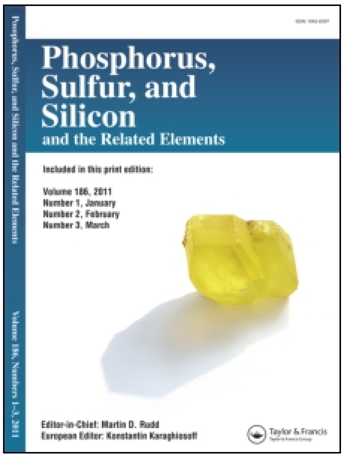

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A NEW STRUCTURAL FORM OF TIN IN A CUBIC CLUSTER

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A NEW STRUCTURAL FORM OF TIN IN A CUBIC CLUSTER

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We have reported new forms of tin comprised of oligomeric oxotin carboxylates that are based on the compositions $[R'Sn(O)O_2CR]_6$[1–5] and $[(R'Sn(O)O_2CR)_2$-$R'Sn(O_2CR)_3]_2$.[2–5] These have "drum" and "ladder" structures, respectively. We also reported the oxygen-capped cluster, $[(n\text{-}BuSn(OH)O_2PPh_2)_3O]$-$[Ph_2PO_2]$,[6] which has tin in a partial cubic array surrounded by chelating phosphinate groups. In all of these forms, tin generally is octahedrally coordinated. One useful synthetic route for their formation employs the interaction of an alkyl or aryl stannoic acid with either a carboxylic acid or a phosphorus-containing acid.

The number of tin atoms in these oligomers is either three or six. We now have obtained an additional form containing four tin atoms. The present report concerns the synthesis and structural characterization of this novel substance.

The reaction of *n*-butylstannoic acid with dicyclohexylphosphinic acid proceeds according to eq 1 to give a 20% yield of the oxotin

$$4n\text{-}BuSn(O)OH + 4(C_6H_{11})_2P(O)OH \rightarrow [n\text{-}BuSn(O)O_2P(C_6H_{11})_2]_4 + 4H_2O \quad (1)$$

composition, mp 263–265 °C.[7] Colorless arrowhead-shaped crystals for X-ray diffraction analysis[8] were grown from a CH_2Cl_2/hexane solution. Anal. Calcd for $C_{64}H_{124}O_{12}P_4Sn_4$: C, 45.64; H, 7.37. Found: C, 45.68; H, 7.28.

As shown in Figure 1, the core of the molecule is defined by tin atoms and trivalent oxygen atoms which occupy the corners of a distorted cube, each face of which is defined by a four-membered $(\text{—Sn—O—})_2$ stannoxane ring. The top and bottom faces of the cube are open, while each of its four sides is spanned diagonally by a phosphinate bridge between two tin atoms. The phosphinate bridges are required by symmetry to be symmetrical. The sides of the cube are not planar but, as in the "drum" class,[1–5] are folded along the Sn—Sn vectors so that the oxygen atoms are directed toward the interior of the cube. This is apparent in Figure 2. The geometry about the tin atoms is distorted octahedral (Table I), where the distortions are occasioned by the constraints of stannoxane rings and the bridging phosphinate groups.

The formation of the cube arrangement instead of the drum structure of the

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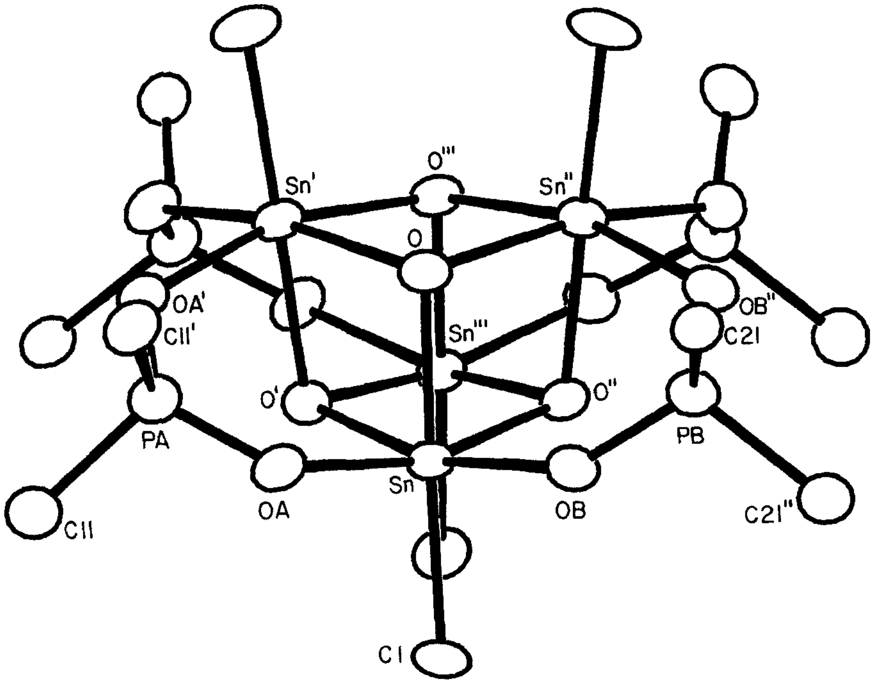

FIGURE 1 ORTEP plot of $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$ with all pendant carbon atoms of the cyclohexyl and *n*-Bu groups omitted for purposes of clarity. Symmetry operators: $' = \frac{1}{4} - x, y, \frac{1}{4} - z$; $'' = \frac{1}{4} - x, \frac{1}{4} - y, z$; $''' = x, \frac{1}{4} - y, \frac{1}{4} - z$.

same empirical composition is most likely aided by the presence of the bulky cyclohexane units attached to the phosphinate ligands (Figure 2). The hydrogen atoms of adjacent cyclohexyl groups are already in van der Waals contact, 2.326 Å for the closest such distance in the cube compared to 2.4 Å for the van der Waal's sum. In the cube, the interligand phosphinate O—Sn—O angles (OA—Sn—OB) are 94.4 (2)°, whereas this angle in the related drum compound $[n\text{-BuSn(O)O}_2\text{P(OPh)}_2]_6$[10] is 79.9 (2)°. Thus, steric crowding would be encountered if the drum formed instead of the cube since the expected decrease in this angle, close to 15°, could force the dicyclohexyl phosphinate groups into even closer proximity.

The tetramer has crystallographic D_2 symmetry in which each of the two crystallographically independent phosphorus atoms is constrained to lie on a twofold axis. However, the idealized molecular symmetry, D_{2d}, indicates that the phosphorus atoms as well as the tin atoms should be chemically equivalent. The latter is consistent with solution ^{119}Sn NMR data which shows a single resonance in $CDCl_3$ with triplet character centered at -462.8 ppm (^2J ^{119}Sn—O—^{31}P = 116 Hz).

The common structural unit in all of the oligomeric forms described so far is the four-membered dimeric distannoxane ring, Sn_2O_2. Related work[11] shows that this unit is present by itself in compounds that have hexacoordinated tin atoms. Thus, the number of tin atoms found in these structures ranges from two to six, excluding five. In a somewhat analogous sense, four-coordinated aluminum–nitrogen

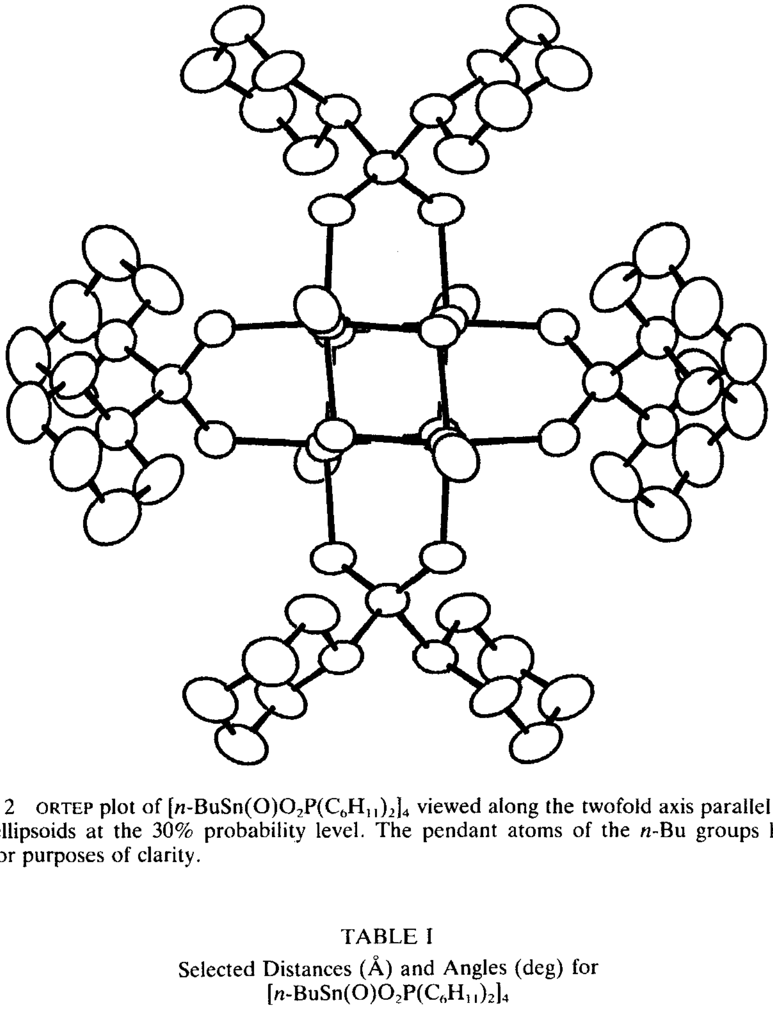

FIGURE 2 ORTEP plot of $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$ viewed along the twofold axis parallel to x, with thermal ellipsoids at the 30% probability level. The pendant atoms of the n-Bu groups have been omitted for purposes of clarity.

TABLE I

Selected Distances (Å) and Angles (deg) for $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$

Sn–O	2.046 (6)	Sn–OA	2.136 (7)
Sn–O′	2.129 (6)	Sn–OB	2.148 (6)
Sn–O″	2.148 (6)	Sn–Cl	2.13 (1)
PA–OA	1.518 (7)	PB–OB	1.519 (7)
Sn–Sn′	3.179 (1)	O–O′	2.686 (8)
Sn–Sn″	3.181 (1)	O–O″	2.710 (8)
Sn–Sn‴	3.253 (1)	O–O‴	2.757 (8)
O–Sn–O′	80.1 (2)	Sn–O–Sn′	99.2 (2)
O–Sn–O″	80.5 (2)	Sn–O–Sn″	98.6 (2)
O′–Sn–O″	80.3 (2)	Sn′–O–Sn″	99.0 (2)
avg	80.3 (2)	avg	98.9 (2)
O–Sn–Cl	178.2 (4)	O–Sn–OA	84.7 (2)
O′–Sn–OB	164.7 (2)	O–Sn–OB	86.1 (2)
O″–Sn–OA	163.8 (2)	O′–Sn–OA	90.8 (2)
O′–Sn–Cl	101.6 (4)	O″–Sn–OB	91.0 (2)
O″–Sn–Cl	99.1 (4)		
OA–Sn–OB	94.4 (2)	Sn–OA–PA	130.7 (4)
OA–Sn–Cl	95.9 (4)	Sn–OB–PB	129.7 (4)
OB–Sn–Cl	92.2 (4)		

[a] esd's are in parentheses. The atom labeling scheme is shown in Figure 1.

compounds[12,13] form oligomers with the number of aluminum atoms ranging from two to eight excluding five. It is to be expected that additional structural forms of organostannoxane derivatives will most likely be uncovered in the near future.

ACKNOWLEDGEMENT

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Supplementary Material Available: Atomic coordinates (Table S1) and anisotropic thermal parameters (Table S2) for non-hydrogen atoms and atomic coordinates and isotropic thermal parameters for hydrogen atoms (Table S3) (3 pages). Ordering information given on any current masthead page.

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7. A mixture of *n*-butylstannoic acid (2.08 g, 10 mmol) and dicyclohexyl phosphinic acid (2.30 g, 10 mmol) were heated together in toluene (85 mL) for 3 h with the azeotropic removal of water by using a Dean Stark apparatus. Toluene was removed from the homogeneous solution, and diethyl ether (30 mL) was added. A crystalline precipitate was obtained.
8. The tetrameric stannoxane $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$ crystallizes in the orthorhombic space group *Fddd* (origin taken at $\bar{1}$)[9] with a = 20.200 (2) Å, b = 46.656 (6) Å, c = 15.969 (2) Å, Z = 8, and $\mu_{\text{Mo K}\bar{\alpha}} = 1.45\ \text{mm}^{-1}$. The crystal used in the X-ray study had maximum dimensions of approximately 0.15 mm × 0.20 mm × 0.40 mm. A total of 2373 independent reflections $(+h, +k, +l)$ were measured at room temperature with use of the θ–2θ scan mode and graphite monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å), for $3° \leq 2\theta_{\text{Mo K}\bar{\alpha}} \leq 43°$, on an Enraf-Nonius CAD4 diffractometer. No corrections were made for absorption. Full-matrix least-squares refinement (non-hydrogen atoms anisotropic, cyclohexyl group hydrogen atoms riding isotropic, butyl hydrogen atoms omitted, function minimized $\Sigma w(|F_0| - |F_c|)^2$, $w^{1/2} = 2F_0L_p/\sigma_1$) led to R = 0.043 and R_w = 0.052 for the 1411 reflections having $I \geq 2\sigma_I$. Mean atomic scattering factors were taken from ref 9, 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. All calculations were performed on a Microvax II computer by using the Enraf-Nonius CAD4 SDP system of programs.
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