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Organotin Cluster Chemistry

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A rich cluster chemistry of organotin compounds has recently emerged 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. In the development of the underlying chemistry, it was discovered that some members exhibit catalytic activity on transesterification and potentially in polymerization processes. Further, as new cluster compositions were uncovered, analogies became apparent with other cluster chemistries, particularly those involving aluminum–nitrogen and iron–sulfur systems. What follows is a description of the emerging cluster chemistry of these interesting new classes of organotin compounds, their interconversions, and possible applications.

Early work in this area 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 $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$. Although there has been an occasional report on substances related to Lambourne's early work, no advances in structural assignment have been forthcoming.[3] The long dormant period 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, with the advent of modern instrumentation providing routine examination of solution high resolution NMR spectra of ^{119}Sn, a low abundant nucleus, and allowing X-ray structures to be determined on a routine basis, we became interested in the possibility of systematically probing the stereochemistry of these organooxotin compositions.

Drum and Ladder Carboxylates

Our entry into the field of organotin cluster chemistry began in 1985 when Dr. Chandrasekhar observed a small amount of crystalline material forming during the purification of triphenyltin cyclohexanecarboxylate, $Ph_3SnO_2C(C_6H_{11})$. Subsequent X-ray analysis showed it to have the composition $[PhSn(O)O_2CC_6H_{11}]_6$ and possess a hexagonal prismatic or "drum" arrangement (Figure 1).[4] This proved to be the first example of a new structural class for tin. Evidently the crystals were produced as a minor hydrolysis product in which phenyl–tin bond cleavage occurred, eq 1.

$$Ph_3SnO_2C(C_6H_{11}) + H_2O \rightarrow \frac{1}{6}[PhSn(O)O_2CC_6H_{11}]_6 + 2C_6H_6 \quad (1)$$

Additional drum derivatives were formed more directly by condensing an organostannonic acid with a carboxylic acid, e.g., $[R'Sn(O)O_2CR]_6$ where $R' = n\text{-Bu}$ and $R = C_6H_4NO_2\text{-}2$, C_5H_9, or C_6H_{11}[5,6] or $R' = R = Me$:[7]

$$6R'Sn(O)OH + 6RCO_2H \rightarrow [R'Sn(O)O_2CR]_6 + 6H_2O \quad (2)$$

A similar condensation reaction also was carried out that gave the alternate composition reported by Lambourne,[1,2] e.g., $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$ ($R' = Me$ and $R = C_6H_{11}$,[5] C_2H_5[8]). More generally, this composition was obtained from the reaction of an alkyltin trichloride with the silver salt of the carboxylic acid ($R' = n\text{-Bu}$ and $R = C_6H_{11}$,[6] C_6H_5,[5] or CH_3[5]), eq 3. X-ray analysis showed these organooxotin derivatives to have "ladder" ("open drum") structures (Figure 2).[5,6] In general, the drum and ladder compounds form in high yield, >70%. All are soluble in organic solvents except the initially isolated drum, $[PhSn(O)O_2CC_6H_{11}]_6$.[4]

$$6R'SnCl_3 + 10Ag^+,RCO_2^- + 4H_2O \rightarrow [(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2 + 10AgCl + 8HCl \quad (3)$$

^{119}Sn NMR studies fully support retention of the structures in solution.[5-7] A single resonance is obtained for the drum and three signals of comparable intensity for the open-drum formulation, all of which are in the hexacoordinated region. For example, the ^{119}Sn NMR signal for the drum $[n\text{-BuSn}(O)O_2CC_6H_{11}]_6$ in $CDCl_3$ is at −486.2 ppm (relative to Me_4Sn).[6] The ^{119}Sn NMR shifts in $CDCl_3$ for the open-drum form [(*n*-BuSn-

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(1) Lambourne, H. *J. Chem. Soc.* **1922**, *121*(2), 2533.

(2) Lambourne, H. *J. Chem. Soc.* **1924**, *125*, 2013.

(3) Other stannoxane derivatives with carboxylate ligands having the composition $PhSn(O)O_2CR$, where $R = (CH_2)_8CH{=}CH_2$ and $(CH_2)_{16}Me$, were reported earlier: Ford, B. F. E.; Liengme, B. V.; Sams, J. R. *J. Organomet. Chem.* **1969**, *19*, 53–65. Like Lambourne,[1] Ford et al. favored cyclic trimeric structures but containing pentacoordinated tin atoms instead of tetracoordinated ones. For related derivatives $PhSn(O)O_2CR$ where $R = t\text{-Bu}$, CCl_3, and CF_3, polymeric structures containing bridging oxygen atoms were suggested: Poller, R. C.; Ruddick, J. N. R.; Taylor, B.; Toley, D. L. B. *J. Organomet. Chem.* **1970**, *24*, 341–346. More recently, Roy and Ghosh suggested linear or cyclic polymeric structures for carboxylate compositions, e.g., $[PhSn(OH)_2O_2CMe]_n$ and $[PhSn(O)O_2CMe]_n$: Roy, A.; Ghosh, A. K. *Inorg. Chim. Acta* **1978**, *29*, L275–L277; *Ibid.* **1977**, *24*, L89–L91. Otera et al. obtained butyltin triphosphate $BuSn[O_2P(OBu)_2]_3$ as an oil.[30]

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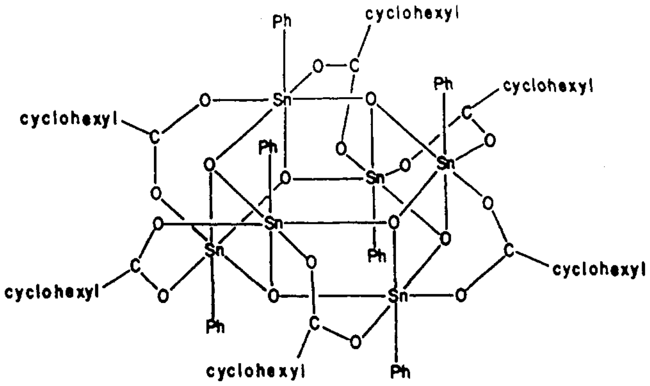

Figure 1. Hexagonal prismatic or "drum" structure of [PhSn-(O)O$_2$CC$_6$H$_{11}$]$_6$. Reprinted with permission from ref 4. Copyright 1985 American Chemical Society.

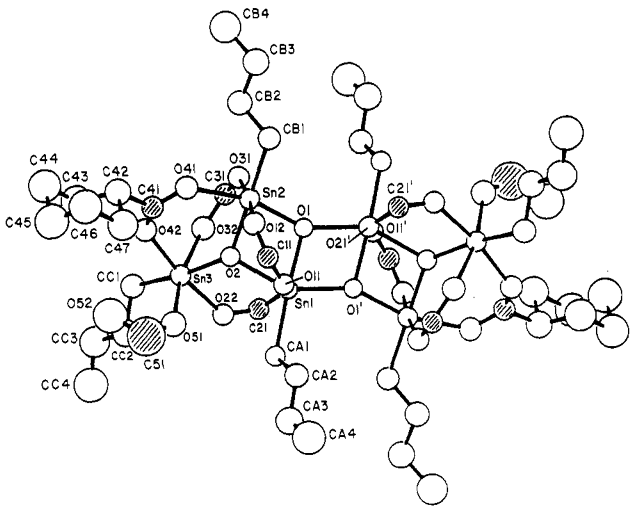

Figure 2. Ladder (open-drum) structure of [(n-BuSn-(O)O$_2$CC$_6$H$_{11}$)$_2$$n$-BuSn(O$_2CC_6H_{11}$)$_3$]$_2$. Carbon atoms of only two of the cyclohexyl groups are shown. Reprinted with permission from ref 6. Copyright 1987 American Chemical Society.

(O)O$_2$CC$_6$H$_{11}$)$_2$(n-BuSn(O$_2$CC$_6$H$_{11}$)$_3$)]$_2$ appear at −524, −552, and −630 ppm.[6]

For the latter drum and open-drum forms, we have demonstrated their reversible interconversion by ^{119}Sn NMR.[6] Hydrolytically, the drum formulation is a more stable form than the open-drum structure, as illustrated in eq 4.

$$[(\mathrm{R'Sn(O)O_2CR})_2\mathrm{R'Sn(O_2CR)_3}]_2 + 2\mathrm{H_2O} \rightarrow [\mathrm{R'Sn(O)O_2CR}]_6 + 4\mathrm{RCO_2H} \quad (4)$$

Although the mechanism of the transformation is not known, alkyltin tricarboxylates R′Sn(O$_2$CR)$_3$ have been identified accompanying the conversion. For example, when the drum compound [n-BuSn(O)O$_2$CMe]$_6$[9] in chloroform solution is reacted with acetic acid, a mixture of the ladder and tricarboxylate forms results. With the use of excess acetic acid, tricarboxylate remains as the final product. Exposing the latter tricarboxylate product to atmospheric moisture causes the appearance of the drum and ladder. Equation 5 summarizes the interconversions.

$$[n\text{-}\mathrm{BuSn(O)O_2CMe}]_6 \underset{\mathrm{H_2O}}{\overset{\mathrm{MeCO_2H}}{\rightleftharpoons}} [(n\text{-}\mathrm{BuSn(O)O_2CMe})_2(n\text{-}\mathrm{BuSn(O_2CMe)_3})]_2 \underset{\mathrm{H_2O}}{\overset{\mathrm{MeCO_2H}}{\rightleftharpoons}} n\text{-}\mathrm{BuSn(O_2CMe)_3} \quad (5)$$

Heating of the ladder composition is another way in which conversion to a drum takes place. The ladder [(MeSn(O)O$_2$CEt)$_2$MeSn(O$_2$CEt)$_3$]$_2$ melts at 180–183 °C, but on further heating, it solidifies.[8,9] The products formed correspond to a transformation to the related drum and tricarboxylate, eq 6. Confirmation of the

$$^3/_2[(\mathrm{MeSn(O)O_2CEt})_2\mathrm{MeSn(O_2CEt)_3}]_2 \xrightarrow{\Delta} [\mathrm{MeSn(O)O_2CEt}]_6 + 3\mathrm{MeSn(O_2CEt)_3} \quad (6)$$

tricarboxylate as a monomeric unit was obtained by synthesizing MeSn(O$_2$CPh)$_3$ in crystalline form.[9,11] Its X-ray structure reveals a heptacoordinate tin center.[9,11]

Clusters with Phosphorus-Based Acids

When stannonic acids are reacted with phosphorus-based acids instead of carboxylic acids, a much wider variety of organotin clusters results. Although ladder forms have not been prepared this way, those that have formed include drums,[7] cubes,[12,13] oxygen-capped clusters,[7,13,14] butterfly formations,[13] crowns,[15] and extended clusters,[15] to name a few. Examples are depicted in Figure 3.

Their synthesis involves variations in stoichiometry in the reactions already discussed, the principal one being the reaction of a stannonic acid with a phosphorus acid. In some cases, reaction is facilitated by starting with a drum composition and treating this with the phosphorus acid, e.g., synthesis of the methyltin crown in a hydrolysis scheme with di-*tert*-butylphosphinic acid,[15] eq 7.

$$2[(\mathrm{MeSn(O)O_2CMe})(\mathrm{MeSn(O)O_2P}(t\text{-}\mathrm{Bu})_2)]_3 + 9(t\text{-}\mathrm{Bu})_2\mathrm{PO_2H} + 6\mathrm{MeOH} + 6\mathrm{H_2O} \rightarrow 3[(\mathrm{MeSn(O)O_2P}(t\text{-}\mathrm{Bu})_2)(\mathrm{MeSn(OH)}(\mathrm{OMe})\mathrm{O_2P}(t\text{-}\mathrm{Bu})_2)]_2[\mathrm{H}][\mathrm{O_2P}(t\text{-}\mathrm{Bu})_2]\cdot 4\mathrm{MeOH}\cdot 2\mathrm{H_2O} + 6\mathrm{MeCO_2H} \quad (7)$$

A related crown cluster prepared in 20% yield from n-butylstannonic acid and di-*tert*-butylphosphinic acid[15] exhibited a mixture of products as seen from the ^{119}Sn NMR spectrum in Figure 4(a). Successive recrystallizations resulted in a pure product (Figure 4(b)). The doublet of doublets centered at −535.3 ppm in Figure 4(b) is the expected ^{119}Sn pattern for the crown cluster as it contains two kinds of phosphorus atoms. The low-field triplet at −474.9 ppm, ^2J (Sn–O–P) = 128 Hz, in the ^{119}Sn NMR spectrum in Figure 4(a) corresponds to the cube derivative [n-BuSn(O)O$_2$P(t-Bu)$_2$]$_4$, which was independently synthesized and characterized by X-ray analysis.[13] The triplet at −513 ppm ^2J (Sn–O–P) = 151 Hz was not identified but may correspond to the oxygen-capped cluster [(n-BuSn(OH)O$_2$P(t-

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[9] Kumara Swamy, K. C.; Schmid, C. G.; Nadim, H.; Burton, S. D.; Day, R. O.; Holmes, R. R. *Abstracts of Papers*, 3rd Chemical Congress of North America, Toronto, Canada; June 1988; INOR 508.

[10] Earlier, Anderson observed that organotin tricarboxylates hydrolyzed to give the formulation [R′Sn(O)O$_2$CR]$_n$, where n was undetermined: Anderson, H. H. *Inorg. Chem.* **1964**, *3*, 912.

[11] Kumara Swamy, K. C.; Day, R. O.; Holmes, R. R., unpublished work.

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[14] Day, R. O.; Holmes, J. M.; Chandrasekhar, V.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 940.

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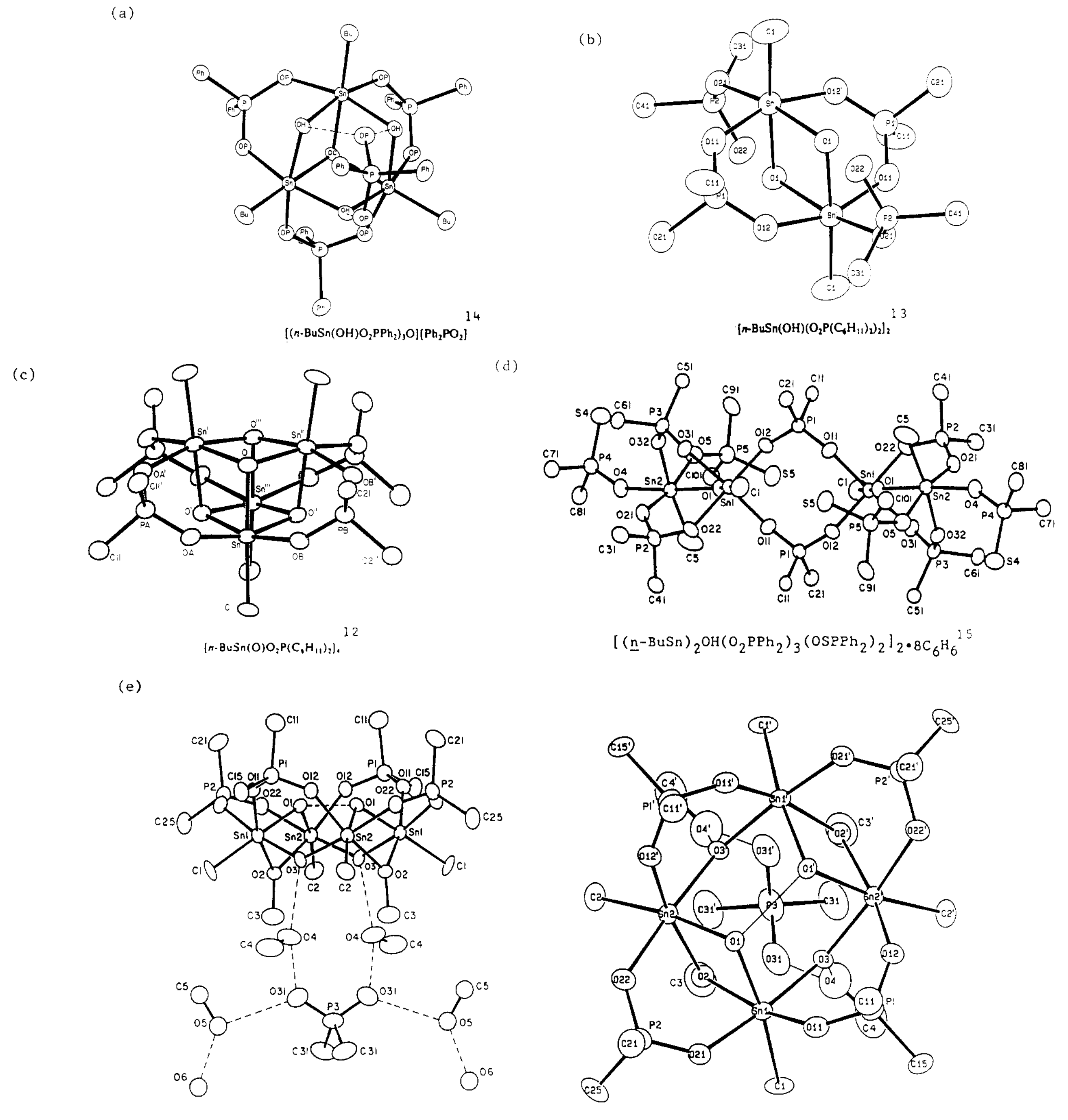

(a) $[(n\text{-BuSn(OH)O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$ 14

(b) $[n\text{-BuSn(OH)(O}_2\text{P(C}_6\text{H}_{11})_2)_2]_2$ 13

(c) $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$ 12

(d) $[(n\text{-BuSn})_2\text{OH(O}_2\text{PPh}_2)_3(\text{OSPPh}_2)_2]_2\cdot 8\text{C}_6\text{H}_6$ 15

(e) $[(\text{MeSn(O)O}_2\text{P}(t\text{-Bu})_2)(\text{MeSn(OH)(OMe)O}_2\text{P}(t\text{-Bu})_2)]_2[\text{H}][\text{O}_2\text{P}(t\text{-Bu})_2]\cdot 4\text{MeOH}\cdot 2\text{H}_2\text{O}$ 15

Figure 3. Examples of organotin clusters belonging to the following structural types (references are indicated by superscripts): (a) an oxygen-capped cluster, (b) a butterfly formation, (c) a cube, (d) an extended form, and (e) a crown cluster (left view perpendicular to the crystallographic two-fold axis; right view looking down the two-fold axis). Pendant atoms and some solvent molecules have been removed for clarity. In addition, the hydrogen atoms attached to O1 and O1′ have been deleted. Reprinted with permission from ref 12–15. Copyrights 1987 and 1988 American Chemical Society.

Bu)$_2$)$_3$O][O$_2$P(t-Bu)$_2$]. The range of chemical shifts for known oxygen-capped derivatives is −498 to −509 ppm[13] extending to near the value under discussion.

Like the above, many of the reactions yield a mixture of products. These are separated, when possible, by taking advantage of solubility differences in solvent mixtures. Table I lists the ^{119}Sn chemical shifts for a variety of butyloxotin clusters. These shifts combined with the characteristic splitting patterns and number of kinds of tin atoms present usually give an unambiguous assignment.

Drums vs Cubes

Even though the drum and cube have the same elemental composition, they are readily differentiated by their ^{119}Sn chemical shift. An important factor that guides which of these clusters result stems from steric considerations. The cube geometry offers greater accommodation for larger groups attached to the phosphorus ligand. The only drums prepared thus far with a phosphorus-based acid are [n-BuSn(O)O$_2$PMe$_2$]$_6$,[16]

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(16) Burton, S. D.; Day, R. O.; Holmes, R. R., unpublished work.

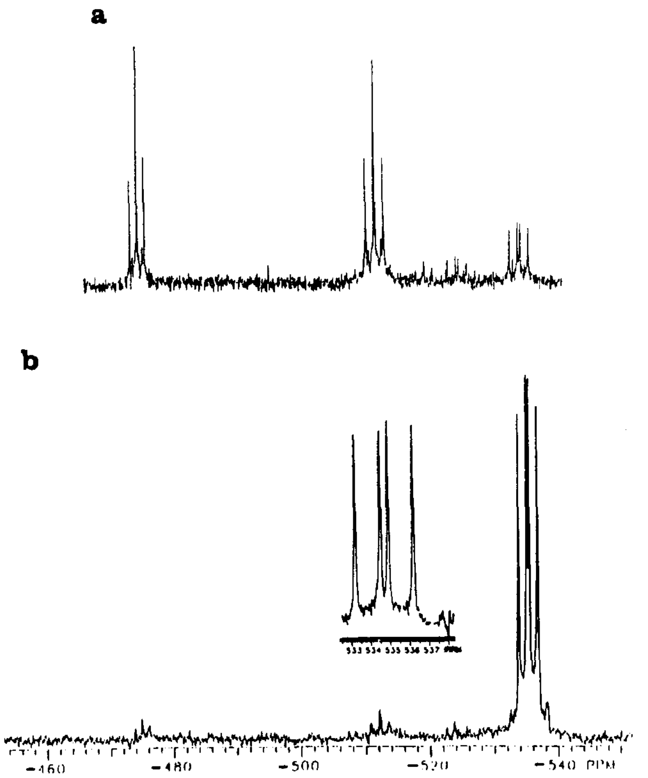


Figure 4. ^{119}Sn NMR spectra of the crown cluster $[(n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2)(n\text{-BuSn(OH)}_2\text{O}_2\text{P}(t\text{-Bu})_2)]_2[\text{H}][\text{O}_2\text{P}(t\text{-Bu})_2]$, (a) from a recrystallization from a benzene–methylene chloride–ether mixture after reaction of a 1:2 molar ratio of n-BuSn(O)OH and $(t\text{-Bu})_2\text{PO}_2\text{H}$ and (b) on the final product. The insert shows an enlarged spectrum of a pure sample. Reprinted with permission from ref 15. Copyright 1988 American Chemical Society.

Table I
^{119}Sn Chemical Shifts for n-Butyloxotin Clusters in $CDCl_3$[a]

cluster[b]	av δ[b]	ref
cube (3)	−466.1 ± 4.7	12, 13
drum (6)	−487.9 ± 1.8	4, 7
crown (2)	−525.4 ± 10	15
O-capped (4)	−501.1 ± 3.9	7, 13, 14
ladder (5)	−523.5 ± 2.2 −549.4 ± 2.8 −621.9 ± 10.7	4, 5
butterfly (1)	−547.4	13
extended (1)	−575	
	−614	15

[a] Except the cube $[n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2]_4$, which was studied in C_6D_6. [b] Numbers in parentheses represent number of compounds studied.

$[n\text{-BuSn(O)O}_2\text{P(OPh)}_2]_6$,[7] and the mixed-drum species, $[(\text{MeSn(O)O}_2\text{CMe})(\text{MeSn(O)O}_2\text{P}(t\text{-Bu})_2)]_3$.[13] 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. Some cube formulations are $[n\text{-BuSn(O)O}_2\text{PR}_2]_4$ where R = C_6H_{11},[12] t-Bu,[13] CH_2Ph.[13]

Interconversions to O-Capped Clusters

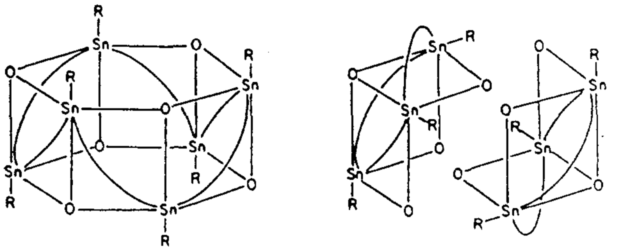
Figure 5 shows a ^{119}Sn NMR spectrum of a reaction mixture of n-butylstannonic acid with dicyclohexylphosphinic acid in $CDCl_3$ indicating the presence of a cube at −462.8 ppm, $[n\text{-BuSn(O)O}_2\text{P}(\text{C}_6\text{H}_{11})_2]_4$, an O-capped cluster at −499.5 ppm, $[(n\text{-BuSn(OH)O}_2\text{P}(\text{C}_6\text{H}_{11})_2)_3\text{O}][(\text{C}_6\text{H}_{11})_2\text{PO}_2]$, and a butterfly formulation at −547.5 ppm, $[n\text{-BuSn(OH)O}_2\text{P}(\text{C}_6\text{H}_{11})_2)_2]_2$.[13] All of these have been isolated in pure form. Study of ^{119}Sn and ^{31}P NMR spectral changes with time indicates that both the cube and butterfly forms, in general, hydrolyze in the presence of atmospheric moisture to give the O-capped cluster, eq 8 and 9, respectively.[13] The cube $[n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2]_4$, however, exists in stable form in solution.

$$\underset{\text{cube }(\text{R}' = \text{Bu, R} = \text{CH}_2\text{Ph})}{[\text{R}'\text{Sn(O)O}_2\text{PR}_2]_4} + 2\text{H}_2\text{O} \rightarrow \underset{\text{O-capped cluster}}{[(\text{R}'\text{Sn(OH)O}_2\text{PR}_2)_3\text{O}][\text{R}_2\text{PO}_2]} + \text{R}'\text{Sn(O)OH} \quad (8)$$

$$3\underset{\text{butterfly }(\text{R}' = \text{Bu, R} = \text{C}_6\text{H}_{11})}{[\text{R}'\text{Sn(OH)(O}_2\text{PR}_2)_2]_2} + 2\text{H}_2\text{O} \rightarrow 2\underset{\text{O-capped cluster}}{[(\text{R}'\text{Sn(OH)O}_2\text{PR}_2)_3\text{O}][\text{R}_2\text{PO}_2]} + 4\text{R}_2\text{PO}_2\text{H} \quad (9)$$

The products obtained on heating the O-capped derivatives appear related to the relative stabilities of cubes, drums, and butterfly forms and perhaps other clusters as yet unidentified. For example, the butyltin cube containing dimesitylphosphinic acid, $[n\text{-BuSn(O)O}_2\text{PMes}_2]_4$, is stable relative to the corresponding drum. Heating the O-capped cluster $[(n\text{-BuSn(OH)O}_2\text{PMes}_2)_3\text{O}][\text{O}_2\text{PMes}_2]$ in this case yields the cube exclusively.[9] Heating the O-capped cluster formed with diphenylphosphinic acid, $[(n\text{-BuSn(OH)O}_2\text{PPh}_2)_3\text{O}][\text{O}_2\text{PPh}_2]$, produces a mixture of the cube and butterfly in addition to some component not identified.[9] Heating the O-capped cluster made up from dibenzylphosphinic acid, $[(n\text{-BuSn(OH)O}_2\text{P}(\text{CH}_2\text{Ph})_2)_3\text{O}][\text{O}_2\text{P}(\text{CH}_2\text{Ph})_2]$, gives the cube and drum derivatives and possibly the butterfly.[9]

The schematic for a drum indicates how it is related to two O-capped molecules (from ref 14).[33]



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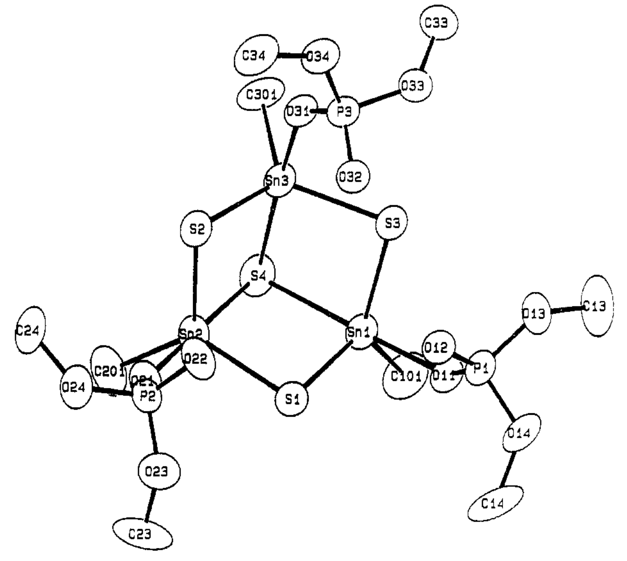
Organotin Sulfur Clusters

Introduction of sulfur in place of oxygen atoms in the organotin framework leads to additional varieties of cluster molecules. A sulfur-capped cluster, $[(n\text{-BuSn(S)OP(OH)(O-}t\text{-Bu)}_2)_3\text{S}][\text{O}_2\text{P(O-}t\text{-Bu)}_2]\cdot 2\text{H}_2\text{S}\cdot\text{H}_2\text{O}$,[17,33] prepared by passing H_2S through a benzene solution of the triphosphate $n\text{-BuSn}[\text{O}_2\text{P(O-}t\text{-Bu)}_2]_3$ at room temperature, eq 10, exhibits two principal differences relative to oxygen-capped clusters.

$$3n\text{-BuSn}[\text{O}_2\text{P(O-}t\text{-Bu)}_2]_3 + 4\text{H}_2\text{S} \rightarrow [(n\text{-BuSn(S)OP(OH)(O-}t\text{-Bu)}_2)_3\text{S}][\text{O}_2\text{P(O-}t\text{-Bu)}_2] + 5(\text{O-}t\text{-Bu})_2\text{PO}_2\text{H} \quad (10)$$

First, the tin atoms are pentacoordinate. Second, the ligands are monodentate and contain dangling P–O–H units. In the oxygen-capped clusters, oxygen atoms other than the capping oxygen are present as OH groups, whereas in the sulfur-capped derivative, sulfur atoms occupy both types of framework sites.

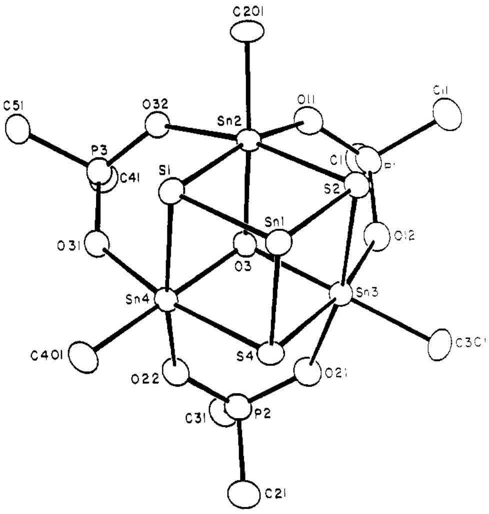


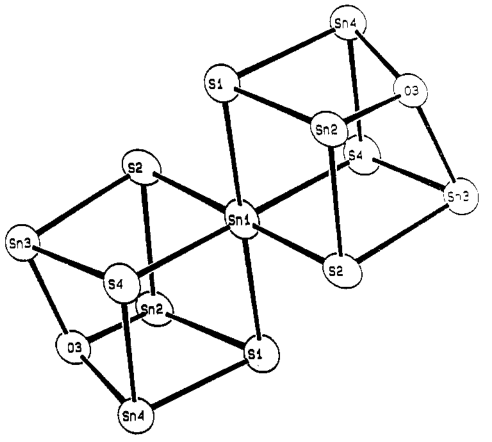
$[(n\text{-BuSn(S)OP(OH)(O-}t\text{-Bu)}_2)_3\text{S}][\text{O}_2\text{P(O-}t\text{-Bu)}_2]\cdot 2\text{H}_2\text{S}\cdot\text{H}_2\text{O}$

These features may be partly a consequence of the presence of larger sulfur atoms producing a greater tin–tin distance that the phosphates need to span to act as bidentate ligands. Secondly, the tin centers should be less acid with framework Sn–S compared to Sn–O bonding, resulting in weaker tin–phosphate coordination.

The first heptanuclear tin–sulfur cluster[18] was obtained from the reaction described by eq 11. X-ray analysis revealed a unique double cube arrangement, which ^{119}Sn and ^{31}P NMR spectra indicate is retained in solution.[18] The geometry at each cube center is depicted on the top and the core structure on the bottom (from ref 18a).[33]

$$24\text{Ph}_2\text{P(OH)} + 3\text{S}_8 + 28n\text{-BuSn(O)OH} \xrightarrow[\text{reflux}]{\text{toluene}} 4[[n\text{-BuSnS(O}_2\text{PPh}_2)]_3\text{O}]_2\text{Sn} + 24\text{H}_2\text{O} + 4n\text{-BuH} \quad (11)$$





With carboxylate ligands, a trinuclear tin cluster containing a Sn–S–Sn bridge was prepared by passing hydrogen sulfide through a CCl_4 solution of n-butyltin tribenzoate at room temperature in the presence of atmospheric moisture, eq 12.[17,33] X-ray analysis showed an almost planar Sn_3O system. Consistent with the solid-state structure, ^{119}Sn NMR shows two kinds of tin resonances in solution in a 2:1 ratio while ^{13}C NMR shows three different types of carboxylate carbons in a 2:2:1 ratio.[17]

$$3n\text{-BuSn(O}_2\text{CPh)}_3 + \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow [(n\text{-BuSn})_3\text{(S)(O)(O}_2\text{CPh)}_5] + 4\text{PhCO}_2\text{H} \quad (12)$$

Analogies with Other Cluster Systems

Table II lists the structural type as a function of metal nuclearity for the organotin clusters which are

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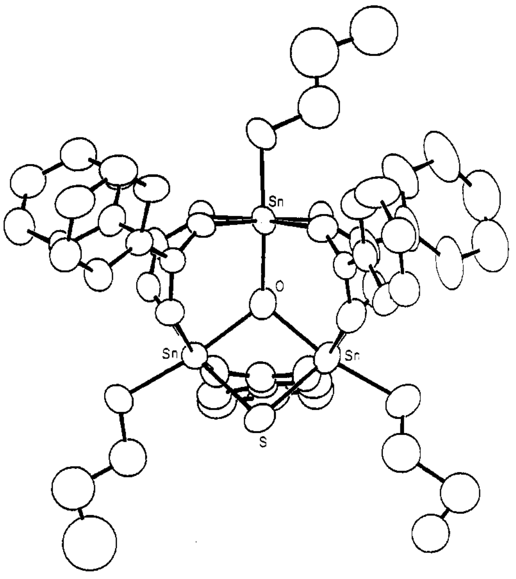
(31) (a) Tsuruta, T.; Hagiwara, T.; Ishimori, M. *Op. cit.* in ref 29, p 45. (b) Hagiwara, T.; Ishimori, M.; Tsuruta, T. *Makromol. Chem.* **1981**, *182*, 501.

(32) Otera, J., personal communication.

(33) The following drawings were reprinted with permission from the source indicated. Schematic of drum and two O-capped molecules: ref 14. Copyright 1987 American Chemical Society. $[(n\text{-BuSn(S)OP(OH)(O-}t\text{-Bu)}_2)_3\text{S}][\text{O}_2\text{P(O-}t\text{-Bu)}_2]\cdot 2\text{H}_2\text{S}\cdot\text{H}_2\text{O}$: ref 17. Copyright 1989 Gordon and Breach Science Publishers. Cube center and core structure of $[[n\text{-BuSnS(O}_2\text{PPh}_2)]_3\text{O}]_2\text{Sn}$: ref 18a. Copyright 1988 American Chemical Society. $[(n\text{-BuSn})_3\text{(S)(O)(O}_2\text{CPh)}_5]$: ref 17. Copyright 1989 Gordon and Breach Science Publishers.



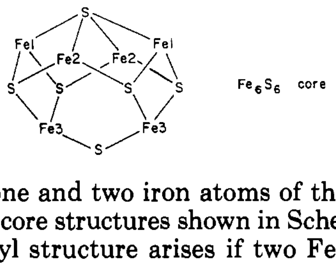
[$(n\text{-BuSn})_3(\text{S})(\text{O})(\text{O}_2\text{CPh})_5$]

compared with similar data for the oligomeric series of aluminum–nitrogen clusters,[19] $(\text{RAlNR}')_n$, $n = 4$ and 6–8, and iron–sulfur clusters.[20] All of these clusters comprise four- and six-membered rings for the most part. In each series, examples with the somewhat rare nuclearity of five are missing. Even though the tin atoms normally achieve a coordination number of six compared to four for aluminum and, in some cases, four for iron, an analogy exists between the topology of the tin, aluminum, and iron units. This analogy may prove especially significant in view of the relevance of the iron–sulfur systems to the chemistry of metallobiomolecules.

The cube geometry which is present in all three series probably represents the most common structural arrangement listed here. Recent examples shown to have a cubane-like core are the azastibacubane $(\text{MeNSbCl}_3)_4$[21] and the molybdenum–sulfur cluster $\text{Mo}_4\text{S}_4(\text{S}_2\text{PEt}_2)_6$,[22] containing dithiophosphinato ligands. Although also present in all three series, the drum geometry is a lesser known structural type. More common is the oxygen-capped, or sulfur-capped, trinuclear cluster. It is listed in both the tin and iron series in Table II and is found in a number of other transition-metal clusters as well.[23] The planar Sn_3O geometry present in the sulfur-bridged molecule [$(n\text{-BuSn})_3(\text{S})(\text{O})(\text{O}_2\text{CPh})_5$] discussed earlier also has analogies in the recently reported manganese complexes $\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6\text{py}_3$[24] and [$\text{Mn}_9\text{O}_4(\text{O}_2\text{CPh})_8\text{sal}_4(\text{salH})_2\text{py}_4$].

Recent work has shown core conversions among Fe_4S_4, Fe_6S_6, and Fe_7S_6 clusters.[20a] In some respects, these conversions resemble core conversion found among the organotin cubes, drums, and oxygen-capped clusters. For example, on the basis of interconversions among the organotin clusters discussed above, i.e., drum and cube to oxygen-capped species, it is not unlikely that a sulfur-capped species would be involved in the drum to cube conversion occurring in the iron–sulfur systems. There already exist iron–sulfur derivatives having the relevant geometries, e.g., $\text{Fe}_3\text{S}_2[\text{S}_2\text{C}_2(\text{CF}_3)_2]_4$[20b] (Table II).

In general, iron should be able to adopt all the geometrical forms exhibited by tin and vice versa. The tetranuclear crown form, for example, found for two members of the organotin series, is absent in the iron–sulfur series. By examination of structural relations of clusters of higher nuclearity, insight into the likelihood of forms of lower nuclearity may result. According to this approach, with the Fe_6S_6 core found in $\text{Fe}_6\text{S}_6[(n\text{-Bu})_3\text{P}]_4\text{Cl}_2$,[20a] i.e., a formal buildup or decomposition of its structure, several tetranuclear clusters may be formed depending on the kinds of iron atoms that are removed. There are three types of iron atoms, labeled 1–3.



Removal of one and two iron atoms of the same type results in the core structures shown in Scheme I. Here the adamantyl structure arises if two Fe1 atoms are

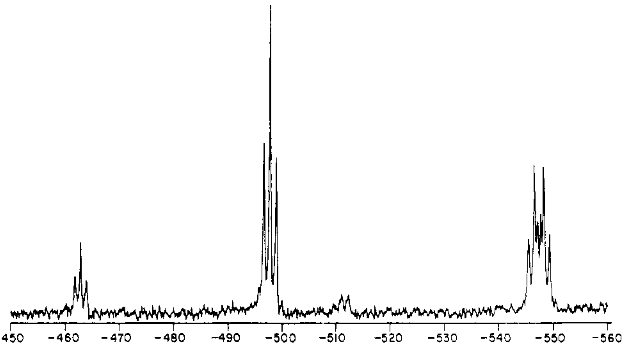


Figure 5. ^{119}Sn NMR spectrum (CDCl_3 solution) of a reaction product of n-butylstannonic acid with dicyclohexylphosphinic acid in a 1:1.5 molar ratio, respectively. The three resonance patterns with increasing shielding are the cube [$n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2]_4$ at −462.8 ppm, the O-capped cluster [$(n\text{-BuSn}(\text{OH})\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2)_3\text{O}][(\text{C}_6\text{H}_{11})_2\text{PO}_2]$ at −499.5 ppm, and the butterfly formulation [$n\text{-BuSn}(\text{OH})(\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2)_2]_2$ at −547.5 ppm. Reprinted with permission from ref 13. Copyright 1988 American Chemical Society.

Scheme I

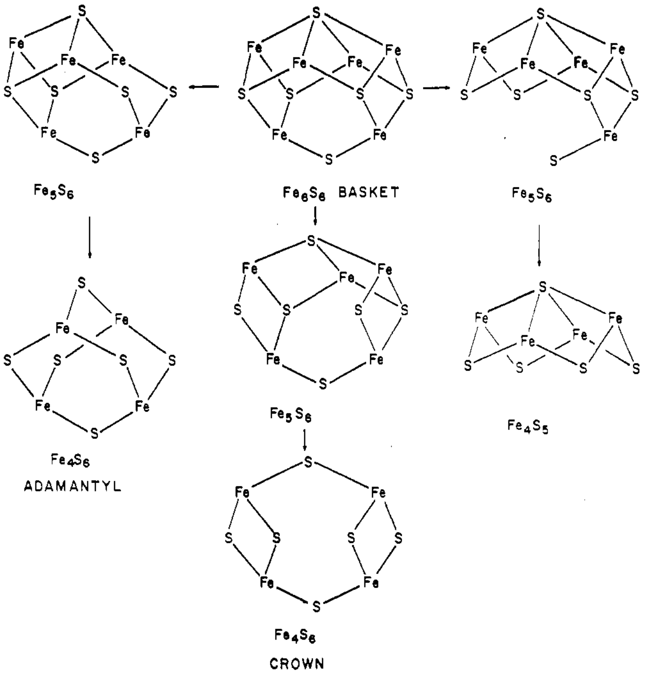
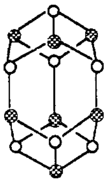
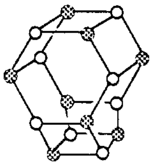
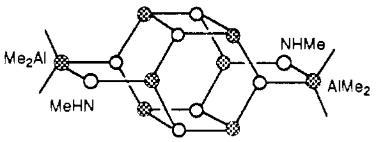


Table II
Comparison of Cluster Formulations in the Organotin–Oxygen, Aluminum–Nitrogen, and Iron–Sulfur Systems

representative formula	cluster type	no. of metal atoms	no. of rings: four membered	six membered	eight membered	ref
$[RSn(OH)(O_2PR'_2)_2]_2$	butterfly	2	1			13
$[(RSn(OH)O_2PR'_2)_3O][R'_2PO_2]$	O-cap	3	3	1		13, 14
$[(RSn)_3(S)(O)(O_2CPh)_5]$	$[(\mu_3\text{-}O)Sn_3](\mu_2\text{-}S)$	3	1			17
$[RSn(O)(O_2PR'_2)]_4$	cube	4	6			12, 13
$[(RSn(O)O_2PR'_2)RSn(OH)(OR'')O_2PR'_2]_2[H][O_2PR'_2]$	crown	4	2		2	15
$[RSn(O)(O_2PR'_2)]_6$	drum	6	6	2		4, 5, 7
$[(RSn(O)O_2CR')_2RSn(O_2CR')_3]_2$	ladder	6	3			5, 6
$[(RSn(S)O_2PR'_2)_3O]_2Sn$	double cube	7	12			18
$(Me_2AlNMe_2)_2$	–	2	1			19a
cis-$(Me_2AlNHMe)_3$	–	3		1		19a,b
$(MeAlN\text{-}i\text{-}Pr)_4$	cube	4	6			19a,c
$(HAlN\text{-}i\text{-}Pr)_6$	drum	6	6	2		19d
$(MeAlNMe)_7$	 $(MeAlNMe)_7$[a]	7	6	3		19e
$(MeAlNMe)_8$	 $(MeAlNMe)_8$[a]	8	6	4		19a,b
$[(Me_2AlNHMe)_2(MeAlNMe)_6]$	 $[(Me_2AlNHMe)_2(MeAlNMe)_6]$[a]	8	2	6		19a
$[Fe_3S(1,2\text{-}(SCH_2)_2C_6H_4)_3]^{2-}$ and $Fe_3S_2[S_2C_2(CF_3)_2]_4$	S-cap	3	3	1		20b
$[Fe_4S_4Cl_4]^{2-}$	cube	4	6			20a
$[Fe_4(SPh)_{10}]^{2-}$	adamantane	4		4		20b
$[Fe_6S_6Cl_6]^{3-}$	drum (or prismane)	6	6	2		20c
$Fe_6S_6[(n\text{-}Bu)_3P]_4Cl_2$	basket	6	6	2		20a
$[Fe_6S_8(PEt_3)_6]^{2+}$	S-capped octahedron	6	12			20d
$[Fe_6S_9(SCH_2Ph)_2]^{4-}$	interlocking partial cubes	6	8	2	1	20e
$[Fe_6O_2(OH)_2(OH_2)(O_2CPh)_{12}(1,4\text{-dioxane})]$	$[(\mu_3\text{-}O)Fe_3](\mu_2\text{-}OH)_2[(\mu_3\text{-}O)Fe_3]$	6			1	20f
$[Fe_7S_6(Et_3P)_4Cl_3]$	Fe-capped drum	7	9	1		20a,g
$[Fe_8S_6I_8]^{3-}$	S-capped cube	8	12			20h
$\{[(tacn)_6Fe_8(O)_2(OH)_{12}]Br_7(H_2O)\}Br\cdot 8H_2O$ (tacn = 1,4,7-triazacyclononane)	complex	8	5	8		20i
$[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$	fused tri-drum	11	9	6		20j

[a] Core representations.

removed, whereas the crown structure, analogous to that formed in the tin series, arises if two Fe2 atoms are removed from the Fe_6S_6 core. It might be possible to synthesize these forms in the iron system like that already obtained in the tin–oxygen system under appropriate experimental conditions.

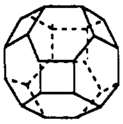
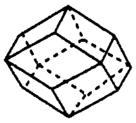
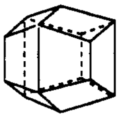
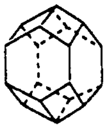
Thus far, the nuclearity of tin systems has not exceeded seven. However, there is no apparent reason limiting the formation of larger units. For example, examination of the space-filling solids illustrated here[28] suggests other possible forms (Table III).

The iron-capped drum core, Fe_7S_6, approaches the rhombic dodecahedron. Capping the opposite face of the Fe_7S_6 core results in the latter polyhedron. A representative formula for this structural type might be $Fe_8S_6(PR_3)_2Cl_6$. The "fused tri-drum" cluster, $Fe_{11}O_6(OH)_6(O_2CPh)_{15}$, having a core formula of $M_{11}X_{12}$ with nine four-membered and six six-membered rings, shows a resemblance to the hypothetical $M_{12}X_{12}$ core as a truncated octahedron comprising six four-membered and eight six-membered rings. Additional work likely will reveal new forms of organotin clusters of increasing nuclearity related to one or more of these space-filling models.

Catalysis

Recent work[29,30] has shown that organotin triphosphates and pyrophosphates when subjected to

Table III

ring size	 truncated octahedron	 rhombic dodecahedron	 twist rhombic dodecahedron	 rhombhex dodecahedron
		no. of rings		
four membered	6	12	6	8
five membered			6	
six membered	8			4
		Core Formulas		
	$M_{12}X_{12}$	$M_8X_6(M_6X_8)$	$M_8X_6(M_6X_8)$	$M_{10}X_8(M_8X_{10})$

thermal treatment act as effective catalysts in the polymerization of epoxides. However, neither the structure of these phosphates nor the nature of the products formed in the thermal reaction is known. It is possible that the thermal treatment may produce a structural form related to one or more of the types discussed in this Account. The field remains open for investigation and one which should be pursued.

In this regard, it is noted that the organozinc complex $[Zn(OMe)_2(EtZnOMe)_6]$ is a very effective catalyst for the polymerization of methyloxirane at 80 °C giving a near quantitative yield of poly(oxypropylene) consisting of equal numbers of D- and L-selective polymer molecules.[31] It would be interesting to learn if the analogous organotin complex, $[(n\text{-}BuSnS(O_2PPh_2))_3O]_2Sn$,[18] has catalytic activity. Otera,[32] in preliminary work, has observed that some of our drum and ladder carboxylate derivatives show catalytic activity for transesterification resulting in yields in excess of 90%. It remains to fully assess the range of catalytic properties of this new area of organooxotin stereochemistry.

Conclusion

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

I express my sincere appreciation to Dr. K. C. Kumara Swamy, Professor V. Chandrasekhar, and my students, Dr. Charles G. Schmid, Sarah D. Burton, and Haleh Nadim, who have made the development of this area possible. Special thanks are due to Dr. Kumara Swamy for his innovative approaches to syntheses and to Professor Roberta O. Day for the crystallographic work, assisted by Joan M. Holmes, giving definition to where we were at. Support of this research from grants by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation is gratefully acknowledged.