Main-Group-Metal Clusters

Molecular $\{(SnO)_6\}$ Trapped by Two $\{R_2Si_2O_3\}$ Fragments: X-ray Single-Crystal Structure of $[(SnO)_6(R_2Si_2O_3)_2]$**

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Dedicated to Professor Oskar Glemser on the occasion of his 93rd birthday

We have a long-standing interest in the design and synthesis of molecular assemblies that contain the {Si-O-M} motif.[1] This interest is motivated, in part, by the possibility of these soluble metallasiloxanes functioning as structural models for the more-complex naturally occurring metallasilicates or synthetic metal-modified zeolites.[2] Another reason for our interest stems from the opportunity provided by molecular metallasiloxane structural frameworks for incorporating basic structural motifs of inorganic oxides as part of the larger cage or ring structures.[3] Such systems can be viewed as organic-soluble solids that contain the inorganic oxide core enveloped by a sheath of lipophilic organic exterior.[3] Although tin(II) alkoxide cage structures have been known for some time, there is a relative paucity of the corresponding tin(II) siloxane cages.[4] In contrast molecular stannasiloxanes that contain tin(IV) have been widely studied.[5] Herein, we describe the synthesis and structural characterization of $[(SnO)_6(R_2Si_2O_3)_2]$ $[R = (2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)]$ **1.** This compound represents the first example of a hexatin(II) cage that contains siloxane ligands. Interestingly compound **1** contains a central embedded tin oxide, in the form of a molecular $\{(SnO)_6\}$ motif between two $\{R_2Si_2O_3\}$ fragments. To the best of our knowledge, there has been no previous report on the isolation and structural characterization of any molecular tin(II) oxide.

The reaction of the tin amide[6] $[Sn\{N(SiMe_3)_2\}_2]$ with the N-bonded silanetriol[7] $RSi(OH)_3$ $[R = (2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)]$ in a 1.5:1 stoichiometric ratio afforded **1** in about 65% yield (Scheme 1). The reaction proceeds under elimination of $HN(SiMe_3)_2$ with a concomitant Si-O-Sn bond formation. Colorless crystals of **1** were obtained after four

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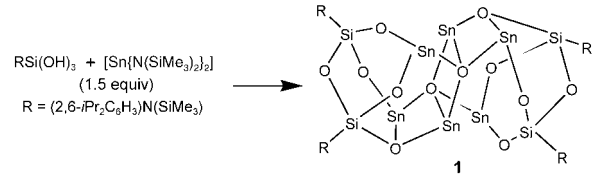

Scheme 1. Synthesis of compound **1**.

days at room temperature. Compound **1** is highly lipophilic and is soluble in a large number of common organic solvents, including hydrocarbons such as hexane. Compound **1** has been fully characterized by means of analytical, spectroscopic, and single-crystal X-ray diffraction studies.[8] A remarkable feature of the stannasiloxane **1** is its high thermal stability. It is stable up to 307 °C, at which point the compound turns black brown. The EI-mass spectrum of **1** shows a highly intense peak at 1740 (100%) $[M^+-18\,CH_3]$ thus indicating that the $\{Sn_6Si_4O_{12}\}$ core is stable under these conditions. The corresponding ^{29}Si NMR spectrum shows the presence of two resonances at $\delta = 7.3$ and -70.2 ppm. The latter corresponds to δ SiO_3N while the former is assigned to δ $SiMe_3N$. The ^{119}Sn NMR of **1** shows three signals ($\delta = -138.6$, -290.5 and -393.1 ppm), which correspond to the three types of tin centers present in **1**.

Compound **1** is formed as a result of the reaction of the in situ generated disiloxanetetrol $[RSi(OH)_2]_2O$ with $[Sn\{N(SiMe_3)_2\}_2]$. Such self-condensation of silanetriols has been previously reported by us.[9] Furthermore, the water liberated from the condensation of the two silanetriol molecules assists in the formation of SnO from $[Sn\{N(SiMe_3)_2\}_2]$.

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ along with two molecules of THF and one molecule of hexane in the asymmetric unit. The molecular structure of **1** is shown in Figure 1. The core structure of **1** along with selected metric parameters are given in Figure 2.

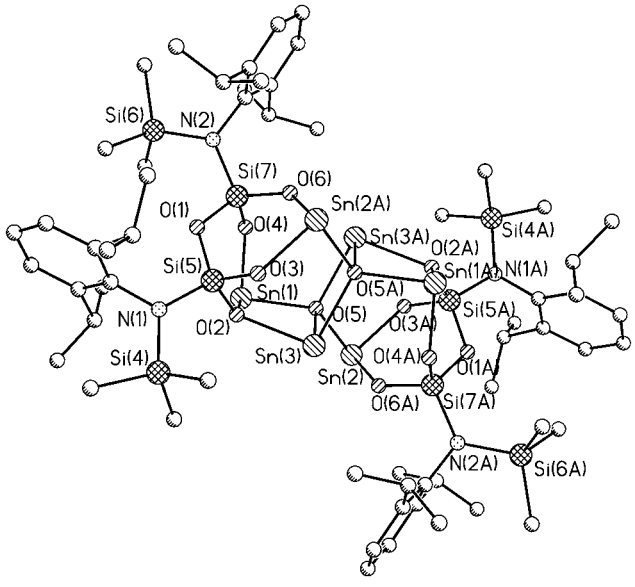

Figure 1. Molecular structure of **1** in the crystal.

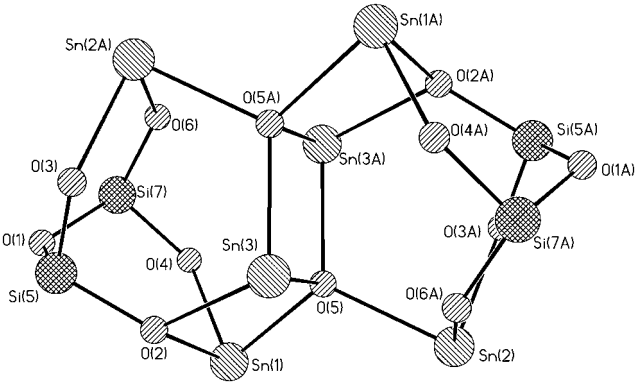

Figure 2. Core structure of **1**. The substituents on silicon have been omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Sn(1)-O(5) 2.190(2), Sn(1)-O(2) 2.141(2), Sn(1)-O(4) 2.025(2), Sn(2)-O(5) 2.184(2), Sn(2A)-O(6) 2.095(2), Sn(2A)-O(3) 2.060(2), Sn(3)-O(2) 2.288(2), Sn(3)-O(5) 2.190(2), Sn(3)-O(5A) 2.287(2), Sn(3A)-O(5) 2.287(2); Sn(1)-O(2)-Sn(3) 102.42(6), Sn(2)-O(5)-Sn(1) 112.66(7), Sn(2)-O(5)-Sn(3) 107.34(6), Sn(1)-O(5)-Sn(3) 104.08(6), Sn(2)-O(5)-Sn(3A) 115.21(6), Sn(1)-O(5)-Sn(3A) 112.82(7), Sn(3)-O(5)-Sn(3A) 103.47(6), Sn(7)-O(6)-Sn(2A) 132.46(9), O(2)-Sn(3)-O(5A) 98.77(6), O(2)-Sn(3)-O(5) 73.40(6), O(2)-Sn(1)-O(5) 76.36(6), O(3A)-Sn(2)-O(5) 87.34(6), O(4)-Sn(1)-O(2) 92.17(6), O(4)-Sn(1)-O(5) 91.39(6), O(5)-Sn(3)-O(5A) 76.53(6), O(6A)-Sn(2)-O(3A) 92.49(6), O(6A)-Sn(2)-O(5) 81.30(6).

The structure of **1** contains two centrosymmetrically related siloxane ligands that bind a central hexatin motif (Figure 2). The tin core consists of three mutually perpendicular $\{Sn_2O_2\}$ four-membered rings. The two oxygen atoms of the central distannoxane are linked further to two other tin centers (Sn 2 and Sn 2A). It is important to note that none of the tin atoms have any other ligands in their coordination environment except oxygen. Thus, the $\{(SnO)_6\}$ motif may be considered as representing a trapped molecular form of tin(II) oxide. All six tin centers in **1** are tricoordinate. It is noteworthy that in the solid-state structure of tin(II) oxide, the coordination environment of the tin atom is four, and the tin atom is positioned in the apex of a square pyramid.[10] The shortest Sn–O distances in **1** are for the Sn(1)–O(4) [2.025(2) Å] and Sn(2A)–O(3) bonds [2.060(2) Å] while the longest distances are found for the Sn(3)–O(5A) [2.287(2) Å] and Sn(3)–O(2) bonds [2.288(2) Å]. It is interesting to compare these distances with those observed in other tin(II) siloxanes. Thus, in $[\{Sn\text{-}(\mu\text{-}OtBu)(OSiPh_3)\}_2]$, which contains a four-membered $\{Sn_2O_2\}$ ring with an Sn–O distance of 2.084(4) Å.[5g] In the case of $[Ca\{Sn(\mu\text{-}OSiMe_2tBu)_3\}_2]$, which contains two $\{SnO_3\}$ motifs binding to a central calcium atom, the average Sn–O distance is 2.106(7) Å.[5i] However, in tin(II) oxide itself, the Sn–O distance was reported as 2.21 Å.[10]

The bond angles around Sn(3) in **1** add up to 249° while those at Sn(1) and Sn(2) add up to 260° and 263°, respectively. There are three different kinds of oxygen environments in the structure of **1**. Thus, there are four dicoordinate oxygen atoms that bridge Si and Sn atoms [O(3), O(4), O(6)] or Si and Si atoms [O(1)]. The angles at all these oxygen atoms are much less than 180°, the largest being at O(6) (132.42°) and the smallest at O(1) (121.20°). There is only one tricoordinate

oxygen atom, O(2), that caps one silicon and two tin atoms. The other oxygen atom, O(5), is tetracoordinate and bridges four tin centers.

In conclusion, we report a novel hexameric stannasiloxane **1** that contains a tin atom in a formal oxidation state of +2. The structure of **1** contains a central $\{(SnO)_6\}$ motif enclosed by two outer $R_2Si_2O_3$ siloxane ligands.

Experimental Section

1: $[Sn\{N(SiMe_3)_2\}_2]$ (2.02 g, 4.59 mmol) was slowly added to a stirred suspension of the silanetriol (1.0 g, 3.06 mmol) in hexane (25 mL) and THF (10 mL). After the addition was complete, the reaction mixture was stirred for 1 h at room temperature. Subsequently, the reaction mixture was refluxed for 1 h. The volatile components were removed to obtain a white solid. To this solid, a mixture of hexane (10 mL) and THF (1 mL) was added. Colorless crystals of **1** were obtained after four days at room temperature (1.12 g, 65.4%); mp 307 °C (dec); ^{1}H NMR (500 MHz, C_6D_6, TMS): $\delta = 0.20$ (s, 36H, $Si(CH_3)_3$), 1.40, 1.42 (d, 48H, $CH(CH_3)_2$), 3.70 (sept, 8H, $CH(CH_3)_2$), 7.05–7.12 ppm (m, 12H, aromatic); ^{29}Si NMR (99 MHz, C_6D_6, TMS): $\delta = 7.3$ ($SiMe_3$), −70.2 ppm (SiO_3); ^{119}Sn NMR (186 MHz, C_6D_6, TMS): $\delta = -138.6$, −290.5, −393.1 ppm; IR (Nujol): $\tilde{\nu} = 1316$ (w), 1259 (s), 1247 (s), 1179 (m), 1104 (m), 1073 (w), 1042 (s), 1007 (m), 969 (s), 954 (s), 907 (m), 876 (m), 836 (s), 801 (s), 752 (w), 721 (w), 685 (w), 641 (w), 603 (w), 543 (w), 521 (m), 501 (w), 466 (m) cm^{-1}; MS (70 eV): *m*/*z* (%): 1740 (100) $[M^+ - 18\,CH_3]$; Elemental analysis calcd (%) for $C_{60}H_{104}N_4O_{12}Si_8Sn_6$ (2010.43): C 35.85, H 5.21, N 2.79; found: C 36.94, H 5.57, N 2.79.

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[8] Crystal data for compound $\mathbf{1}\cdot 2\,C_4H_8O\cdot C_6H_{14}$: $C_{74}H_{134}N_4O_{14}Si_8Sn_6$, $M_r = 2240.71$, monoclinic, space group $P2(1)/c$, $a = 14.5130(7)$ Å, $b = 17.3237(9)$ Å, $c = 19.8882(10)$ Å, $\alpha = 90°$, $\beta = 105.986(4)°$, $\gamma = 90°$, $V = 4806.9(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.548$ mg m^{-3}, $F(000) = 2260$, $T = 133(2)$ K, μ ($Mo_{K\alpha}$) = 1.690 mm^{-1}. The data were collected using the ω scan mode in the range of $1.59 \le \theta \le 24.81$, $-17 \le h \le 17$, $-20 \le k \le 20$, $-23 \le l \le 23$. Of 47029 reflections collected, 8260 were unique. Final $R1$ ($I > 2\sigma(I)$) = 0.0195; $wR2$ (all data) = 0.0498. Maximum and minimum heights in the final Fourier difference map were 0.583 and −0.411 e A^{-3}. Colorless single crystals of compound $\mathbf{1}\cdot 2\,C_4H_8O\cdot C_6H_{14}$ suitable for X-ray diffraction studies were obtained from hexane/THF at room temperature. Diffraction data were collected on an IPDS II Stoe image-plate diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELX-97)[11] and refined against F^2 on all data by full-matrix least squares with SHELX-97.[12] The heavy atoms were refined anisotropically. Hydrogen atoms were included by using the riding model with U_{iso} tied to the U_{iso} of the parent atoms. CCDC 232378 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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