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

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

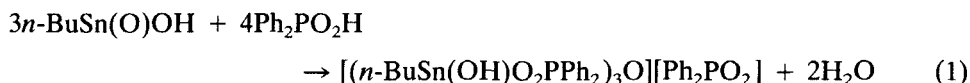
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Recently we have shown that oligomeric organotin oxycarboxylates based on the compositions $[R'Sn(O)O_2CR]_6$ and $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$ have "drum"^{1–3} and "ladder"^{2,3} structures, respectively. Reaction of *n*-butylstannoic acid with diphenylphosphoric acid instead of a carboxylic acid results in the formation of an analogous drum composition, $[n\text{-BuSn}(O)O_2P(OPh)_2]_6$.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,



brick-shaped crystals for X-ray diffraction analysis were grown from hot ether. Anal. Calcd for $C_{60}H_{70}O_{12}P_4Sn_3$: 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 × 0.30 mm × 0.33 mm, triclinic space group $P\bar{1}$ (C_1^1 , No. 2),⁶ $a = 11.260$ (2) Å, $b = 12.672$ (2) Å, $c = 22.804$ (2) Å, $\alpha = 96.98$ (1)°, $\beta = 99.36$ (1)°, $\gamma = 98.64$ (1)°, $Z = 2$, $\mu(MoK\alpha) = 1.353$ mm^{−1}. Independent reflections (7044) were measured at $23 \pm 2^\circ\text{C}$ on an Enraf-Nonius CAD4 automated diffractometer, using graphite monochromated Mo $K\alpha$ radiation and the θ - 2θ scan mode to a maximum $2\theta_{MoK\alpha}$ of 43° . The structure was solved by using Patterson and difference Fourier techniques. Full-matrix least-squares refinement⁷ (anisotropic refinement of 76 non-hydrogen 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 $I \geq 2\sigma_1$.

X-ray analysis shows tin (IV) present in an oxygen-capped cluster molecule. The basic framework consists of a trisannoxane 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

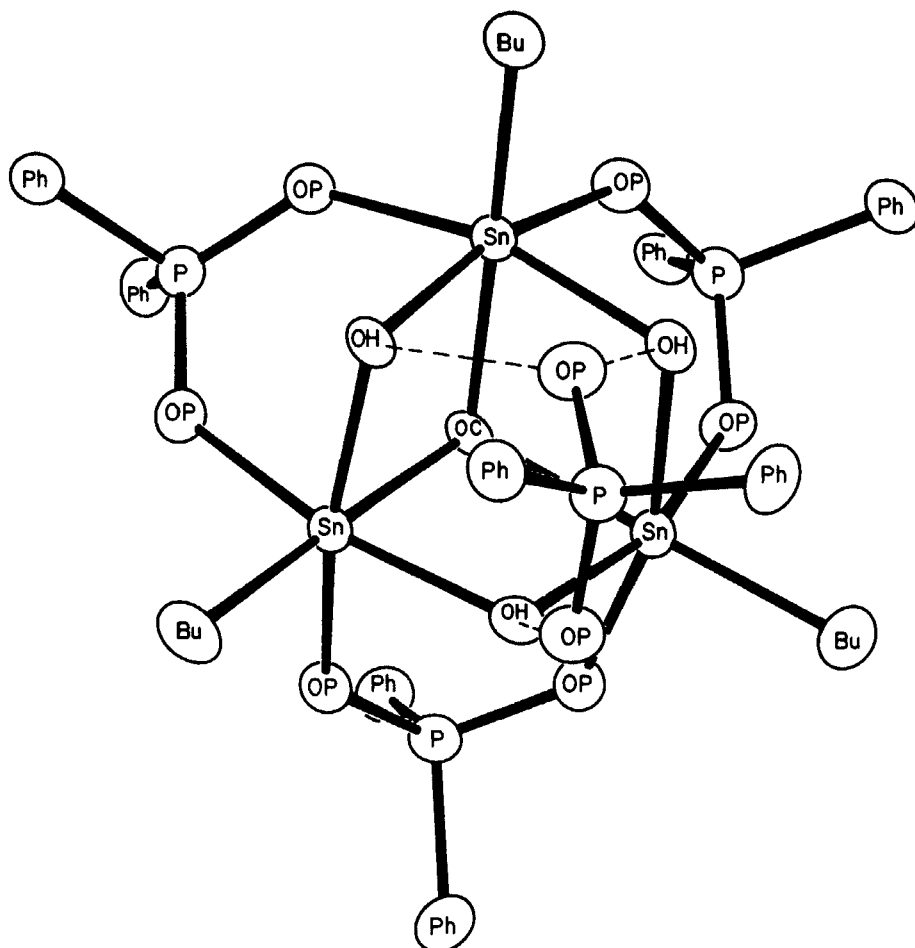
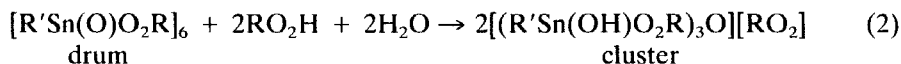
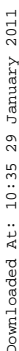


FIGURE 1 ORTEP plot of $[(n\text{-BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$ with thermal ellipsoids shown at the 30% probability level. Pendant atoms of the three *n*-Bu groups and of the eight Ph groups are omitted for purposes of clarity. Hydrogen-bonding interactions 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

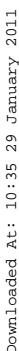
The oxygen-capped cluster can be viewed as a hydrolysis product of the drum just as the drum is viewed as a hydrolysis product of the ladder,² i.e., eq 2 and 3, respectively. The drum





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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. Diethyl 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 $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_o Lp/\sigma_I$. 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.