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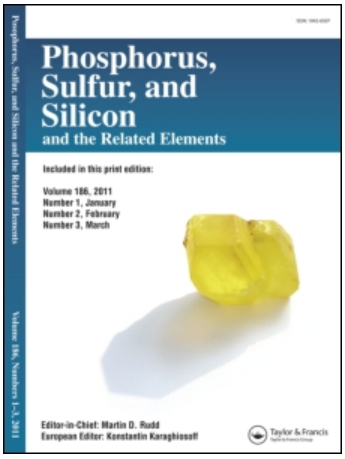

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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OXO CARBOXYLATE TIN LADDER CLUSTERS. A NEW STRUCTURAL CLASS OF ORGANOTIN COMPOUNDS

Robert R. Holmes[a]; Charles G. Schmid[a]; V. Chandrasekhar[a]; Roberta O. Day[a]; Joan M. Holmes[a]
[a] Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

To cite this Article Holmes, Robert R. , Schmid, Charles G. , Chandrasekhar, V. , Day, Roberta O. and Holmes, Joan M.(1995) 'OXO CARBOXYLATE TIN LADDER CLUSTERS. A NEW STRUCTURAL CLASS OF ORGANOTIN COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 99: 1, 49 — 63
To link to this Article: DOI: 10.1080/10426509508031336
URL: http://dx.doi.org/10.1080/10426509508031336

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Phosphorus, Sulfur, and Silicon, 1995, Vol. 99, pp. 49–63
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OXO CARBOXYLATE TIN LADDER CLUSTERS. A NEW STRUCTURAL CLASS OF ORGANOTIN COMPOUNDS[1]

ROBERT R. HOLMES,* CHARLES G. SCHMID,[2]
V. CHANDRASEKHAR, ROBERTA O. DAY, and JOAN M. HOLMES
Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

(Received September 2, 1986)

The hexameric *n*-butyloxotin benzoate, $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2\cdot 2]_6\cdot 3\text{C}_6\text{H}_6$, **1**, and the dimeric methyloxotin cyclohexanoate, $[(\text{MeSn(O)O}_2\text{CC}_6\text{H}_{11})_2\text{MeSn(O}_2\text{CC}_6\text{H}_{11})_3]_2$, **4**, 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, $[(n\text{-BuSn(O)O}_2\text{CR})_2\text{-}n\text{-BuSn(O}_2\text{CR})_3]_2$, **2** (R = Ph) and **3** (R = Me). These represent new substances and, as found by X-ray analysis, form a new structural class of organotin compounds for **2–4** having "unfolded drum" or "ladder" structures. The hexamer composition **1** exists in "drum" form. ^{119}Sn NMR data show that the drum and ladder structures interconvert reversibly. **1** crystallizes in the rhombohedral/space group $R\bar{3}$ with a_H = 15.283 (4) Å, c_H = 34.683 (9) Å, and Z = 3. **2** crystallizes in the triclinic space group $P\bar{1}$ with a = 13.657 (6) Å, b = 14.104 (2) Å, c = 14.559 (4) Å, α = 99.14 (2)°, β = 111.73 (3)°, γ = 101.57 (3)°, and Z = 1. **3** crystallizes in the orthorhombic space group *Pbca* with a = 10.721 (1) Å, b = 23.833 (5) Å, c = 25.138 (5) Å, and Z = 4. **4** crystallizes in the triclinic space group $P\bar{1}$ with a = 12.549 (2) Å, b = 13.368 (3) Å, c = 15.301 (4) Å, α = 82,12 (2)°, β = 67.24 (1)°, γ = 72.80 (2)°, and Z = 1. The conventional unweighted residuals were 0.037 (**1**), 0.033 (**2**), 0.043 (**3**), and 0.077 (**4**).

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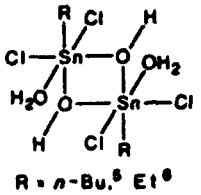
Recently, we reported[3] the first example of a new structural form of tin octahedrally coordinated in a drum-shaped molecule. An X-ray structure of hexameric phenyloxotin cyclohexane-carboxylane, $[\text{PhSn(O)O}_2\text{CC}_6\text{H}_{11}]_6$, showed that the faces of the drum are comprised of six-membered $(\text{—Sn—O—})_3$ tristannoxane rings, and the sides contain four-membered $(\text{—Sn—O—})_2$ distannoxane rings. The hexameric composition apparently formed as a result of slow hydrolysis of triphenyltin cyclohexanoate, $\text{Ph}_3\text{SnO}_2\text{C(C}_6\text{H}_{11})$, the major reaction product of Ph_3SnOH and cyclohexane carboxylic acid.

Formation of distannoxane rings seems to be an integral component of hydrolysis products of many organotin compounds.[4] For example, monoalkyltin halides hydrolyze to give distannoxanes of the type



R = *n*-Bu,[5] Et[6]

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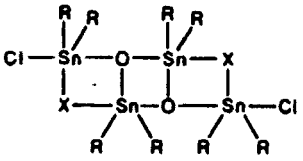
whereas diorganotin halides give dimeric distannoxanes as end products. This possess "ladder"[4,7,8] or "stair case"[9] structures. Here the tin atoms are pentacoordinated.



Similar structural units are found in aluminum chemistry. In the series, $(R_xAlNR)_n$,[10] where n = 4, 6, 7, 8, all the observed structures have components consisting of four- and six-membered rings, including drum compounds[10a,11] (n = 6) analogous to the tin derivative, cubane structures, expanded drums, and an unique heptamer cage structure, $(MeAlNMe)_7$.[10b]

The cubane structure, observed for $(R_2AlNR)_4$[12] so far has no counterpart in stannoxane chemistry. However, an unstable organostannylphosphine, $Ph_4Sn_4P_4$,[13] exists with a proposed cubane form. Further, for tin-sulfur derivatives, admantyl structures are known, e.g., $(MeSn)_4S_6$,[14] which possess six-membered (—Sn—S—)$_3$ rings, as does the cyclic structure found for trimeric $(R_2SnS)_3$ compounds.[8] The latter are similar to the structure of oxygen analogues, e.g., $(t\text{-}Bu_2SnO)_3$.[15]

The above analogies suggest that additional structural forms for tin are possible containing either four- or six-membered rings or both.[26] Toward that end, we have characterized condensation products resulting from the reaction of either a stannoic acid, RSn(O)OH (R = *n*-Bu, Me), with a carboxylic acid or caused coupling between n-$BuSnCl_3$ and silver salts of benzoic acid and acetic acid.

The latter reaction was used by Anderson[16] and led to the isolation of tricarboxylates, $R'Sn(O_2CR)_3$. The former reaction is one employed earlier by Lambourne[17] in the synthesis of crystalline $Me_3Sn_3(O_2(O_2CR)_5$ derivatives.

We report the reaction of n-BuSn(O)OH with o-nitrobenzoic acid which resulted in a drum derivative, $[n\text{-BuSn-(O)}(O_2CC_6H_4NO_2\text{-}2]_6 \cdot 3C_6H_6$, **1**, sparingly soluble in hot THF. The other reactions reported here produced new derivatives with the composition described by Lambourne.[17] However, as a result of X-ray analysis, this formulation is better represented as a mixed oxycarboxylate-tricarboxylate, $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$. Accordingly, the compounds we prepared with this formula represent members of this new structural class of oxycarboxylate tin compounds. Relative to this formula, the members are R′ = n-Bu and R = Ph, **2**; R′ = n-Bu and R = Me, **3**; R′ = Me and R = C_6H_{11}, **4**. All of these are found to have an open-drum or "ladder" structure.

^{119}Sn NMR data indicate that the compounds retain their structures in chloroform solution in the absence of perturbing influences. Additional NMR evidence indicates that these ladder forms can be made to undergo a reversible reaction leading to the drum form.

EXPERIMENTAL

Chemicals were obtained from Aldrich and Ventron and used without further purification. Methylstannoic acid was prepared according to the procedure given by Lambourne.[17] n-Butylstannoic acid

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was a gift from Koriyama Kasei Co.; LTD. (Japan) and was purified by using excess KOH in $CHCl_3$ to remove a small amount of n-$BuSn(OH)Cl_2$ and/or n-$BuSn(OH)_2Cl$ suspected[18] as a contaminant. Solvents used were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.

^1H and ^{119}Sn NMR spectra (proton decoupled) were recorded on a Varian X-L 300 FT/NMR spectrometer equipped with a multinuclear broadband probe and operated at 300 MHz and 11.862 MHz, respectively. Resonances are referenced vs. tetramethylsilane (^1H) and tetramethyltin (external standard, ^{119}Sn). Infrared spectra were recorded by using KBr windows on a Perkin-Elmer Model 180 spectrometer.

Synthesis. Hexameric n-Butyloxotin o-Nitrobenzoate $[n\text{-}BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6\cdot 3C_6H_6$ (**1**). n-Butylstannoic acid, n-BuSn(O)OH, (2.17 g, 10.4 mmol) was added to a stirred solution of methylene chloride (50 mL) and benzene (80 mL). o-Nitrobenzoic acid (1.74 g, 11.4 mmol) was added, and the mixture was refluxed for 18 h. A Dean-Stark separator was used to azeotropically remove the water generated in the reaction. The clear yellow solution originally present turned to a cream-white cloudy suspension. Upon standing 24 h, a white powder containing small clear crystals was present. This was filtered and washed with benzene. On standing, larger crystals grew from the filtrate. These were isolated. Both the crystals and the powder had the same melting point: mp 295–305°C dec (total yield 3.65 g, 98%); IR (Nujol) (cm^{-1}) 1530, 1550 ν_{COO}; 563, ν_{Sn-O} 530. Prior to analysis the solid was dried. Anal. Calcd for $C_{66}H_{78}O_{30}N_6Sn_6$: C, 36.91; H, 3.66; N, 3.91. Found: C, 36.43; H, 3.43; N, 3.82.

Dimeric Bis(n-butyloxotin benzoato)-n-butyltin Tribenzoate, $[(n\text{-}BuSn(O)O_2CPh)_2\text{-}n\text{-}BuSn(O_2CPh)_3]_2$ (**2**). n-Butyltin trichloride (1.44 g, 5.09 mmol) was dissolved in carbon tetrachloride (50 mL), and to this solution was added silver benzoate (3.75 g, 16.37 mmol). Reflux of this heterogeneous mixture under nitrogen for 3 h and filtration of the silver chloride gave a clear solution. Removal of the solvent yielded a soft cream-colored solid assumed to be n-$BuSn(O_2CPh)_3$. From a small portion of this solid dissolved in a CH_2Cl_2/hexane mixture, two types of crystals grew long clear needlelike crystals, identified as benzoic acid, and large clear chunky crystals of $[(n\text{-}BuSn(O)O_2CPh)_2\text{-}n\text{-}BuSn(O_2CPh)_3]_2$. Hydrolysis of the remaining soft solid with wet acetonitrile precipitated a white powder which was collected, washed with cold acetonitrile and dried. This powder had an identical melting point and infrared spectrum to the large chunky crystals [mp 302–303°C dec (yield 1.68 g, 85.0%); ^{119}Sn NMR ($CDCl_3$) (ppm) −520 (m), −536 (s), −548 (m), −606 (br)]. The signal at −536 ppm suffered a relative decrease in intensity with time: IR (Nujol) (cm^{-1}) 1560, 1535 ν_{COO}, 610, 580 ν_{Sn-O}. Anal. Calcd for $C_{94}H_{104}O_{24}Sn_6$: C, 48.45; H, 4.50. Found: C, 48.23; H, 4.53.

Dimeric Bis(n-butyloxotin acetato)-n-butyltin Triacetate, $[(n\text{-}BuSn(O)O_2CMe)_2\text{-}n\text{-}BuSn(O_2CMe)_3]_2$ (**3**). n-Butyltin trichloride (1.23 g, 4.38 mmol) was dissolved in CH_2Cl_2 (40 mL) followed by the addition of silver acetate (2.24 g, 13.43 mmol). The mixture was refluxed 4 h. The silver chloride formed was filtered off, and the solvent was removed to give a tan colored solid. Upon sitting for 2 days in the reaction flask, clear crystals grew. These were removed and washed with cold ether. The rest of the tan colored solid was hydrolyzed with 95% ethanol to give additional crystals and a white powder. Both the white powder and the crystals had the same melting point and infrared spectra: mp 292–295°C dec (total yield 1.07 g, 86.2%); ^{119}Sn NMR ($CDCl_3$) (ppm) recorded on a sample one week after preparation; −486 (s), −522 (s), −533 (s), −549 (s); IR (Nujol) (cm^{-1}) 1595, 1560 ν_{COO}, 610, 575 ν_{Sn-O}, 543. Anal. Calcd for $C_{44}H_{84}O_{24}Sn_6$: C, 30.92; H, 4.95. Found: C, 30.94; H, 4.84.

Dimeric Bis(methyloxotin cyclohexanoato)methyltin Tricyclohexanoate, $[(MeSn(O)O_2CC_6H_{11})_2MeSn(O_2CC_6H_{11})_3]_2$ (**4**). Methylstannoic acid, MeSn(O)OH (1.0 g, 6.0 mmol), was taken in a conical flask under an atmosphere of nitrogen. Cyclohexanecarboxylic acid (2.31 g, 18.0 mmol) was added to it, and the mixture was heated to 100°C. More cyclohexanecarboxylic acid (4.6 g, 36.0 mmol) was added to the reaction mixture, and heating was continued up to a temperature of 160°C when a clear solution was formed. It was kept at this temperature for 2 h and allowed to cool. A thick oily mass was the product. It was heated with 50 mL of anhydrous ether to remove excess cyclohexanecarboxylic acid and filtered. The residue was heated with methylene chloride and filtered. A whitish semicrystalline material was obtained, both from the ether extract and the methylene chloride extract. They both had a melting point of 200–260°C. They were recrystallized separately, both from a mixture of methylene chloride and Skelly B (1:1) at room temperature, to yield needle like crystals. Crystals obtained from both batches were found to be the same: mp 268–270°C (total yield of the crystalline solid 0.75 g, 35%); ^1H NMR ($CDCl_3$) (ppm) 1.24–2.24 (m, aliphatic resonances of cyclohexyl group), 0.60 (s, Sn—CH_3); ^{119}Sn NMR ($CDCl_3$) (ppm) −500.9 (s), −527.0 (s), −607.4 (s); two additional lines of low intensity appeared at −465.9 and −515.6; IR (Nujol) (cm^{-1}) 1580, 1545 ν_{COO}, 590, 560 ν_{Sn-O}. Anal. Calcd for $C_{76}H_{128}O_{24}Sn_6$: C, 42.70; H, 6.03. Found: C, 41.70; H, 5.90.

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X-ray Studies. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation (λ Kα_1 = 0.70930, λ Kα_2 = 0.71359 Å) at an ambient temperature of 23 ± 2°C. Details of the experimental and computational procedures have been described previously.[19]

Crystals were mounted inside of thin-walled glass capillaries which were sealed as a precaution against moisture. The structures were solved by using standard Patterson and difference Fourier techniques and were refined by using full-matrix least-squares.[20]

X-ray Crystallographic Study for $[n\text{-}BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6\cdot 3C_6H_6$ (**1**). The colorless crystal used for the X-ray study was cut from a larger polycrystal and was nearly a triangular prism with edge lengths of 0.23 mm and a height of 0.13 mm.

Crystal Data. $(C_{11}H_{13}O_5NSn)_6\cdot 3C_6H_6$, rhombohedral space group $R\bar{3}$ [C^2_{3i}—No. 148],[21] hexagonal setting, a_H = 15.283 (4) Å, c_H = 34.683 (9) Å, Z = 3 and $\mu_{Mo\ K\bar{\alpha}}$ = 1.671 mm^{-1}. A total of 3052 independent reflections ($+h$, $+k$, $\pm l$) was measured by using the θ-2θ scan mode for 3° ≤ $2\theta_{Mo\ K\bar{\alpha}}$ ≤ 50°. No corrections were made for absorption.

The 21 independent non-hydrogen atoms were refined anisotropically. The 13 hydrogen atoms with positions which could be inferred from the molecular geometry were included in the refinement as fixed isotropic scatterers whose coordinates were updated as refinement converged so that the final C—H bond lengths were 0.98 Å. Positions for the three independent methyl hydrogen atoms were obtained from a difference Fourier synthesis, and these atoms were also included in the refinement as fixed isotropic scatterers. The final agreement factors[22] were R = 0.037 and R_w = 0.049 for the 2187 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Study for $[(n\text{-}BuSn(O)O_2CPh)_2\text{-}n\text{-}BuSn(O_2CPh)_3]_2$ (**2**). The colorless crystal used for the X-ray study was cut from a larger polyfaceted crystal and had dimensions of 0.20 × 0.28 × 0.33 mm.

Crystal Data. $[(n\text{-BuSn(O)O}_2\text{CPh})_2\text{-}n\text{-BuSn(O}_2\text{CPh)}_3]_2$, **2**, triclinic space group $P\bar{1}$ [C^1_i—No. 2],[23] a = 13.657 (6) Å, b = 14.104 (2) Å, c = 14.559 (4) Å, α = 99.14 (2)°, β = 111.73 (3)°, γ = 101.57 (3)°, Z = 1, and $\mu_{Mo\ K\bar{\alpha}}$ = 1.566 mm^{-1}. A total of 5628 independent reflections ($+h$, $\pm k$, $\pm l$) was measured by using the θ-2θ scan mode for 3° ≤ $2\theta_{Mo\ K\bar{\alpha}}$ ≤ 43°. No corrections were made for absorption.

The 62 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were omitted from the refinement. The final agreement factors[22] were R = 0.033 and R_w = 0.047 for the 4715 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Study for $[(n\text{-}BuSn(O)O_2CMe)_2\text{-}n\text{-}BuSn(O)_2CMe)_3]_2$ (**3**). The colorless crystal used for the X-ray study was cut from a fused mass of chunky crystals and had dimensions of 0.23 × 0.24 × 0.25 mm.

Crystal Data. $[(n\text{-BuSn(O)O}_2\text{CMe})_2\text{-}n\text{-BuSn(O}_2\text{CMe)}_3]_2$, **3**, orthorhombic space group *Pbca* [D^{15}_{2h}—No. 61],[24] a = 10.721 (1) Å, b = 23.833 (5) Å, c = 25.138 (5) Å, Z = 4, and $\mu_{Mo\ K\bar{\alpha}}$ = 2.375 mm^{-1}. A total of 3666 independent reflections ($+h$, $+k$, $+l$) was measured by using the θ-2θ scan mode for 3° ≤ $2\theta_{Mo\ K\bar{\alpha}}$ ≤ 43°. No corrections were made for absorption.

Of the 37 independent non-hydrogen atoms, 35 were refined anisotropically in full occupancy. Two sets of positions were found for CA2 and CA3 of the *n*-Bu group attached to Sn1, and these two atoms were refined anisotropically in half occupancy for each of their two positions. Hydrogen atoms were omitted from the refinement. The final agreement factors[22] were R = 0.043 and R_w = 0.054 for the 2323 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Study for **4**. The crystal used for data collection was cut from an elongated hexagonal prism, which was a twin, and had dimensions of 0.15 × 0.30 × 0.35 mm.

Crystal Data. $[(MeSn(O)O_2CC_6H_{11})_2MeSn(O_2CC_6H_{11})_3]_2$, **4**, triclinic space group $P\bar{1}$,[23] a = 12.549 (2) Å, b = 13.368 (3) Å, c = 15.301 (4) Å, α = 82.12 (2)°, β = 67.24 (1)°, γ = 72.80 (2)°, Z = 1. A total of 5162 independent reflections ($+h$, $\pm k$, $\pm l$) was measured for 2° ≤ $2\theta_{Mo\ K\bar{\alpha}}$ ≤ 43°. Of the 53 independent non-hydrogen atoms, the 23 which were not part of cyclohexyl groups were refined anisotropically. Although it was possible to find positions for the 30 carbon atoms of the five independent cyclohexyl groups which had marginally reasonable initial geometry, refinement including these atoms as isotropic scatterers would not converge. The agreement factors[22] converged to R = 0.077 and R_w = 0.106 for the 3356 reflections having $I \geq 2\sigma_I$.

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RESULTS

The molecular geometry and atom labeling scheme for **1** is shown in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I, while selected bond lengths and angles are given in Table II. The corresponding information for **2** and **3** is given in Figures 2 and 3 and Tables III, IV, and V. Figure 4 displays the structural form of **4**. The basic structure of **1** resembles a "drum" whereas **2–4** are "unfolded drums" or, more descriptively, "ladders."

Thermal parameters and additional bond lengths and angles for **1**, **2**, and **3** and hydrogen atom parameters for **1** are provided as Supplementary Material.

DISCUSSION

Synthesis

Two routes were used to prepare the oxocarboxylates **1–4.** For the derivatives having the drum composition **1** or the ladder formulation **4** a condensation reaction between the stannoic acid and carboxylic acid proceeded according to eq 1 and 2, respectively.

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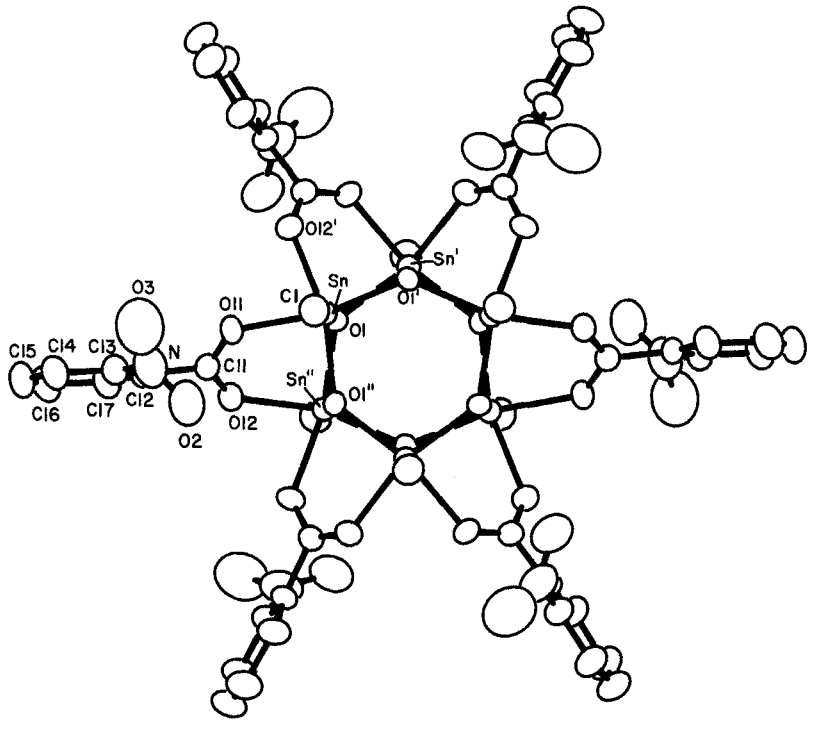

FIGURE 1 ORTEP plot of $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-2}]_6 \cdot 3\text{C}_6\text{H}_6$, **1** with thermal ellipsoids at the 30% probability level. The three terminal atoms of the *n*-Bu groups (C2, C3, and C4) and the benzene of solvation have been omitted for purposes of clarity. The coordinates of the labeled symmetry related atoms are derived from those in the coordinate list by $' = y, y - x, -z$ and $'' = x - y, x, -z$.

TABLE I

Atomic coordinates in crystalline $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2]_6 \cdot 3\text{C}_6\text{H}_6$ (1)[a]

atom[b]	10^4x	10^4y	10^4z
Sn1	1639.4 (3)	1066.5 (3)	336.8 (1)
O1	1427 (3)	931 (3)	-259 (1)
O2	2452 (6)	3840 (5)	858 (2)
O3	3935 (7)	4171 (6)	1018 (2)
O11	2686 (3)	2688 (3)	251 (1)
O12	1938 (3)	3090 (3)	-219 (1)
N	3350 (7)	4232 (5)	799 (2)
C1	1820 (5)	1230 (5)	947 (2)
C2	2640 (7)	1076 (7)	1119 (2)
C3	2411 (8)	5 (7)	1119 (3)
C4	3213 (9)	-150 (9)	1310 (3)
C11	2589 (5)	3298 (5)	41 (2)
C12	3364 (5)	4404 (5)	93 (2)
C13	3770 (5)	4821 (5)	449 (2)
C14	4526 (6)	5818 (6)	490 (3)
C15	4880 (7)	6398 (6)	167 (3)
C16	4516 (7)	6022 (6)	-188 (3)
C17	3733 (6)	5020 (5)	-229 (2)
CA	2903 (10)	5637 (7)	1670 (4)
CB1	491 (36)	982 (13)	2051 (5)
CB2	1023 (12)	504 (34)	2044 (4)

[a] Numbers in parentheses are esd's. [b] Atoms are labeled to agree with Figure 1. The terminal atoms of the independent *n*-Bu group omitted from Figure 1 are C2–C4. The independent carbon atom for the benzene of solvation having crystallographic S_6 symmetry is CA. The two independent carbon atoms for the benzene of solvation having crystallographic C_3 symmetry are CB1 and CB2.

TABLE II

Selected bond lengths (Å) and bond angles (deg) for $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2]_6 \cdot 3\text{C}_6\text{H}_6$ (1)[a]

Sn–O1	2.085 (3)	Sn–O11	2.197 (4)
Sn–O1′	2.088 (4)	Sn–O12′	2.193 (4)
Sn–O1″	2.097 (4)	C11–O11	1.249 (7)
Sn–Cl	2.132 (6)	C11–O12	1.259 (7)
Cl–Sn–O1	177.8 (2)	Cl–Sn–O11	91.4 (2)
O1′–Sn–O11	160.2 (2)	Cl–Sn–O12′	96.3 (2)
O12′–Sn–O1″	155.7 (2)	Cl–Sn–O1′	103.0 (2)
O1′–Sn–O1″	105.0 (2)	Cl–Sn–O1″	100.0 (2)
O1′–Sn–O1	78.0 (2)	O11–Sn–O12′	76.3 (2)
O1″–Sn–O1	77.8 (1)	O11–Sn–O1″	85.3 (2)
Sn′–O1–Sn″	131.5 (2)	O11–Sn–O1	77.8 (1)
Sn′–O1–Sn	100.3 (2)	O12′–Sn–O1′	88.6 (2)
Sn″–O1–Sn	100.6 (2)	O12′–Sn–O1	85.7 (2)

[a] Numbers in parentheses are esd's. Atoms are labeled to agree with Figure 1.

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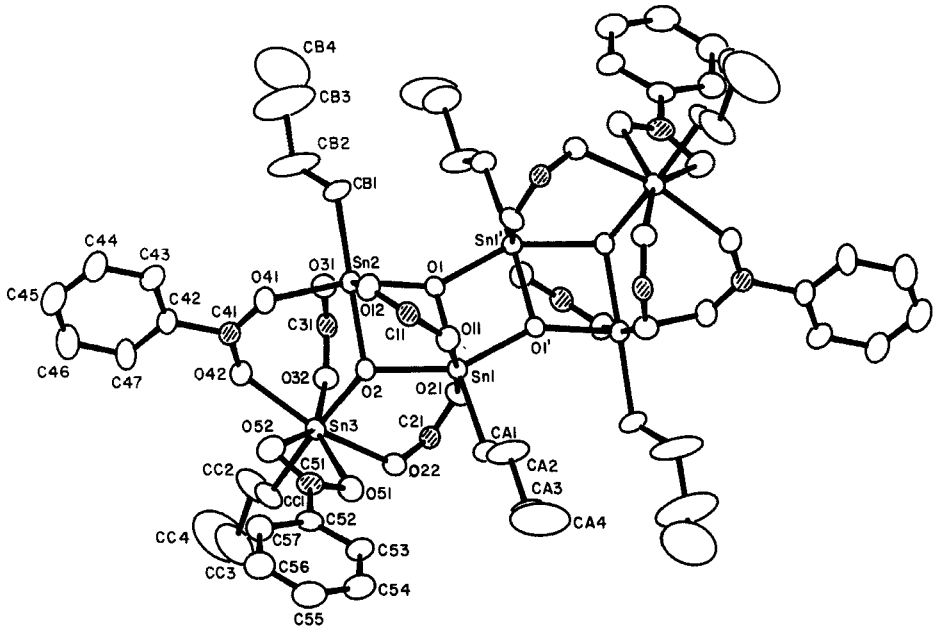

FIGURE 2 ORTEP plot of $[(n\text{-BuSn(O)O}_2\text{CPh})_2\text{-}n\text{-BuSn(O}_2\text{CPh)}_3]_2$, **2**, with thermal ellipsoids at the 30% probability level. Six of the ten phenyl group have been omitted for purposes of clarity. Carbon atoms of the carboxyl groups are shaded. Primed atoms are related to unprimed ones by the inversion operation.

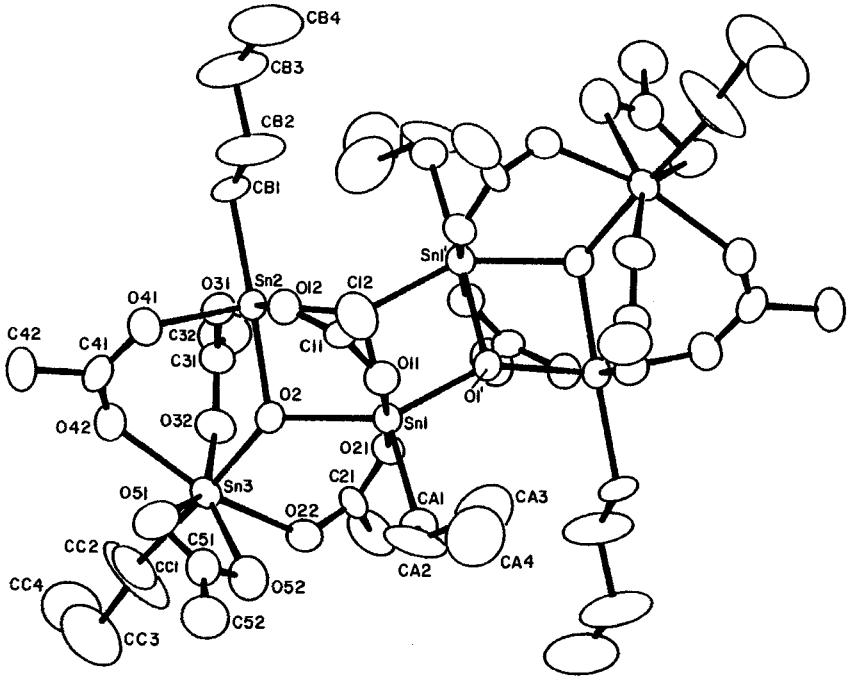

FIGURE 3 ORTEP plot of $[(n\text{-BuSn(O)O}_2\text{CMe})_2\text{-}n\text{-BuSn(O}_2\text{CMe)}_3]_2$, **3**, with thermal ellipsoids at the 30% probability level. Primed atoms are related to unprimed ones by the inversion operation. For purposes of clarity, only one set of positions for the disordered CA2 and CA3 is shown.

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TABLE III

Atomic coordinates in crystalline $\{[n\text{-BuSn(O)O}_2\text{CPh}]_2[n\text{-BuSn(O}_2\text{CPh)}_3]\}_2$ (2)[a]

atom[b]	10^4x	10^4y	10^4z
Sn1	40.7 (3)	154.1 (3)	1152.7 (3)
Sn2	1738.5 (4)	2173.3 (3)	1261.0 (3)
Sn3	387.8 (4)	2485.9 (3)	1956.1 (3)
O1	564 (3)	903 (3)	242 (3)
O2	906 (3)	1663 (3)	2101 (3)
O11	1686 (3)	−99 (3)	1733 (3)
O12	2859 (3)	1366 (3)	1978 (3)
O21	−1472 (3)	567 (3)	610 (3)
O22	−1241 (3)	1318 (3)	2177 (3)
O31	668 (4)	3075 (3)	769 (3)
O32	−491 (4)	2918 (3)	1527 (3)
O41	2802 (4)	3367 (3)	2598 (3)
O42	1597 (4)	3863 (3)	3124 (3)
O51	552 (4)	1374 (3)	3889 (3)
O52	1987 (4)	2663 (4)	4478 (4)
C11	2637 (5)	489 (5)	2102 (5)
C12	3561 (5)	135 (5)	2716 (5)
C13	4622 (6)	807 (6)	3215 (6)
C14	5487 (7)	474 (8)	3798 (6)
C15	5308 (7)	−493 (7)	3912 (6)
C16	4252 (8)	−1167 (7)	3407 (6)
C17	3377 (7)	−841 (6)	2817 (6)
C21	−1816 (5)	994 (5)	1220 (5)
C22	−2937 (5)	1107 (5)	789 (4)
C23	−3523 (6)	867 (6)	−272 (5)
C24	−4553 (7)	1019 (8)	−695 (6)
C25	−5006 (7)	−1421 (8)	56 (7)
C26	−4422 (7)	1651 (8)	1009 (6)
C27	−3394 (6)	1478 (6)	1430 (5)
C31	−232 (6)	3116 (4)	824 (5)
C32	−1051 (6)	3417 (5)	−13 (5)
C33	−730 (8)	3751 (6)	−751 (6)
C34	−1509 (9)	3999 (8)	−1557 (7)
C35	−2574 (10)	3891 (8)	−1616 (7)
C36	−2880 (8)	3559 (8)	−847 (8)
C37	−2097 (6)	3332 (6)	−28 (6)
C41	2514 (5)	3994 (5)	3106 (4)
C42	3387 (5)	4968 (5)	3720 (5)
C43	4429 (6)	5124 (5)	3738 (5)
C44	5243 (7)	6021 (6)	4310 (6)
C45	5011 (8)	6749 (6)	4867 (7)
C46	3954 (8)	6610 (6)	4842 (7)
C47	3119 (7)	5692 (5)	4270 (6)
C51	1498 (5)	1856 (5)	4572 (5)
C52	1974 (5)	1457 (5)	5475 (4)
C53	1495 (6)	473 (6)	5425 (5)
C54	1908 (6)	106 (6)	6301 (6)
C55	2777 (6)	725 (7)	7186 (6)
C56	3259 (6)	1710 (7)	7225 (6)
C57	2858 (6)	2083 (6)	6362 (5)
CA1	−424 (6)	−731 (5)	2079 (5)
CA2	251 (9)	−1426 (7)	2431 (8)
CA3	−173 (10)	−2035 (7)	3073 (9)
CA4	599 (16)	−2591 (13)	3608 (13)
CB1	2702 (7)	2623 (6)	448 (6)
CB2	2846 (18)	3580 (11)	297 (16)
CB3	3636 (24)	3853 (15)	−169 (22)
CB4	3247 (22)	4238 (24)	−952 (19)
CC1	−296 (6)	3286 (6)	3808 (5)
CC2	−1012 (8)	3898 (8)	3265 (7)
CC3	−1678 (9)	4203 (9)	3882 (9)
CC4	−2407 (14)	4796 (14)	3352 (9)

[a] Numbers in parentheses are esd's. [b] Atoms are labeled to agree with Figure 2. The carbon atoms of the three independent phenyl groups omitted from Figure 2 are labeled C12–C17 (C12 bonded to C11), C22–C27 (C22 bonded to C21), and C32–C37 (C32 bonded to C31).

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TABLE IV

Atomic coordinates in crystalline $\{[n\text{-BuSn(O)O}_2\text{CMe}]_2[n\text{-BuSn(O}_2\text{CMe)}_3]\}_2$ (3)[a]

atom[b]	10^4x	10^4y	10^4z
Sn1	733.7 (8)	-34.4 (4)	567.9 (3)
Sn2	1907.5 (9)	1040.0 (3)	-28.2 (3)
Sn3	1906.4 (9)	1102.4 (4)	1411.4 (3)
O1	474 (7)	471 (3)	-82 (3)
O11	2321 (8)	-364 (3)	134 (3)
O12	3199 (8)	380 (4)	-227 (3)
O2	1850 (8)	691 (3)	726 (3)
O21	-857 (8)	356 (3)	949 (3)
O22	196 (8)	636 (4)	1655 (3)
O31	659 (8)	1694 (3)	214 (3)
O32	309 (9)	1602 (4)	1082 (4)
O41	3560 (8)	1482 (4)	213 (4)
O42	2990 (9)	1770 (3)	1027 (4)
O52	4093 (11)	864 (5)	1494 (4)
O51	2657 (10)	351 (4)	1831 (4)
C11	3110 (13)	-138 (6)	-157 (5)
C12	4046 (13)	-520 (6)	-425 (6)
C21	-824 (14)	555 (5)	1411 (5)
C22	-2022 (12)	681 (8)	1703 (6)
C31	56 (14)	1785 (6)	628 (6)
C32	-1149 (16)	2107 (8)	569 (7)
C41	3738 (14)	1755 (6)	639 (7)
C42	4939 (14)	2098 (7)	666 (6)
C51	3776 (17)	451 (7)	1748 (6)
C52	4775 (14)	51 (7)	1985 (7)
CA1	1048 (13)	-601 (6)	1213 (5)
CA2[c]	1519 (31)	-1194 (12)	1021 (11)
CA2'[c]	2291 (44)	-957 (16)	1210 (12)
CA3[c]	2931 (31)	-1186 (18)	1167 (16)
CA3'[c]	2070 (45)	-1440 (16)	871 (19)
CA4	3331 (23)	-1774 (9)	921 (10)
CB1	1986 (14)	1426 (5)	-802 (5)
CB2	2727 (22)	1108 (9)	-1206 (6)
CB3	2655 (28)	1442 (10)	-1724 (8)
CB4	2985 (39)	1129 (11)	-2150 (10)
CC1	1882 (16)	1603 (7)	2111 (6)
CC2	835 (22)	1869 (12)	2270 (8)
CC3	751 (21)	2176 (10)	2806 (9)
CC4	0 (28)	2618 (12)	2745 (10)

[a] Numbers in parentheses are esd's. [b] Atoms are labeled to agree with Figure 3. [c] Half occupancy.

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

$$[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-}2]_6\cdot 3\text{C}_6\text{H}_6 + 6\text{H}_2\text{O} \quad (1)$$

$$6\text{MeSn(O)OH} + 10\text{C}_6\text{H}_{11}\text{CO}_2\text{H} \rightarrow$$

$$[(\text{MeSn(O)O}_2\text{CC}_6\text{H}_{11})_2\text{MeSn(O}_2\text{CC}_6\text{H}_{11})_3]_2 + 8\text{H}_2\text{O} \quad (2)$$

In contrast, the preparation of **2** and **3** was achieved by reacting *n*-butyltin trichloride with the silver salt of the corresponding acid, followed by hydrolysis as expressed in eq 3. Anderson[16] has shown

$$6n\text{-BuSnCl}_3 + 10\text{Ag}^+\text{RCO}_2^- + 4\text{H}_2\text{O} \rightarrow$$

$$[(n\text{-BuSn(O)O}_2\text{CR})_2\text{-}n\text{-BuSn(O)}_2\text{CR})_3]_2 + 10\text{AgCl} + 8\text{HCl} \quad (3)$$

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TABLE V

Selected bond lengths (Å) and bond angles (deg) for $[(n\text{-BuSn(O)O}_2\text{CR})_2\text{-}n\text{-BuSn(O}_2\text{CR)}_3]_2$ (**2**), (R = Ph) and (**3**) R = Me[a]

compound	2	3	compound	2	3
O1-Sn1	2.051 (4)	2.049 (7)	O41-Sn2	2.147 (5)	2.148 (9)
O1-Sn2	2.060 (4)	2.054 (7)	O42-Sn3	2.189 (5)	2.194 (9)
O1-Sn1′	2.079 (5)	2.061 (7)	O51-Sn3	2.218 (5)	2.229 (10)
O2-Sn1	2.161 (4)	2.140 (7)	O52-Sn3	2.407 (5)	2.421 (12)
O2-Sn2	2.067 (4)	2.072 (7)	C11-O11	1.253 (8)	1.241 (4)
O2-Sn3	1.985 (4)	1.983 (7)	C11-O12	1.268 (8)	1.251 (14)
Sn1-CA1	2.154 (7)	2.137 (12)	C21-O21	1.275 (9)	1.254 (13)
Sn2-CB1	2.143 (8)	2.153 (11)	C21-O22	1.257 (8)	1.269 (14)
Sn3-CC1	2.129 (7)	2.126 (12)			
O11-Sn1	2.210 (4)	2.169 (9)	C31-O31	1.272 (8)	1.243 (15)
O12-Sn2	2.149 (5)	2.159 (8)	C31-O32	1.264 (8)	1.252 (14)
O21-Sn1	2.161 (4)	2.166 (8)	C41-O41	1.263 (8)	1.267 (16)
O22-Sn3	2.242 (5)	2.230 (9)	C41-O42	1.252 (8)	1.264 (16)
O31-Sn2	2.130 (5)	2.143 (8)	C51-O51	1.269 (8)	1.241 (17)
O32-Sn3	2.232 (4)	2.244 (9)	C51-O52	1.242 (8)	1.221 (17)
Sn1-O1-Sn1′	104.8 (2)	105.2 (3)	O2-Sn2-O41	87.9 (2)	87.9 (3)
Sn1-O1-Sn2	103.7 (2)	103.5 (3)	O2-Sn2-O12	84.7 (2)	86.5 (3)
Sn2-O1-Sn1′	148.2 (2)	147.4 (4)	O2-Sn2-O31	90.4 (2)	90.7 (3)
Sn1-O2-Sn2	99.7 (2)	99.8 (3)	CB1-Sn2-O1	103.0 (3)	104.6 (4)
Sn3-O2-Sn2	126.0 (2)	126.6 (4)	CB1-Sn2-O41	95.1 (3)	90.8 (5)
Sn3-O2-Sn1	125.9 (2)	125.3 (4)	CB1-Sn2-O12	89.7 (3)	94.4 (4)
CA1-Sn1-O1	174.5 (2)	176.4 (4)	CB1-Sn2-O31	91.7 (3)	88.3 (4)
O11-Sn1-O21	173.7 (2)	174.8 (3)	O1-Sn2-O12	93.5 (2)	89.1 (3)
O2-Sn1-O1′	150.4 (2)	150.4 (3)	O1-Sn2-O31	91.6 (2)	91.8 (3)
O1-Sn1-O2	75.2 (1)	75.5 (3)	O41-Sn2-O12	83.2 (2)	83.9 (3)
O1-Sn1-O1′	75.2 (2)	71.8 (3)	CC1-Sn3-O2	175.2 (3)	174.9 (5)
O1-Sn1-O11	85.5 (2)	85.3 (3)	O51-Sn3-O2	86.8 (2)	91.4 (3)
O1-Sn1-O21	90.1 (1)	89.6 (3)	O52-Sn3-O2	91.9 (2)	89.3 (4)
CA1-Sn1-O2	107.7 (2)	106.3 (4)	O51-Sn3-O22	76.1 (20)	76.5 (4)
CA1-Sn1-O1′	101.9 (2)	103.3 (4)	O52-Sn3-O22	131.7 (2)	131.0 (3)
CA1-Sn1-O11	90.1 (1)	91.7 (4)	O51-Sn3-O42	129.5 (2)	126.9 (4)
CA1-Sn1-O21	94.5 (2)	93.4 (4)	O52-Sn3-O42	73.9 (2)	72.3 (4)
O2-Sn1-O11	84.5 (2)	87.0 (3)	O51-Sn3-CC1	92.3 (2)	93.7 (5)
O2-Sn1-O21	90.1 (2)	90.6 (3)	O52-Sn3-CC1	91.5 (2)	94.2 (5)
			O51-Sn3-O52	55.7 (2)	54.6 (4)
O1′-Sn1-O11	94.8 (2)	90.7 (3)	O32-Sn3-O2	85.0 (2)	85.3 (3)
O1′-Sn1-O21	88.5 (2)	89.1 (3)	O32-Sn3-O22	75.5 (2)	74.8 (3)
CB1-Sn2-O2	174.4 (3)	178.3 (4)	O32-Sn3-O42	79.0 (2)	81.8 (4)
O12-Sn2-O31	171.9 (2)	176.8 (3)	O32-Sn3-CC1	93.5 (3)	89.9 (5)
O1-Sn2-O41	165.0 (2)	163.6 (3)	O2-Sn3-O42	92.1 (2)	89.6 (3)
O2-Sn2-O1	77.1 (2)	76.9 (3)	O2-Sn3-O22	87.3 (2)	88.1 (3)
O41-Sn2-O31	90.2 (2)	94.5 (3)	CC1-Sn3-O42	92.1 (3)	87.9 (5)
O32-Sn3-O51	150.7 (2)	151.2 (4)	CC1-Sn3-O22	87.8 (3)	92.4 (5)
O32-Sn3-O52	152.5 (2)	153.5 (4)			
O22-Sn3-O42	154.4 (2)	156.6 (3)			

[a]Numbers in parentheses are esd's. Atoms are labeled to agree with Figures 3 and 4.

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that organotin tricarboxylates can be distilled in high yield from the reaction of organotin trichlorides and silver salts of carboxylic acids. Further, he established that the tricarboxylates readily hydrolyze in a reversible reaction leading to an oxycarboxylate composition of unspecified degree of polymerization, e.g., eq 4.

$$n\text{-BuSn(O}_2\text{CR)}_3 + \text{H}_2\text{O} \rightarrow {}^1/_x(n\text{-BuSn(O)O}_2\text{CR})_x + 2\text{RCO}_2\text{H} \qquad (4)$$

In one instance, Lambourne[17a] isolated $(\text{MeSn(O)O}_2\text{CMe})_3$ for which the trimer formulation was given based on cryoscopic measurements in phenol.

For $[\text{MeSn(O)O}_2\text{CR}]_6$, R = Et, Pr, *i*-Pr, Lambourne[17b] obtained hexamer compositions from cryoscopic molecular weight determinations in benzene. The isolation of different reaction products by us and by Anderson[16] using similar reactants, according to eq 3, suggest that the tricarboxylate formulation, $\text{R'Sn(O}_2\text{CR)}_3$, is an intermediate in the reaction sequence leading to the oxocarboxylate compositions, **1–4.**

Not only do the tricarboxylate compositions readily hydrolyze, eq 4, but as our NMR data show, a reversible reaction is established in some cases between the drum and ladder forms. Subtraction of eq 2 from eq 1, in general form, leads to

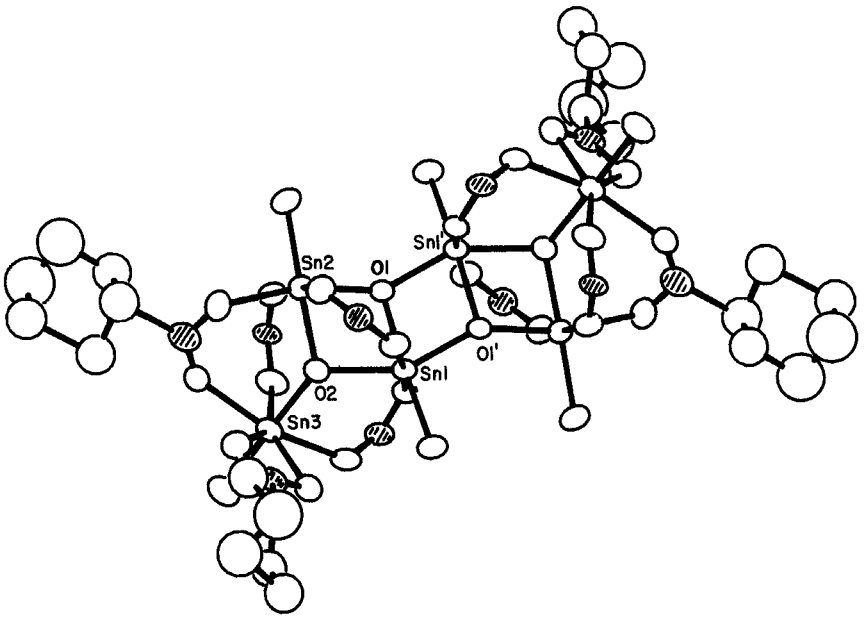

FIGURE 4 ORTEP plot showing the partially refined structure of $[(MeSn(O)_2CC_6H_{11})_2MeSn(O_2CC_6H_{11})_3]_2$, **4**, with thermal ellipsoids at the 20% probability level. Six of the ten cyclohexyl groups are omitted for purposes of clarity. Carbon atoms of the carboxyl groups are shaded. Primed atoms are related to unprimed ones by the inversion operation.

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the hydrolysis traction of eq 2 from eq 1, in general form, leads to the hydrolysis reaction in eq 5. Hence, the drum is a hydrolysis product further

$$[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2 + 2H_2O \rightarrow [R'Sn(O)O_2CR]_6 + 4RCO_2H \quad (5)$$

along the sequence from the tricarboxylate composition than is the ladder. Whereas it takes 1 mol of H_2O per mol of tricarboxylate to form the drum structure (eq 4), only $\frac{2}{3}$ of a mol of H_2O are required to form the ladder.

^{119}Sn NMR Data

NMR evidence showing partial conversion of ladders to drums has been obtained for the mixed oxocarboxylate tricarboxylates **2–4.** For example, three major ^{119}Sn signals for **4** 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 structure. 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 5, 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[18] is -478 to -485 ppm for butylstannoic acid derivatives. It is reasonable that the lower field signal at -465.9 ppm for **4** is due to the drum formed in the hydrolysis of eq 5. Addition of carboxylic acid to a solution of pure drum causes the appearance of ^{119}Sn NMR signals associated with the ladder formulation.[18]

These data are in agreement with earlier work of Lambourne[17a] suggesting the presence of the reversibility of eq 5. He found that the "pentacetyl" derivative, $Me_3Sn_3(O)_2(O_2CMe)_5$, (identified in our work as the ladder structure, $[(R'Sn(O)O_2CR)_2\,R'Sn(O_2CR)_3]_2$) underwent partial hydrolysis to produce a much more stable "triacetyl" compound, $(MeSn(O)O_2CMe)_3$ (in our work, we have established drum compositions $[R'Sn(O)O_2CR]_6$). Further he showed that the original "pentacetyl" compound was formed by prolonged action of excess glacial acetic acid on the "triacetyl" derivative.

Similar to **4**, the three ^{119}Sn NMR signals recorded as broad at -606 ppm and as multiplets at -548 and -520 ppm for the benzoate derivative **2** 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.

For the week old sample of the acetate compound **3** the high field signal assignable to the terminal tin atoms of the ladder was not observed. This agrees with the presence of only weak intensity signals at -522 and -549 ppm which are assigned to the two other types of tin atoms in **3**. Correspondingly, a strong signal at -486 ppm supports the formation of the drum structure in this sample according to eq 5. The relatively weak signal at -533 ppm is assigned to an intermediate.

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IR Data

Infrared bands corresponding to the bridging carboxyl groups and the Sn—O stretching vibration are very useful in discriminating between the drum and ladder forms. For drum structures, the carboxyl absorption, ν_{COO}, appears as a symmetrical doublet centered near 1550 cm^{-1}, whereas the ladders have an unsymmetrical doublet absorption in this same region. A very strong band around 600 cm^{-1}, characteristic of the Sn—O—Sn linkage,[25] is assigned to ν_{Sn-O} for the drum form. Ladders, however, give two bands in this region of the spectrum. The infrared data recorded here for **1–4** are consistent with these patterns that have been observed on additional derivatives of both structural forms.[18]

Structural Details

The drum compound **1** has crystallographic S_6 symmetry, so that the six tin atoms are both crystallographically and chemically equivalent. The hexacoordinated tin atoms have distorted octahedral geometry. For each hexamer in the unit cell there are three benzene molecules of solvation, one with crystallographic S_6 symmetry and two with crystallographic C_3 symmetry.

The ladder or "unfolded drum" compounds **2** and **3** have crystallographic C_i symmetry, which corresponds to the idealized molecular symmetry. There are,

therefore, three chemically nonequivalent types of Sn atoms in the molecules. 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 CCl in axial positions. For **2**, the five ligand atoms and the Sn3 atom comprising the equatorial plane are coplanar to within ±0.081 Å, while the axial angle O2—Sn3—CCl is 175.2 (3)°. For **3**, these values are ±0.057 Å and 174.9 (5)°.

The general structural features of the methyloxotin cyclohexanoate **4** are very similar to those of **2** and **3**, as shown in Figure 4. This compound also has crystallographic C_i symmetry.

The Sn—O framework of the "drum" in **1** is shown in Figure 5. The general features of this framework are the same as for the other drum shaped molecules which have been structurally characterized[3,18]: the six-membered rings have a chair conformation while the four-membered rings are not planar due to the fact that the oxygen atoms are tilted toward the center of the cavity, relative to the tin atoms. The Sn—O bond lengths in the framework are 2.088 (4) and 2.097 (4) Å for the six-membered rings and 2.085 (3) Å for the four-membered rings. The bonds are shorter than the Sn—O bonds to the bridging carboxyl oxygen atoms which have values of 2.197 (4) and 2.193 (4) Å.

The Sn—O framework for the unfolded species **2** is shown is Figure 6. In Figure 6b deviations from planarity for this framework can be visualized. Atom Sn1,O1, Sn1′, and O1′ are required by symmetry to be coplanar. The symmetry related O2 atoms lie very nearly in this plane while the Sn2 atoms and the Sn3 atoms are progressively more displaced from this plane in opposite directions. The geometry about the trivalent oxygen atoms, however, tends toward planarity. For **2**, the sum

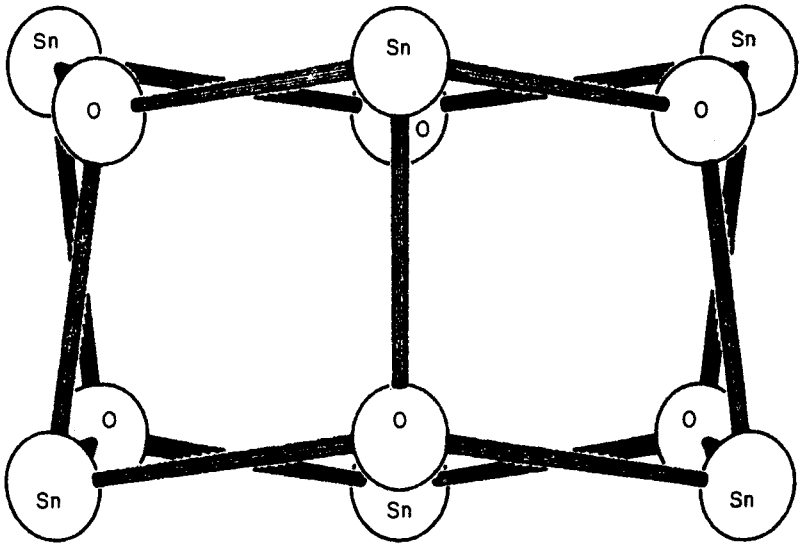

FIGURE 5 ORTEP plot showing the Sn—O framework of the "drum" in $[n\text{-BuSn(O)}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-}2]_6\cdot 3\text{C}_6\text{H}_6$, **1**.

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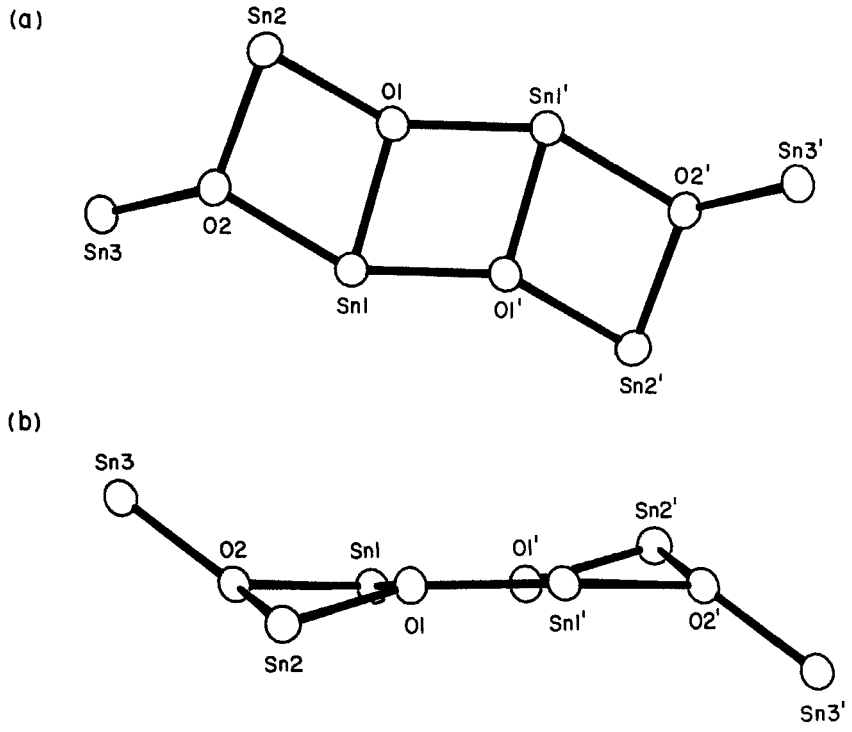

FIGURE 6 ORTEP plot showing the Sn—O framework of the "unfolded drum" in $[(n\text{-BuSn(O)O}_2\text{CPh})_2\text{-}n\text{-BuSn(O}_2\text{CPh)}_3]_2$, **2**: (a) viewed normal to the central Sn_2O_2 plane and (b) viewed parallel to the central Sn_2O_2 plane.

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of the angles about O1 is 356.7° and about O2 is 351.6°. For **3**, these values are 356.1° and 351.7°.

As in the case of the drum **1** the framework Sn—O bonds tend to be shorter than the Sn—O bonds to bridging carboxylate groups, with the exception of the Sn1—O2 framework bond. For **2**, the framework Sn—O bonds range from 1.985 (4) to 2.067 (4) Å except for the Sn1—O2 bond length of 2.161 (4) Å, while the bridging Sn—O bond lengths range from 2.189 (5) to 2.242 (5) Å. For **3**, these values are 1.983 (7) to 2.072 (7), 2.140 (7), and 2.143 (8) to 2.244 (9) Å. For both **2** and **3**, the shortest Sn—O bond length is the axial bond of the heptacoordinated Sn3.

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation CHE-8504737 and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged, as is the generous allocation of computing time by the University of Massachusetts Computing Center.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom parameters, and additional bond lengths and angles (Tables S1–S3, respectively, for **1**), anisotropic thermal parameters and additional bond lengths and angles (Tables S4 and S5, respectively, for **2**, and Tables S6 and S7, respectively, for **3**), deviations from selected least-squares mean planes (Tables S8 and S9 for **2** and **3**, respectively) (13 pages); a listing of observed and calculated structure factors for **1–3** (36 pages). Ordering information is given on any current masthead page.

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