

# Transformations of the polycyclic Alumosiloxane $\text{Al}_2(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3$ into new Polycycles and Co(II) and In(III) derivatives of $(\text{Ph}_2\text{SiO})_8[\text{Al}(\text{O})\text{OH}]_4$

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Dedicated to Prof. Hansgeorg Schnökel on the occasion of his 80<sup>th</sup> birthday.

In the presence of water and amines the etherate of bicyclic  $\text{Al}_2(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3$  (**IIa**) can be used to generate novel alumosiloxane polycycles like  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)_2\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2\text{O})_2] \cdot 2 \text{H}_2\text{N}^+\text{Et}_2$  (**1**),  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)_2\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiO})_2]_2 \cdot 2 \text{HN}^+\text{Et}_3$  (**2**),  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)_2\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2\text{O})_2]_2 \cdot 2 \text{HN}^+\text{Et}_3$  (**3a**, **3b**), which crystallizes in two different phases, and  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)_2\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2\text{O})_2]_2 \cdot 2 \text{HN}^+(\text{CH}_2\text{CH}_2)_3\text{N}$  (**4**). As a common structural feature of these compounds two aluminum atoms which are incorporated in six-membered  $[\text{Al}(\text{OSiPh}_2\text{OSiPh}_2\text{O})_2]$  rings are connected as spiro cyclic centers through oxygen and/

or siloxane bridges  $[(\text{OSiPh}_2)_n\text{O}]$  ( $n = 1, 2$ ) to form an assembly of three fused rings at the aluminum corners. The central ring is either eight- (**1**, **2**) or twelve-membered (**3**, **4**). Alkyl ammonium cations balance the charges and form hydrogen bridges to oxygen atoms of the six membered rings. The pentacyclic  $(\text{Ph}_2\text{SiO})_8[\text{Al}(\text{O})\text{OH}]_4$  (**I**) can be used indirectly (addition of water) and directly as chelating ligand versus  $\text{Co}(\text{II})\text{Cl}$  and  $\text{In-CH}_3$  fragments as shown with the isolated and structurally characterized compounds  $(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3][\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-}$  (**5a**, **5b**) and  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2(\text{InCH}_3) \cdot 2 \text{O}(\text{CH}_2)_4$  (**6**).

## Introduction

The incorporation of metallic elements in siloxanes or silsesquioxanes has been widely studied since more than 70 years.<sup>[1–4]</sup> Within the molecular metallo-siloxanes the alumosiloxanes, also often addressed as molecular alumosiloxides, have attracted special attention because of their structural and chemical diversity. When aluminum is linked to one or several diphenyl siloxy groups,  $(\text{Ph}_2\text{SiO})_n$  cycles and polycycles can be generated with different geometries and with various applications.<sup>[5,6,7]</sup> When  $(\text{Ph}_2\text{SiO})_n$  is combined with  $\text{OAl}(\text{OH})$  the compounds become proton acidic. With tripodal silanols this property has been used to trap aluminum hydroxide clusters,<sup>[8]</sup> or such functionalized compounds serve as catalysts in olefin isomerization comparable to active sites in zeolites.<sup>[9]</sup>

For many years we have looked at the hydrogen reactivity in the polycycle  $(\text{Ph}_2\text{SiO})_8[\text{Al}(\text{O})\text{OH}]_4$  (**I**) resulting in Lewis acid-base adducts with  $\text{O-H}\cdots\text{Q}$  bridges ( $\text{Q} = \text{base}$ ) which even may lead to

supramolecular structures.<sup>[10,11]</sup> In view of molecular analogues to alumo-silicates we have studied metal derivatives of **I** by replacing the hydrogen atoms on the hydroxide groups by Li, Na,  $\text{Ge}(\text{II})$ ,  $\text{Sn}(\text{II})$ ,  $\text{Pb}(\text{II})$ ,  $\text{Zn}(\text{II})$ .<sup>[12,13,14]</sup> Because of its defined  $\text{O-Al}(\text{OH})-\text{O}$  substructure **I** may also be used to mimic aluminum hydroxide surface reactivity as recently shown with the amino acid lysine.<sup>[15]</sup> Finally, this pentacyclic **I** as well as the bicyclic  $\text{Al}_2(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3 \cdot 2\text{Q}$  (**II**)<sup>[16]</sup> (see Figure 1), which can only be generated under strict exclusion of water and air, react with small amounts of water to form a multitude of polycyclic molecules which even incorporate complex building blocks like  $[\text{Al}_2(\text{OH})_8]^{2-}$ .<sup>[17]</sup>

Intrigued by the transformations of the polycycles **I** and **II** into complex structures we had a closer look on the formation of cyclic compounds during hydrolysis and condensation of **I** and **II**. In earlier studies we have reported about possible intermediates in these reactions.<sup>[16,18]</sup> Here we describe the hydrolysis of **IIa** in the presence of amines like diethyl amine, triethyl amine and 1,4-diazabicyclo[2.2.0]octane. Furthermore, we have succeeded to use **I** as ligand towards  $\text{Co}^{2+}$  as the first example of an 3d open shell element and describe the monomethyl indium derivative of **I** generated by the replacement of two hydrogen atoms at the hydroxy sites of **I** by the  $\text{In-CH}_3$  moiety.

## Results and Discussion

### Syntheses

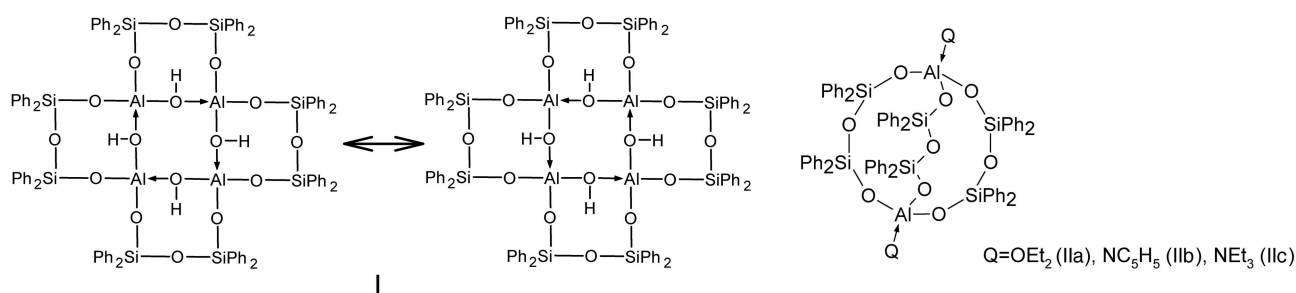
We have performed several hydrolyses of  $\text{Al}_2(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3 \cdot 2 \text{OEt}_2$  (**IIa**)<sup>[16]</sup> using different amines as co-reactants. In the case of diethyl amine, the alumosiloxane **IIa** is

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**Figure 1.** Two-dimensional bonding description of  $(\text{Ph}_2\text{SiO})_8[\text{Al}(\text{O})\text{OH}]_4$  (I)<sup>[11]</sup> and  $\text{Al}_2(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3 \cdot 2\text{Q}$  (II)<sup>[16]</sup> with “dative bonds” represented by arrows. The hydrogen atoms in I are coordinated in the crystal by bases like  $\text{OEt}_2$ , pyridine etc. (for more details see [10]).

first dissolved in toluene. To this solution a mixture of diethyl amine with few drops of water is slowly added resulting in the new di-spiro aluminosiloxane **1** (Scheme 1).

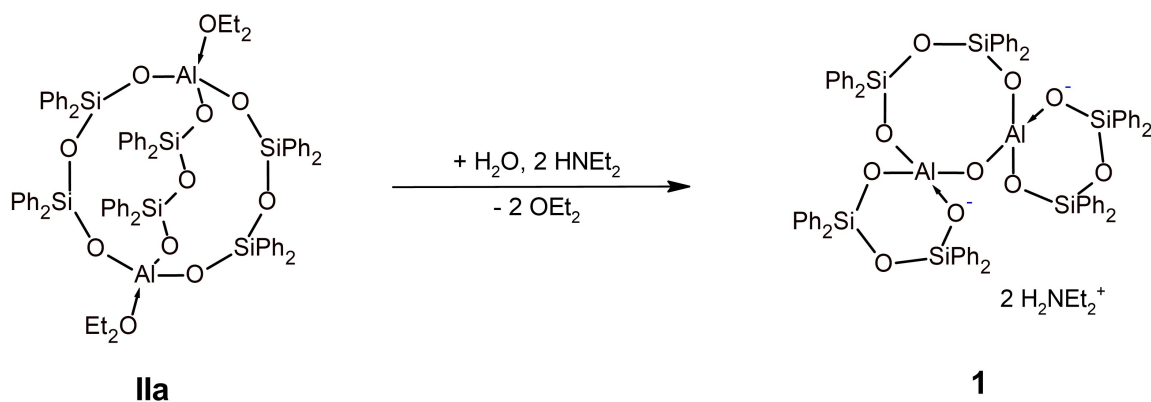
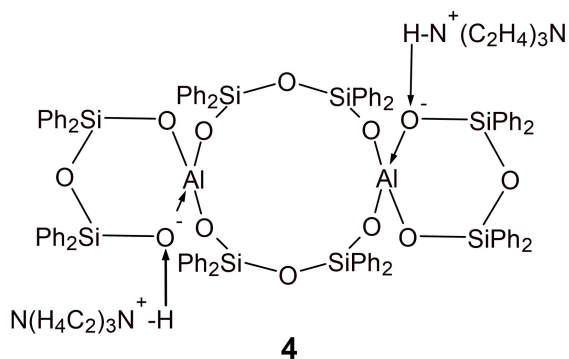
The new colorless compound **1** is isolated from this solution by crystallization. In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of redissolved **1** apart of the resonances of phenyl groups also those of the ethyl groups can be identified in accordance with diethyl amine being part of the molecule. In the  $^{29}\text{Si}$  NMR spectrum only two resonances are registered indicating a higher molecular symmetry. It follows from the X-ray diffraction analysis (see below) that **1** has the composition  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2\text{O}[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}] \cdot 2\text{H}_2\text{N}^+\text{Et}_2$  with 1.25 toluene molecules per formula unit serving as space-fillers in the van-der-Waals lattice.

When diethyl amine is replaced by triethyl amine, all other reaction conditions being like in the reaction of Scheme 1, two other compounds form as may be deduced from Scheme 2.

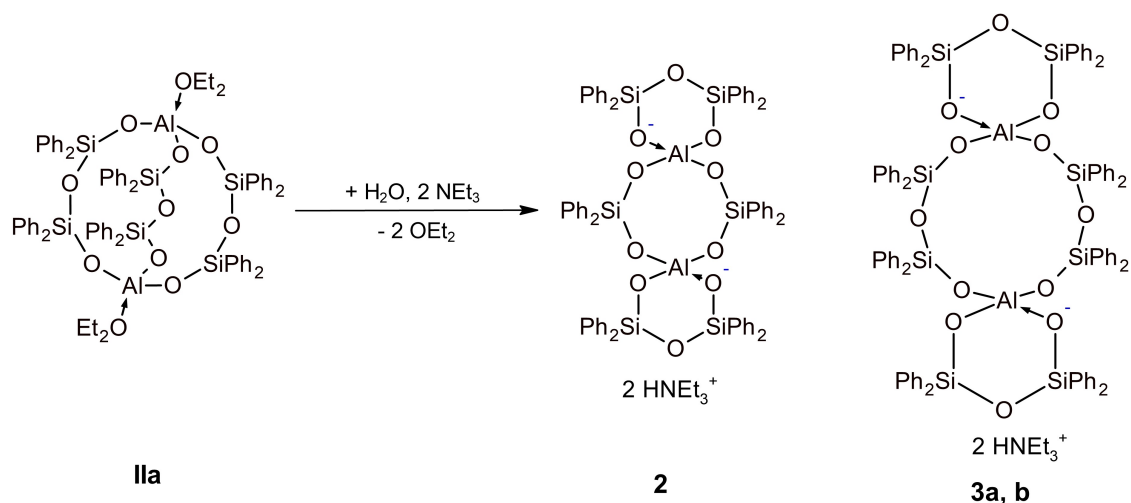
The main product is **3**, which can be isolated in two different crystalline forms **3a** and **3b**, whereas **2** is only obtained in exceedingly small yields. The formation of **2** is most likely explained by a hydrolytic degradation of the  $\text{O}-\text{SiPh}_2-\text{O}-\text{SiPh}_2-\text{O}$  chain which could have been occurred due to excess water in the reaction.<sup>[19]</sup> In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** the resonances of ethyl groups of the triethyl amine and the phenyl groups of the  $\text{Ph}_2\text{Si}$  groups show up. As in **1** only two signals are found in the

$^{29}\text{Si}$  NMR spectrum, indicating a higher symmetry of the molecule in solution. The X-ray structure analyses reveal, that **2** and **3** are tricyclic with the aluminum atoms connecting the six-eight-six (**2**), respectively six-twelve-six membered (**3**) cycles as spiro centers; their compositions are  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{Si})\text{O}]_2 \cdot 2\text{HN}^+\text{Et}_3 \cdot \text{C}_7\text{H}_8$  (**2**) and  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2 \cdot 2\text{HN}^+\text{Et}_3$  (**3**).

On replacing triethylamine by 1,4-diazabicyclo[2.2.0]octane in the reaction with **IIa** a similar compound to **3** can be obtained: in this new compound **4** the places of the two triethyl amine molecules are taken by two 1,4-diazabicyclo[2.2.0]octanes, as may be seen from the two-dimensional formula drawn below.



**Scheme 1.** Hydrolysis of **IIa** in the presence of diethyl amine.



**Scheme 2.** Hydrolysis of **IIa** in the presence of triethyl amine.

The formula for **4**,  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2 \cdot 2 \text{HN}^+(\text{CH}_2\text{CH}_2)_3\text{N} \cdot 2 \text{C}_7\text{H}_8$ , is based on the X-ray structure determination (vide infra). From the NMR spectral data ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR) it can be concluded, that diphenyl silyl groups are present. Interestingly the  $^{29}\text{Si}$  NMR spectrum of **4** contains three resonances whereas the  $^{29}\text{Si}$  NMR spectrum of **3** contains only two.

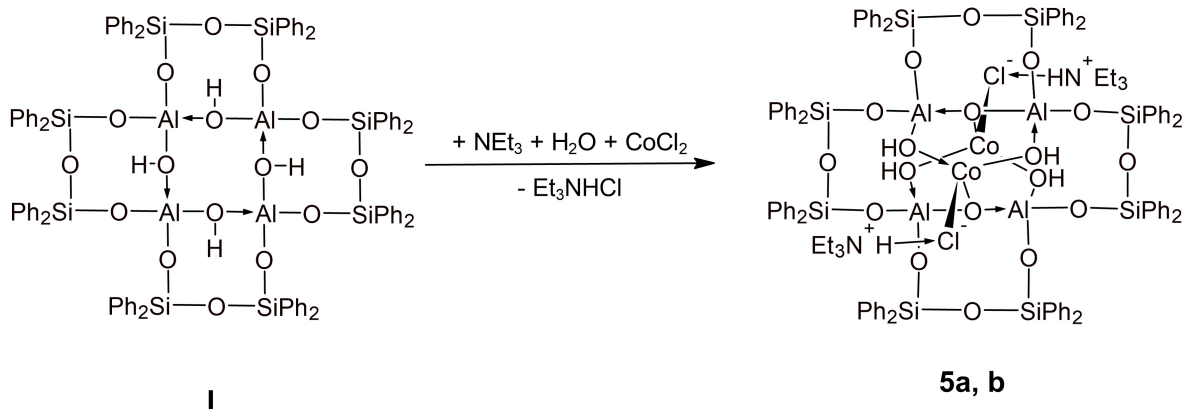
Although we have tried to transform the aluminosiloxane **I** in metal derivatives by replacement of the hydrogen atoms in the inner  $\text{Al}_4[\text{O}(\text{H})]_4$  cycle of **I** by metallic elements like Li, Na, Ge(II), Sn(II), Pb(II) Zn(II)<sup>[12–14]</sup>, we have never used transition metals with an open d-shell or another metallic element of group 13. In scheme 3 the reaction of **I** with  $\text{CoCl}_2$  is depicted using triethyl amine as HCl acceptor.

As result of the reaction the blue compound **5** is obtained, which crystallizes in two different crystal structures as **5a** and **5b** (see experimental section). Triethyl ammonium chloride is formed as expected but is incorporated in the molecule. In the UV/vis spectrum the three absorption maxima at 628, 663, 693 nm are indicative of  $\text{Co}^{2+}$ , so the oxidation state of the

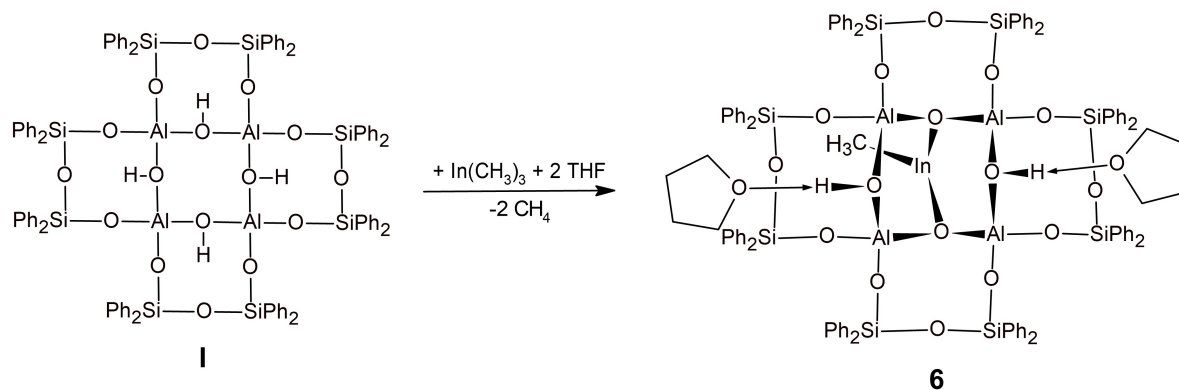
metal has not changed during reaction. The composition of **5** due to the X-ray structure analyses is  $(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2][\text{CoCl}]_2\}^{2-}$ . The central core of the structure is similar to the compound  $[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2][\text{Zn}(\text{OEt}_2)_2]$ , which we have described some years ago (for further discussion see next chapter).<sup>[13]</sup>

For the synthesis of an indium derivative of **I** the metal-organic trimethyl indium diethyl etherate is used in view of an indium-oxygen bond formation at the acidic OH group through elimination of methane. The overall reaction, which is run in a THF solution, is shown in Scheme 4.

As intended, indium is included in the molecule **I** and the compound  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2(\text{InCH}_3)_2 \cdot 2 \text{O}(\text{CH}_2)_4 \cdot \text{C}_7\text{H}_8$  (**6**) can be obtained by crystallization (see below). We have tried several molar ratios between trimethyl indium and **I**, but could only isolate **6** as product, although other derivatives of **I** might be accessible with more indium atoms replacing the remaining protonic hydrogen atoms in **6**. Indeed, with tin(II) in the place of  $\text{In-Me}$  we found two compounds:  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2\text{Sn} \cdot 2 \text{O}(\text{CH}_2)_4$  and  $(\text{Ph}_2\text{SiO})_8[\text{AlO}_2]_4\text{Sn}_2$  as mono- and



**Scheme 3.** Reaction scheme of **I** with cobalt(II) chloride.



**Scheme 4.** Reaction of **1** (dative bonds not drawn) with trimethyl indium.

di-substitutes of the ring hydrogen atoms, the first one differing structurally from **6** by the replacement of  $\text{In-CH}_3$  by  $\text{Sn}$ .<sup>[12]</sup> We can not exclude that a similar di-substituted compound also forms in the reaction of Scheme 4, as in the <sup>29</sup>Si NMR of the crude product four resonances can be detected. The structurally similar monosubstituted compound  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2\text{Sn} \cdot 2 \text{O}(\text{CH}_2)_4\text{O}$  has only two resonances in organic solvents.<sup>[12]</sup>

### Structures

The result of the structure analysis on  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)_2\text{O}]_2\text{Al}_2\text{O}[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)_2\text{O}] \cdot 2 \text{H}_2\text{N}^+\text{Et}_2$  (**1**) is depicted in Figure 2. The compound crystallizes with two independent molecules and with 2.5 toluene molecules in the asymmetric unit of the centrosymmetric triclinic cell. The toluene molecules (some are disordered) serve as space fillers and have no other than van der Waals contacts to the polycycles. The molecule **1** consists of three rings (two are six-membered and one eight-membered) which are spiro-cyclically connected through two aluminum atoms. Moreover, the  $\alpha$ -oxygen atoms of the six-membered rings are engaged in hydrogen bridging to diethyl ammonium ions forming two  $\text{O}^- \cdots \text{Al} \cdots \text{O} \cdots \text{H} \cdots \text{N}^+ \cdots \text{H} \cdots$  eight membered rings. The molecules have approximately  $\text{C}_2$  point symmetry, the pseudo two-fold axis running through the two oxygen atoms, (Si)O(Si) and (Al)O(Al), of the central rings. In the solution the point-symmetry might even be  $\text{C}_{2v}$  in accordance with two <sup>29</sup>Si resonance lines.

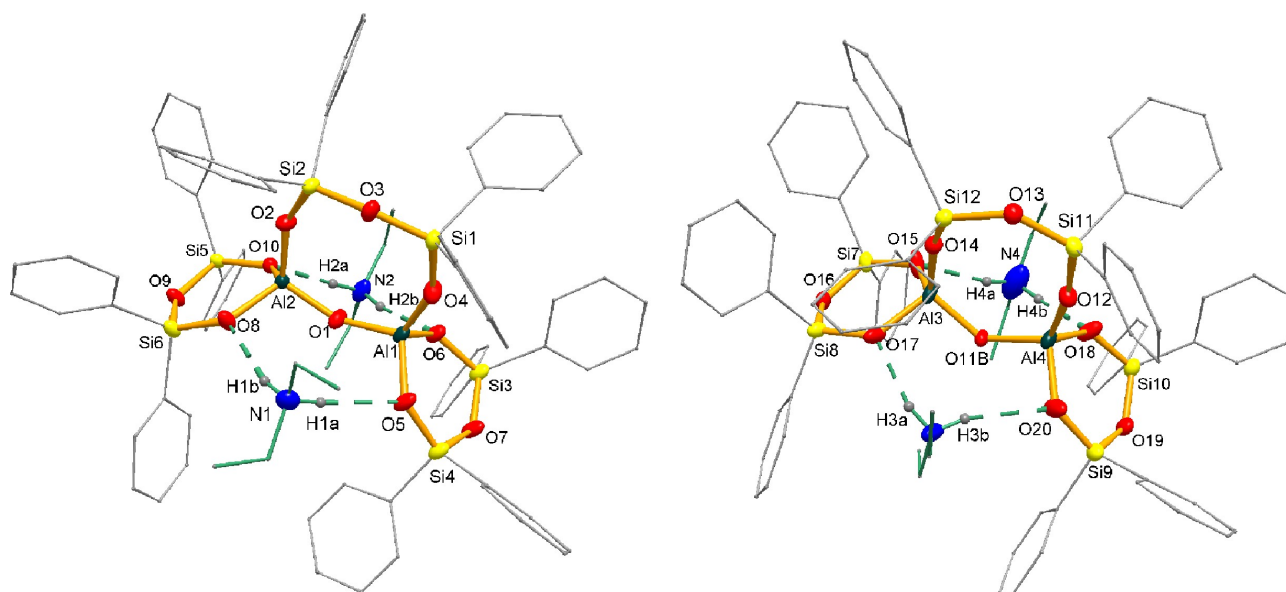
Apparently, compound **1** has been formed by addition of a water molecule to **IIa** followed by ring opening and reclosure. From the original three  $-\text{O}-\text{SiPh}_2-\text{O}-\text{SiPh}_2-\text{O}-$  chains only one has been maintained, while the two other ones have added a proton on terminal oxygen atoms. The oxygen atom of the water molecule is bonded to the two aluminum atoms closing the inner  $\text{Al}-\text{O}-\text{SiPh}_2-\text{O}-\text{SiPh}_2-\text{O}-\text{Al}-\text{O}$  cycle. The OH terminated  $-\text{O}-\text{SiPh}_2-$  chains bind back to the same aluminum atoms forming six-membered  $\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}$  loops. The role of the diethyl amine is two-fold: it serves as acceptor for the proton of the hydroxy group and connects through double

hydrogen bridging the diethyl ammonium entities to the oxygen atoms O(5)/O(8), O(6)/O(10), O(15)/O(18) and O(17)/O(20) (see Figure 2).

In all structure determinations within this paper, we have always found the hydrogen atoms near the nitrogen atoms and far from the oxygen atoms when a hydrogen bridge between O–H and N was detected. This is not unexpected, as the proton affinities of the bases used in our reactions are among the highest (diethyl amine: 932, triethyl amine: 982, 1,4-diazabicyclo[2.2.0]octane 963 kJ/Mol in the gas phase).<sup>[20]</sup> We therefore use the formula  $\text{O}^- \cdots \text{H}-\text{N}^+$  to describe these bridges, although we are aware that the small electron density difference is not an irrevocable criterion. We also performed refinement tests, putting the hydrogen atoms in the position between N and O and found in all cases that on refinement the hydrogen atoms moved back to the original positions at the nitrogen atoms. As all these compounds are highly hydrophilic it is difficult to use IR-spectroscopy of the crystals to distinguish between the different hydrogen bonding. Although we tried to perform measurements under inert gases, we could not obtain reproducible results.

The  $\text{O}^- \cdots \text{H}-\text{N}^+ \cdots \text{H}-\text{O}$  bridges in **1** are quite symmetrical, although they show a tendency to approach more on one side, as may be seen by comparing the O $\cdots$ N distances in the caption of Figure 2. There is nevertheless no indication of a bonding preference to one of the sides, as the O–Al bond lengths of the oxygen atoms engaged in hydrogen bonding are almost equal (mean value 1.772(4) in molecule **1** $\alpha$  with Al(1/2) and 1.764(2) Å in molecule **1** $\beta$  with Al(3/4)). The very small deviations in the Al–O bond lengths suggest that the negative charge is equally distributed on the oxygen atom pairs O(5)/O(6), O(8)/O(10), O(15)/O(17) and O(18)/O(20) within the rings.

The orientations of the best planes of the six membered cycles with respect to the eight membered in **1** are almost orthogonal with a mean value of 88.1(9)° (**1** $\alpha$ ) and 84(2)° (**1** $\beta$ ). The aluminum atoms are in the centers of slightly distorted tetrahedral oxygen environments with angles varying between 106.8 to 112.3° apart from angles within the six-membered rings (mean O–Al–O: 104.9(4)°) and those of the eight-membered rings (mean O–Al–O (114.5(3)°) caused by different



**Figure 2.** Molecular structures of the two independent molecules  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2\text{O})_2\text{Al}_2\text{O}[\text{O}(\text{Ph}_2\text{SiOSiPh}_2\text{O})_2] \cdot 2 \text{H}_2\text{N}^+\text{Et}_2$  (**1**), left molecule  $\alpha$ , right  $\beta$ , with thermal ellipsoids (50%) at Si, Al, O, N, and stick models for other atoms (the toluene molecules in the crystal lattice are omitted for clarity, hydrogen atoms bonded to carbon are not drawn). The bonds within the diethyl amine molecules are in green. Only one of the two split positions of O(11) has been drawn. Some pertinent bond lengths/Å and angles/°: Al(1)–O(1) 1.698(2), Al(1)–O(4) 1.718(2), Al(1)–O(5,6) mean: 1.771(1), Al(2)–O(1) 1.696(2), Al(2)–O(2) 1.729(2), Al(2)–O(8,10) mean: 1.773(4), Al(3)–O(14) 1.714(2), Al(3)–O(11 A) 1.724(5), Al(3)–O(11B) 1.738(5), Al(3)–O(15,17) mean: 1.767(1), Al(4)–O(12) 1.717(2), Al(4)–O(11 A) 1.720(5), Al(4)–O(11B) 1.739(5), Al(4)–O(18,20) mean: 1.762(2); Al(2)–O(1)–Al(1) 155.2(1), Si(2)–O(2)–Al(2) 150.2(1), Si(1)–O(3)–Si(2) 158.8(1), Si(1)–O(4)–Al(1) 152.5(1), Si(4)–O(5)–Al(1) 130.0(1), Si(3)–O(6)–Al(1) 128.0(1), Si(3)–O(7)–Si(4) 132.0(1), Si(6)–O(8)–Al(2) 129.7(1), Si(5)–O(9)–Si(6) 133.9(1), Si(5)–O(10)–Al(2) 127.9(1), Al(4)–O(11 A)–Al(3) 140.0(4), Al(3)–O(11B)–Al(4) 137.1(3), Si(11)–O(12)–Al(4) 167.2(1), Si(12)–O(13)–Si(11) 143.3(1), Si(12)–O(14)–Al(3) 157.5(1), Si(7)–O(15)–Al(3) 130.7(1), Si(8)–O(16)–Si(7) 130.8(1), Si(8)–O(17)–Al(3) 128.4(1), Si(10)–O(18)–Al(4) 130.6(1), Si(10)–O(19)–Si(9) 131.1(1), Si(9)–O(20)–Al(4) 130.8(1). Hydrogen bonds: O(5)⋯N(1) 3.014(4), O(8)⋯N(1) 2.930(4), O(10)⋯N(2) 2.833(4), O(17)⋯N(3) 2.828(6), O(20)⋯N(3) 3.128(6), O(15)⋯N(4) 2.947(6), O(18)⋯N(4) 2.910(6), N(1)–H(1<sup>a</sup>)⋯O(5) 165.7(4), N(1)–H(1<sup>b</sup>)⋯O(8) 162.5(4), N(2)–H(2<sup>b</sup>)⋯O(6) 169.2(4), N(2)–H(2<sup>a</sup>)⋯O(10) 176.1(4), N(3)–H(3<sup>a</sup>)⋯O(17) 162.9(4), N(3)–H(3<sup>b</sup>)⋯O(20) 153.0(4), N(4)–H(4<sup>a</sup>)⋯O(15) 166.6(4), N(4)–H(4<sup>b</sup>)⋯O(18) 172.1(4).

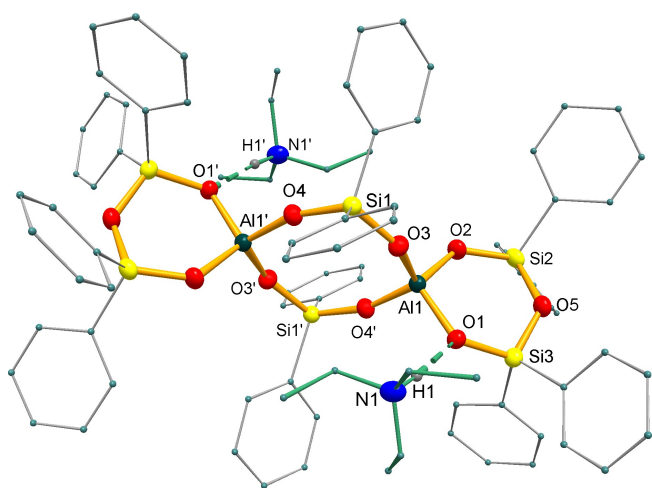
ring strains. The bond angles at the oxygen atoms are generally more acute in the six-membered rings compared to the eight-membered (see caption of Figure 2) for the same reasons.

Whereas the four six-membered rings in the two molecules **1α** and **1β** differ only slightly in their dimensions and are almost planar (sum of angles within the six-membered rings: 714.5(5)° and 715.3(5)° [**1α**], 713.2(5)° and 716.7(5)° [**1β**]) the eight-membered rings show remarkable differences. In a crude approximation the aluminum and silicon atoms in **1α** and **1β** are similarly located in the corners of a distorted square (**1α**: Si–Si = 3.200(1), Al–Al = 3.315(1), Si–Al = 3.205(1)/3.206(1) Å; **1β**: Si–Si = 3.104(1), Al–Al = 3.236(1), Si–Al = 3.238(1)/3.286(1) Å). In contrast to this situation the oxygen atoms are differently displayed as may be seen from the trans-annular distances O(1)⋯O(3) 3.777(2) versus O(2)⋯O(4) 4.027(2) in **1α** or the corresponding O(11)⋯O(13) 4.285(4) versus O(12)⋯O(14) 3.519(2) Å distances in **1β**, which have an opposite relation. This remarkable difference may also be seen by inspection of the Al–O(1, 11)–Al, Al–O(2, 4, 12, 14)–Si and Si–O(3, 13)–Si angles which differ considerably in the two molecules (see caption of Figure 2), as they show larger angles in **1α** at places in which they are more acute in **1β**. Whereas molecule **1α** has an elongated eight-membered ring in the O(2)⋯O(4) direction,

the contrary is true for **1β** which has its elongation in the O(11)⋯O(13) direction. Apparently, the two different conformations found for the eight-membered rings in **1α** and **1β** are only separated by a low activation energy, as they appear together in a lattice, in which only small van-der-Waals forces are acting. It should be recalled that the flexibility of cyclic siloxane and metallo-siloxane rings is high due to small energy differences between conformers (also compare discussion on **3b** and **4** below).<sup>[21]</sup>

In Figure 3 the molecular structure of  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2\text{O})_2\text{Al}_2\text{O}[\text{O}(\text{Ph}_2\text{SiO})_2] \cdot 2 \text{HN}^+\text{Et}_3$  (**2**) is shown, which has been obtained as a minor byproduct of Scheme 2. Like compound **1** it crystallizes with a toluene molecule which behaves as space filler in the lattice. The compound **2** has  $C_i$  point symmetry and its deviation of the higher symmetry  $C_{2h}$  (the pseudo  $C_2$  axis passing through Si(1) and Si(1')) is only small. As already mentioned above, we believe that the O–SiPh<sub>2</sub>–O group has been formed through hydrolysis of the longer O–SiPh<sub>2</sub>–O–SiPh<sub>2</sub>–O chain, a process which is well known in siloxane chemistry.<sup>[19]</sup>

In comparison to **1** in molecule **2** the aluminum spiro centers are symmetrically connected by two –O–SiPh<sub>2</sub>–O–bridges the resulting eight-membered cycle being nearly planar



**Figure 3.** Molecular structure of  $[O(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{Si})\text{O}]_2 \cdot 2 \text{HN}^+\text{Et}_3 \cdot \text{C}_7\text{H}_8$  (**2**) with thermal ellipsoids (50%) at Si, Al, O, N and ball and stick models for other atoms. The bonds and the carbon atoms within the triethyl amine molecules are in green, the toluene molecule as well as hydrogen atoms bonded to carbon are not drawn. Some pertinent bond lengths/Å and angles/°: Al(1)–O(3) 1.722(2), Al(1)–O(4') 1.723(2), Al(1)–O(2) 1.754(2), Al(1)–O(1) 1.782(2), Si(1)–O(3,4) mean: 1.600(2), Si(2)–O(2) 1.600(2), Si(3)–O(1) 1.620(2), Si(2,3)–O(5) mean: 1.643(2); O(3)–Al(1)–O(4') 112.86(8), O(2)–Al(1)–O(1) 106.52(7), Si(3)–O(1)–Al(1) 127.05(9), Si(2)–O(2)–Al(1) 130.1(1), Si(1)–O(3)–Al(1) 148.3(1), Si(1)–O(4)–Al(1') 161.6(1), Si(3)–O(5)–Si(2) 128.7(1). Hydrogen bonding: N(1)⋯O(1) 2.849(5); O(1)⋯H(1)–N(1) 172.8(6).

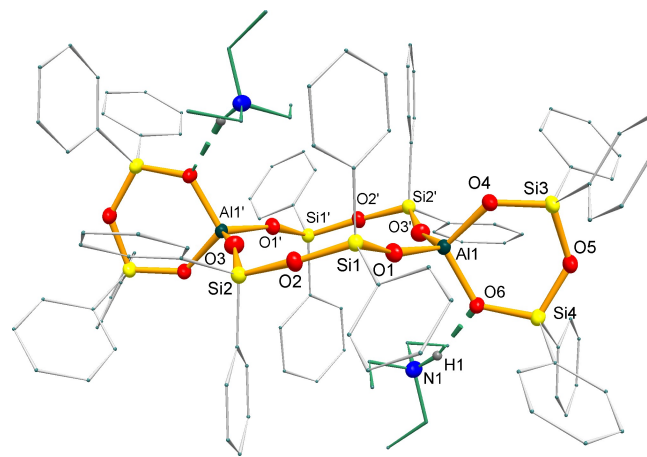
with a  $14.3(2)^\circ$  kink of the O(3)–Al(1)–O(4') sub-plane with respect to the remaining atoms. Using best planes for the six- and eight-membered cycles of **2** the inter-planar angle is  $87.2^\circ$  similar to compound **1**. The six-membered rings are somewhat twisted as can be deduced from the dihedral angles Al(1)–O(1)–Si(3)–O(5) ( $-25.6^\circ$ ) and Al(1)–O(2)–Si(2)–O(5) ( $1.9^\circ$ ).

Contrarily to the bidentate hydrogen coordination of diethyl ammonium ions in **1** the spirocyclic molecule **2** has only monodentate triethyl ammonium groups. Consequently, only one of the oxygen atoms adjacent to aluminum in the six-membered rings serves as hydrogen bridge to the protonic sides of the cations. As can be seen from the Al–O distances in the caption of Figure 3 the Al(1)–O(2) bond length is by 0.028 Å shorter than Al(1)–O(1) (a significant value compared to the triple standard deviation). This elongation for Al(1)–O(1) is expected as O(2) is only two-coordinate whereas O(1) is three-coordinate forming a hydrogen bridge to N(1), which withdraws electron-density from O(1). The situation such differs from the structure of **1**, where the adjacent O–Al bonds in the six-membered cycles have almost equal lengths (see above), as both oxygen atoms are engaged in hydrogen bridging.

The eight-membered ring in **2** has normally shorter bond lengths and larger Al–O–Si and Si–O–Si angles compared to those in the six-membered rings as already stated in the case of molecule **1** (see caption Figure 3). The N⋯O distance in **2** is in the same order of magnitude as in **1**.

The molecular structure of the almost exclusive product of Scheme 2,  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2 \cdot 2 \text{HN}^+\text{Et}_3$  (**3**), crystallizes in two different forms **3a** and **3b**, which differ only slightly in their molecular dimensions. When crystallized directly from the reaction solution compound **3a** forms, which has no further solvent molecules in the crystal lattice, whereas **3b** forms when the solid reaction residue is redissolved in toluene and recrystallized (Figure 4). The structure of **3a** has already been shortly described before.<sup>[16]</sup> The formation of **3** (Scheme 2) may be rationalized by partial hydrolysis of **IIa** liberating HO–SiPh<sub>2</sub>–O–SiPh<sub>2</sub>–OH, which then adds back to the starting compound to form **3a, b**.

We restrict our structure description for **3b** only to the comparison to **1, 2** and **4** (see below). In compound **3b** two spiro-cyclic aluminum centers, again both being part of six-membered  $\text{AlO}_3\text{Si}_2$  rings, are connected through O–SiPh<sub>2</sub>–O–SiPh<sub>2</sub>–O chains to obtain a twelve-membered central cycle (Figure 4). The point symmetry of molecule is  $C_i$  (with a small deviation from  $C_{2h}$ , the pseudo  $C_2$  passing through O(2) and O(2')) and two toluene molecules are incorporated in the unit cell. The central twelve-membered ring can be divided in three different planes (*plane1*: Al(1), O(1), O(3'), *plane2* (highest deviation of this plane 0.014 Å): O(1), Si(1), O(3'), Si(2'), *plane3* (highest deviation of this plane 0.019 Å): Si(1), O(2), Si(2), Si(1'), O(2'), Si(2')). The interplanar angles are: *plane1/plane2*:  $32.7^\circ$  and *plane2/plane3*:  $54.7^\circ$  (the corresponding interplanar angles in **3a** are *plane1/plane2*:  $38.0^\circ$  and *plane2/plane3*:



**Figure 4.** A section of the crystal structure of  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2 \cdot 2 \text{HN}^+\text{Et}_3 \cdot 2 \text{C}_7\text{H}_8$  (**3b**) with thermal ellipsoids (50%) at Si, Al, O, N and ball and stick models for other atoms omitting the two toluene molecules incorporated in the crystal and the hydrogen atoms at the carbon atoms. The bonds and the carbon atoms within the triethyl amine molecules are in green. Some pertinent bond lengths/Å and angles/°: Al(1)–O(1) 1.717(1), Al(1)–O(3') 1.721(1), Al(1)–O(4) 1.742(1), Al(1)–O(6) 1.785(1), Si(1,2)–O(2) mean: 1.625(1), Si(1)–O(1)/Si(2)–O(3) mean: 1.590(1), Si(3)–O(4) 1.601(1), Si(3)–O(5) 1.650(1), Si(4)–O(6) 1.622(1), Si(4)–O(5) 1.635(1); O(1)–Al(1)–O(3') 109.25(6), O(4)–Al(1)–O(6) 105.35(5), Si(1)–O(1)–Al(1) 160.37(8), Si(1)–O(2)–Si(2) 168.69(8), Si(2)–O(3)–Al(1') 163.03(8), Si(3)–O(4)–Al(1) 130.76(7), Si(4)–O(5)–Si(3) 131.92(7), Si(4)–O(6)–Al(1) 128.98(7). Hydrogen bonding: N(1)⋯O(6) 2.821(5); O(6)⋯H(1)–N(1) 161.8(3).

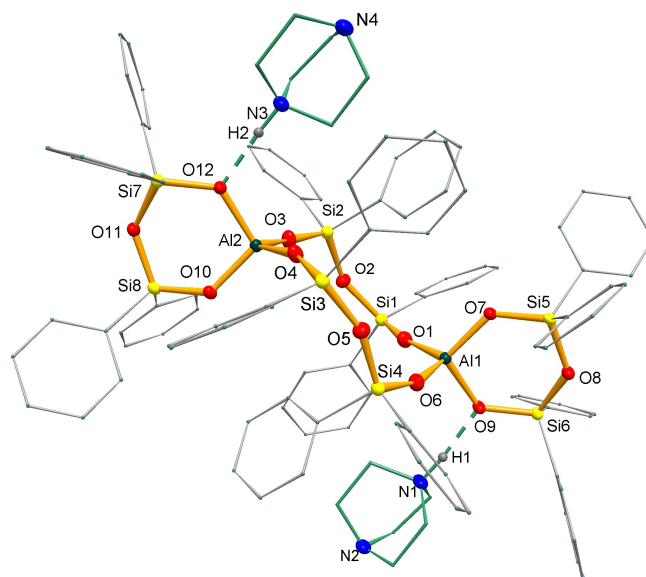
60.8°<sup>[16]</sup>). The conformation of the inner twelve-membered ring can therefore be described as a “double chair” in the two structures. The structural differences between **3a** and **3b** are minor as can be seen not only by inspection of the intramolecular bond lengths and angles (compare caption of Figure 4 with<sup>[16]</sup>) but also from the N...O–Al angles (105.73(6)° (**3a**) versus 107.94(6)°) and the corresponding N...O distances (2.805(6) (**3a**) and 2.821(5) Å).

The triethyl ammonium ions in **3b** bind in the same way through hydrogen bridges to the oxygen atoms O(6, 6') of the six-membered rings as found for **2**. The N...O distance is with 2.821(5) Å in the same range as found for **2**. Again, the Al(1)–O(6) bond length is longer by 0.043 Å than the corresponding Al(1)–O(4) (see caption Figure 4), a little bit more pronounced as discussed above. The larger inner cycle also affects the Al–O bond lengths as may be seen by comparison the Al–O bonds in the central ring (they are smaller) with those in the six-membered rings (they are larger): in molecule **1** (eight membered central ring) the mean difference compared to the six-membered ring is 0.051(5) Å, in molecule **2** (eight membered central ring) it is 0.047(2) Å and in **3b** (twelve-membered central ring) it is 0.045(2) Å.

In compound  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2 \cdot 2 \text{HN}^+(\text{CH}_2\text{CH}_2)_3\text{N}$  (**4**), depicted in Figure 5, the triethyl ammonium cations of **3b** are substituted by protonated 1,4-diazabicyclo[2.2.0]octane molecules. The compound **4** is synthesized in a similar way to **3b**, has the same di-spirocyclic structure, and the configuration of bases with respect to the polycycle are alike.

The molecule **4** crystallizes in a van-der-Waals lattice with toluene molecules serving as space fillers and has no higher point symmetry. The 1,4-diazabicyclo[2.2.0]octane molecules are protonated at N(1) and N(3) and form shorter N–H...O hydrogen bridges (mean: 2.692(3) Å) compared to **2** (2.849(5) Å) or **3b** (2.821(5) Å). The impact of the hydrogen bridge can, like in the other molecules **2** and **3b**, be shown on comparing the Al–O bond lengths Al(1)–O(7)/Al(1)–(9) and Al(2)–O(10)/Al(2)–O(12) (see caption of Figure 5).

The most remarkable property of **4** is the different conformation of the central ring with respect to compound **3b**. Already by inspecting the Figures 4 and 5 one can easily distinguish on one side (**3b**) a double chair conformation of the twelve-membered ring with almost parallel Si–O–Si edges and large Si–O–Si angles (168.7(1)°) from the twisted conformation in **4** on the other side with more acute Si–O–Si angles (154.5(9)°). Indeed, by putting a best plane into the silicon atoms Si(1, 2, 3, 4) (mean deviation from the plane: 0.06 Å), the distance to this plane for the oxygen atoms O(2) and O(5) is –0.38 and 0.29 Å. Using the plane designation *plane1* (AlO<sub>2</sub>) and *plane2* (Si<sub>2</sub>O<sub>2</sub>) as defined for compound **3b** (see above), we find in **4** small interplanar angles (9.7 and 16.2°) whereas the interplanar angles between *plane2* and the Si<sub>4</sub>-plane are 47.6 and 51.5° (compare above for **3b**). The biggest difference between the eight-membered rings in the two molecules **3b** and **4** is found for the central Si<sub>4</sub>O<sub>2</sub> units (Si(1, 2, 1', 2') and O(2, 2') in **3b**; Si(1, 2, 3, 4) and O(2, 5) in **4**). In **3b** these atoms are almost in one plane (see above), whereas in **4** the Si–O–Si



**Figure 5.** A molecular sketch of  $[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2\text{Al}_2[\text{O}(\text{Ph}_2\text{SiOSiPh}_2)\text{O}]_2 \cdot 2 \text{HN}^+(\text{CH}_2\text{CH}_2)_3\text{N} \cdot 2 \text{C}_7\text{H}_8$  (**4**) with thermal ellipsoids (50 %) at Si, Al, O, N and ball and stick models for other atoms. The bonds and the carbon atoms within the 1,4-diazabicyclo[2.2.0]octane molecules are in green. The space filling toluene molecules and the hydrogen atoms at the carbon atoms are not drawn. Some pertinent bond lengths/Å and angles/°: Al(1)–O(1) 1.716(1), Al(1)–O(6) 1.725(1), Al(1)–O(7) 1.738(1), Al(1)–O(9) 1.782(1), Al(2)–O(3) 1.717(1), Al(2)–O(4) 1.717(1), Al(2)–O(10) 1.742(1), Al(2)–O(12) 1.785(1), Si(1)–O(1)/Si(2)–O(3)/Si(3)–O(4)/Si(4)–O(6) mean: 1.591(1), Si(1,2)–O(2) mean: 1.624(1), Si(3,4)–O(5) mean: 1.620(1), Si(5)–O(7)/Si(8)–O(10) mean: 1.600(1), Si(5)–O(8) 1.650(1), Si(6)–O(9)/Si(7)–O(12) mean: 1.627(1), Si(6)–O(8) 1.636(1), Si(7)–O(11) 1.641(1), Si(8)–O(11) 1.653(1); O(1)–Al(1)–O(6) 111.71(6), O(7)–Al(1)–O(9) 104.19(5), O(3)–Al(2)–O(4) 112.61(6), O(10)–Al(2)–O(12) 104.34(5), Si(1)–O(1)–Al(1) 164.96(8), Si(2)–O(2)–Si(1) 150.03(7), Si(2)–O(3)–Al(2) 166.47(8), Si(3)–O(4)–Al(2) 159.82(7), Si(4)–O(5)–Si(3) 158.88(8), Si(4)–O(6)–Al(1) 161.48(8), Si(5)–O(7)–Al(1) 130.47(7), Si(6)–O(8)–Si(5) 130.69(7), Si(6)–O(9)–Al(1) 129.25(6), Si(8)–O(10)–Al(2) 129.78(7), Si(7)–O(11)–Si(8) 128.72(7), Si(7)–O(12)–Al(2) 127.35(6). Hydrogen bonding: N(1)···O(9) 2.688(5), N(3)···O(12) 2.695(5); O(9)···H(1)–N(1) 173.5(4), O(12)···H(3)–N(3) 172.7(5).

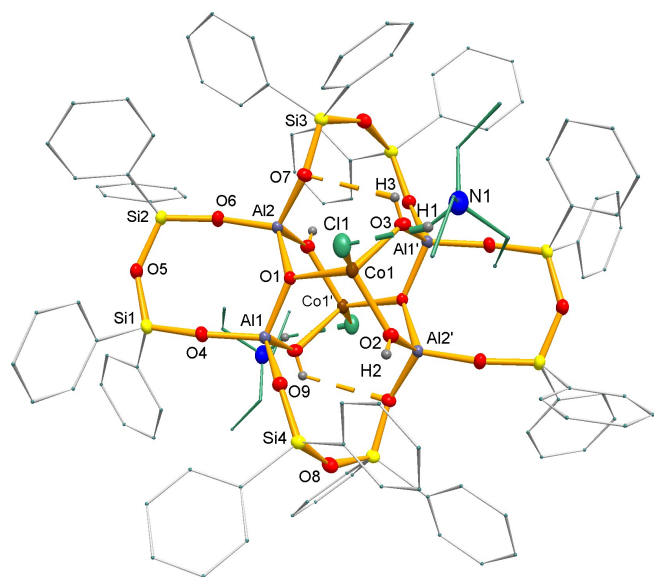
substructures show interplanar angles of 65.3 and 83.6° to the Si<sub>4</sub>-plane.

The different conformations of the central rings in **3b** and **4** must be attributed to the different bases coordinated to oxygen atoms of the six-membered cycles, which as consequence of their unequal spatial requirements seem to influence the conformations encountered in the crystal lattices. When the bases are alike, crystal structures like in the case of **3a** and **3b** may be different concerning the crystal packing but show almost similar conformations of their polycycles (see also<sup>[16]</sup>). An exploratory analysis through molecular mechanics calculation of the respective anions in **3b** and **4** (omitting the cations) reveals that the energy differences between the two conformers is around 20 kJ/Mol.<sup>[22]</sup>

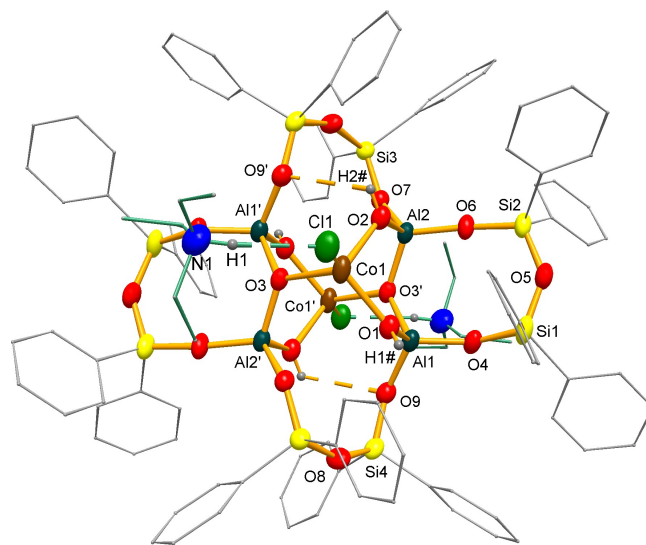
The product of the reaction between **1** and CoCl<sub>2</sub>, in the presence of small quantities of water (Scheme 3), has the

composition  $(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-}$  and crystallizes in two different forms **5a** (toluene) and **5b** (benzene) depending on the solvent incorporated in the crystal (Figures 6 and 7).

Both molecules **5a** and **5b** have a crystallographic inversion center as point symmetry. In a purely formal description, the polycycle **I** has on its reaction pathway added two CoO and two triethylammonium chloride entities. The original inner  $\text{Al}_4(\text{OH})_4$  eight-membered cycle of **I** has been cleaved at two opposite Al–O(H)–Al edges to form four Al–OH groups while at the remaining Al–O(H)–Al edges two cobalt atoms have replaced the hydrogen atoms. The cobalt atoms are displaced on both sides of the polycyclic system and have further bonds to two OH groups forming a tripodal pyramidal arrangement. The fourth coordination site of the tetrahedrally distorted cobalt atoms is occupied by a chloride anion which has a hydrogen bond to the triethylammonium cation. Whereas in **5a** this hydrogen bonding is oriented opposite to the oxygen atom O(1), it points in **5b** in the same direction of O(3) which is an equivalent position to O(1) in **5a**.



**Figure 6.** Molecular structure of  $(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-} \cdot 2 \text{C}_7\text{H}_8$  (**5a**) with thermal ellipsoids (50%) at Al, Cl, N, O and Si. The phenyl and ethyl groups are represented in a simplified fashion (without hydrogen atoms), the solvent molecules are omitted. The triethyl ammonium ions are in green. Some pertinent bond lengths/Å and angles/°: Co(1)–O(1) 1.970(1), Co(1)–O(2) 1.988(2), Co(1)–O(3) 2.004(2), Co(1)–Cl(1) 2.2503(6), Al(1)–O(4) 1.717(2), Al(1)–O(9) 1.722(2), Al(1)–O(1) 1.764(2), Al(1)–O(3') 1.792(2), Al(2)–O(6) 1.707(2), Al(2)–O(7) 1.726(2), Al(2)–O(1) 1.763(2), Al(2)–O(2') 1.787(2), Si(1)–O(4)/Si(2)–O(6) mean: 1.593(1), Si(1)–O(5) 1.626(2), Si(2)–O(5) 1.639(2), Si(3)–O(7)/Si(4)–O(9) mean: 1.602(2), Si(3)–O(8')/Si(4)–O(8) mean: 1.636(2); O(1)–Co(1)–O(2) 107.66(6), O(1)–Co(1)–O(3) 114.24(6), O(2)–Co(1)–O(3) 99.40(6), O(1)–Co(1)–Cl(1) 115.80(5), O(2)–Co(1)–Cl(1) 110.10(5), O(3)–Co(1)–Cl(1) 108.36(5), Al(2)–O(1)–Al(1) 123.52(9), Al(2)–O(1)–Co(1) 113.76(8), Al(1)–O(1)–Co(1) 119.98(8), Al(2')–O(2)–Co(1) 120.81(8), Al(1')–O(3)–Co(1) 119.85(8). Hydrogen bonding: N(1)···Cl(1) 3.148(5), O(3)···O(7) 3.000(8); Cl(1)···H(1)–N(1) 155.2(4), O(7)···H(3)–O(3) 118.5(8).



**Figure 7.** The molecular structure of  $(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-} \cdot \text{C}_6\text{H}_6$  (**5b**) with thermal ellipsoids (50%) at Al, Cl, N, O and Si. The phenyl and ethyl groups are represented in a simplified fashion (without hydrogen atoms). The triethyl ammonium cations and their coordination to chlorine are in green. The intercalated benzene molecule as well as split-positions are not shown. Some pertinent bond lengths/Å and angles/°: Co(1)–O(3) 1.974(3), Co(1)–O(1) 1.988(3), Co(1)–O(2) 1.990(3), Co(1)–Cl(1) 2.276(1), Al(1)–O(4) 1.721(3), Al(1)–O(9) 1.733(3), Al(1)–O(3') 1.767(3), Al(1)–O(1) 1.788(3), Al(2)–O(6) 1.708(3), Al(2)–O(7) 1.721(3), Al(2)–O(3') 1.767(3), Al(2)–O(2) 1.795(3), Si(1)–O(4)/Si(2)–O(6) mean: 1.595(1), Si(1)–O(5) 1.625(4), Si(2)–O(5) 1.635(4), Si(3)–O(7)/Si(4)–O(9) mean: 1.601(2), Si(3)–O(8') 1.631(3), Si(4)–O(8) 1.624(3); O(3)–Co(1)–O(1) 112.3(1), O(3)–Co(1)–O(2) 107.9(1), O(1)–Co(1)–O(2) 98.0(1), O(3)–Co(1)–Cl(1) 112.31(9), O(1)–Co(1)–Cl(1) 113.70(9), O(2)–Co(1)–Cl(1) 111.73(9), Al(2')–O(3)–Al(1') 122.4(2), Al(2')–O(3)–Co(1) 116.5(2), Al(1')–O(3)–Co(1) 118.2(2). Hydrogen bonding: N(1)···Cl(1) 3.210(5), O(3)···O(7) 2.975(8); Cl(1)···H(1)–N(1) 172.5(4), O(7)···H(3)–O(3) 115.3(8).

Several years ago, we have found a similar structure to **5a, b** with the zinc derivative  $\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2]\text{Zn}_2\} \cdot 2 \text{OEt}_2$ .<sup>[13]</sup> The polycyclic alumosiloxane part of the zinc derivative is very similar to **5a, b** and even the zinc oxygen bond lengths show the same tendency (Zn–O(Al, Al) = 1.949(2), Zn–O(H, Al) = 1.969(2)) with shorter bonds to the oxygen atom bound to the two aluminum atoms like in the cobalt derivatives (mean values from **5a, b**: Co–O(Al, Al) = 1.972(2), Co–O(H, Al) = 1.993(8) Å, see also captions of Figures 6, 7). The differences in the transition metal oxygen bond lengths do not reflect the difference of the ionic radii for  $\text{Co}^{2+}$  (0.72 Å) and  $\text{Zn}^{2+}$  (0.74 Å) in tetrahedral coordination spheres, as longer bond lengths are found for cobalt in **5a** and **5b**.<sup>[23]</sup> This discrepancy must come from the charged chloride ligand at cobalt, whereas in the zinc derivative the fourth coordination sites at zinc are occupied by uncharged diethyl ether.

The two molecules **5a** and **5b** have almost equal Co–O bond lengths (mean: 1.987(9) (**5a**), 1.984(5) Å (**5b**)) but differ in their Co–Cl bond lengths by 0.026 Å. The shorter Co–Cl bond



length in **5a** is accompanied by a flatter  $\text{CoO}_3$  pyramid (sum of angles:  $321.3^\circ$ ) compared to **5b** ( $318.2^\circ$ ; see also captions of Figures 6 and 7). In general, the bond lengths and  $\text{Cl}\cdots\text{N}$  distances found for **5a, b** compare well with those found in comparable structures like tris(ethylene)diammonium cobalt tetrachloride ( $\text{Co}-\text{Cl}$  2.27(1),  $\text{Cl}\cdots\text{N}$  3.18(1) Å) and bis(triethylammonium) tetrachloro-cobalt(II) ( $\text{Co}-\text{Cl}$  2.265(9),  $\text{Cl}\cdots\text{N}$  3.215(5) Å) as may be seen by inspection of the captions of Figures 6 and 7.<sup>[24,25]</sup>

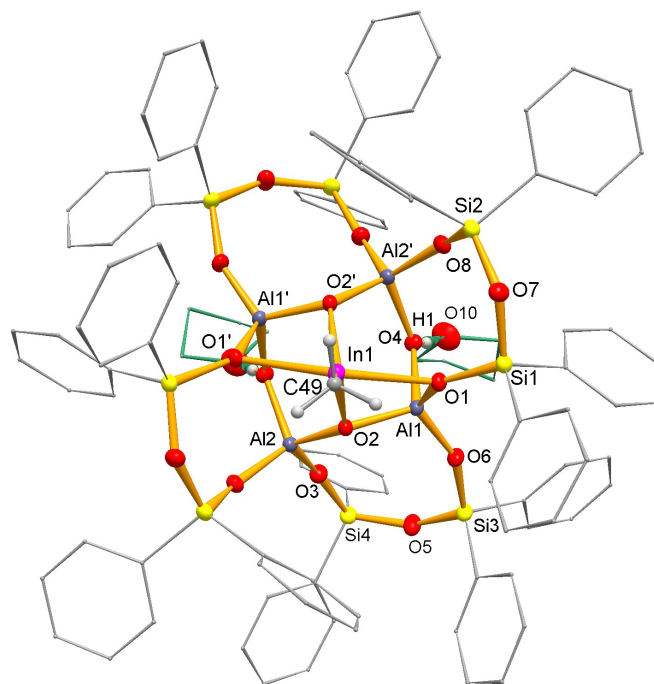
Concerning the polycyclic sub-structures in the two molecules **5a** and **5b** they are remarkably similar and strongly resemble the configuration first characterized for  $\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2]\text{Zn}_2\} \cdot 2 \text{OEt}_2$ .<sup>[13]</sup> Even the hydrogen bridge ( $\text{O}(3)-\text{H}(3)\cdots\text{O}(7')$  in **5a**,  $\text{O}(2)-\text{H}(2\#)\cdots\text{O}(9')$  in **5b**) is also present in the zinc derivative (not addressed explicitly in the published paper,  $\text{O}\cdots\text{O}$  2.87(1) Å) and comparable (see captions of Figures 6, 7). Another remarkable structural detail is the almost planar configuration by the metal atoms  $\text{Al}(1)$ ,  $\text{Al}(2)$ ,  $\text{Co}(1)$  around  $\text{O}(1)$  (**5a**) and  $\text{Al}(1')$ ,  $\text{Al}(2')$ ,  $\text{Co}(1)$  around  $\text{O}(3)$  (**5b**) with an angular sum of  $357.3^\circ$  respectively  $357.1^\circ$ . Again, these values compare well with the angular sum found for the zinc compound ( $356.1^\circ$ ).<sup>[13]</sup>

To resume, the minor structural differences between **5a** and **5b** show that the orientation of the triethylammonium cations has almost no impact to the structure of the anion. In comparison to the **3a/3b** case, in which the solvent molecules almost hardly affect the mutual orientation of the cation and anion, the different solvent molecules in the crystals of **5a** and **5b** trigger these orientations effectively.

In contrast to the reaction of **I** with  $\text{CoCl}_2$ , the reaction with trimethyl indium etherate (Scheme 4) leaves the eight-membered ring in **I** intact. By substitution of two hydrogen atoms in **I** by  $\text{In}-\text{CH}_3$  forming a  $\text{O}-\text{In}(\text{CH}_3)-\text{O}$  bridge a new compound  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2(\text{InCH}_3) \cdot 2 \text{O}(\text{CH}_2)_4$  (**6**) forms, which is displayed in Figure 8.

The molecule **6** crystallizes with toluene as space filler in the crystal and has crystallographic  $C_2$  point symmetry, the axis running through  $\text{In}(1)$  and  $\text{C}(49)$  (the hydrogen atoms of the methyl show a two-fold splitting). The two OH groups which have not reacted are coordinated by tetrahydrofuran molecules. The indium atom, in a first approximation, is five-coordinate with  $\text{C}(49)$ ,  $\text{O}(2)$  and  $\text{O}(2')$  in the equatorial plane and with  $\text{O}(1)$  and  $\text{O}(1')$  on the axis of a distorted trigonal bipyramid ( $\text{O}(1)-\text{In}(1)-\text{O}(1')$   $150.71(6)^\circ$ , although  $\tau_5$ -value of 0.22 is indicative for a quadratic pyramid.<sup>[26]</sup> This has nevertheless no structural meaning, as, apart the methyl ligand, the oxygen atoms are incorporated in the polycycle: the coordination sphere around indium is therefore dominated by geometric constrains, which can be seen for example from the narrow "bite angle"  $\text{O}(2)-\text{In}(1)-\text{O}(2')$  of  $84.60(6)^\circ$ . On the same line, the  $\text{In}-\text{O}$  bond lengths show a considerable difference with respect to the equatorial and axial positions ( $\Delta=0.223$  Å), so the coordination figure around  $\text{In}(1)$  can also be described as 3+2 [trigonal planar ( $\text{C}(49)$ ,  $\text{O}(2)$ ,  $\text{O}(2')$ ) + 2 almost orthogonal contacts ( $\text{O}(1)$  and  $\text{O}(1')$ ] (compare caption of Figure 8).

The compound **6** is structurally remarkably similar to the tin (II) derivative  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2\text{Sn} \cdot 2 \text{O}(\text{CH}_2)_4$  and crystal-



**Figure 8.** The molecular structure of  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2(\text{InCH}_3) \cdot 2 \text{O}(\text{CH}_2)_4 \cdot \text{C}_7\text{H}_8$  (**6**) with thermal ellipsoids (50%) at Al, In, O and Si. The phenyl and butyl groups are represented in a simplified fashion. The tetrahydrofuran molecules are in green. The intercalated toluene molecule as well as split positions at THF and the methyl group are not shown. Hydrogen atoms bonded to the carbon atoms (apart  $\text{C}(49)$ ) have been omitted. Some pertinent bond lengths/Å and angles/ $^\circ$ :  $\text{In}(1)-\text{C}(49)$  2.104(3),  $\text{In}(1)-\text{O}(2)$  2.130(1),  $\text{In}(1)-\text{O}(1)$  2.353(1),  $\text{Al}(1)-\text{O}(6)$  1.687(1),  $\text{Al}(1)-\text{O}(1)$  1.765(1),  $\text{Al}(1)-\text{O}(2)$  1.768(1),  $\text{Al}(1)-\text{O}(4)$  1.790(1),  $\text{Al}(2)-\text{O}(3)$  1.706(1),  $\text{Al}(2)-\text{O}(8')$  1.715(1),  $\text{Al}(2)-\text{O}(2)$  1.763(1),  $\text{Al}(2)-\text{O}(4')$  1.811(1),  $\text{Si}(1)-\text{O}(1)$  1.638(1),  $\text{Si}(2)-\text{O}(8)/\text{Si}(3)-\text{O}(6)/\text{Si}(4)-\text{O}(3)$  mean: 1.605(1),  $\text{Si}(1,2)-\text{O}(7)/\text{Si}(3,4)-\text{O}(5)$  mean: 1.634(4);  $\text{C}(49)-\text{In}(1)-\text{O}(2)$   $137.70(3)$ ,  $\text{O}(2)-\text{In}(1)-\text{O}(2')$   $84.60(6)$ ,  $\text{C}(49)-\text{In}(1)-\text{O}(1)$   $104.65(3)$ ,  $\text{O}(2)-\text{In}(1)-\text{O}(1)$   $70.02(4)$ ,  $\text{O}(2')-\text{In}(1)-\text{O}(1)$   $88.15(4)$ ,  $\text{O}(1)-\text{In}(1)-\text{O}(1')$   $150.71(5)$ . Hydrogen bonding:  $\text{O}(4)\cdots\text{O}(10)$  2.564(5);  $\text{O}(10)\cdots\text{H}(1)-\text{O}(4)$  166.8(1).

lizes isotypically in the same space group with similar lattice constants.<sup>[12]</sup> In these two compounds tin and indium occupy similar coordination figures, the methyl ligand at indium taking formally the place of the lone pair at the tin atom. Compared to **6** the difference in the equatorial to axial positions in the tin compound are somewhat larger ( $\text{Sn}-\text{O}_e$  2.150(3),  $\text{Sn}-\text{O}_a$  2.432(3),  $\Delta=0.282$  Å<sup>[12]</sup>), which is not surprising as two-coordinate base-free tin(II) compounds (stannylenes) are well known since many years, even in the crystalline state.<sup>[27]</sup>

## Conclusions

The transformations of polycyclic aluminosiloxanes **I** or **II** into either metal derivatives (**5a**, **5b**, **6**) or new polycycles (**1**, **2**, **3a, b**, **4**) have been evaluated. By hydrolysis of  $\text{Al}(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3\text{Al} \cdot 2 \text{OEt}_2$  (**IIa**) new tricyclic aluminosiloxanes

can be obtained which all are spirocyclic with different central ring sizes and structures. The choice of the amine in the reaction is crucial. Whereas with diethyl amine the central ring is asymmetric with an oxygen respectively O–SiPh<sub>2</sub>–O–SiPh<sub>2</sub>–O linkage between the two aluminum atoms (**1**), with triethylamine the central ring has two diphenyl siloxane linkers, which can be shorter (**2**) or longer (**3**). With 1,4-diazabicyclo[2,2,0]octane exclusively one compound (**4**) can be isolated. The compounds **3a** and **3b** crystallize in different lattices due to the absence or presence of solvent molecules in the crystal, which has almost no impact to the conformations of the constituent rings.

The role of the amines is two-fold: they function as proton acceptors and by hydrogen bridging, they stabilize the anions, which is nicely shown with diethyl ammonium in compound **1** in comparison to triethyl ammonium in **2** or **3b**. There is also an influence of the bases on the conformers as found by checking the twelve-membered inner cycles in **3b** (triethylammonium ion) and **4** (protonated 1,4-diazabicyclo[2,2,0]octane).

The two new metal derivatives of (Ph<sub>2</sub>SiO)<sub>8</sub>[Al(O)OH]<sub>4</sub> (**I**), the di-cobalt derivatives **5a, b** and the indium derivative **6** have in a structural sense both predecessors and show that irrespective of the metal atom the coordination ability of **I** depends on charge and size of the metal element and on reaction conditions. The two bonding forms of triethyl ammonium towards the [(Ph<sub>2</sub>Si)<sub>2</sub>O<sub>3</sub>]<sub>4</sub>[Al<sub>4</sub>(OH)<sub>4</sub>O<sub>2</sub>](CoCl)<sub>2</sub><sup>2-</sup> anions, generating coordination isomers **5a** and **5b**, illustrate impressively the potential role of solvent molecules as space fillers in van-der-Waals lattices.

## Experimental Section

All manipulations were performed in a nitrogen atmosphere under exclusion of water and air. Solvents were purified prior to use by distillation and were kept over sodium wire. NMR spectra were obtained with Bruker AC200F/AC200P, FT-IR with a Varian 2000 and UV-Vis spectra with a Lambda 35 of Perkin-Elmer. The data sampling for single crystal X-ray diffraction analyses was performed with a Bruker X8 Apex II CCD using Mo-K<sub>α</sub> radiation. The structures were solved and refined using the SHELX-system in the graphical user interface *ShelXle* and are graphically represented using the *Diamond* program.<sup>[28,29]</sup>

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies from the data can be obtained free of charge on quoting the depository numbers CCDC-2072837 (**1**), CCDC-2072839 (**2**), CCDC-2072856 (**3b**), CCDC-2072838 (**4**), CCDC-2072857 (**5a**), CCDC-2072858 (**5b**), CCDC-2072833 (**6**). (Fax: +44 1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sup>-</sup><sub>2</sub>Al<sub>2</sub>[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sub>2</sub>·2 H<sub>2</sub>N<sup>+</sup>Et<sub>3</sub>·1.25 C<sub>7</sub>H<sub>8</sub> (**1**): To a solution of 0.495 g (0.3438 mMol) [O(SiPh<sub>2</sub>)O(SiPh<sub>2</sub>)O]<sub>3</sub>Al<sub>2</sub>·2 OEt<sub>2</sub> (**IIa**)<sup>[16]</sup> in 15 mL toluene a mixture of 1.5 mL (14.6 mMol) diethyl amine and 0.02 mL (1.2 mMol) water is dropped under stirring. After 0.5 h the volatiles are pumped off under reduced pressure and the residue is redissolved in 5 mL toluene under warming. After 12 h standing at 4 °C 0.116 g (0.13 mMol, 38 %) of colorless crystals **1** are obtained. C<sub>80</sub>H<sub>84</sub>Al<sub>2</sub>N<sub>2</sub>O<sub>10</sub>Si<sub>6</sub>·1.25 C<sub>7</sub>H<sub>8</sub> (1571.16). No correct analyses because

of high reactivity. <sup>1</sup>H NMR (C<sub>7</sub>H<sub>8</sub>/C<sub>6</sub>D<sub>6</sub>): δ = 1.12 (t, CH<sub>3</sub>CH<sub>2</sub>N); 3.25 (q, CH<sub>3</sub>CH<sub>2</sub>N); 6.96–7.17 (m, H-phenyl). <sup>13</sup>C NMR (C<sub>7</sub>H<sub>8</sub>/C<sub>6</sub>D<sub>6</sub>): δ = 11.38 (s, CH<sub>3</sub>CH<sub>2</sub>N); 47.4 (s, CH<sub>3</sub>CH<sub>2</sub>N); 125.6–135.4 ppm (m, C-Phenyl). <sup>29</sup>Si NMR (THF): δ = -35.9, -47.5. **X-ray data:** Triclinic, P-1, a = 14.3602(5), b = 24.2059(8), c = 25.3231(8) Å, α = 88.189(2), β = 82.243(2), γ = 74.939(2)°, V = 8422.2(5) Å<sup>3</sup>, Z = 4. Measuring temperature: 122 K. Structure refinement: 36696 reflections (R(int) = 0.0382; θ [°] = 1.48 to 27.00; completeness to θ = 27.0: 99.8%; max. and min. transmission: 0.982 and 0.906); refinement method: full matrix least squares on F<sup>2</sup>; 2315 parameters (1334 restraints); final R indices [I > 2σ(I)]: R<sub>1</sub> = 0.0476, wR<sub>2</sub> = 0.1110; largest diff. peak and hole: [e Å<sup>-3</sup>] 1.59 and -0.74. There is a B-alert in the checkcif file concerning the largest diff. peak (see above), which is due to atom splitting within molecule **1b**.

[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sup>-</sup><sub>2</sub>Al<sub>2</sub>[O(Ph<sub>2</sub>Si)O]<sub>2</sub>·2 HN<sup>+</sup>Et<sub>3</sub> (**2**), [O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sup>-</sup><sub>2</sub>Al<sub>2</sub>[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sub>2</sub>·2 HN<sup>+</sup>Et<sub>3</sub> (**3a, 3b**). 0.4 g (0.2778 mMol) [O(SiPh<sub>2</sub>)O(SiPh<sub>2</sub>)O]<sub>3</sub>Al<sub>2</sub>·2 OEt<sub>2</sub> (**IIa**)<sup>[16]</sup> are dissolved in 20 mL toluene under warming. To this solution a mixture of 0.15 mL (1.08 mMol) triethyl amine and 0.02 mL (1.1 mMol) water is added slowly. The mixture is stirred for 1 h at 50–60 °C. On 12 h standing at ambient temperature 0.302 g (0.1583 mMol; 57 %) of colorless crystals are obtained, which are almost entirely compound **3a**. Within the crystals very few of a different habitus (less block like) can be sorted out under the microscope which turn out (after X-ray structure analysis) to be compound **2**. When crystals of **3a** are redissolved in toluene, a second crystallization leads to phase **3b** which differs from **3a** in the crystal packing and space group due to solvent molecules incorporated in the crystal.

[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sup>-</sup><sub>2</sub>Al<sub>2</sub>[O(Ph<sub>2</sub>Si)O]<sub>2</sub>·2 HN<sup>+</sup>Et<sub>3</sub>·C<sub>7</sub>H<sub>8</sub> (**2**). No analytical data due to small number of crystals. C<sub>91</sub>H<sub>100</sub>Al<sub>2</sub>N<sub>2</sub>O<sub>10</sub>Si<sub>6</sub> (1604.22). **X-ray data:** Triclinic, P-1, a = 11.643(1), b = 12.689(1), c = 15.432(2) Å, α = 74.431(5), β = 73.483(6), γ = 85.099(6)°, V = 2105.3(4) Å<sup>3</sup>, Z = 1. Measuring temperature: 152 K. Structure refinement: 9107 reflections (R(int) = 0.0259; θ [°] = 1.424 to 27.00; completeness to θ = 25.24: 99.4%; max. and min. transmission: 0.957 and 0.970); refinement method: full matrix least squares on F<sup>2</sup>; 660 parameters (84 restraints); final R indices [I > 2σ(I)]: R<sub>1</sub> = 0.0439, wR<sub>2</sub> = 0.1224; largest diff. peak and hole: [e Å<sup>-3</sup>] 0.373 and -0.527.

[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sup>-</sup><sub>2</sub>Al<sub>2</sub>[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sub>2</sub>·2 HN<sup>+</sup>Et<sub>3</sub> (**3a**). C<sub>108</sub>H<sub>112</sub>Al<sub>2</sub>N<sub>2</sub>O<sub>12</sub>Si<sub>8</sub> (1908.68): calcd. C 67.96, H 5.91, N 1.47%; found C 67.83, H 6.22, N 1.54%. <sup>1</sup>H NMR (C<sub>7</sub>H<sub>8</sub>/C<sub>6</sub>D<sub>6</sub>): δ = 0.47 (t, CH<sub>3</sub>CH<sub>2</sub>N); 2.24 (q, CH<sub>3</sub>CH<sub>2</sub>N); 6.89–7.21 (H-phenyl). <sup>13</sup>C NMR (C<sub>7</sub>H<sub>8</sub>/C<sub>6</sub>D<sub>6</sub>): δ = 7.92 (s, CH<sub>3</sub>CH<sub>2</sub>N); 44.91 (s, CH<sub>3</sub>CH<sub>2</sub>N); 128.1 ppm (p-C-phenyl), 135.0 ppm (o-C-phenyl), 140.5 (Si-C-phenyl) <sup>29</sup>Si NMR (THF): δ = -39.3, -53.6. **X-ray data**<sup>[16]</sup>.

[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sup>-</sup><sub>2</sub>Al<sub>2</sub>[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sub>2</sub>·2 HN<sup>+</sup>Et<sub>3</sub>·2 C<sub>7</sub>H<sub>8</sub> (**3b**). C<sub>128</sub>H<sub>128</sub>Al<sub>2</sub>N<sub>2</sub>O<sub>12</sub>Si<sub>8</sub> (2092.96). Spectroscopic data as **3a**. **X-ray data:** Monoclinic, P2<sub>1</sub>/n, a = 13.018(1), b = 25.578(2), c = 17.411(2) Å, β = 100.78(1)°, V = 5694.9(2) Å<sup>3</sup>, Z = 2. Measuring temperature: 152 K. Structure refinement: 13883 reflections (R(int) = 0.0304); θ [°] = 1.432 to 28.115; completeness to θ = 25.242°: 100%; max. and min. transmission: 0.914 and 0.965; refinement method: full matrix least squares on F<sup>2</sup>; 722 parameters (1 restraints); final R indices [I > 2σ(I)]: R<sub>1</sub> = 0.0407, wR<sub>2</sub> = 0.1007 largest diff. peak and hole: [e Å<sup>-3</sup>] 0.557 and -0.394.

[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sup>-</sup><sub>2</sub>Al<sub>2</sub>[O(Ph<sub>2</sub>SiOSiPh<sub>2</sub>)O]<sub>2</sub>·2 HN<sup>+</sup>(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N·2 C<sub>7</sub>H<sub>8</sub> (**4**). The procedure is similar to the synthesis of **3a/b** replacing triethyl amine by 1,4-diazabicyclo[2.2.0]octane. With 0.503 g (0.349 mMol) of **IIa** 0.29 g (43 %) of colorless crystals **4** could be obtained.

C<sub>108</sub>H<sub>106</sub>Al<sub>2</sub>N<sub>4</sub>O<sub>12</sub>Si<sub>8</sub>·2 C<sub>7</sub>H<sub>8</sub> (2114.92). No analytical data due to high reactivity. <sup>1</sup>H NMR (C<sub>7</sub>H<sub>8</sub>/C<sub>6</sub>D<sub>6</sub>): δ = 2.41 (s, NCH<sub>2</sub>CH<sub>2</sub>N); 7.05–7.24

(m, H-phenyl).  $^{13}\text{C NMR}$  ( $\text{C}_7\text{H}_8/\text{C}_6\text{D}_6$ ):  $\delta = 40.4$  ( $\text{NCH}_2\text{CH}_2\text{N}$ ); 125.5–137.6 ppm (m, C-Phenyl).  $^{29}\text{Si NMR}$  (THF):  $\delta = -35.9$ ,  $-36.8$ ,  $-51.3$ . **X-ray data:** Monoclinic,  $\text{P}2_1/c$ ,  $a = 22.9874(8)$ ,  $b = 24.7312(4)$ ,  $c = 19.7939(3)$  Å,  $\beta = 92.692(1)$ ,  $V = 11240.5(3)$  Å $^3$ ,  $Z = 4$ . Measuring temperature: 122 K. Structure refinement: 39233 reflections ( $R(\text{int}) = 0.0591$ );  $\theta$  [ $^\circ$ ] = 1.21 to 32.09; completeness to  $\theta = 25.242^\circ$ : 100.0%; max. and min. transmission: 0.970 and 0.932; refinement method: full matrix least squares on  $F^2$ ; 1343 parameters (0 restraints); final R indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0512$ ,  $wR_2 = 0.1085$ ; largest diff. peak and hole: [ $e \text{ \AA}^{-3}$ ] 0.531 and  $-0.358$ .

$(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-} \cdot 2 \text{C}_7\text{H}_8$  (**5a**),  $(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-} \cdot \text{C}_6\text{H}_6$  (**5b**). To a solution of 0.960 g (0.452 mMol) alumosiloxane  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4 \cdot 4 \text{OEt}_2$  ( $I$ ) $^{[11]}$  in 30 mL toluene a mixture of 0.3 mL (2.16 mMol) triethyl amine and 0.02 mL (1.1 mMol) water is added slowly. This solution is further dropped to a suspension of 0.117 g (0.901 mMol) cobalt dichloride in 10 ml toluene. The bright blue reaction mixture is held during 30 m under reflux. The reaction medium turns into a clear dark blue solution. After stirring for 10 h half of the solution is kept at ambient temperature, whereas from the other half the solvent and volatiles are separated under reduced pressure resulting in a blue solid. From the original solution blue crystals of **5a** form, while the solid redissolved in benzene transforms in blue crystals **5b**. The overall yield (20%) is small as other crystalline products like  $\text{CoCl}_2 \cdot 2 \text{NEt}_3$  and  $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4 \cdot 2 \text{NEt}_3$  $^{[10]}$  form as well.

$(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-} \cdot 2 \text{C}_7\text{H}_8$  (**5a**).  $\text{C}_{122}\text{H}_{132}\text{Al}_4\text{Cl}_2\text{Co}_2\text{N}_2\text{O}_{18}\text{Si}_8$  (2435.74): calcd. C 60.16, H 5.46, N 1.15, Co 4.83%; found C 59.11, H 5.79, N 2.04, Co 5.61%. **UV/vis:** 628, 663, 693 nm. **X-ray data:** Triclinic,  $\text{P}-1$ ,  $a = 11.3900(4)$ ,  $b = 15.2485(5)$ ,  $c = 17.8686(6)$  Å,  $\alpha = 97.293(2)$ ,  $\beta = 93.222(2)$ ,  $\gamma = 93.868(2)^\circ$ .  $V = 3064.7(2)$  Å $^3$ ,  $Z = 1$ . Measuring temperature: 122 K. Structure refinement: 13515 reflections ( $R(\text{int}) = 0.0503$ );  $\theta$  [ $^\circ$ ] = 1.35 to 27.39; completeness to  $\theta = 25.242^\circ$ : 99.5%; max. and min. transmission: 0.939 and 0.801; refinement method: full matrix least squares on  $F^2$ ; 793 parameters (233 restraints); final R indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0391$ ,  $wR_2 = 0.0826$ ; largest diff. peak and hole: [ $e \text{ \AA}^{-3}$ ] 0.446 and  $-0.283$ .

$(\text{HN}^+\text{Et}_3)_2\{[(\text{Ph}_2\text{Si})_2\text{O}_3]_4[\text{Al}_4(\text{OH})_4\text{O}_2](\text{CoCl})_2\}^{2-} \cdot \text{C}_6\text{H}_6$  (**5b**).  $\text{C}_{114}\text{H}_{122}\text{Al}_4\text{Cl}_2\text{Co}_2\text{N}_2\text{O}_{18}\text{Si}_8$  (2329.57). **X-ray data:** Monoclinic,  $\text{P}2_1/n$ ,  $a = 17.827(1)$ ,  $b = 18.978(1)$ ,  $c = 18.160(1)$  Å,  $\beta = 105.829(2)^\circ$ .  $V = 5910.9(6)$  Å $^3$ ,  $Z = 2$ . Measuring Temperature: 122(2) K. Structure refinement: 12912 reflections ( $R(\text{int}) = 0.079$ );  $\theta$  [ $^\circ$ ] = 1.419 to 26.999; completeness to  $\theta = 25.242^\circ$ : 100%; max. and min. transmission: 0.9252 and 0.894; refinement method: full matrix least squares on  $F^2$ ; 882 parameters (667 restraints); final R indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0584$ ,  $wR_2 = 0.1345$ ; largest diff. peak and hole: [ $e \text{ \AA}^{-3}$ ] 0.86 and  $-0.37$ .

$(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_2[\text{AlO}]_2(\text{InCH}_3) \cdot 2 \text{O}(\text{CH}_2)_4 \cdot \text{C}_7\text{H}_8$  (**6**). A solution of 0.247 g (1.06 mMol) diethyl etherate of indium trimethyl  $(\text{Me}_3\text{In} \cdot \text{OEt}_2)^{[30]}$  in 2 mL tetrahydrofuran (THF) is slowly dropped to a solution of 1.12 g (0.528 mMol) alumosiloxane  $I$  $^{[11]}$  in 8 mL THF under stirring. The colorless solution is further stirred for 5 h; then the solvents are removed under reduced pressure obtaining a white solid (1.214 g, 97% with reference to **I**). This solid is redissolved in 3 mL toluene from which colorless crystals form at  $-15^\circ\text{C}$ .  $\text{C}_{105}\text{H}_{107}\text{Al}_4\text{InO}_{18}\text{Si}_8 \cdot \text{C}_7\text{H}_8$  (2190.47): calcd. In 5.24, found In 4.55% (C,H-analytical values were not satisfactory due to high reactivity).  $^1\text{H NMR}$  (THF/ $\text{C}_6\text{D}_6$ , crystals):  $\delta = -0.5$  (s,  $\text{InCH}_3$ ); 2.28 (s,  $\text{C}_6\text{H}_5\text{-CH}_3$ ); 6.8–7.8 (m, H-phenyl); 9.3 (s,  $\text{Al-OH}$ ).  $^{13}\text{C NMR}$  (THF/ $\text{C}_6\text{D}_6$ , crystals):  $\delta = -5.0$  ( $\text{InCH}_3$ ); 21.0 ( $\text{C}_6\text{H}_5\text{-CH}_3$ ); 125.5–137.9 ppm (m, C-Phenyl).  $^{29}\text{Si NMR}$  (THF, solid reaction residue before crystallization):  $\delta = -32.8$ ,  $-43.0$ ,  $-45.8$ ,  $-46.5$ . **X-ray data:** Monoclinic,  $\text{C}2/c$ ,  $a = 19.9703(17)$ ,  $b = 21.0495(17)$ ,  $c = 26.166(2)$  Å,  $\beta = 93.355(6)^\circ$ ,  $V = 10980(2)$  Å $^3$ ,  $Z = 4$ . Measuring temperature: 130 K. Structure refinement: 20841 reflections ( $R(\text{int}) = 0.0322$ );  $\theta$  [ $^\circ$ ] = 1.407 to 33.15;

completeness to  $\theta = 25.242^\circ$ : 100%; max. and min. transmission: 0.908 and 0.812; refinement method: full matrix least squares on  $F^2$ ; 662 parameters (44 restraints); final R indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0388$ ,  $wR_2 = 0.0948$ ; largest diff. peak and hole: [ $e \text{ \AA}^{-3}$ ] 1.60 and  $-0.789$ .

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