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A NEW STRUCTURAL FORM OF TIN IN AN OXYGEN-CAPPED CLUSTER

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Recently we have shown that oligomeric organotin oxycarboxylates based on the compositions $[R'Sn(O)O_2CR]_6$ and $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$ have "drum" ¹⁻³ and "ladder" ^{2,3} structures, respectively. Reaction of *n*-butylstannoic acid with diphenylphosphoric acid instead of a carboxylic acid results in the formation of an analogous drum composition, $[n-BuSn(O)O_2P(OPh)_2]_6$. ⁴ However, when diphenylphosphinic acid is reacted with *n*-butylstannoic acid under reflux in toluene, a new structural form of tin is obtained. This report concerns the synthesis and structural characterization of this novel substance.

The reaction proceeds according to eq 1 giving the stable oxide composition in 90% yield, mp 198–208°C dec.⁵ Colorless,

3n-BuSn(O)OH + $4Ph_2PO_2H$

$$\rightarrow [(n-BuSn(OH)O_2PPh_2)_3O][Ph_2PO_2] + 2H_2O$$
 (1)

brick-shaped crystals for X-ray diffraction analysis were grown from hot ether. Anal. Calcd for C₆₀H₇₀O₁₂P₄Sn₃: C, 49.25; H, 4.82. Found: C, 49.01; H, 4.97.

Crystal data for $[(n\text{-BuSn}(OH)O_2PPh_2)_3O][Ph_2PO_2]$, crystal dimensions 0.30 mm \times 0.30 mm \times 0.33 mm, triclinic space group $P\bar{1}$ (C_1^1 , No. 2), $^6a = 11.260$ (2) Å, b = 12.672 (2) Å, c = 22.804 (2) Å, $\alpha = 96.98$ (1)°, $\beta = 99.36$ (1)°, $\gamma = 98.64$ (1)°, Z = 2, $\mu(MoK\bar{\alpha}) = 1.353$ mm⁻¹. Independent reflections (7044) were measured at $23 \pm 2^{\circ}C$ on an Enraf-Nonius CAD4 automated diffractometer, using graphite monochromated Mo $K\bar{\alpha}$ radiation and the θ -2 θ scan mode to a maximum $2\theta_{MoK\bar{\alpha}}$ of 43°. The structure was solved by using Patterson and difference Fourier techniques. Full-matrix least-squares refinement 7 (anisotropic refinement of 76 nonhydrogen atoms, isotropic refinement of three n-Bu carbon atoms, hydrogen atoms omitted) led to a conventional unweighted residual $R = \Sigma ||F_o|| - |F_c||/\Sigma |F_o||$ of 0.051 for the 6038 reflections having $I \ge 2\sigma_1$.

X-ray analysis shows tin (IV) present in an oxygen-capped cluster molecule. The basic framework consists of a tristannoxane ring in a cyclohexane chair arrangement. Hydroxyl groups comprise the oxygen components of the ring system. A tricoordinated oxygen atom caps one side of this framework while three additional diphenylphosphinate groups bridge adjacent hexacoordinated tin atoms.

It is noted that three distannoxane ring units form as a consequence of the

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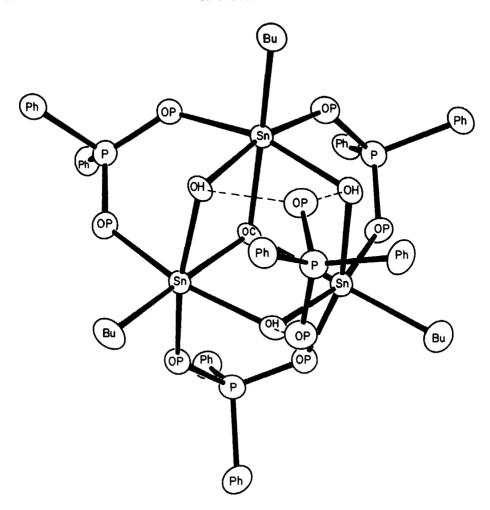


FIGURE 1 ORTEP plot of $[(n-BuSn(OH)O_2PPh_2)_3O][Ph_2PO_2]$ with thermal ellipsoids shown at the 30% probability level. Pendant atoms of the three n-Bu groups and of the eight Ph groups are omitted for purposes of clarity. Hydrogen-bonding interactions are shown as dashed lines. Average bond lengths (Å): Sn—OC = 2.075 (5); Sn—OH = 2.128 (6); Sn—OP = 2.122 (6); Sn—Bu = 2.15 (1). Average bond angles (deg): OC—Sn—OH = 77.2 (2); OC—Sn—OP = 85.3 (2); OC—Sn—Bu = 178.4 (3); OH—Sn—OH = 91.3 (2); OH—Sn—OP = 162.7 (2), 86.8 (2); OH—Sn—Bu = 102.1 (3); OP—Sn—OP = 90.1 (2); OP—Sn—Bu = 95.0 (3); Sn—OC—Sn = 103.6 (2); Sn—OH—Sn = 100.1 (2).

presence of the unique capping oxygen atom. These three four-membered rings contain the latter atom and form a portion of a cube. The presence of four- and six membered rings also is a primary structural feature of the drum structure.^{1,2} The ladder framework, however, only possesses four-membered rings.²

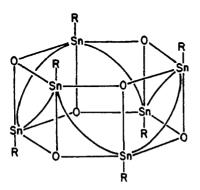
The oxygen-capped cluster can be viewed as a hydrolysis product of the drum just as the drum is viewed as a hydrolysis product of the ladder,² i.e., eq 2 and 3, respectively. The drum

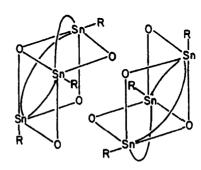
$$[R'Sn(O)O2R]6 + 2RO2H + 2H2O \rightarrow 2[(R'Sn(OH)O2R)3O][RO2]$$
 (2)
drum cluster

$$[(R'Sn(O)O_2R)_2R'Sn(O_2R)_3]_2 + 2H_2O \rightarrow [R'Sn(O)O_2R]_6 + 4RO_2H$$
(3)
ladder drum
$$R = R''C \text{ or } R''_2P$$

to ladder conversion has been followed by ¹¹⁹Sn NMR and shown to be reversible. ^{2b} The ¹¹⁹Sn NMR spectrum for the oxygen-capped cluster exhibits a single resonance with triplet character centered at -498.5 ppm ($^2J^{119}Sn-O-^{31}P=132.0$ Hz). This observation is consistent with the presence of three equivalent tin atoms provided by a cluster unit which has the hydrogen-bonded anionic phosphinate undergoing fast exchange among the three hydroxyl groups of the tristannoxane ring.

The schematic for a drum indicates how it is related to two cluster molecules.





Formally, two bridging phosphinates rearrange, two oxygen atoms are added, four Sn—O bonds are cleaved, the six Sn—O—Sn linkages become Sn(OH)Sn units, and two phosphinates are added to hydrogen bond to the hydroxyls.

The discovery of these three novel types of stannoxane structural entities, the drum, ¹⁻³ the ladder, ^{2,3} and the oxygen-capped cluster, suggests that additional cluster arrangements remain to be discovered possessing interesting properties.

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Supplementary Material Available: Atomic coordinates (Table S1) and isotropic thermal parameters (Table S2) (5 pages). Ordering information is given on any current masthead page.

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- 4. Chandrasekhar, V.; Holmes, J. M.; Day, R. O.; Holmes, R. R., unpublished work.
- 5. A suspension of n-butylstannoic acid (1.05 g, 5.03 mmol), Koriyama Kasei Co., Ltd., Japan, and diphenylphosphinic acid (1.10 g, 5.04 mmol), Aldrich, was heated in toluene (125 mL) at reflux for 4 h. A Dean-Stark apparatus was used to azeotropically remove water. Removal of solvent yielded a semisolid. Diethy ether (30 mL) was added, and the mixture heated, and then filtered. Needlelike crystals formed from the filtrate.
- 6. International Tables for X-ray Crystallography; Kynoch: Birmingham, England, 1969; Vol. I, p 75.
 7. The function minimized was Σw(|F_o| |F_c|)², where w^{1/2} = 2F_oLp/σ₁. Mean atomic scattering factors were taken from ref 6, 1974; Vol. IV, pp 72-98. Real and imaginary dispersion corrections for Sn, O, and P were taken from the same source, pp 149-150.