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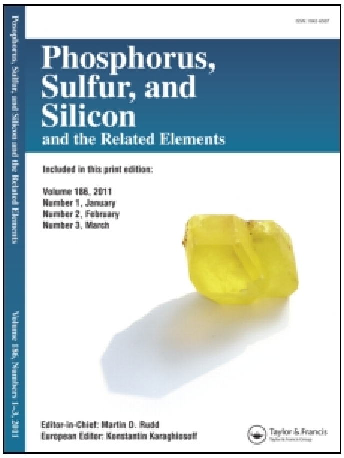

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Structural Correlations of Organooxotin Compounds

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A review of the basic structural features of organooxotin cluster chemistry is followed by a presentation of more recent work that illustrates interrelationships apparent on examining other chemistries that exhibit similar structural types. For examples, ladders, partial cubes, cubes, and double cubes are now more extensively known that incorporate a mixture of elements other than tin. Some compositions of organotin clusters that combine different elements are the ladder form, $[Fe_6(\mu_3\text{-}S)_4(\mu_2\text{-}SR)_4]$ core, the cube forms, $[n\text{-}BuSn(O)O_2AsMe_2]_4$, $[Mo_3(SnCl_3)Se_4(NCS)_9]^{6-}$, the butterfly compounds, $[n\text{-}BuSn(OH)\text{-}(O_2AsMe_2)OP(O)Me_2]_2$ and $[n\text{-}BuSn(OH)(O_2AsMe_2)_2]_2$ and the double cubes, $[\{n\text{-}BuSn(S)O_2P(p\text{-}ClC_6H_4)_2\}_3O]_2Sn$, $[\{(H_2O)_9Mo_3S_4\}\ Sn]^{8+}$, and $[Mo_6AsS_8(H_2O)_{18}]^{8+}$. Also of interest are double cubanes with sulfur or oxygen bridges, e.g., $[(Fe_4S_4Cl_3)_2S]^{4-}$and adamantyl derivatives, e.g., $(t\text{-}Bu)_4Ge_4S_6$ and $[Fe_4(SPh)_{10}]^{2-}$. By taking advantage of the insight gained from such comparisons, synthetic procedures may reveal themselves in not only extending the chemistry of organotin compounds but that of other chemistries based on related clusters.

Keywords: organooxotin clusters; ladders; cubes; double cubes; adamantyl derivatives

INTRODUCTION

Early work on organooxotin clusters traces back to 1921 when Lambourne[1,2] established compositions of organooxotin compounds resulting from the condensation reactions of alkylstannonic acids with carboxylic acids. These were of two types, the oligomers $[R'Sn(O)O_2CR]_n$, with $n = 3$ or 6, and those based on the formula $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$. A long dorment period followed which may be related partly to the difficulty in working with this class of substances. Intermediates form in the condensation process giving mixtures sometimes resulting as an oil. Interconversions also occur during the reaction sequence that further complicate the isolation of pure materials. However, the use of x-ray diffraction techniques and the ability to obtain ^{119}Sn by NMR spectra of solutions provided powerful probes which led to the development of a rich cluster chemistry of organotin compounds based on Sn-O-Sn and Sn-S-Sn bonding formed in reactions of stannonic acids with carboxylic and phosphorus-based acids as participating ligands.[3] New cluster forms were characterized as ladders, drums (or prismanes), partial cubes, double cubes, and butterfly derivatives. More complex structures also were obtained and characterized. The tin nuclearity extended up to seven in the double cube. Each of these basic clusters will be described including their interconversions and thermal behavior. Afterwards, more recent applications of tin cluster chemistry will be outlined and interrelationships with related chemistries, particularly the biologically important Fe-S clusters, will be discussed.

DRUM (OR PRISMANE)

During the course of our work[5,6] 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 present in a mixture of products:

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

$$\downarrow\ \mathrm{+ H_2O}$$

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

Although a pure product was not 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 appeared that the hexamer is hydrolytically and thermally stable. The schematic in Figure 1 portrays the drum-shaped structure resulting from the x-ray analysis and shows the atom labeling.

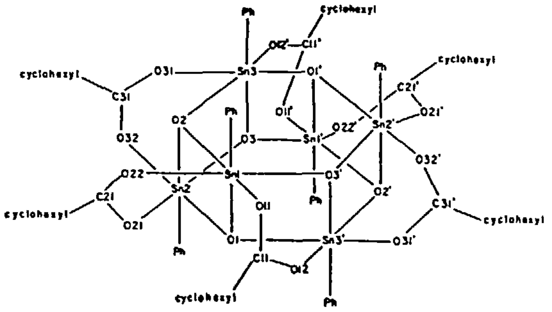


FIGURE 1 Schematic representation of the drum structure of $[\mathrm{PhSn(O)O_2CC_6H_{11}}]_6$.

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 structures are reminiscent of the ladder arrangement in dimeric distannoxanes. 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. 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. 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[7] of 1.50 Å for oxygen, the interior of the cavity could thus host a species with a radius of approximately 0.69 Å. This prismane provided the first example of tin atoms symmetrically bridged by a carboxylate group.[4]

Additional "drum" compositions were synthesized by reaction of an alkylstannonic acid with either a carboxylic acid or a phosphorus-based acid.[8] Both the drum-containing acetate ligands $[\text{MeSn(O)O}_2\text{CMe}]_6$ (**1**) and the drum with phosphate ligands $[n\text{-BuSn(O)O}_2\text{P(OPh)}_2]_6$ (**2**) were synthesized by a condensation reaction of the organostannonic acid with the ligand acid (eq 1).

$$6R'Sn(O)OH + 6RO_2H \longrightarrow [R'Sn(O)O_2R]_6 + 6H_2O \qquad (1)$$

$$R' = Me, R = MeC\ (\mathbf{1});\ R' = n\text{-}Bu, R = P(OPh)_2\ (\mathbf{2})$$

The ligand itself, glacial acetic acid, was used as a solvent in synthesizing **1** while benzene was used in the preparation of **2**. The reaction of the acetate drum **1** with di-*tert*-butylphosphinic acid gave the mixed drum **3** in which half of the acetate ligands were replaced by phosphinate ligands (eq 2). The reaction was conducted in a toluene-methanol solvent mixture (7:1). In toluene alone, no reaction occurred.

$$\underset{\mathbf{1}}{[MeSn(O)O_2CMe]_6} + 3t\text{-}BuPO_2H \longrightarrow$$

$$\underset{\mathbf{3}}{[(MeSn(O)O_2CMe)(MeSn(O)O_2P(t\text{-}Bu)_2]_3} + 3MeCO_2H \qquad (2)$$

Figure 2 shows the alternation of the two kinds of ligands around the outside of the drum. The unique formation of the mixed-drum structure **3** here is attributed to the inability of the drum to accommodate six bulky phosphinate ligands containing *tert*-butyl groups. This is supported by the values obtained for the interligand O-Sn-O angles. The O-Sn-O angle in the mixed-drum **3** averages 78.4(2)°. The latter value is very close to 79.9(2)° found in the drum structure **2** containing all phosphate ligands. Hence, there exists a potentially greater compression between adjacent ligands in the drum compared to the cube accompanying the approximate decrease in the interligand O-Sn-O angle of 15°.

The drum compounds are thermally quite stable with melting points above 300°C for most derivatives[3] although **2**, which is the only one containing all phosphate ligands, melts the lowest, at 245-247°C.

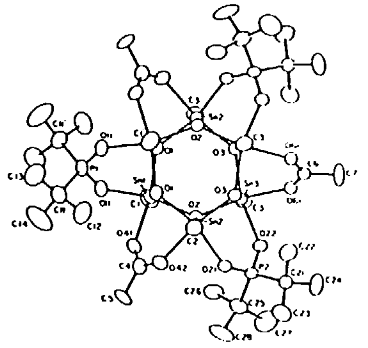


FIGURE 2 ORTEP plot of $[(MeSn(O)O_2CMe)(MeSn(O)O_2P(t\text{-}Bu)_2]_3$ (3).

However, the mixed-drum 3 with both carboxylate and phosphate ligands did not melt up to 370°C.

The interesting conversion of the oxygen-capped derivative[8] $[(n\text{-}BuSn(OH)O_2P(OPh)_2)_3O][(PhO)_2PO_2]$ (4) to the drum formulation 2 on heating (Figure 3b) corresponds to the reaction in eq 3. The drum 2 on standing for 5 days at 25°C slowly transforms to the oxygen-capped cluster 4 (Figure 3d), showing that eq 3 is reversible.[9] The latter conversion undoubtedly involves the slow pickup of moisture by the $CDCl_3$ solvent. The phosphate acid may come from partial hydrolytic cleavage of drum 2 corresponding to a reversal of eq 1 to the initial reactants. It is apparent that the oxygen-capped cluster is hydrolytically more stable than the drum.

$$\underset{\text{cluster}}{2[(R'Sn(OH)O_2PR_2)_3O][R_2PO_2]} \longrightarrow \underset{\text{drum}}{[R'Sn(O)O_2PR_2]_6} + 2R_2PO_2H + 2H_2O \qquad (3)$$

$$R' = n\text{-Bu};\ R = OPh\ (4)$$

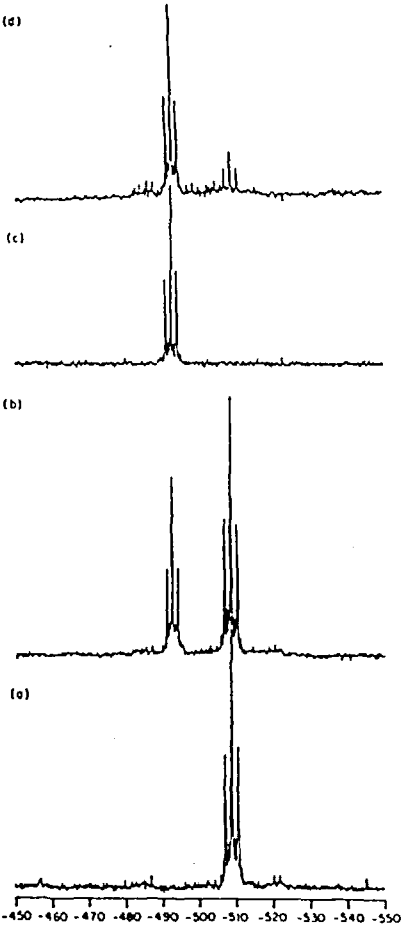


FIGURE 3 $^{119}Sn\{^1H\}$ NMR spectra of (a) the oxygen-capped cluster $[(n\text{-}BuSn(OH)O_2P(OPh)_2)_3O][(PhO)_2PO_2]$ (4), (b) partial conversion (40%) of the oxygen-capped cluster 4 to drum 2 on heating 4 in benzene for 1/2 h, (c) a $CDCl_3$ solution of the crystals of the drum $[n\text{-}BuSn(O)O_2P(OPh)_2]_6$ (2) obtained from heating the product shown in part b with toluene for 24 h, and (d) the same $CDCl_3$ solution used in part c but after 5 days at 25°C, showing partial conversion of drum 2 to the oxygen-capped cluster 4.

^{119}Sn NMR Data

There is little doubt that the drum compounds **2** and **3** retain their structure in solution at 25°C. The slow transformation of drum **2** to the oxygen-capped cluster **4** occurs at 250°C, Figure 3d. The mixed drum **3** shows a single doublet at -470.7 ppm, the doublet due to $^2J(^{119}Sn\text{-}O\text{-}^{31}P)$ coupling. Although this is the expected pattern for the cubic structure of the same empirical composition, the chemical shift normally appears at slightly lower field.[3] The average chemical shift value for three cubic forms that will be discussed in a subsequent section is -466 ± 5 ppm and that for six drum compounds is -488 ± 2 ppm.

LADDER (OR UNFOLDED DRUM)[3,10,11]

The hexameric *n*-butyloxotin benzoate, $[n\text{-}BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6 \cdot 3C_6H_6$, **5**, and the dimeric methyloxotin cyclohexanoate, $[(MeSn(O)O_2CC_6H_{11})_2MeSn(O_2CC_6H_{11})_3]_2$ **6** were prepared by condensing the stannoic acid with the respective carboxylic acid. Reaction of *n*-butyltin trichloride with the silver salt of the respective carboxylic acid gave the dimeric *n*-butyloxotin carboxylate compositions, $[(n\text{-}BuSn(O)O_2CR)_2\text{-}n\text{-}BuSn(O_2CR)_3]_2$, **7** (R = Ph) and **8** (R = Me). These represented new substances and, as found by x-ray analysis, form a new structural class of organotin compounds for **6-8** having "unfolded drum" or "ladder" structures. The hexamer composition **5** exists in "drum" form. ^{119}Sn NMR data show that the drum and ladder structures interconvert reversibly.

Two routes were used to prepare the oxocarboxylates **5-8**. For the derivatives having the drum composition **5** or the ladder formulation **6**, a condensation reaction between the stannoic acid and carboxylic acid proceeded according to eq 4 and 5, respectively.

$$6n\text{-BuSn(O)OH} + 6\text{HO}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-2} \xrightarrow{\text{C}_6\text{H}_6} [n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-2}]_6\bullet 3\text{C}_6\text{H}_6 + 6\text{H}_2\text{O} \qquad (4)$$

$$6\text{MeSn(O)OH} + 10\text{C}_6\text{H}_{11}\text{CO}_2\text{H} \longrightarrow [(\text{MeSn(O)O}_2\text{CC}_6\text{H}_{11})_2\text{MeSn(O}_2\text{CC}_6\text{H}_{11})_3]_2 + 8\text{H}_2\text{O} \qquad (5)$$

In contrast, the preparation of 7 and 8 was achieved by reacting *n*-butyltin trichloride with the silver salt of the corresponding acid, followed by hydrolysis as expressed in eq 6.

$$6n\text{-BuSnCl}_3 + 10\text{Ag}^+\text{RCO}_2^- + 4\text{H}_2\text{O} \longrightarrow [(n\text{-BuSn(O)O}_2\text{CR})_2\text{-}n\text{-BuSn(O}_2\text{CR})_3]_2 + 10\text{AgCl} + 8\text{HCl} \qquad (6)$$

The basic structure of **5** resembles a "drum" whereas **6**-**8** are "unfolded drums" or, more descriptively, "ladders". An ORTEP plot of **7** is shown in Figure 4 as representative of the ladder structures.

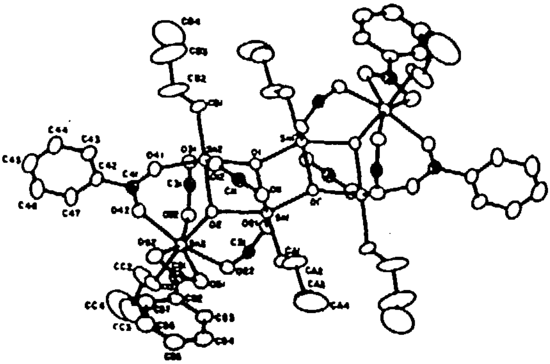


FIGURE 4 ORTEP plot of $[(n\text{-BuSn(O)O}_2\text{CPh})_2\text{-}n\text{-BuSn(O}_2\text{CPh})_3]_2$, **7**, with thermal ellipsoids at the 30% probability level. Six of the ten phenyl groups have been omitted for purposes of clarity. Carbon atoms of the carboxyl groups are shaded.

The tricarboxylate compositions readily hydrolyze and NMR data show that a reversible reaction is established in some cases between the drum and ladder forms. Subtraction of eq 5 from eq 4, in general form, leads to the hydrolysis reaction in eq 7. Hence, the drum is a hydrolysis product further along the sequence from the tricarboxylate composition than is the ladder.

$$[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2 + 2H_2O \longrightarrow [R'Sn(O)O_2CR]_6 + 4RCO_2H \qquad (7)$$

NMR evidence showing partial conversion of ladders to drums has been obtained for the mixed oxocarboxylate tricarboxylates **6**-**8**. For example, three major ^{119}Sn signals for **6** at -500.9, -527.0, and -607.4 ppm are assignable to the three nonequivalent tin sites in this ladder structure. The most shielded tin atoms are obviously the pair of terminal tins which are seven-coordinated. It seems reasonable to assign the successively observed lower field peaks to pairs of tin atoms located progressively toward the center of the ladder structures. Two additional ^{119}Sn signals of low intensity are present at -465.9 and -515.6 ppm. The former signal may be due to the drum, $[MeSn(O)O_2CC_6H_{11}]_6$, formed by loss of carboxylic acid, eq 7, whereas the signal at 515.6 ppm may be due to an intermediate on the way to the formation of the drum.

The range of ^{119}Sn chemical shifts observed for drums[3,8] is -478 to -485 ppm for butylstannoic acid derivatives. It is reasonable that the lower field signal at -465.9 ppm for **6** is due to the drum formed in the hydrolysis of eq 7. Addition of carboxylic acid to a solution of pure drum causes the appearance of ^{119}Sn NMR signals associated with the ladder formulation.[3,8]

Similar to **6**, the three ^{119}Sn NMR signals recorded as broad at -606 ppm and as multiplets at -548 and -520 ppm for the benzoate derivative

7 are assigned to the "ladder", and the signal at -536 ppm is assigned to an intermediate. The components of the multiplet at -548 ppm are -545, -548, and -550 ppm while the components of the multiplet at -520 ppm are -517, -520, -522, and -523 ppm.

There are three chemically nonequivalent types of Sn atoms in the molecules 7 and 8. Both compounds have similar geometries in which Sn1 and Sn2 are both hexacoordinated and have distorted octahedral geometry. The terminal Sn3, however, is heptacoordinated and has pentagonal bipyramidal geometry with O2 and CC1 in axial positions.

The general structural features of the methyloxotin cyclohexanoate 6 are very similar to those of 7 and 8. The Sn-O framework for the unfolded species 7 is shown in Figure 5. In Figure 5b deviations from planarity for this framework can be visualized.

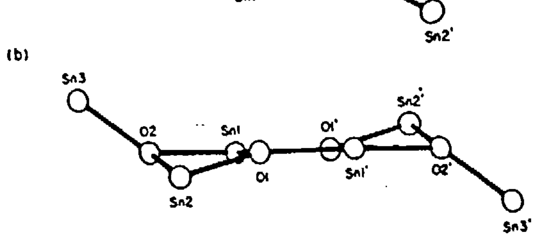


FIGURE 5 ORTEP plot showing the Sn-O framework of the "unfolded drum" in $[(n\text{-BuSn(O)O}_2\text{CPh})_2\text{-}n\text{-BuSn(O}_2\text{CPh})_3]_2$, 7 (a) viewed normal to the central Sn_2O_2 plane and (b) viewed parallel to the central Sn_2O_2 plane.

Additional drum structures,[11] hexameric *n*-butyloxotin cyclopentanoate $[n\text{-BuSn(O)O}_2\text{CC}_5\text{H}_9]_6\bullet\text{C}_6\text{H}_6$ (**9**) and hexameric *n*-butyloxotin cyclohexanoate $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11}]_6\bullet\text{C}_6\text{H}_6$ (**10**), were prepared by reacting *n*-butylstannanoic acid with the corresponding carboxylic acid. An additional ladder structure was obtained by the reaction of *n*-butyltin trichloride with the silver salt of cyclohexanecarboxylic acid which gave the dimeric composition $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (**11**). The synthesis of a novel chloro derivative, $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)-}(\text{O}_2\text{CPh})_2)]_2$ (**12**), having a "ladder" structure also was obtained.

PARTIAL CUBE OR OXYGEN-CAPPED CLUSTER[3,12]

Reaction of diphenylphosphinic acid with *n*-butylstannonic acid under reflux in toluene yielded a new structural form of tin characterized as a partial cube or oxygen-capped cluster.[12] The reaction proceeds according to eq 8 giving the stable oxide composition in 90% yield, mp 198-208°C dec. The basic framework consists of a tristannoxane ring in

$$3n\text{-BuSn(O)OH} + 4\text{Ph}_2\text{PO}_2\text{H} \longrightarrow [(n\text{-BuSn(OH)O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2] + 2\text{H}_2\text{O} \qquad (8)$$

a cyclohexane chair arrangement, Figure 6. 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 presence of the unique capping oxygen atom. These units which contain the capping oxygen atom are arranged essentially at right angles to one another giving a cube with one corner missing.

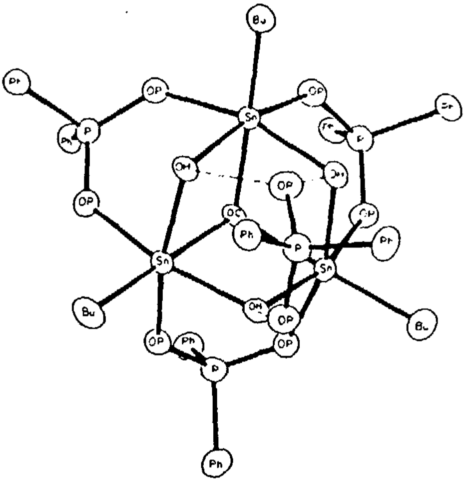


FIGURE 6 ORTEP plot of $[(n\text{-BuSn(OH)O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$. Pendant atoms of the three n-Bu groups and of the eight Ph groups are omitted for purposes of clarity. Hydrogen-bonding interactions are shown as dashed lines.

The presence of four- and six-membered rings also is a primary structural feature of the drum structure.[4,11,13] The ladder framework, however, only possesses four-membered rings.[11]

The oxygen-capped cluster can be viewed as a hydrolysis product of the drum just as the drum is viewed as a hydrolylsis product of the ladder,[11] i.e., eq 9 and 10, respectively. The drum to ladder conversion has been followed by ^{119}Sn NMR and shown to be

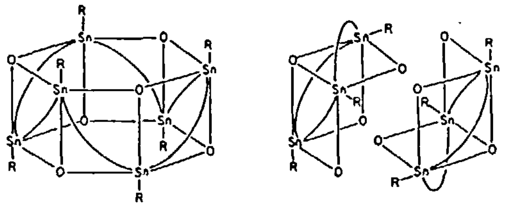
$$\underset{\text{drum}}{[\text{R}'\text{Sn(O)O}_2\text{R}]_6} + 2\text{RO}_2\text{H} + 2\text{H}_2\text{O} \longrightarrow \underset{\text{cluster}}{2[(\text{R}'\text{Sn(OH)O}_2\text{R})_3\text{O}][\text{RO}_2]} \qquad (9)$$

$$\underset{\text{ladder}}{[(R'Sn(O)O_2R)_2R'Sn(O_2R)_3]_2} + 2H_2O \longrightarrow \underset{\text{drum}}{[R'Sn(O)O_2R]_6} + 4RO_2H \qquad (10)$$

$$R = R''C \text{ or } R''_2P$$

reversible.[11] The ^{119}Sn 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 oxygen-capped clusters. 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.



CUBE[3,14]

The reaction of *n*-butylstannoic acid with dicyclohexylphosphinic acid proceeds according to eq 11 to give a 20% yield of the oxotin composition, mp 263-265°C. Solution ^{119}Sn NMR data shows a single

$$4n\text{-BuSn(O)OH} + 4(\text{C}_6\text{H}_{11})_2\text{P(O)OH} \longrightarrow [n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4 + 4\text{H}_2\text{O} \qquad (11)$$

resonance in $CDCl_3$ with triplet character centered at -462.8 ppm (^2J $^{119}Sn\text{-}O\text{-}^{31}P$ = 116 Hz).

As shown in Figure 7, 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 (-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,[4,8,11,13] are folded along the Sn-Sn vectors so that the oxygen atoms are directed toward the interior of the

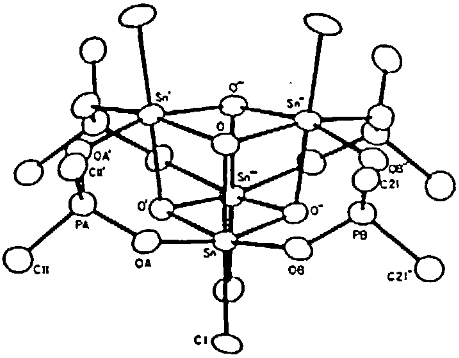


FIGURE 7 ORTEP plot of [n-BuSn(O)O$_2$P(C$_6$H$_{11}$)$_2$]$_4$ with all pendant carbon atoms of the cyclohexyl and n-Bu groups omitted for purposes of clarity.

cube. This is apparent in Figure 8. The geometry about the tin atoms is distorted octahedral, 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 same empirical composition is most likely aided by the presence of the bulky cyclohexane units attached to the phosphinate ligands (Figure 8). 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 Waals' sum.[7] 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-BuSn(O)$O_2P(OPh)_2]_6$[8] is 79.9(2)°. Thus, steric crowding would be encountered if the drum formed instead of the cube since the expected

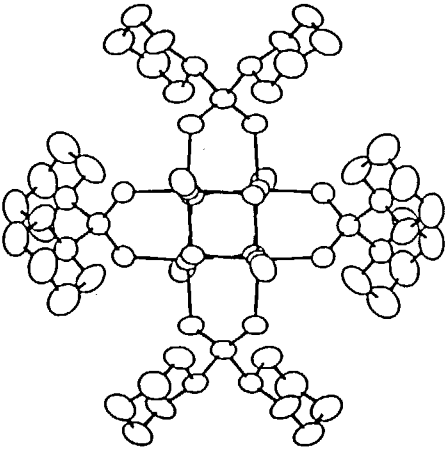


FIGURE 8 ORTEP plot of [n-BuSn(O)$O_2P(C_6H_{11})_2]_4$ viewed along the twofold axis parallel to x.

decrease in this angle, close to 15°, could force the dicyclohexyl phosphinate groups into even closer proximity.

ADDITIONAL CUBES AND A BUTTERFLY CLUSTER[15]

Reaction of *n*-butylstannoic acid with the phosphinic acids, R_2PO_2H, where R = *tert*-butyl, benzyl, and cyclohexyl, led to new types of structural forms for hexacoordinated tin: two cubic clusters, [*n*-$BuSn(O)O_2P(t\text{-}Bu)_2]_4$ (**13**) (Figure 9) and [*n*-$BuSn(O)O_2P(CH_2Ph)_2]_4$ (**14**), respectively, and a "butterfly" cluster, [*n*-$BuSn(OH)(O_2P(C_6H_{11})_2)_2]_2$ (**15**) (Figure 10). Interesting transformations of cubes and the butterfly derivative yield oxygen-capped cluster formulations, $[(R'Sn(OH)O_2PR_2)_3O][R_2PO_2]$, where R′ = *n*-Bu and R = C_6H_{11} or CH_2Ph. ^{119}Sn and ^{31}P NMR show these structural characteristics in solution. Although the butterfly cluster **15**

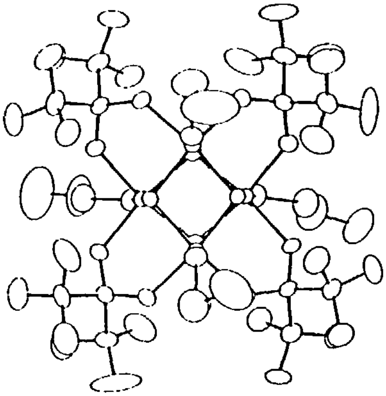


FIGURE 9 ORTEP plot of [*n*-$BuSn(O)O_2P(t\text{-}Bu)_2]_4$ (**13**). The view is down the pseudo S_4 axis.

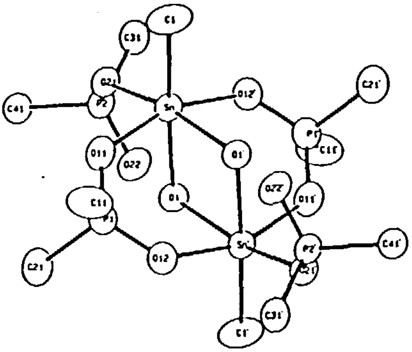


FIGURE 10 ORTEP plot of $[n\text{-BuSn(OH)}(O_2P(C_6H_{11})_2)_2]_2$ (**15**). Hydrogen atoms and pendant carbon atoms are omitted for purposes of clarity.

was prepared by both reaction of *n*-butylstannoic acid with the appropriate phosphinic acid and reaction of *n*-butyltin trichloride with the silver salt of the phosphinic acid, **13** and **14** were formed only by the former reaction (eq 12). The former reaction has been used to

$$4n\text{-BuSn(O)OH} + 4R_2PO_2H \longrightarrow [n\text{-BuSn(O)}O_2PR_2]_4 + 4H_2O \qquad (12)$$

$$R = t\text{-Bu } (\mathbf{13}),\ CH_2Ph\ (\mathbf{14})$$

prepare open-drum (or ladder) oxotin compounds[10,11] containing carboxylate ligands. The condensation reaction of stannoic acid with phosphinic acid in forming the cubic structures, **13** and **14**, requires a 1:1 stoichiometry (eq 12) whereas this reaction leading to the butterfly cluster, **15**, proceeds in a 1:2 stoichiometric ratio of tin acid to phosphorus acid (eq 13). The drum composition $[R'Sn(O)O_2P(OR)_2]_6$ also results from a 1:1 reaction of tin acid to phosphorus-based acids.[8]

$$2n\text{-BuSn(O)OH} + 4(C_6H_{11})_2PO_2H \longrightarrow [n\text{-BuSn(OH)}(O_2P(C_6H_{11})_2)_2]_2 + 2H_2O \qquad (13)$$

However, as previously observed,[8,14] the cube geometry offers greater accommodation for larger groups attached to the phosphinate ligand. The alteration in ligand type around the outside of the drum in the latter structure presumably allows the relaxation of any steric effect from the di-*tert*-butylphosphinate ligands. It is reasonable that derivatives with all carboxylate ligands have not yielded any cubic arrays.[10,11] Here, steric effects should be minimal between carboxylate groups due to the presence of only one R group and the near planarity associated with the RCO_2 unit. Instead, a competition arises between drum an dopen-drum forms leading to reversible equilibria.[11]

In the present case with phosphinate ligands, interconversions of a different kind are found. Although the cube **13**, containing the di-*tert*-butylphosphinate ligands (depicted in Figure 1) exists in stable form in solution, both the cube **14** and butterfly **15** undergo transformations with adventitious water. The hydrolysis of **15** proceeds more slowly than that for **14**. Both yield an oxygen-capped cluster as demonstrated by their $CDCl_3$ solution-state ^{119}Sn and ^{31}P NMR spectra. For the cube **14** a new triplet appeared at -499.2 ppm in the ^{119}Sn spectrum and increased in intensity at the expense of the triplet at -464.4 ppm. The ^{31}P NMR spectrum behaves similarly. The ^{119}Sn chemical shift is especially diagnostic of the type of structure present. As Table I indicates, each formulation falls in a rather narrow chemical shift range with no overlap between ranges.

Figure 11 shows a ^{119}Sn NMR spectrum of a reaction mixture of *n*-butylstannoic acid with dicyclohexylphosphinic acid in $CDCl_3$.

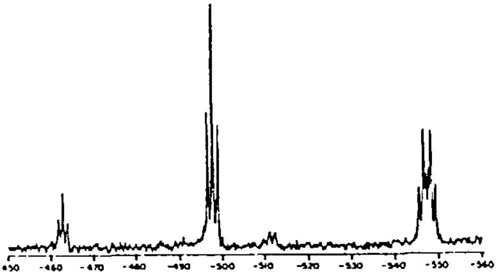


FIGURE 11 ^{119}Sn NMR spectrum ($CDCl_3$ solution) of a reaction product of *n*-butylstannoic acid with dicyclohexylphosphinic acid in a 1:1.5 molar ratio, respectively. The three resonance patterns with increasing shielding are the cube **16** at -462.8 ppm, the O-capped cluster **17** at -499.5 ppm, and the butterfly formulation **15** at -547.5 ppm.

The cube $[n\text{-BuSn(O)}O_2P(C_6H_{11})_2]_4$ (**16**) low-field triplet at -462.8 ppm, the O-capped cluster $[(n\text{-BuSn(OH)}O_2P(C_6H_{11})_2)_3O]$-$[(C_6H_{11})_2PO_2]$ (**17**) higher field triplet at -499.5 ppm, and the butterfly cluster **15** highest field doublet of triplets at -547.5 ppm, are readily identified with reference to Table I. As can be seen from Figure 11, the butterfly derivative **15** is formed in significant quantities, although the yield of the isolated pure product is very low. Of course, in this case, the cube **16** and butterfly cluster**15** were independently synthesized and have had their x-ray structures determined, **16** reported earlier[14] and **15** here.

The conversion of **15** to **17** is illustrated by the ^{31}P NMR spectra in Figure 12 obtained in less than 1 h after solution preparation and also after 6 days. The two types of phosphinate signals with ^{119}Sn satellites for the butterfly **15**, resonating at 56.0 and 47.6 ppm (1:1 intensity), decrease in intensity as the ^{31}P signal, with ^{119}Sn satellites indicative

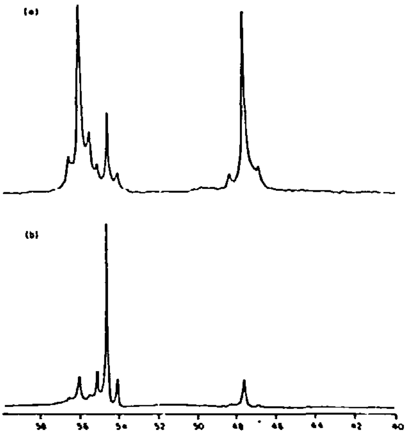


FIGURE 12 ^{31}P NMR spectrum ($CDCl_3$ solution) of the same reaction product as in Figure 11 (a) obtained in less than 1 h after sample preparation showing two equal intensity triplets at 56.0 ppm (bridging phosphinate) and at 47.6 ppm (dangling phosphinate) corresponding to the butterfly **15** and a low-intensity triplet at 54.6 ppm associated with the cation of the *o*-capped cluster **17** and (b) obtained after 6 days showing the growth of the O-capped triplet at 54.6 ppm and the diminished intensity due to the two triplets arising from the butterfly **15**.

of the O-capped cluster **17**, grows in at 54.6 ppm. The ^{31}P resonance expected at 44.0 ppm for the phosphinate anion most likely is absent due to fast exchange with phosphinic acid released in the hydrolysis. This conversion proceeds to over 95%. The reactions generating the O-capped cluster follow eq 14 and 15 for **14** and **15**, respectively. In the

$$[R'Sn(O)O_2PR_2]_4(\text{cube } \mathbf{14}\ (R' = Bu, R = CH_2Ph)) + 2H_2O \longrightarrow$$
$$[(R'Sn(OH)O_2PR_2)_3O][R_2PO_2](\text{O-capped cluster})$$
$$+\ R'Sn(O)OH \qquad (14)$$

$$\begin{aligned}&3[R'Sn(OH)(O_2PR_2)_2]_2(\text{butterfly } \mathbf{15}\ (R' = Bu, R = C_6H_{11})) + 2H_2O\\ &\longrightarrow 2[(R'Sn(OH)O_2PR_2)_3O][R_2PO_2](\text{O-capped cluster } (\mathbf{17}))\\ &\quad + 4R_2PO_2H \qquad (15)\end{aligned}$$

TABLE I ^{119}Sn chemical shifts for *n*-butyloxotin clusters in $CDCl_3$

cluster [b]	av δ^c	Sn/ligand [d]	H_2O/Sn [e]
cube (3)	-466.1 ± 4.6	1	1
drum (6)	-487.9 ± 1.8	1	1
crown (2)	-525.4 ± 10	4/5	1/2
O-capped (4)	-501.1 ± 3.9	3/4	2/3
ladder (5)	-523.5 ± 2.2 -549.4 ± 2.8 -621.9 ± 10.7	3/5	4/3
butterfly (1)	-547.4	1/2	1
extended (1)	-575		
	-614	2/5	3/2

[a] Summarized here are ^{119}Sn chemical shifts for clusters containing mainly phosphinate and carboxylate ligands. References are found in Table 1 of ref. 3. [b] Numbers in parentheses represent number of compounds studied. [c] All in $CDCl_3$ except the cube $[n\text{-}BuSn(O)O_2P(t\text{-}Bu)_2]_4$, which was studied in C_6D_6. [d] Mole ratio of the stoichiometric amount of the organostannoic acid in reaction with the ligand acid. [e] Mole ratio of water formed to stannoic acid used in the condensation reaction of stannoic acid with ligand acid.

former process, hydrolysis proceeds with the generation of stannoic acid, while in the latter hydrolysis, phosphinic acid is formed. The ^{119}Sn and ^{31}P chemical shifts and coupling constants giving rise to the transformation indicated in Figure 12 correspond to the O-capped cluster **(17)**, identified as such in the conversion of the dicyclohexyl cube **16** to this species. In accord with eq 14 and 15 then, the O-capped cluster arrangement is hydrolytically more stable than either the cube or butterfly compositions.

An additional cube form is pictured schematically in Figure 13. Its low yield synthesis is outlined by two different routes. It is unique compared to the others in that sulfur atoms in the cube framework have formally replaced oxygen atoms for those atoms bonded to tin.

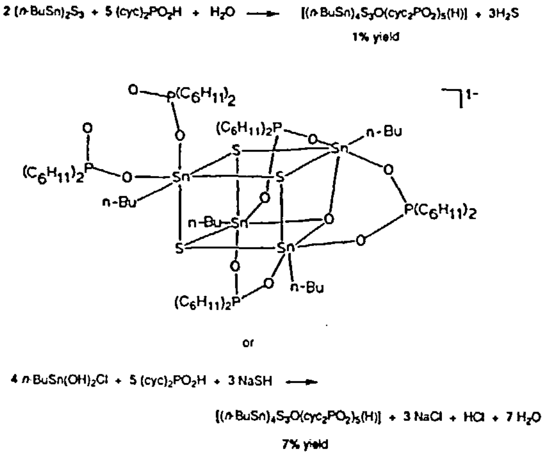


FIGURE 13 Phosphinate chelated tin-sulfur cube.[16]

DOUBLE CUBE

A heptanuclear tin-sulfur cluster formed from the reaction of *n*-butylstannonic acid, diphenyl phosphine oxide, and elemental sulfur.[17]

$$24Ph_2P(OH) + 3S_8 + 28n\text{-}BuSn(O)OH \xrightarrow[\text{reflux}]{\text{toluene}} 4[\{n\text{-}BuSnS(O_2PPh_2)\}_3O]_2Sn + 24H_2O + 4n\text{-}BuH$$

X-ray analysis revealed a double cube arrangement which was the first such structural entity uncovered for a main group element. An analogous core structure exists for a zinc complex, however, $Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6$.[18] The latter is a polymerization catalyst. Figure 14 shows the chelating phosphinate ligand arranged around the outside of one of the symmetry-related Sn-O cubes. The relation

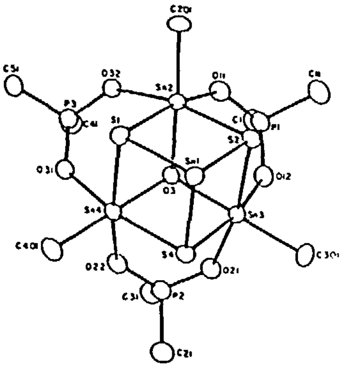


FIGURE 14 ORTEP plot of the asymmetric unit of the $[(n\text{-}BuSn(S)O_2PPh_2)_3O]_2Sn$ molecule. Atom Sn1 lies on a crystallographic inversion center. Pendant carbon atoms of the six phenyl groups and of the three *n*-butyl groups are omitted for purposes of clarity.

between this geometry and the oxygen-capped (or partial cube) formulation may be seen by the formal removal of Sn1 and the introduction of hydrogen atoms on S1, S2, and S4, with S-H bonds replacing S-Sn1 bonds. This results in an SH analogue of the O-capped cluster, $[n(\mathrm{BuSn(OH)O_2PPh_2})_3\mathrm{O}]^+$.

The core of the molecule is shown in Figure 15 as a double cube connected at the corners occupied by Sn1. Distortions away from cubic geometry are caused primarily by the geometric requirements of the

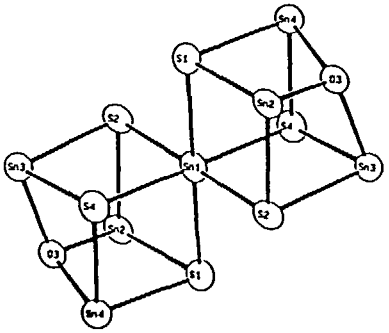


FIGURE 15 ORTEP plot showing the tin-sulfur-oxygen core of the $[(n\mathrm{BuSn(S)O_2PPh_2})_3\mathrm{O}]_2\mathrm{Sn}$ molecule.

oxygen atom O3. The four-membered $(\mathrm{Sn\text{-}S})_2$ rings are nearly planar (± 0.044 Å maximum deviation) with angles that deviate only slightly from 90° (av values from 89.41(4)° to 90.18(4)°). The angles at O3, however, are nearly tetrahedral (av 109.4(1)°), and the four-membered rings containing O3 are not planar. For these, O3 is displaced 0.4Å out of the plane defined by the remaining three atoms in a direction toward the center of the cube. The angles at Sn and S in these rings average 82.2(1)° and 83.38(4)°, respectively.

$^{119}\mathrm{Sn}$ and $^{31}\mathrm{P}$ NMR indicate that the double cube structure is retained in solution. A single tin signal with triplet character due to phosphorus atom coupling appearing in the hexacoordinated region is assigned to the six equivalent tin atoms. A $^{119}\mathrm{Sn}$ NMR signal due to the unique tin atom connected to six sulfur atoms was not observed. This also was the case for two other double cubes that were synthesized, $[(n\text{-}BuSn(S)O_2P(n\text{-}Bu)_2)_3O]_2Sn$[19] and $[(n\text{-}BuSn(S)O_2P(p\text{-}ClC_6H_4)_2)_3O]_2Sn$.[20] Consistent with the presence of equivalent phosphorus atoms, one phosphorus signal with tin satellites is observed in the ^{31}P NMR spectrum.

ADDITIONAL OXYGEN- AND SULFUR-CAPPED ORGANOTIN CLUSTERS[21]

The synthesis and structural features of the oxygen-capped cluster, $[(n\text{-}BuSn(OH)O_2P(O\text{-}t\text{-}Bu)_2)_3O][O_2P(O\text{-}t\text{-}Bu)_2]$ (**18**), are compared to that of the analogous formulations containing framework sulfur atoms in place of oxygens, $[(n\text{-}BuSn(S)(OH)OP(O\text{-}t\text{-}Bu)_2)_3S][O_2P(O\text{-}t\text{-}Bu)_2]\bullet 2H_2S\bullet H_2O$ (**19**) and $[(n\text{-}BuSn)_3(S)(O)(O_2CPh)_5]$ (**20**). Solution NMR, ^{119}Sn and ^{31}P, indicate that the solid state structures determined by x-ray analysis are retained in solution.

The oxygen-capped cluster $[(n\text{-}BuSn(OH)O_2P(O\text{-}t\text{-}Bu)_2)_3O][O_2P(O\text{-}t\text{-}Bu)_2]$ (**18**) was prepared by condensation of *n*-butylstannonic acid with di-*tert*-butyl phosphoric acid at room temperature in benzene solution, eq 16.

$$3n\text{-}BuSn(O)OH + 4(O\text{-}t\text{-}Bu)_2PO_2H \longrightarrow [(n\text{-}BuSn(OH)O_2P(O\text{-}t\text{-}Bu)_2)_3O][O_2P(O\text{-}t\text{-}Bu)_2] + 2H_2O \quad (16)$$

The sulfur-capped cluster $[(n\text{-}BuSn(S)(OH)OP(O\text{-}t\text{-}Bu)_2)_3S]\text{-}[O_2P(O\text{-}t\text{-}Bu)_2]\text{-}\bullet 2H_2S\bullet H_2O$ (**19**) was prepared by passing hydrogen sulfide through a benzene solution of $n\text{-}BuSn[O_2P(O\text{-}t\text{-}Bu)_2]_3$ at room temperature, eq 17.

$$3n\text{-BuSn}[O_2P(O\text{-}t\text{-Bu})_2]_3 + 4H_2S \longrightarrow$$
$$[(n\text{-BuSn}(S)OP(OH)(O\text{-}t\text{-Bu})_2)_3S][O_2P(O\text{-}t\text{-Bu})_2]$$
$$+ 5(O\text{-}t\text{-Bu})_2PO_2H \qquad (17)$$

For the preparation of $[(n\text{-BuSn})_3(S)(O)(O_2CPh)_5]$ (**20**), hydrogen sulfide was passed through a CCl_4 solution of *n*-butyltin tribenzoate at room temperature in the presence of atmospheric moisture.

$$3n\text{-BuSn}(O_2CPh)_3 + H_2S + H_2O \longrightarrow$$
$$[(n\text{-BuSn})_3(S)(O)(O_2CPh)_5] + 4PhCO_2H$$

Clusters **18** and **19** are partial cubes. X-ray analysis of **18** reveals that the cation portion contained a trinuclear oxygen-capped cluster which is similar to others discussed earlier.[3,12] This cation also contains bridging hydroxide and phosphate ligands between the tin atoms. The anion consists of a phosphate unit that is hydrogen bonded to the hydroxides. This molecule is structurally similar to other O-capped derivatives.[12,15] A ^{119}Sn NMR spectrum shows a triplet centered at -507.7 ppm. The chemical shift is consistent with the presence of a hexacoordinated tin atom. Two-bond tin-phosphorus coupling was measured to be 189 Hz. The ^{31}P NMR spectrum shows a singlet with tin satellites at -12.8 ppm due to the bridging phosphate ligands and another singlet at -5.7 ppm assigned to the phosphate anion.

An x-ray diffraction study of **19** revealed the molecular formula, $[(n\text{-BuSn}(S)OP(OH)(O\text{-}t\text{-Bu})_2)_3S][O_2P(O\text{-}t\text{-Bu})_2]\bullet 2H_2S\bullet H_2O$, corresponding to a trinuclear sulfur-capped organotin cluster containing sulfide bridges and monodentate di-*tert*-butylphosphate ligands (Figure 16).

Several structural features differentiate this sulfur-capped molecule from the oxygen-capped species (18). First, the tin atoms are pentacoordinate. This is borne out in solution as well. The ^{119}Sn NMR

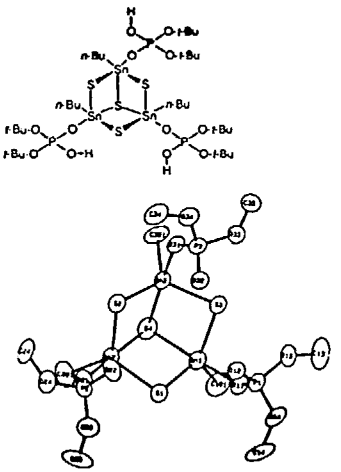
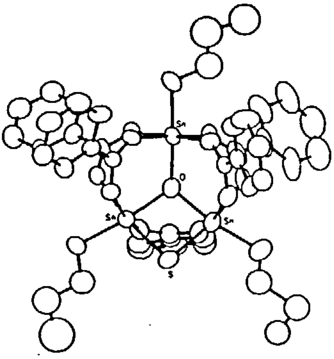


FIGURE 16 An ORTEP drawing of the cation of 19 with pendant atoms removed for clarity.

spectrum reveals a broad resonance at -205 ppm with no observable tin-phosphorus coupling. The ^{31}P NMR spectrum shows only a single broad resonance, centered at -12.0 ppm. This might imply a rapid exchange of the coordinated phosphate ligands with the capping phosphate anion. Only a slight broadening of the signal is observed upon lowering the temperature to -90°C. Second, the ligands are monodentate. They reach out above the face of the cage instead of angling back towards the capping atom as in the O-capped analog. This leaves little space for a close interaction between the sulfur atoms of the cation and the solvate molecules. Instead, there arises an involved network of hydrogen bonding between the dangling P-O-H moieties of the coordinated phosphates, the two H_2S solvates, the H_2O solvate, and the anionic capping phosphate.

X-ray analysis of **20** revealed a trinuclear cluster with a tricoordinate oxygen atom joining the three tin centers (Figure 17). Five carboxylate groups span the tin atoms with one Sn-S-Sn linkage present to form a mixed Sn-S-Sn-O ring system. The ^{119}Sn NMR spectrum shows two



$[(n\text{-}BuSn)_3(S)(O)(O_2CPh)_5]$

FIGURE 17 An ORTEP drawing of **20**.

kinds of tin centers present in a 2:1 ratio. One resonance appears at -414.1 ppm and contains two sets of tin-tin satellites, $^{2}J(^{119}Sn\text{-}^{117}Sn)$ = 178 Hz and $^{2}J(^{119}Sn\text{-}^{119}Sn)$ = 222 Hz. A second resonance, one half the intensity of the first, occurs at -593.4 ppm. It has a single set of tin satellites, $^{2}J(^{119}Sn\text{-}^{119}Sn)$ = 222 Hz, which are twice as intense as the corresponding satellites of the first signal. An inverse gated decoupled ^{13}C NMR spectrum shows three different carboxylate carbons in a 2:2:1 ratio.

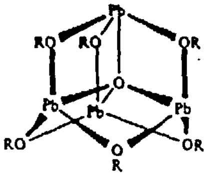
It is apparent that sulfur insertion into organotin-capped clusters causes structural difference compared to oxygen-capped analogs. This is noted particularly in the sulfur-capped, Sn-S-Sn bridged cluster (**19**) showing both five-coordinated tin atoms and monocoordinated phosphate ligands. A rearrangement of hydrogen bonding effects in **19** compared to that in the O-capped cluster (**18**) appears partly responsible for these differences.

MORE RECENT WORK

In the following sections, more recent literature is discussed that either takes advantage of previous knowledge or shows structural correlations with regard to organooxotin cluster chemistry. The development is not comprehensive but supplies sufficient comparisons that might prove useful in providing insight for advances in this intriguing area.

Adamantyl Derivatives

Adamantyl formulations are known for germanium, tin, and lead. For example, $Pb_4O(OSiPh_3)_6$[22] has an adamantane-like structure showing four-fold coordination about the central oxygen atom. The local geometry about Pb(II) is pseudo-trigonal bipyramidal. The $OSiPh_3$ groups occupy equatorial sites and the unique oxygen atom and a lone pair occupy axial sites. More recently, $Pb_4O(O\text{-}t\text{-}Bu)_6$, was reported as having a similar adamantyl structure (Figure 18).[23]



$Pb_4O(O\text{-}t\text{-}Bu)_6$

FIGURE 18 A lead oxo alkoxide in an oxygen-encapsulated adamantane structure.

Likewise germanium and tin enter into this formulation. Pohl[24] found $Ge_4S_6Br_4$ to be adamantyl while Ando and coworkers[25] summarized adamantane interrelationships for organogermanium derivatives (Figure 19).

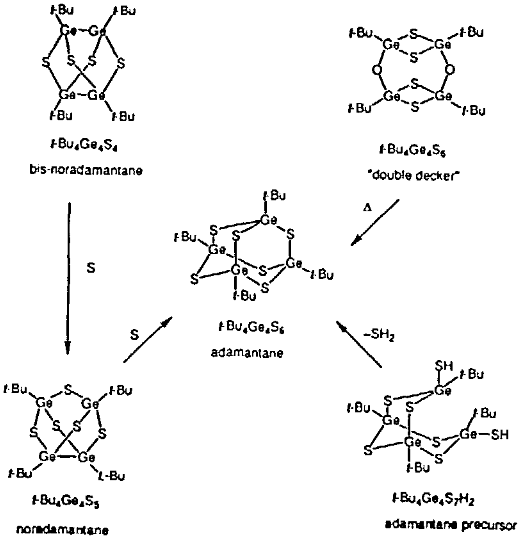


FIGURE 19 Germanium adamantane interrelationships.

Recent work by Jurkschat, Dakternieks, and coworkers[26] illustrated adamantyl and noradamantyl-like compositions of organooxotin compounds (Figure 20).

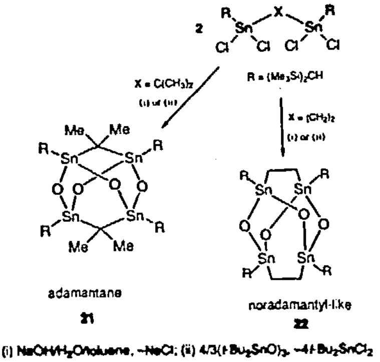
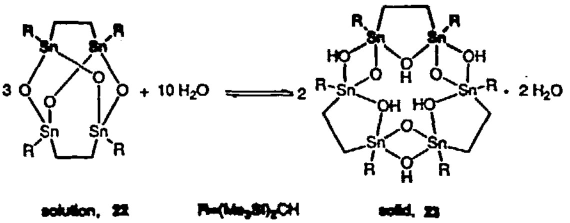


FIGURE 20 **Adamantyl derivatives of tin.**

An x-ray determination of **21** was obtained while the structure of **22** was deduced from the reversible equilibrium expressed in eq 18 giving **23** whose x-ray structure was established.



Related Cluster Chemistries

Several presentations at the International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead (ICCOC-GTL-9)[27] dealt with ladder, cube, and partial cube formulations. From their work, it is apparent that current interest in this field has led to a diversity of applications.

Mixed Double Cubes

In recent work, double cubes analogous to those already discussed have been formed which contain other atoms in addition to tin in the cube frameworks. Also the atom that links the two cubes may be other than a tin atom. Some examples, **24-26**, that have had their structures established by x-ray analysis are shown in Figures 21[28] and 22[29,30] where syntheses are also included.

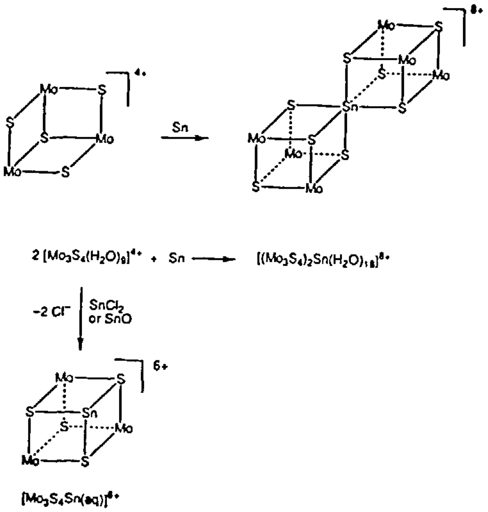
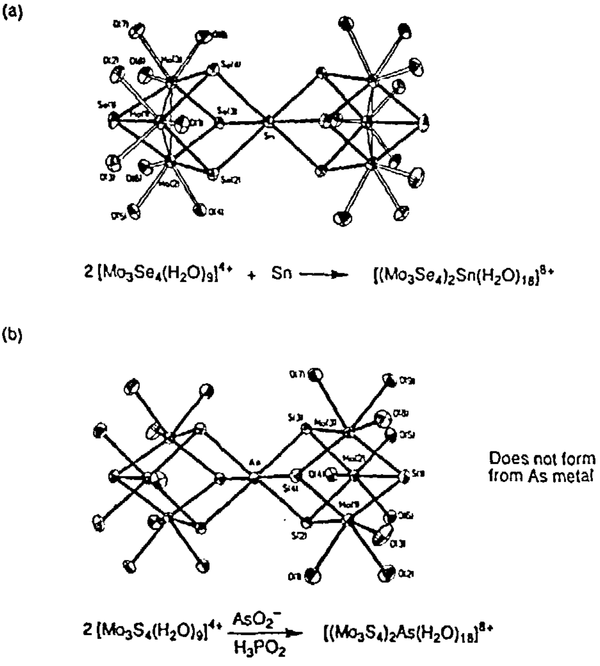


FIGURE 21 Synthesis of the cube $[Mo_3S_4Sn(aq)]^{6+}$ and the double cube $[(Mo_3S_4)_2Sn(H_2O)_{18}](pts)_8{\bullet}26H_2O$[28] (24) from a partial cube. Shown are core representations (pts = *p*-toluenesulfonate, $CH_3C_6H_4SO_3$).



Does not form from As metal

FIGURE 22 Synthesis and ORTEP of the double cube (a) $[(Mo_3Se_4)_2Sn(H_2O)_{18}]\text{-}(pts)_8 \bullet 2H(pts) \bullet 28H_2O$[29] (25) and (b) $[(Mo_3S_4)_2As(H_2O)_{18}](pts)_8 \bullet 28H_2O$[30] (26) (pts = *p*-toluenesulfonate, $CH_3C_6H_4SO_3$).

An analogous composition to the arsenic containing double cube is the antimony derivative, $[(Mo_3S_4)_2Sb(H_2O)_{18}]^{8+}$ [31] (27), which has the same basic structure.

As will be apparent in our discussion of iron-sulfur clusters to follow, no double cubes of the type outlined here have been prepared. Instead, Fe-S cubes are linked by cube edges or Fe-S-Fe bridges.

Iron-Sulfur Clusters

Some simple iron-sulfur formulations that bear a close resemblance to related oxotin clusters are depicted in Figure 23. These consist of a ladder,[32] a drum,[33] a cube,[34] and an adamantane[35] structure. Other members exist in these classes (see ref. 3).

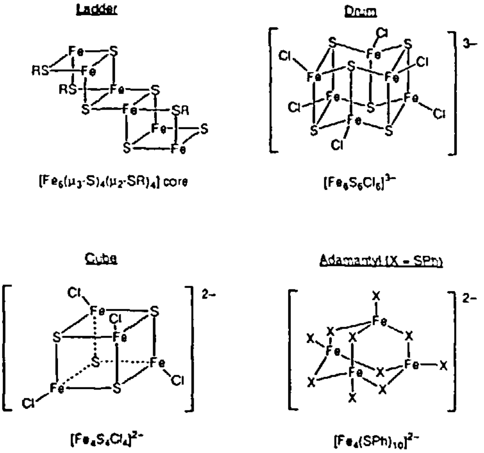


FIGURE 23 Some iron-sulfur clusters.

The stair-like ladder structure (Figure 24) was prepared from the binuclear iron complex $[\{Fe(\text{"}EtN_2S_2\text{"})\}_2]$ ("EtN_2S_2" = *N,N'*-diethyl-3,7-diazanonane-1,9-ditholate). The latter reacts with the $[Fe_4S_4I_4]^{2-}$ cubane cluster to form the neutral hexanuclear cluster $[\{Fe(\text{"}EtN_2S_2\text{"})\}_2Fe_4S_4I_2]$ (28), which contains the hexanuclear stair-like $[Fe_6(\mu_3\text{-}S)_4(\mu_2\text{-}SR)_4]$ core.[32] Apparent in the core is the presence of two partial cubes linked by two sulfur bridges.

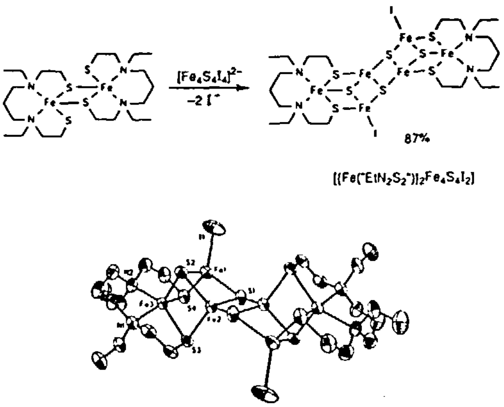
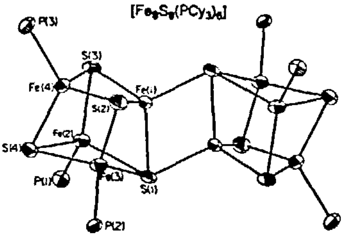


FIGURE 24 Synthesis and ORTEP of the stair-like ladder structure 28.[32]

The stair-like ladder structure 28 (Figure 24) bears a resemblance with the edge connected "dicubane", $[\{Fe_4S_4(Pcyc_3)_3\}_2]$ (29).[36]



29

This formulation has two cubes attached to each other by two Fe-S bonds producing a stair-like arrangement of Fe_2S_2 faces. One can envision capping the two partial cubes, i.e., the Fe_3S_4 fragments of **28**, with an additional Fe atom on each.

When $[\{Fe(\text{“}EtN_2S_2\text{”})_2\}Fe_4S_4]_2$ is dissolved in polar aprotic solvents, e.g., DMF, decomposition occurs and a new cluster cyrstallizes out, $[\{Fe(\text{“}EtN_2S_2\text{”})\}_2Fe_4S_5]\bullet 2DMF$[32] (30) (Figure 25).

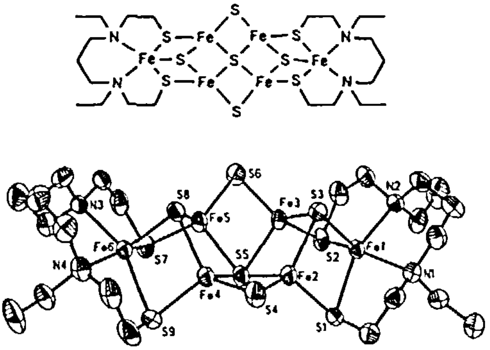


FIGURE 25 Schematic and ORTEP representation of the structure of $[\{Fe(\text{“}EtN_2S_2\text{”})\}_2Fe_4S_5]\bullet 2DMF$[32] (30).

Cluster **30**, like **28**, consists of two partial cubes but differ in the number and type of sulfur bridges. For **30**, one sulfur atom is bonded to four iron atoms while the other sulfur atoms act as bridges to two iron atoms (Figure 25).

In addition to the edge-connected "double cube" **29**, two cubes joined with Fe-S-Fe and Fe-O-Fe bridges have been prepared,[37] e.g., the synthesis of $\{[R_3MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$ [38] (31) (Figure 26). The structure of this class was deduced from NMR and electrochemical data.[37] However, an x-ray analysis of a similar iron-sulfur cluster, $[(Fe_4S_4Cl_3)_2S]^{4-}$ [39] (32) yielded the structural representation depicted in Figure 26.

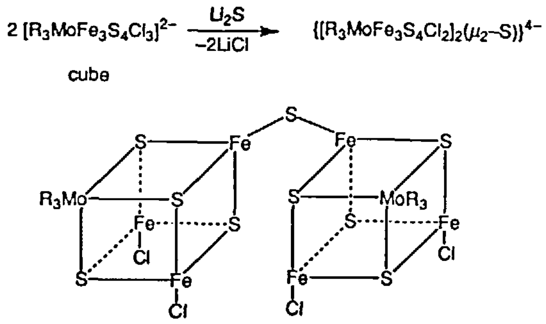


FIGURE 26 Synthesis and structural representation of $(Et_4N)_4$-$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}\bullet 2LiCl$ (**31**) showing single cubes joined with an Fe-S-Fe bridge.[38] Others have been similarly characterized from NMR and electrochemical data.[37] Meida = R_3 = *N*-methylimidodiacetate(2-).

A great deal of effort has been expended in searching for synthetic routes to prepare "double cubane" clusters with sulfur bridges in the iron-sulfur system. Most importantly is their relation to the proposed nitrogenase cofactor in its role as an internal redox center in the FeMo protein of nitrogenase (Figure 27).[40]

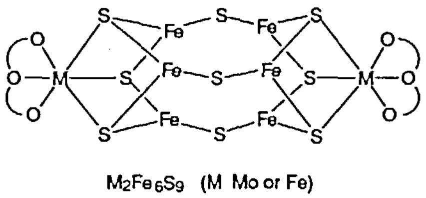


FIGURE 27 A proposed model for the nitrogenase cofactor that consists of two partial cubes bridged by three sulfur atoms.[40]

The systematic exploration of organotin cluster chemistry along with a study of the interconversions has provided a basis for interpreting structural relationships of cluster geometries common to both transition and main group elements. These comparisons suggest directions, as yet unexplored, leading to new applications of potential significance in both enzymatic and nonenzymatic chemistry.

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