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Synthesis of the first four-membered ring compound containing three tin atoms and one oxygen. The crystal structure of the species $[O\{Sn(C_6H_3Et_2\text{-}2,6)_2\}_3]$

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Abstract

Aerial oxidation of the novel homocyclic tetratin species $[\{SnAr_2\}_3SnArBr]$ (**1**) [1] (Ar = $C_6H_3Et_2$-2,6) affords the tritin heterocycle $[O\{Sn(C_6H_3Et_2\text{-}2,6)_2\}_3]$ (**2**), which has been crystallographically characterised; **2** is the first reported oxatristannacyclobutane, and the first heterocyclic tin species having both tin–tin and tin–heteroatom bonds.

Discrete tin heterocycles with three or four members have been reported with ring types Sn_4 [1], Sn_2O_2 [2], Sn_3 [3], and Sn_2OS [4]. For the lighter elements of group 14, a more extensive range is known. In addition to the above types, rings with E–E bonds have also been reported, e.g., Ge_2S [5], Si_2C [6], Si_2O [7], and Si_2S [8], but to date such compounds are unknown for tin, and only the three-membered ring systems above have been structurally characterised for Si or Ge.

We now report that an oxatritin species can be obtained by atmospheric oxidation of $[\{SnAr_2\}_2SnArBr]$ (**1**) [1] (Ar = $C_6H_3Et_2$-2,6) to give $[O\{Sn(C_6H_3Et_2\text{-}2,6)_2\}_3]$ (**2**). Thus solutions of **1** on standing in air afford **2** slowly in good yield; however, a quicker procedure is to pass a concentrated solution of **1** down a column containing silica, under air, which also gives a good yield. The latter procedure gives the product in pure, crystalline form *. Spectroscopic data are not particularly informative, though the IR spectrum shows a single intense, sharp absorption at 807 cm^{-1} [ν(Sn–O–Sn)]. At 300 MHz the NMR spectrum is complicated by the overlapping of the groups on the differing tin atoms, and further by the evidently restricted rotation of the aryl substituents in this crowded molecule. Yet a further problem is that the compound is not soluble in common NMR solvents, with the

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* IR: 3054,s; 2965,s; 2934,s; 2875,s; 1567,m; 1453,s; 1426,w; 1375,m; 1326,w; 1262,w; 1227,w; 1167,w; 1120,w; 1071,w; 1055,w; 1048,w; 807,s; 778,s; 732,m; 685,w; 644,m; 485,m; 341,w; 219,w.
NMR: 300 MHz ($CDCl_3$) δ 0.597m, 0.777m (together 6H); 2.51m, 2.61m, 2.77m (together 4H); 6.91m, 7.11m (together 3H); in ppm downfield from internal TMS.
M.p. dec. above 180 °C (in air).

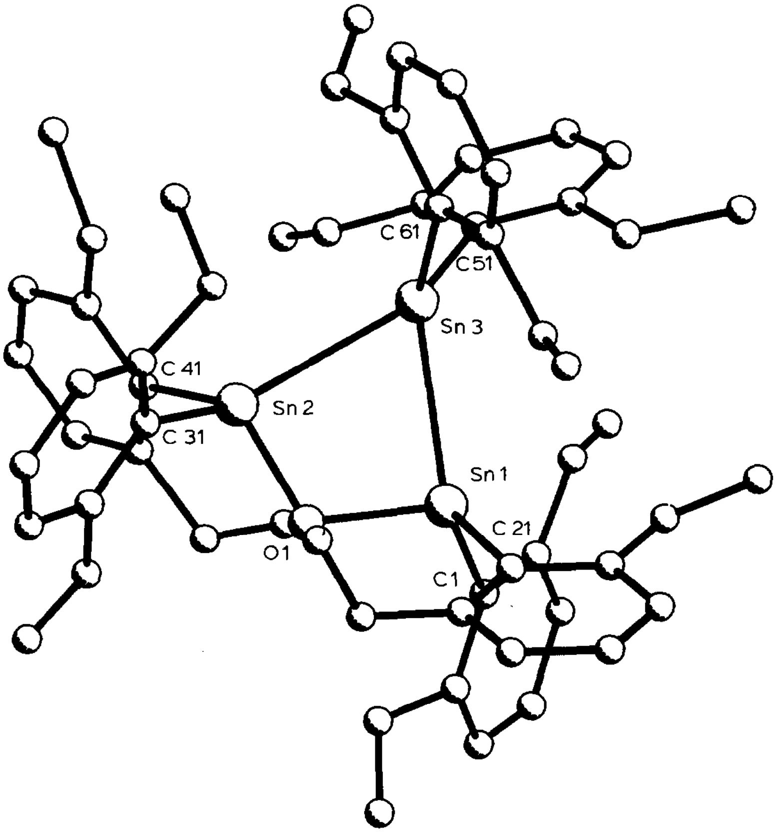

Fig. 1. A single molecule of **2** viewed normal to the Sn_3O plane. Salient bond lengths (Å) and angles (°): Sn(2)–Sn(1) 3.263(5); Sn(3)–Sn(1) 2.918(5); Sn(3)–Sn(2) 2.962(5); O(1)–Sn(1) 1.976(27); O(1)–Sn(2) 1.926(26); Sn(1)–C(1) 2.173(14); Sn(1)–C(2) 2.164(11); Sn(2)–C(31) 2.187(13); Sn(2)–C(41) 2.174(11); Sn(3)–C(51) 2.185(13); Sn(3)–C(61) 2.207(13); Sn(3)–Sn(1)–Sn(2) 56.2(2); O(1)–Sn(1)–Sn(3) 88.9(6); Sn(3)–Sn(2)–Sn(1) 55.9(2); O(1)–Sn(2)–Sn(3) 89.6(6); Sn(2)–Sn(3)–Sn(1) 67.9(0); Sn(2)–O(1)–Sn(1) 113.5(7); C(1)–Sn(1)–C(21) 107.0(6); C(31)–Sn(2)–C(41) 107.7(6); C(51)–Sn(3)–C(61) 106.1(6).

exception of deuterochloroform, in which it slowly decomposes, so that total freedom from traces of impurity is not possible. When allowance is made for this the integrations are almost quantitative.

The single-crystal structure analysis of **2** revealed the geometry shown in Fig. 1. The three tin atoms and the oxygen are essentially coplanar, and the framework is shaped like an arrow-head, with Sn(2) forming the tip. Bond lengths and angles do not deviate significantly from normal, though the Sn–C vectors are tilted very slightly from the normals to the Sn_3O plane. The geometries about the three tin atoms differ only very slightly, being essentially tetrahedral in all cases. One small difference is the angle subtended at the metal atom by the ligating carbons of the aromatic ligands. This is marginally smaller for Sn(3) than for the other two, [106.1(6)° compared with 107.7(6)° and 107.0(6)°], in agreement with our previous observations that the corresponding angle is invariably larger when the metal is attached to electronegative centres.

Since the tristannoxane of the same ligand, hexakis(2,6-diethylphenyl)tristannoxane, has been obtained by aerial oxidation of the tristannane in solution [9], we attempted aerial oxidation of **2** in solution, but recovered unchanged material. We have also attempted to study the aerial oxidation of hexakis(2,4,6-triisopropylphenyl)-*cyclo*-tristannane in chloroform and in hexane. Our results show that in the light, the *cyclo*-tristannoxane is produced, but we have not obtained evidence of the intermediate mono- or dioxo-species. In the dark, the reaction takes a different course, and complex, possibly polymeric products result. These results parallel those obtained on the oxidation of octakis(2,6-diethylphenyl)octastannacubane [10], where the peroxygenated species has been reported, but none of the (presumed) intermediates.

In the light of the above observations, it is interesting to consider how the present monooxo species can be obtained from **1**, but apparently not from the *cyclo*-tristannane. Although the crystal structure of **1** shows that the tin–tin bonds to the unique tin atom [Sn(Br)Ar] are significantly shorter than the others [1], they are presumably substantially more polar than the other metal–metal interactions, and hence it is this metal with its attached ligands which is lost on reaction with dioxygen.

Crystal data

$C_{60}H_{78}OSn_3$, $M_r = 1171.358$. Orthorhombic, $Pna2_1$ no. 33, $a = 13.366(1)$, $b = 20.150(2)$, $c = 20.579(4)$ Å. $U = 5542.5(1.2)$ Å^3. $D_c = 1.40$ g cm^{-3}, $Z = 4$; $F(000) = 2408$, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 13.9$ cm^{-1}.

Data collection

A yellow crystal of approximate size $0.3 \times 0.2 \times 0.2$ mm^3 was mounted on an Enraf–Nonius CAD4 diffractometer, and the intensities of 3810 reflections in the range $1 < \theta < 22°$ were measured using Mo-K_α radiation with a graphite monochromator. The cell co-ordinates were determined by refining the setting angles of 25 reflections in the range $16 < \theta < 18°$, final cell dimensions were obtained from the celdim routine. The data were corrected for decay, and reduced to give 3224 reflections (merging $R = 0.0224$) of which 2745 had $|F_{obs}| > 4\sigma(F_{obs})$ and were used in structure solution and refinement.

Structure solution and refinement

The structure was solved by the Direct method of SHELXS and refined by full-matrix least squares, 203 variables, to a conventional R-factor of 0.0601, and a final average shift of 0.021. The six-membered rings were refined as rigid groups with the hydrogen atoms placed geometrically. The three tin atoms were given anisotropic temperature factors. The weighting scheme was also refined to an R_w of 0.0652 and a goodness of fit of 1.94. The final difference Fourier had a largest peak in the map of 1.16 e Å^{-3}. The final structure is shown in Fig. 1, along with salient bond lengths and angles. Lists of atom coordinates, bond lengths and angles, and isotropic and anisotropic temperature factors are available from the Cambridge Crystallographic Data Centre.

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