the X-ray crystal structure determination. We are grateful to Dr. Egbert Keller for providing a copy of his SCHAKAL program.

Registry No. **1**, 96212-33-8; **2**, 96212-35-0; $(Mo_2O_7)[(n\text{-}C_4H_9)_4N]_2$, 96211-57-3; MoO_3, 1313-27-5; SiO_2, 7631-86-9.

Supplementary Material Available: Table II (atomic coordinates for non-hydrogen atoms in **1**), Table III (atomic coordinates for hydrogen atoms in **1**), Table IV (thermal parameters for atoms in **1**), Figure 2 (ORTEP drawing of the cation in **1**), and structure factor tables for the X-ray structural study of **1** (17 pages). Ordering information is given on any current masthead page.

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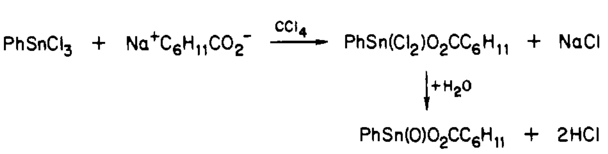
A New Structural Form of Tin Octahedrally Coordinated in a Drum-Shaped Molecule[1]

Sir:

Although oligomeric organotin oxycarboxylates based on the composition $[RSn(O)O_2CR']_n$ have been known for some time,[2] no indications of their possible structural features are available. As early as 1921 some members of this class were reported[3] to be hexameric, e.g., $[CH_3Sn(O)O_2CR]_6$.

We report herein the synthesis and X-ray crystal structure of hexameric phenyltin oxycyclohexanecarboxylate, $[PhSn(O)O_2CC_6H_{11}]_6$. The X-ray characterization shows tin(IV) present in a new structural environment appearing as a drum-shaped molecule containing hexacoordinated tin atoms.

During the course of our work[4,5] on triorganotin esters of carboxylic acids, we first obtained the hexamer while recrystallizing triphenyltin cyclohexanoate, $Ph_3SnO_2C(C_6H_{11})$. Presumably, it formed as a result of slow hydrolysis of the latter compound with the loss of two molecules of benzene. A more direct route involves the reaction of $PhSnCl_3$ with the sodium salt of the acid in CCl_4 solution, followed by a hydrolysis step which gave the compound as a powdery substance in modest yield[6] present in a mixture of products:



$$PhSnCl_3 + Na^+C_6H_{11}CO_2^- \xrightarrow{CCl_4} PhSn(Cl_2)O_2CC_6H_{11} + NaCl$$

$$\big\downarrow{+H_2O}$$

$$PhSn(O)O_2CC_6H_{11} + 2HCl$$

Although a pure product has yet to be obtained by this route, both the crystalline hexamer and the powder had similar Nujol mull infrared spectra, melted with decomposition at 340 °C, and were insoluble in organic solvents and in water. It thus appears that the hexamer is hydrolytically and thermally stable.

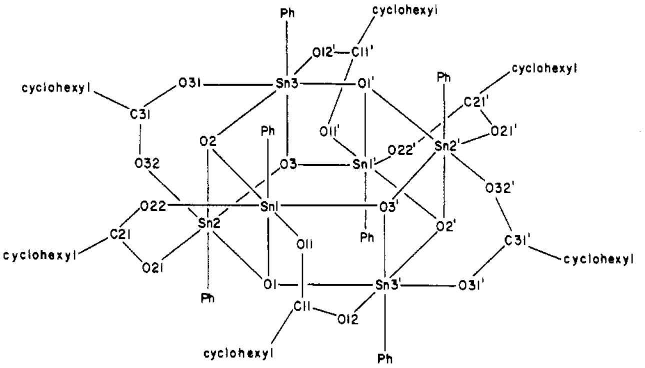


Figure 1. Schematic representation of the drum structure of $[PhSn(O)O_2CC_6H_{11}]_6$.

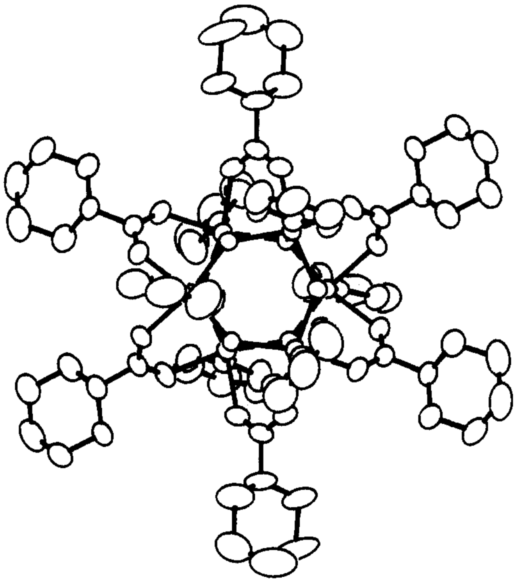


Figure 2. ORTEP plot of $[PhSn(O)O_2CC_6H_{11}]_6$ viewed down the S_6 axis with thermal ellipsoids at the 50% probability level.

The schematic in Figure 1 portrays the drum-shaped structure resulting from the X-ray analysis[7] and shows the atom labeling. The high symmetry associated with the molecule is revealed in Figure 2. The hexamer has crystallographic C_i symmetry. However, the noncrystallographic symmetry of the molecule is higher, namely S_6, assuming free rotation about the C–C single bonds.

The six tin atoms are chemically equivalent, as are the six trivalent oxygen atoms. The Sn–O framework of the molecule can be described as a drum with top and bottom faces each being comprised of a six-membered $(\text{–Sn–O–})_3$ tristannoxane ring.

The drum faces are joined together by six Sn–O bonds containing tricoordinated oxygen atoms. The sides of the drum are thus comprised of six four-membered $(\text{–Sn–O–})_2$ distannoxane rings, each of which is spanned by a carboxylate group that forms a symmetrical bridge between two tin atoms. The sides of the structure are reminiscent of the ladder arrangement in dimeric

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(6) Phenyltin trichloride (1.1 g, 3.6 mmol) and the sodium salt of cyclohexanecarboxylic acid (0.55 g, 3.6 mmol) were reacted in carbon tetrachloride (100 mL) at reflux temperature for 2 h. Filtration of NaCl and removal of the solvent in vacuo yielded a residue that was heated with a mixture of 95% ethanol (10 mL), acetonitrile (10 mL), and water (5 mL) for 2 h. A white insoluble compound was isolated (0.3 g); 25% yield, mp 340 °C dec. The infrared spectrum of this compound in Nujol shows $\nu(CO_2)$ at 1530 cm^{-1}.

(7) The hexameric stannoxane $[PhSn(O)O_2CC_6H_{11}]_6$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.919$ (3) Å, $b = 19.361$ (3) Å, $c = 15.089$ (2) Å; $\beta = 90.81$ (1)°, $Z = 2$, $\mu_{MoK\bar{\alpha}} = 1.891$ mm^{-1}. A total of 5984 independent reflections were measured at room temperature with use of the θ–2θ scan mode and graphite-monochromated Mo$K\bar{\alpha}$ radiation, for $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 47°$, on an Enraf-Nonius CAD4 diffractometer. No corrections were made for absorption. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, hydrogen atoms fixed isotropic, function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{1/2} = 2F_oLp/\sigma_I$) led to $R = 0.030$ and $R_w = 0.044$ for the 5093 reflections having $I \geq 2\sigma_I$.

Table I. Summary of Selected Bond Distances (Å) and Angles (deg) for $[PhSn(O)O_2CC_6H_{11}]_6$

Tristannoxane Ring, $(\text{–Sn–O–})_3$[a]			
Sn3′–O1–Sn2	133.7 (2)	Sn2–O3–Sn1′	135.2 (2)
Sn1–O2–Sn3	133.8 (2)	av	134.2
O3′–Sn1–O2	102.2 (1)	O2–Sn3–O1′	104.1 (1)
O1–Sn2–O3	102.7 (1)	av	103.0
Sn1–O2	2.083 (3)	Sn3–O2	2.080 (3)
Sn1–O3′	2.073 (3)	Sn3–O1′	2.069 (3)
Sn2–O1	2.081 (3)	av	2.079
Sn2–O3	2.089 (3)		
Distannoxane Ring, $(\text{–Sn–O–})_2$			
Sn1–O1–Sn2	99.3 (1)	Sn3–O3–Sn2	99.6 (1)
Sn1–O1–Sn3′	99.6 (1)	Sn3–O3–Sn1′	100.3 (1)
Sn2–O2–Sn1	100.1 (1)	av	99.8
Sn2–O2–Sn3	100.0 (1)		
O1–Sn1–O2	77.7 (1)	O3–Sn3–O2	78.0 (1)
O1–Sn1–O3′	77.6 (1)	O3–Sn3–O1′	78.2 (1)
O2–Sn2–O1	78.4 (1)	av	78.0
O2–Sn2–O3	77.9 (1)		
Sn1–O1	2.124 (3)	Sn3–O3	2.098 (3)
Sn2–O2	2.096 (3)	av	2.106
Carboxylate			
Sn1–O11	2.165 (3)	Sn3–O31	2.139 (4)
Sn1–O22	2.155 (4)	Sn3–O12′	2.149 (4)
Sn2–O21	2.153 (4)	av	2.153
Sn2–O32	2.154 (4)		
C11–O11	1.266 (6)	C31–O31	1.242 (8)
C11–O12	1.261 (6)	C31–O32	1.277 (7)
C21–O21	1.259 (6)	av	1.260
C21–O22	1.252 (6)		

[a] Similar Sn–O–Sn (133.1–134.5°) and O–Sn–O (105.9–106.9°) bond angles and slightly shorter Sn–O bond lengths (1.952–1.978 Å) are present in the oxides $(t\text{-}Bu_2SnO)_3$ and $(t\text{-}Am_2SnO)_3$.[12]

distannoxanes recently found for aryl[8] and alkyl[9,10] derivatives, e.g., $[Ph_2(Cl)SnOSnPh_2(Cl)]_2$. Concomitant with the equivalence of the Sn–O bonds to a particular carboxylate group is the corresponding equivalence of the pairs of C–O carboxylate bond lengths. The hexamer provides the first example of tin atoms symmetrically bridged by a carboxylate group. A summary of important bond parameters are listed in Table I.

The distannoxane ring units of the sides of the drum (i.e., $\overline{\text{Sn1–O1–Sn2–O2}}$) are not planar but are folded along the Sn–Sn vectors so that the oxygen atoms are directed toward the interior of the cavity. This is apparent in Figure 2. Similarly, the tristannoxane ring faces of the drum (i.e., Sn1–O2–Sn3–O1′–Sn2′–O3′) are not planar but have the oxygen atoms directed toward the interior of the cavity an average of 0.24 Å, relative to the Sn atoms. This contrasts with the planar six-membered tin–oxygen rings found in the di-*tert*-butyltin[11,12] and di-*tert*-amyltin[12] oxides, $(t\text{-}Bu_2SnO)_3$ and $(t\text{-}Am_2SnO)_3$, containing tetracoordinate tin. The distance between the plane defined by Sn1, Sn2′, Sn3 and Sn1′, Sn2, Sn3′ is 2.315 Å. The corresponding distance between the planes defined by the oxygen atoms is 1.844 Å.

Thus, the interior of the cavity is defined by a crown of six oxygen atoms, in a trigonal-antiprismatic arrangement, where the average O–O distance is 2.633 Å and the average distance from the center of the cavity to the O atoms is 2.093 Å. On the basis of a van der Waals radius[13] of 1.40 Å for oxygen, the interior of the cavity could thus host a species with a radius of approximately 0.69 Å. The entrance to the cavity is defined by three oxygen atoms arranged as an approximate equilateral triangle with an average edge length (oxygen center to oxygen center) of 3.254 Å. Again with 1.40 Å as the van der Waals radius of oxygen, species with radii up to about 0.5 Å could gain entrance to the cavity. Thus, encapsulation of ions as large as Li^+, Be^{2+}, or Mg^{2+} might be possible.

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Supplementary Material Available: Atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, and bond lengths and bond angles for $[PhSn(O)O_2CC_6H_{11}]_6$ (Tables SI–SIV, respectively) and a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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