in 50 mL toluene cooled with methanol/dry ice (monitored by 31P-NMR) until the conversion is quantitative. After the solution has been allowed to warm up to room temperature, the solvent is removed in vacuo, the residue taken up in a little acetonitrile, and the spontaneous crystallization completed in the refrigerator at ca. \(-2^\circ\mathrm{C}\). Yield: 2.11 g (58%), m. p. \(93^\circ\mathrm{C}\).

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Molecular structure of the gaseous crystals. It is evident from the crystal diffraction data and refined to \(R=6.6\%\) (\(R_m=5.5\%\)) that the gaseous crystals are actually formed in the refrigerator at ca. \(-2^\circ\mathrm{C}\). Yield: 2.11 g (58%), m. p. \(93^\circ\mathrm{C}\).

To establish the mechanism of reaction we have now repeated the thermolysis of 1 in the presence of a potential trapping reagent for 4 or 5; we chose for this purpose the dimeric tin(IV) bis(tert-butoxide) \(\mathrm{Sn}_2\left(\text{OR}\right)_2\) which is loosely bound in solution, for it proved useful in the “trapping” of monomeric thallium(III) tert-butoxide with formation of \(\mathrm{Sn}_2\left(\text{OR}\right)_2\). To the solution of 1 in 50 mL toluene cooled with methanol/dry ice (monitored by 31P-NMR) until the conversion is quantitative. After the solution has been allowed to warm up to room temperature, the solvent is removed in vacuo, the residue taken up in a little acetonitrile, and the spontaneous crystallization completed in the refrigerator at ca. \(-2^\circ\mathrm{C}\). Yield: 2.11 g (58%), m. p. \(93^\circ\mathrm{C}\).

2 \[\mathrm{Me}_2\mathrm{Si}(\text{NR})_2\mathrm{Sn}_2\] + \[\frac{1}{2} \mathrm{Sn}_2(\text{OR})_2\] \(\xrightarrow{\Delta}\) \[\mathrm{Sn}_2\left(\text{NR}\right)_2(\text{OR})_2\] + 2 \[\mathrm{Me}_2\mathrm{Si}(\text{NR})_2\mathrm{Sn}\]

The novel compound \(\mathrm{Sn}_2\left(\text{NR}\right)_2(\text{OR})_2\), which is still stable even above 250°C, is also formed with a twentyfold excess of 6. Its composition is confirmed by elemental analysis, mass spectrum and 1H-NMR spectrum. As the X-ray structure analysis shows, the molecule 7 has a crystallographic plane of symmetry (cf. Figure 1); the deviation from the higher point symmetry \(C_m\) (mm2) is however insignificant, so this symmetry can be assigned to the free molecule. Supporting evidence for this is provided by the 1H-NMR spectrum of 7 in toluene, \(\delta=1.28\) (s, 18H) and 1.58 (s, 18H), which indicates the same chemical environment for each of the pairs of tert-butyl groups at the nitrogen and oxygen atoms independently of the temperature (\(-80\) to \(+40^\circ\mathrm{C}\)).

Purely geometrically, the heptatomic cyclic moiety in 7, which to our knowledge is a novelty in the structural chemistry of cage-like polycycles, can be regarded as made up of two trigonal bipyramids (\(\mathrm{Sn}_2\left(\text{NR}\right)_2\mathrm{Sn}\)) with a common face (\(\mathrm{Sn}_2\mathrm{N}\)). Four of the seven atoms forming the “cage” bear tert-butyl substituents, which are oriented in the direction of the apices of a distorted bisphenoid.

\(\mathrm{Sn}_8(\text{NR})_2(\text{OrBu})_2\), A Molecule with a Novel, Heptaatomic, Polycyclic Framework**

By Michael Veith* and Walter Frank

When strongly heated, the tricyclic compound 1 is quantitatively converted into 2 and 3 (R=tertBu)[1].

\[\begin{align*}
\text{Me}_2\text{Si} & \equiv \text{Sn} & \equiv \text{N} & \equiv \text{R} & \equiv \text{Sn}_4(\text{NR})_4
\end{align*}\]

The rate-determining step of this reaction follows a first order rate law[1]. We therefore assumed that tert-butyliminostannanediyl ("stannylene") is initially formed as an unstable intermediate, from which the stable tetramer 3 is formed stepwise[2].

\[\begin{align*}
2 \left\{\text{SnN} & \equiv \text{R}\right\} & \rightarrow \left\{\text{Sn} & \equiv \text{N}\right\} & \left\{\text{Sn} & \equiv \text{Si}\right\} & \rightarrow & \frac{1}{2} \text{Sn}_4(\text{NR})_4
\end{align*}\]

To the solution of 1 in 50 mL toluene cooled with methanol/dry ice (monitored by 31P-NMR) until the conversion is quantitative. After the solution has been allowed to warm up to room temperature, the solvent is removed in vacuo, the residue taken up in a little acetonitrile, and the spontaneous crystallization completed in the refrigerator at ca. \(-2^\circ\mathrm{C}\). Yield: 2.11 g (58%), m. p. \(93^\circ\mathrm{C}\).

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Two of the three tin atoms in 7 are trigonal-pyramidally coordinated, whereas one (Sn2) has four nearest neighbors. Thus, the usual coordination number 3 for SnIII atoms is not only stepped in larger molecular cages but also in strongly strained systems. The environment at the nitrogen atom is distorted-tetrahedral, that at the oxygen atom trigonal planar. In the chemical formulation of 7 the bonding may simply be described with donor acceptor bonds symbolized by arrows.

\[
\text{7} \\
\text{8}
\]

This description of the structure is not only formal (cf. Table 1). The molecule 7 is therefore to be regarded as a Lewis acid-base adduct of 5 and monomeric 6. Control experiments and kinetic investigations suggest that 5 occurs as intermediate in reaction (a): Thus, e.g., no reaction takes place between 3 and 6, even under extreme conditions (sealed tube, 270°C).

Other heptaatomic polycycles are known, but their structures mostly derive from the "open" norsecocubane. An example of this type of structure is Sn(NR)2(NHR)2. On comparing 8 and 7 there is a very striking similarity in composition, and in a broad sense (replacement of NH by O) they are even isosteric. The sp3 hybridization brought about in 8 by the hydrogen atoms on the nitrogen atoms leads to the norsecocubane-like structure, whereas in 7 the oxygen atoms are sp2 hybridized and thus facilitate the formation of the "closed" polycycle.

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[5] A mixture of 1 (3.14 g, 6.2 mmol) and 6 (0.82 g, 1.55 mmol) is heated without solvent for 30 min at 210°C. 2 is isolated from the solid reaction mixture by condensation (spectroscopic characterization [2]) at 40°C/0.01 torr, while 7 is obtained by sublimation at 80°C/0.001 torr. Recrystallization from toluene furnishes 1.78 g (89%) colorless 7 (m.p. 129°C), which is readily soluble in benzene, hexane, and diethyl ether.


Isolation of a Sulfur-Rich Binary Mercury Species from a Sulfide-Containing Solution: [Hg(S0)2]2+, a Complex with $S_5^{2-}$ Ligands

By Achim Müller*, Jürgen Schimanski, and Uwe Schimanski

The increased solubility of heavy metal sulfides of the "H₂S group" of the analytical separation procedure of the metal cations (e.g. of HgS) in alkaline sulfide-containing solutions is not only of general chemical interest (possible formation of unusual thiometalates) but also of analytical and mineralogical interest. Sulfide mineral ores are mainly formed hydrothermally (from post-magmatic fluids); it appears remarkable that the formation of many ore deposits cannot be conclusively explained because of the very small solubility products (e.g. of α-HgS, cinna-...