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A unique self-assembled tricyclic stannasiloxane containing a planar Sn_3SiO_5 fused 6.4.4 tricyclic ring system

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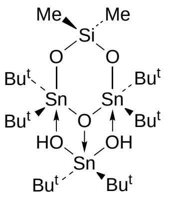
The compound $Bu^t_4Sn_2(Me_2Si)O_3 \cdot Bu^t_2Sn(OH)_2$ displays a unique tricyclic structure consisting of fused six-membered Sn_2SiO_3 and four-membered Sn_2O_2 rings to form a planar $SiSn_3O_4$ skeleton, with severely distorted trigonal bipyramidal co-ordination at tin and tetrahedral co-ordination at silicon.

It was reported recently that accidental reactions with silicon grease result in the incorporation of dimethylsiloxane units into the final product. Two unusual compounds, containing the crown-ether type siloxane complex $[K(Me_2SiO)_7]^+$ have been thus obtained and crystallographically characterized.[1,2] We report now the serendipitous formation of a cyclostannasiloxane, obtained during an attempt to prepare $Bu^t_2Sn[Pb(Mes)_3]_2$ (Mes = mesityl) by treating $Bu^t_2SnCl_2$ with $(Mes)_3Pb^-Li^+$ in tetrahydrofuran (thf) at −78 °C.† The crystalline compound isolated was characterised by IR and NMR spectroscopy and identified by X-ray diffraction as $Bu^t_4Sn_2(Me_2Si)O_3 \cdot Bu^t_2Sn(OH)_2$, a self-assembled supramolecular 1 : 1 adduct, **1**. The source of dimethylsiloxane units is certainly the silicon grease, since repeating the reaction in its absence resulted in the isolation of hexa-*tert*-butylcyclotristannoxane, $(Bu^t_2SnO)_3$, which we identified by NMR spectroscopy and single-crystal X-ray diffraction.



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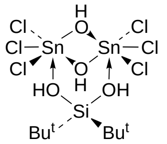
The hydroxyl hydrogen atoms in **1** were not located by X-ray diffraction ‡ but their presence is evident in the infrared spectra (in toluene solution) by an absorption band at 3643 cm^{-1}. These data support the formulation of **1** as a tricyclic species self-assembled through tin–oxygen Lewis acid–base interactions.

The molecular structure of compound **1** is illustrated in Fig. 1(*a*) which shows the perfect planarity of the inorganic Sn–O–Si skeleton. Fig. 1(*b*) shows a 'front-view' of the molecule (only *ipso* carbons of the *tert*-butyl groups are given for clarity) and illustrates the tricyclic system, containing a planar Sn_2SiO_3 ring fused to two planar Sn_2O_2 rings. This structure is unique compared with other Sn–O–Si inorganic ring systems, which contain six-membered Si_2SnO_3,[4,5] and eight-membered Si_3SnO_4 and $Sn_2Sn_2O_4$ rings.[6] The only other compound containing a Sn_2SiO_3 ring reported so far is $Cl_6Sn_2(OH)_2 \cdot Bu^t_2Si(OH)_2$ **2**, obtained from $Bu^t_2Si(OH)_2$ and $SnCl_4$.[7] Recent attempts to prepare $SnSi_2O_3$ rings led to novel ring-opened polymers in the solid state, and cyclic monomers in solution.[8] In addition, compound **1** is the first cyclostannasiloxane containing five-co-ordinate tin.



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In compound **1** the co-ordination around the five-co-ordinate tin atoms can be described as severely distorted trigonal bipyramidal, with oxygen atoms in axial positions and two *tert*-butyl groups and an oxygen in equatorial positions. The distortions are imposed by the four-membered rings, with Sn–O–Sn bond angles in the range 103.8–112.1° and O–Sn–O bond angles in the range 70.0–74.1°. Similar four-membered Sn_2O_2 rings are frequently formed by self-assembly of various organotin–oxygen compounds.[9–11] The distortion of the axial bonds is not so great at Sn(1) [O(1)–Sn(1)–O(2) 163.5°] and Sn(3) [O(3)–Sn(3)–O(4) 163.6°] compared to that at Sn(2) [O(2)–Sn(2)–O(3) 147.0°]. The Sn–O–Si and Sn–O–Sn bond angles in the six-membered Sn_2SiO_3 ring are larger than other related angles in **1**, *i.e.* 142° for the Sn–O–Si angle and 136.5° for the Sn(1)–O(5)–Sn(3) angle. The sum of bond angles at O(5) is 360.0°, demonstrating the perfect planarity of the three O–Sn bonds at this site.

The Sn–O bond length variation in the tricyclic system is worth underscoring. Thus, 'shorter' Sn–O bonds Sn(1)–O(1) 2.006, Sn(3)–O(4) 2.000, Sn(1)–O(5) 2.092 and Sn(3)–O(5) 2.094 Å are observed in the six-membered Sn_2SiO_3 ring, and 'longer' dative O→Sn bonds Sn(1)–O(2) 2.274 and Sn(3)–O(3) 2.279 Å in the four-membered rings. All Sn–O bonds from the three-co-ordinate oxygen to tin are short (*ca.* 2.09 Å).

The structure of compound **1** can be compared with an analogous cycloborastannoxane **3** (R = alkyl, R′ = aryl),[12] which displays very similar bond length variations in the rings (but significantly different bond angles at boron and oxygen in the six-membered Sn_2BO_3 ring). Since in our chemistry the

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† Preparation: di-*tert*-butyltin dichloride, $Bu^t_2SnCl_2$ (0.54 g, 1.77 mmol) in thf (30 cm^3) was treated at −78 °C with a slurry of $(Mes)_3Pb^-Li^+$ [obtained from 1.09 g (0.88 mmol) hexamesityldilead and 0.19 g (14.3 mmol) lithium metal] in thf (30 cm^3), added dropwise during 30 min. Subsequent to complete addition, the colour changed to pale yellow and finally to red. After another 30 min the mixture was allowed to warm to room temperature and further stirred for 2 h. Solvents were removed under vacuum and the orange residue was extracted with toluene (50 cm^3). On evaporation of toluene, a white, waxy material was obtained. It was repeatedly recrystallised from toluene, to give **1** (150 mg) as a white crystalline solid. IR spectrum (toluene): 3643 cm^{-1}. ^1H NMR (in C_6D_6 relative to $SiMe_4$): δ 0.29 ($Si-CH_3$), 1.45 [Bu^t, $J(^{119}Sn-H)$ 45 Hz].

‡ Crystal data: $C_{26}H_{62}O_5SiSn_3$, **1**, M = 838.99, monoclinic, space group $P2_1/n$, a = 9.658(4), b = 19.580(4), c = 19.460(10) Å, β = 91.70(3)°, U = 3678(3) $Å^3$, Z = 4, T = 296 K, μ = 2.089 mm^{-1}, $R(F)$ = 0.0421, wR = 0.0606 using 3106 observed reflections. CCDC reference number 186/791.

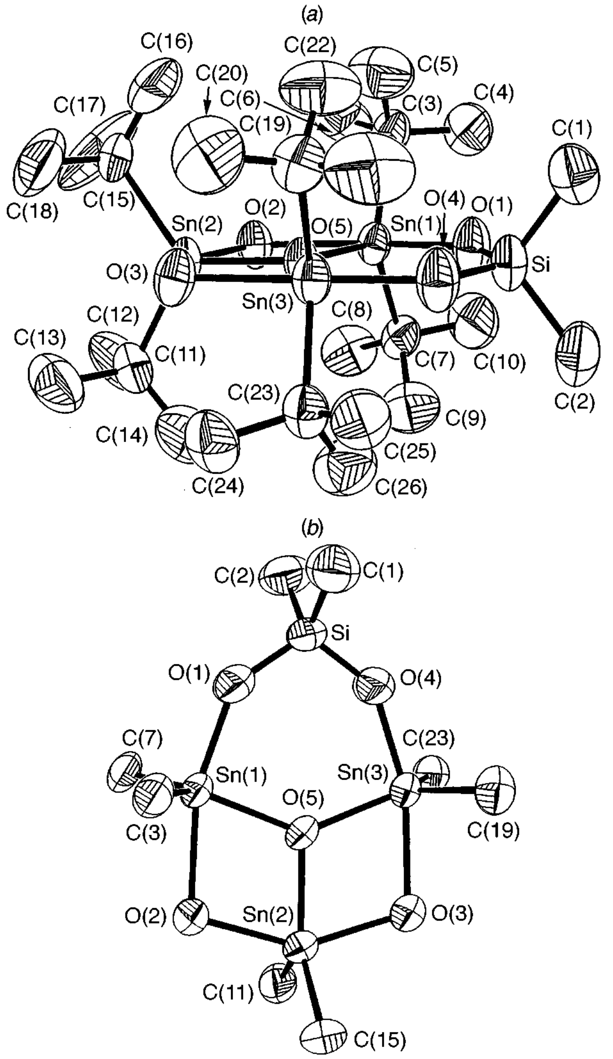
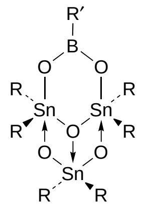


Fig. 1(*a*) An ORTEP[3] diagram of complex **1**, (*a*) side-on and (*b*) front-on, with $\mathrm{Bu^t}$ methyl groups omitted for clarity. Selected bond distances (Å): Si–O(1) 1.598(6), Si–O(4) 1.599(6), Sn(1)–O(1) 2.006(6), Sn(1)–O(2) 2.274(5), Sn(1)–O(5) 2.092(5), Sn(3)–O(4) 2.000(6), Sn(3)–O(3) 2.279(5), Sn(3)–O(5) 2.094(5), Sn(2)–O(2) 2.104(5), Sn(2)–O(3) 2.105(5), Sn(2)–O(5) 2.098(5)



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absence of a source of dimethylsiloxane units results in the formation of hexa-*tert*-butylcyclotristannoxane, $(\mathrm{Bu^t_2SnO})_3$, and noting that the formation of the cycloborastannoxane **3** resulted from a reaction between $(\mathrm{Bu^t_2SnO})_3$ and an arylboronic acid, $\mathrm{R'B(OH)_2}$, we think that the cyclotristannoxane is an intermediate in the formation of the tricyclic systems **1**.[13]

In view of these data it can be expected that tricyclic structures similar to **1** with other non-metals in the six-membered ring, besides boron or silicon, *e.g.* phosphorus, arsenic, antimony, germanium, perhaps sulfur or selenium, could be systematically synthesised under appropriate conditions from $(\mathrm{Bu^t_2SnO})_3$. We are actively pursuing this line of research.

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13 Since completion of this study Professor Klaus Jurkschat has informed us that indeed the reaction between $\mathrm{Ph_2SiCl_2}$ and $(\mathrm{Bu^t_2SnO})_3$ in the presence of NaOH in toluene leads to excellent yields of the diphenylsilyl analog of **1**.

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