

in 50 mL toluene cooled with methanol/dry ice (monitored by  $^{31}\text{P}$ -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.  $-2^\circ\text{C}$ . Yield: 2.11 g (58%), m. p. =  $93^\circ\text{C}$ .

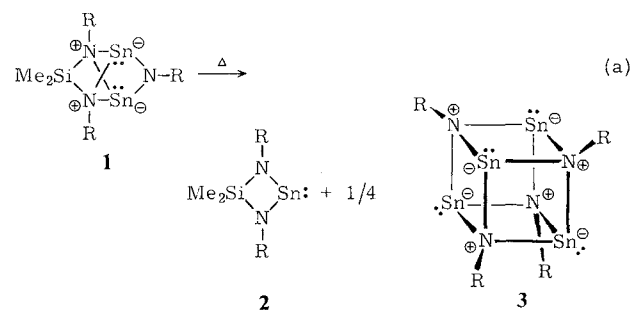
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[5] Molecular structure of **3**: triclinic,  $P\bar{1}$ ,  $a=921.1(4)$ ,  $b=1046.0(4)$ ,  $c=1536.4(11)$  pm,  $\alpha=76.24(4)$ ,  $\beta=83.09(5)$ ,  $\gamma=86.38(3)^\circ$ ,  $V=1426.4 \times 10^6$  pm $^3$ ,  $\rho_{\text{calc}}=1.06$  g/cm $^3$ ,  $Z=2$ . The structure was determined by direct methods (SHELXTL) from 3731 single crystal diffractometer data and refined to  $R=6.8\%$  ( $R_w=5.5\%$ ). Geometry: sum of angles at P =  $359.7^\circ$  (almost planar), angle between the aryl plane and the POC plane  $80^\circ$ ; angles  $C_{\text{aryl}}\text{PO}$   $121.0$ ,  $C_{\text{aryl}}\text{PC}$   $113.1$ ,  $\text{POC}$   $125.6^\circ$ ; distances  $\text{P}=\text{O}$   $145.8(3)$ ,  $\text{P}=\text{C}$   $165.7(4)$ ,  $\text{O}\cdots\text{C}$   $277$  pm (aryl = 2,4,6-tri-*tert*-butylphenyl). Further details on the crystal structure investigation can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen by quoting the depository number CSD 50 591, the names of the authors, and the journal citation.  
[6] Selected NMR parameters:  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ , 32.2 MHz,  $\text{H}_3\text{PO}_4$  ext.):  $\delta=153.7$  (s);  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ , 20.0 MHz, TMS int.):  $\delta=103.8$  (d),  $J(\text{P}=\text{C})=113.2$  Hz.

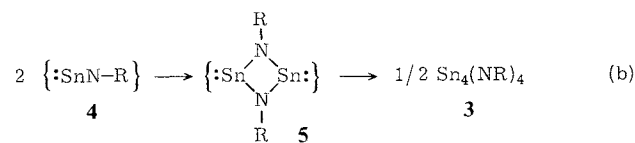
## $\text{Sn}_3(\text{N}t\text{Bu})_2(\text{O}t\text{Bu})_2$ , A Molecule with a Novel, Heptaatomic, Polycyclic Framework\*\*

By Michael Veith\* and Walter Frank

When strongly heated, the tricyclic compound **1** is quantitatively converted into **2** and **3** ( $\text{R} = t\text{Bu}$ )<sup>[1]</sup>.



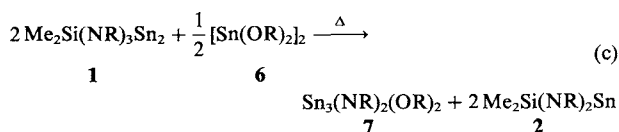
The rate-determining step of this reaction follows a first order rate law<sup>[1]</sup>. We therefore assumed that *tert*-butyliminostannanedyl ("stannylene") is initially formed as an unstable intermediate, from which the stable tetramer **3** is formed stepwise<sup>[2]</sup>.



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[\*\*] Cyclic Diazastannylenes, Part 20. This work was supported by the Fonds der Chemischen Industrie.—Part 19: M. Veith, M. Grosser, V. Huch, *Z. Anorg. Allg. Chem.*, in press.

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(II) bis(*tert*-butoxide) **6**<sup>[3]</sup>, which is loosely bound in solution, for it proved useful in the "trapping" of monomeric thallium(I) *tert*-butoxide with formation of  $\text{Tl}(\text{O}t\text{Bu})_3\text{Sn}^{[4]}$ .



The novel compound **7**<sup>[5]</sup>, which is still stable even above  $250^\circ\text{C}$ , is also formed with a twentyfold excess of **6**. Its composition is confirmed by elemental analysis, mass spectrum and  $^1\text{H}$ -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  $C_{2v}$  ( $\text{mm}2$ ) is however insignificant, so this symmetry can be assigned to the free molecule. Supporting evidence for this is provided by the  $^1\text{H}$ -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  $+40^\circ\text{C}$ ). Purely geometrically, the heptaatomic 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 ( $\text{SnN}_2\text{OSn}$ ) with a common face ( $\text{SnN}_2$ ). 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.

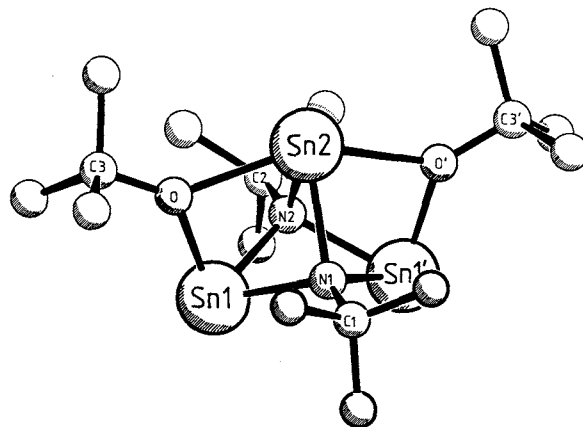
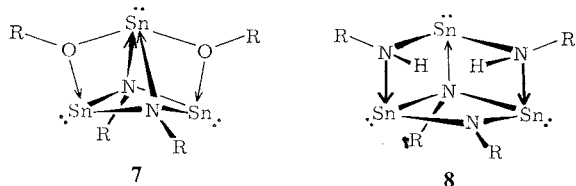


Fig. 1. Molecular structure of **7** in the crystal (orthorhombic, space group  $\text{Cmca}$ ,  $a=1758.6(9)$ ,  $b=1236.7(9)$ ,  $c=2192(1)$  pm,  $Z=8$ ,  $\rho_{\text{exp}}=1.81$  g cm $^{-3}$ ; 1380 independent reflections/115 parameters,  $R=0.054$ ). Further details of the crystal structure investigation are available from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, on quoting the depository number CSD 50 653, the names of the authors, and full citation of the journal.

Table 1. Selected bond lengths [pm] and angles [ $^\circ$ ] in the molecule **7**.

Sn1—O	210.0(5)	O—Sn1—N1	83.4(3)	Sn1—O—Sn2	88.0(2)
Sn1—N1	219.7(6)	O—Sn1—N2	83.4(3)	Sn1—O—C3	135.4(5)
Sn1—N2	219.8(5)	N1—Sn1—N2	68.4(2)	Sn2—O—C3	136.6(5)
Sn2—O	237.4(6)	O—Sn2—O'	147.9(3)	Sn1—N1—Sn2	88.7(3)
Sn2—N1	225.8(9)	O—Sn2—N1	76.2(1)	Sn1—N1—Sn1'	96.2(2)
Sn2—N2	220.1(8)	O—Sn2—N2	77.3(1)	Sn1—N1—C1	123.5(4)
O—C3	142(1)	N1—Sn2—N2	67.3(3)	Sn2—N1—C1	126.3(7)
N1—C1	149(2)			Sn1—N2—Sn2	90.2(2)
N2—C2	154(1)			Sn1—N2—Sn1'	96.2(2)
				Sn1—N2—C2	122.2(3)
				Sn2—N2—C2	127.0(6)

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 Sn<sup>II</sup> atoms is not only overstepped in larger molecular cages<sup>[6]</sup> 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.



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<sup>[7]</sup>. An example of this type of structure is Sn(NR)<sub>2</sub>(NHR)<sub>2</sub> **8**<sup>[8]</sup>. 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 sp<sup>3</sup> 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 sp<sup>2</sup> hybridized and thus facilitate the formation of the "closed" polycycle.

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CAS Registry numbers:

**1**, 71262-29-8; **6**, 84913-53-1; **7**, 88589-48-4.

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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.

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## Isolation of a Sulfur-Rich Binary Mercury Species from a Sulfide-Containing Solution: [Hg(S<sub>6</sub>)<sub>2</sub>]<sup>2-</sup>, a Complex with S<sub>6</sub><sup>2-</sup> Ligands

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The increased solubility of heavy metal sulfides of the "H<sub>2</sub>S group" of the analytical separation procedure of the

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ore deposits cannot be conclusively explained because of the very small solubility products (e.g. of α-HgS, cinnabar)<sup>[3-5]</sup>. We have been able to demonstrate that definite novel complexes of metals such as Cu, Ag, Au, and Hg are

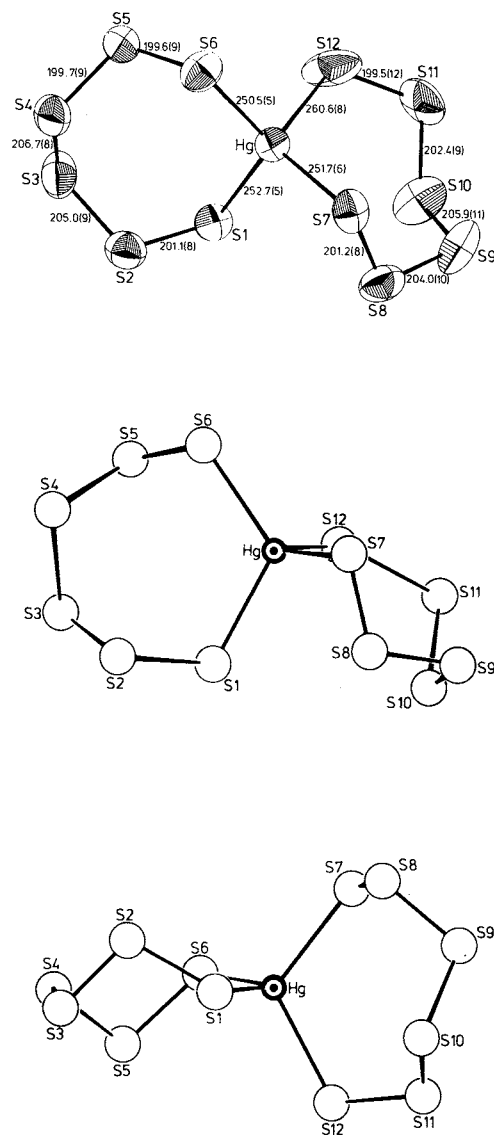


Fig. 1. Structure of the anionic complex **1a** (three projections) in the crystal of the tetraethylammonium salt **1** [space group P2<sub>1</sub>/c, a = 1283.1(5), b = 1762.9(7), c = 1455.6(5) pm, β = 97.42(3)°, Z = 4; Syntex P2<sub>1</sub>, MoKα, R = 0.086 for 3593 independent reflections (F<sub>0</sub> > 3.92σ(F<sub>0</sub>)]. Bond angles: S1-Hg-S6 117.0(2), S1-Hg-S7 109.2(2), S1-Hg-S12 99.6(2), S6-Hg-S7 109.6(2), S6-Hg-S12 107.4(2), S7-Hg-S12 113.9(2), Hg-S-S (mean value) 108.4, S-S-S (mean value) 108.6°. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, on quoting the depository number CSD 50593, the names of the authors, and full citation of the journal.

ore deposits cannot be conclusively explained because of the very small solubility products (e.g. of α-HgS, cinnabar)<sup>[3-5]</sup>. We have been able to demonstrate that definite novel complexes of metals such as Cu, Ag, Au, and Hg are