
OC(C17H15S)
OC(C17H15S)

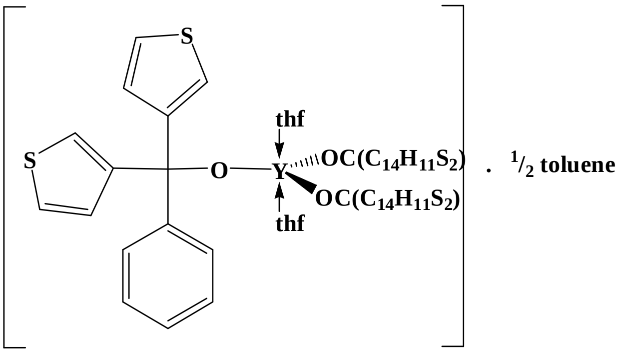
35


H_3C
CH_3
S
S
H
O
Er
O
$OC(C_{17}H_{15}S)$
$OC(C_{17}H_{15}S)$

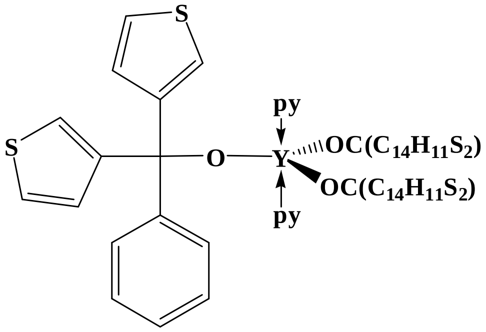
36


$(C_{14}H_{11}S_2)C$
thf
O
Na
thf
$(C_{14}H_{11}S_2)C$
Na
O
Na
O
$C(C_{14}H_{11}S_2)$
O
Na
S
S

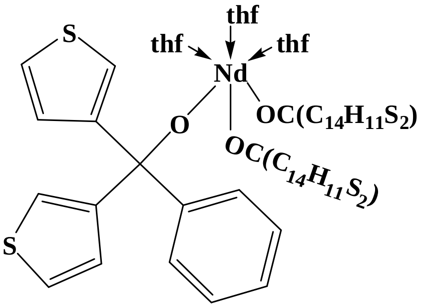
37


S
thf
S
O
Y
$OC(C_{14}H_{11}S_2)$
$OC(C_{14}H_{11}S_2)$
thf
. $^1/_2$ toluene

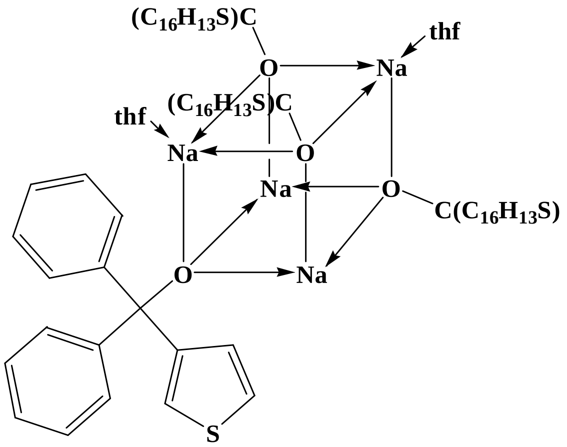
38


S
py
S
O
Y
$OC(C_{14}H_{11}S_2)$
$OC(C_{14}H_{11}S_2)$
py

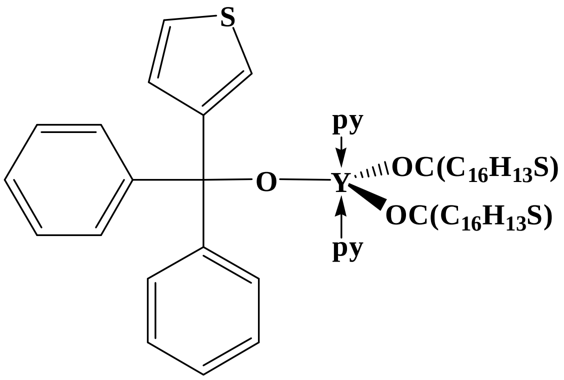
39


thf
S
thf
thf
Nd
O
$OC(C_{14}H_{11}S_2)$
$OC(C_{14}H_{11}S_2)$
S

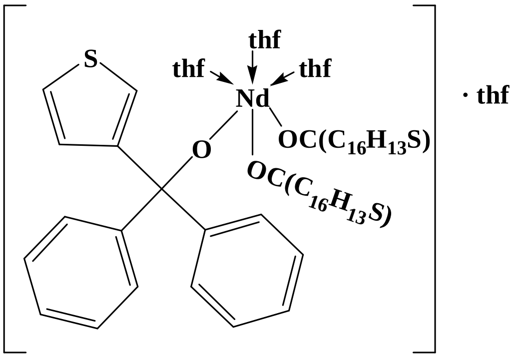
40


(C16H13S)C
thf
O
Na
thf
(C16H13S)C
Na
O
Na
O
C(C16H13S)
O
Na
S

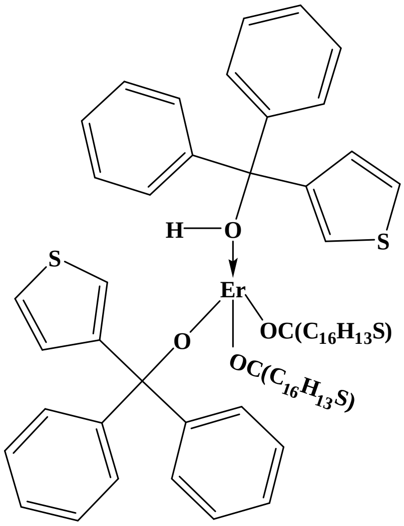
41


S
O
py
Y
OC(C16H13S)
OC(C16H13S)
py

42


S
thf
thf
thf
Nd
O
OC(C16H13S)
OC(C16H13S)
· thf

43


H
O
S
S
Er
O
OC(C16H13S)
OC(C16H13S)

44