Polynuclear Chlorine Containing Organooxotin Clusters[1,2]

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Reaction of n-butyltin dihydroxy chloride, $n\text{-BuSn(OH)}_2\text{Cl}$, with the phosphinic acids $\text{R}_2\text{P(O)OH}$ (R = cyc, *t*-Bu, Ph, Mes) yields the novel chlorooxotin clusters, $[\{n\text{-BuSn(OH)O}_2\text{P(C}_6\text{H}_{11})_2\}_3\text{O}][\{n\text{-BuSnCl}_2\text{O}_2\text{P(C}_6\text{H}_{11})_2\}_2\text{OH}]$ (**1**), $[(n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2)(n\text{-BuSn(OH)}_2\text{O}_2\text{P}(t\text{-Bu})_2)]_2[\text{H}][\text{Cl}][n\text{-BuSnCl(OH)(O}_2\text{P}(t\text{-Bu})_2)]_2$ (**2**), $[\{n\text{-BuSnCl}_2\text{(O}_2\text{PPh}_2)\}\{n\text{-BuSn(OH)(O}_2\text{PPh}_2)_2\}]_2\cdot 2\text{CH}_2\text{Cl}_2$ (**3**), and $[(n\text{-BuSn(OH)O}_2\text{PMes}_2)_3\text{O}]\text{Cl}$ (**4**), respectively, that contain tin nuclearities varying from 2 to 4. All have hydroxyl groups bridging hexacoordinate tin centers and in **1** and **2** these hydroxyl bridges hydrogen bonds to neighboring chlorine atoms. The new compounds **1** and **2** are each composed of two cluster units. In **1** an O-capped cationic cluster hydrogen bonds to a new form of a dinuclear tin anion. Formal replacement of the two phosphinate units attached to each of the central tin atoms of the tetranuclear tin cluster **3** with chlorine atoms generates the new dinuclear tin anion structure of **1**. In **2**, two distinct compounds cocrystallize, a protonated tetranuclear tin crown cluster which is hydrogen bonded to a chloride ion and a neutral dinuclear tin butterfly unit similarly hydrogen bonded to the chloride. Formulation 4 is representative of an O-capped cluster. ^{1}H, ^{119}Sn, and ^{31}P NMR data are consistent with retention of the solid-state structures in solution. Possible routes for the formation of these new oxotin clusters are presented. **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 14.870 (5) Å, b = 15.328 (4) Å, c = 26.117 (8) Å, α = 72.88 (2)°, β = 70.39 (3)°, γ = 70.63 (3)°, and Z = 2. **2** crystallizes in the triclinic space group $P1$ with a = 13.040 (3) Å, b = 14.334 (5) Å, c = 16.536 (3) Å, α = 71.62 (2)°, β = 71.19 (2)°, γ = 77.33 (2)°, and Z = 1. **3** crystallizes in the orthorhombic space group $Pbca$ with a = 23.544 (6) Å, b = 16.608 (4) Å, c = 25.926 (5) Å, and Z = 4. The final conventional unweighted residuals are 0.060 (**1**), 0.056 (**2**), and 0.046 (**3**).

Introduction

Previous work in our laboratory has led to the development of a new area of monoorganotin cluster chemistry based on a stannoxane framework.[4] This has led to the discovery of a variety of structural units involving tin nuclearities from 2 to 7. Particularly prevalent are forms that were uncovered with phosphorus-based acids which acted as bidentate chelating groups spanning adjacent tin(IV) atoms. This usually resulted in hexacoordinated tin containing one organic substituent and oxygen atoms that were either bi- or tricoordinated. Some of the more common clusters obtained were prismanes[5] (drums), O-capped[5–7] and crown[8] clusters, cubes,[6–9] and butterfly[6] formations.

In continuation of this work, we now report more complex organooxotin clusters resulting from the reaction of phosphinic acids with the common reagent *n*-butyldihydroxytin chloride, $n\text{-BuSn(OH)}_2\text{Cl}$. Both $[(\text{n-BuSn(OH)O}_2\text{P(cyc)}_2)_3\text{O}][(\text{n-BuSnCl}_2\text{O}_2\text{P(cyc)}_2)_2\text{OH}]$ (**1**) and $[(n\text{-BuSn(OH)O}_2\text{P}(t\text{-Bu})_2)_4\text{O}_2][\text{H}][\text{Cl}][n\text{-BuSn(OH)ClO}_2\text{P}(t\text{-Bu})_2]_2$ (**2**) are composed of two separate clusters that contain chlorine and hydroxyl groups which enter into hydrogen-bonding interactions with each other. A third derivative, $[(\text{n-Bu})_2\text{Sn}_2\text{Cl}_2\text{(OH)(O}_2\text{PPh}_2)_3]_2\cdot 2\text{CH}_2\text{Cl}_2$ (**3**), isolated in a reaction with diphenylphosphinic acid also contains chlorine and hydroxyl groups and exhibits an extended cluster framework. Solution state ^{1}H, ^{119}Sn, and ^{31}P NMR data in addition to X-ray analyses are reported to fully characterize these interesting species. Possible routes to their formation also are presented showing an interrelationship between components of the various clusters.

Table I. Crystallographic Data for Compounds **1–3**

	1	**2**	**3**
formula	$\text{C}_{80}\text{H}_{159}\text{O}_{15}$-$\text{Cl}_4\text{P}_5\text{Sn}_5$	$\text{C}_{72}\text{H}_{169}\text{O}_{20}$-$\text{Cl}_3\text{P}_6\text{Sn}_6$	$\text{C}_{88}\text{H}_{98}\text{O}_{14}\text{Cl}_4\text{P}_6\text{Sn}_4\cdot 2\text{CH}_2\text{Cl}_2$
fw	2251.282	2359.481	2352.036
space group	$P\bar{1}$ (No. 2)	$P1$ (No. 1)	$Pbca$ (No. 61)
cryst syst	triclinic	triclinic	orthorhombic
a, Å	14.870 (5)	13.040 (3)	23.544 (6)
b, Å	15.328 (4)	14.334 (5)	16.608 (4)
c, Å	26.117 (8)	16.536 (3)	25.926 (5)
α, deg	72.88 (2)	71.62 (2)	
β, deg	70.39 (3)	71.19 (2)	
γ, deg	70.63 (3)	77.33 (2)	
V, Å^3	5176.7	2752.5	10137.6
Z	2	1	4
T, °C	23 (2)	23 (2)	23 (2)
λ, Å	0.71073	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.444	1.421	1.541
μ, cm^{-1}	14.256	15.562	13.393
$R(F_o)^a$	0.060	0.056	0.046
$R_w(F_o)^a$	0.084	0.080	0.063

[a] $R = \sum \| F_o| - |F\| / \sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$.

Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, and Alfa and used without further purification. Di-*tert*-butylphosphinic acid[10] and dicyclohexylphosphinic acid[11] were prepared by literature methods.

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Solvents used were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[12]

^{1}H, ^{31}P, and ^{119}Sn NMR spectra (proton decoupled) were recorded on a Varian XL 300 FT/NMR spectrometer equipped with a multinuclear broad-band probe and operated at 300, 121.4, and 11.862 MHz, respectively. Resonances are referenced vs tetramethylsilane (^{1}H), tetramethyltin (external standard, ^{119}Sn), and 85% orthophosphoric acid (external standard except where noted, ^{31}P).

Preparation of the O-Capped Cluster, $[(n\text{-BuSn(OH)O}_2\text{Pcyc}_2)_3\text{O}][(n\text{-BuSnCl}_2\text{O}_2\text{Pcyc}_2)_2\text{OH}]$ (1). A mixture of *n*-butyldihydroxytin chloride (1.813 g, 6.73 mmol) (Alfa products) and dicyclohexyl phosphinic acid (1.548 g, 6.73 mmol) were heated together in toluene (75 mL) for 2 h with the azeotropic removal of water using a Dean–Stark apparatus. The solvent was removed in vacuo and the residue was dissolved in diethyl ether (100 mL). Evaporation of the solvent at 20 °C gave an oil (~3.1 g). A portion of this oil (2.2 g) was passed through a silica gel (~30 g) column. The first fraction [hexane (1) + dichloromethane (9), 200 mL] was discarded. Solvent was evaporated from the second fraction [dichloromethane (1) + methanol (1), 300 mL], and a mixture of dichloromethane (15 mL) and methyl cyanide (25 mL) was added to the residue. Slow evaporation of the solvent at 20 °C gave crystals of **1**: Mp 182–195 °C (sweats); yield 0.80 g (25%). ^{31}P NMR (C_6D_6, ppm): 55.48 ($^2J(Sn\text{–O–}P)$ = 134.3 Hz), cation; 50.89 ($^2J(^{119,117}Sn\text{–O–}P$ = 207.8, 199.2 Hz), anion. ^{119}Sn NMR (C_6D_6, ppm): −517.29 (t, $^2J(Sn\text{–O–}P)$ = 136.0 Hz), cation; −525.81 (t, $^2J(Sn\text{–O–}P)$ = 209.1 Hz), anion. ^{1}H NMR ($CDCl_3$, ppm): 0.89 (t, J = 7.6 Hz, 3 H, CH_3), 1.10–2.10 (br m, 28 H, CH_2), 6.13 (s, ~1 H, possible O*H*). Anal. Calcd for $C_{80}H_{159}O_{15}Cl_4P_5Sn_5$: C, 42.68; H, 7.07. Found: C, 42.53; H, 6.91.

Preparation of the Crown-Butterfly Cluster, $[(n\text{-BuSn(OH)O}_2\text{P}(t\text{-Bu})_2)_4\text{O}_2][\text{H}][\text{Cl}][n\text{-BuSn(OH)ClO}_2\text{P}(t\text{-Bu})_2]_2$ (2). A mixture of *n*-butyldihydroxytin chloride (1.168 g, 4.34 mmol) and di-*tert*-butylphosphinic acid (0.772 g, 4.34 mmol) in toluene (70 mL) was heated for 2 h with the azeotropic removal of water. The solvent was completely removed in vacuo and the residue crystallized from a mixture of dichloromethane (10 mL), diethyl ether (5 mL), and methyl cyanide (20 mL) over a period of 4 days. The first batch of crystals (0.6 g) showed peaks (^{119}Sn NMR, $CDCl_3$) centered at −523.4 (m), −497.0 (br), −467.0 (d, br) and −438.7 (d) ppm; however the crystals were not suitable for an X-ray study. The residue, after being redissolved in a mixture of dichloromethane (10 mL), diethyl ether (5 mL), and methyl cyanide (20 mL) afforded crystals of **2** suitable for X-ray analysis: Mp 167–172 °C; yield 0.34 g (20%). ^{31}P NMR (C_6D_6, ppm): 59.40 (^2J(Sn–O–P) = 147.0 Hz; P (crown)), 59.55 ($^2J(Sn\text{–O–}P)$ = 183.0 Hz, P (crown)), 64.0 (m, P (dimer)). ^{119}Sn NMR (C_6D_6, ppm): −499.0 (br, dimer), −533.2 (dd, $^2J(Sn\text{–O–}P)$ = 148.4, 191.4 Hz (crown)). ^{1}H NMR ($CDCl_3$, ppm): 0.82–0.96 (2 t, 3 H, CH_2CH_3), 1.16–1.38 (m, 22 H, CH_2, $C(CH_3)_3$), 1.70 (br, 2 H, CH_2). The O*H* protons were not identified, probably due to significant broadening. Anal. Calcd for $C_{72}H_{169}O_{20}Cl_3P_6Sn_6$: C, 36.65; H, 7.16. Found: C, 36.40; H, 6.93.

Preparation of the Extended Tetranuclear Cluster, $[(n\text{-Bu})_2\text{Sn}_2\text{Cl}_2(\text{OH})(\text{O}_2\text{PPh}_2)_3]_2\cdot 2\text{CH}_2\text{Cl}_2$ (3). n-Butyldihydroxytin chloride (1.382 g, 5.13 mmol) and diphenylphosphinic acid (1.198 g, 5.13 mmol) were heated in toluene (90 mL) for 2 h with the azeotropic removal of water. The volume of the solution was reduced to ca. 20 mL and dichloromethane (60 mL) was added. Compound **3** crystallized from the solution upon slow evaporation of the solvent at 20 °C (6 h): mp 258–260; yield 0.46 g (23%). ^{31}P NMR ($CDCl_3$, ppm): 25.27 (s, $^2J(Sn\text{–O–}P)$ = 213.2 Hz, terminal bridge), 22.49 (s, $^2J(^{119,117}Sn\text{–O–}P)$ = 162.2, 155.3 Hz, central bridge). ^{119}Sn NMR ($CDCl_3$, ppm): −507.39 (t, $^2J(Sn\text{–O–}P)$ = 222.8 Hz, Sn (terminal)), −615.36 (m, Sn (central)). ^{1}H NMR ($CDCl_3$, ppm): 0.45–2.30 (m, 36 H; CH_2, CH_3), 4.73 (s, 2H, $^2J(Sn\text{–O–}H)$ = 25.2 Hz), 5.29 (s, 4 H, CH_2Cl_2), 6.90–7.90 (m, 60 H, *H*(Ar)). Two sets of CH_3 groups at 0.49 and 0.97 ppm in the intensity ratio 1:1 were observed, as expected. Anal. Calcd for $C_{90}H_{102}O_{14}Cl_8P_6Sn_4$: C, 45.95; H, 4.34. Found: C, 46.21; H, 4.38.

Preparation of the O-Capped Cluster $[(n\text{-BuSn(OH)O}_2\text{PMes}_2)_3\text{O}]\text{Cl}$ (4). *n*-Butyldihydroxytin chloride (0.375 g, 1.39 mmol) and dimesitylphosphinic acid[13] (0.421 g, 1.39 mmol) were heated in toluene (100 mL) for 2 h with the azeotropic removal of water. ^{119}Sn NMR of the reaction mixture shows **4** as a major component (>65%) at −509.99 (t, *O*-cap), and two minor components: [−519.45 (dd, $^2J(Sn\text{–O–}P)$ = 186.0, 218.2 Hz), indicative of a crown cluster], and [−536.8 (~t, $^2J(Sn\text{–O–}P)$ = 181.4 Hz), unassigned]. The solvent was removed completely in vacuo and the residue crystallized from a mixture of diethyl ether (20 mL), methyl cyanide (10 mL) and dichloromethane (10 mL) to afford **4**: Mp 196–216 °C (some residue); yield, 0.4 g, 56%. ^{1}H NMR ($CDCl_3$, ppm): 0.53 (t, $^3J(H\text{–}H)$ = 6.6 Hz, 3 H, CH_2CH_3), 1.00–2.60 (br m, 24 H, CH_2, $C_6H_2(CH_3)_3$), 6.25–6.90 (m, 5 H, O*H*, *H*(Ar)). ^{31}P NMR ($CDCl_3$, ppm): 37.10 ($^2J(Sn\text{–O–}P)$ = 153.8 Hz). ^{119}Sn NMR ($CDCl_3$, ppm):

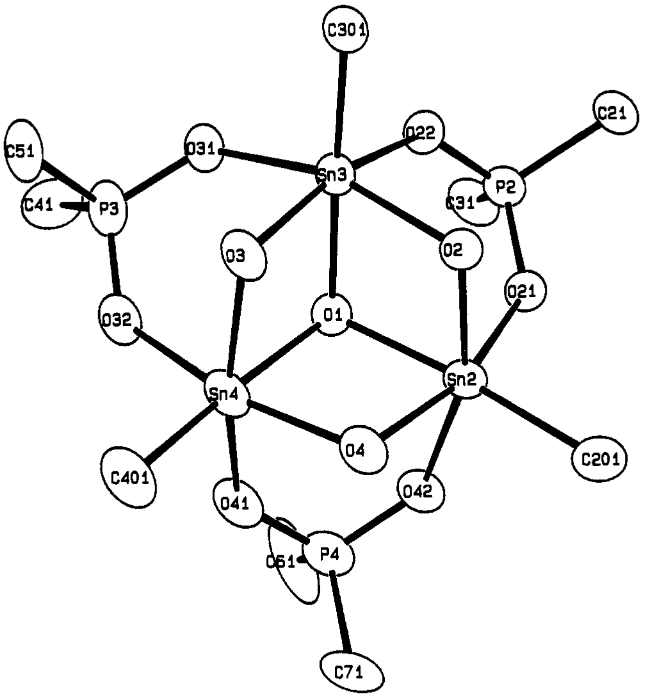

Figure 1. ORTEP plot of the cation in $[(n\text{-BuSn(OH)O}_2\text{P(cyc)}_2)_3\text{O}][(n\text{-BuSnCl}_2\text{O}_2\text{P(cyc)}_2)_2\text{OH}]$ (**1**) with thermal ellipsoids at the 30% probability level. Pendant atoms of the *n*-Bu groups (bound to C201, C301, and C401) and of the cyclohexyl groups (bound to C21, C31, C41, C51, C61, and C71) are omitted for clarity.

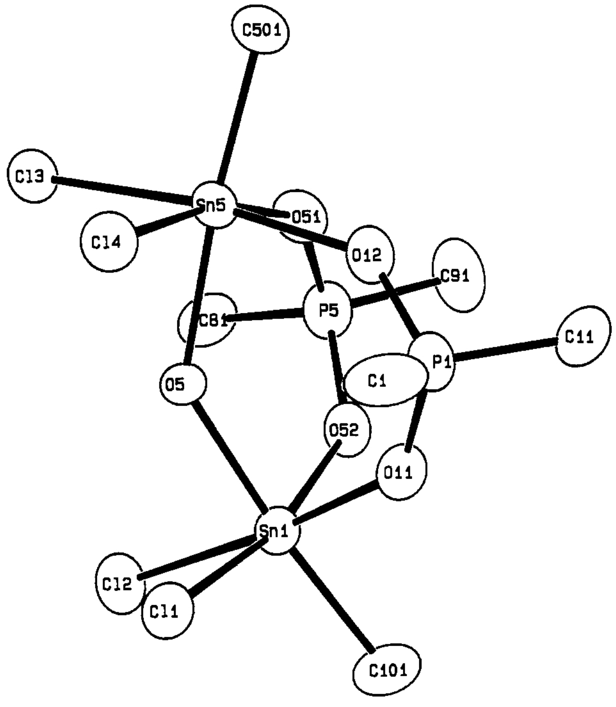

Figure 2. ORTEP plot of the anion in $[(n\text{-BuSn(OH)O}_2\text{P(cyc)}_2)_3\text{O}][(n\text{-BuSnCl}_2\text{O}_2\text{P(cyc)}_2)_2\text{OH}]$ (**1**) with thermal ellipsoids at the 30% probability level. Pendant atoms of the *n*-Bu groups (bound to C101 and C501) and of the cyclohexyl groups (bound to C1, C11, C81, and C91) are omitted for clarity.

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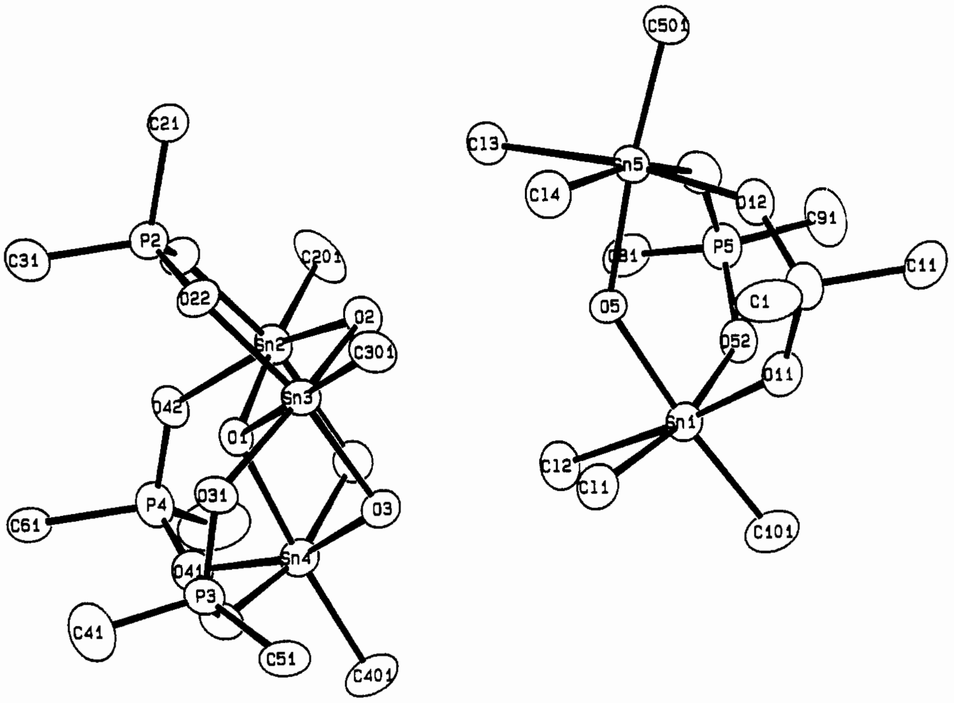

Figure 3. ORTEP plot showing the relative orientation of the frameworks of the cation-anion pair in $[(n\text{-BuSn(OH)O}_2\text{P(cyc)}_2)_3\text{O}][(n\text{-BuSnCl}_2\text{O}_2\text{P(cyc)}_2)_2\text{OH}]$ (**1**).

Table II. Selected Atomic Coordinates in Crystalline $[(n\text{-BuSn(OH)O}_2\text{P(cyc)}_2)_3\text{O}][(n\text{-BuSnCl}_2\text{O}_2\text{P(cyc)}_2)_2\text{OH}]$ (**1**)[a]

atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å^2	atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å^2
Sn1	0.06386 (6)	0.45877 (6)	0.15543 (4)	5.91 (3)	O22	0.0971 (6)	0.0167 (6)	0.3970 (3)	6.4 (2)
Sn2	0.09974 (6)	0.03163 (6)	0.25645 (3)	5.79 (3)	O31	0.3016 (6)	0.0451 (6)	0.3599 (3)	6.9 (3)
Sn3	0.16845 (6)	0.11491 (6)	0.33583 (4)	5.90 (3)	O32	0.4181 (6)	0.0160 (6)	0.2639 (4)	7.7 (3)
Sn4	0.31943 (7)	0.06942 (7)	0.21555 (4)	7.09 (3)	O41	0.3554 (7)	–0.0630 (6)	0.1945 (4)	7.9 (3)
Sn5	–0.18328 (7)	0.42300 (6)	0.26693 (4)	6.38 (3)	O42	0.1868 (6)	–0.0937 (5)	0.2270 (3)	6.5 (3)
Cl1	0.1702 (3)	0.4045 (3)	0.2204 (2)	8.0 (1)	O51	–0.2076 (6)	0.4584 (6)	0.1876 (4)	7.7 (3)
Cl2	0.1358 (3)	0.3052 (3)	0.1246 (2)	8.1 (1)	O52	–0.0469 (6)	0.4891 (6)	0.1175 (4)	7.1 (3)
Cl3	–0.1701 (3)	0.2572 (3)	0.2728 (2)	8.8 (1)	C1	–0.061 (1)	0.613 (1)	0.2900 (6)	11.0 (6)
Cl4	–0.1126 (3)	0.3756 (3)	0.3467 (2)	9.3 (1)	C11	–0.158 (1)	0.738 (1)	0.1998 (9)	13.0 (8)
P1	–0.0988 (3)	0.6193 (3)	0.2304 (2)	7.1 (1)	C21	–0.0804 (9)	–0.0212 (9)	0.4369 (5)	6.6 (4)
P2	0.0445 (3)	–0.0506 (3)	0.3936 (1)	5.9 (1)	C31	0.101 (1)	–0.173 (1)	0.4188 (5)	8.2 (5)
P3	0.4079 (3)	0.0253 (3)	0.3229 (2)	7.6 (1)	C41	0.481 (1)	–0.082 (1)	0.3527 (7)	10.4 (6)
P4	0.2908 (3)	–0.1179 (3)	0.1905 (2)	7.4 (1)	C51	0.457 (1)	0.124 (1)	0.3185 (7)	9.8 (6)
P5	–0.1443 (3)	0.4621 (3)	0.1280 (2)	7.4 (1)	C61	0.349 (1)	–0.242 (1)	0.221 (1)	14.1 (8)
O1	0.2169 (5)	0.0182 (5)	0.2851 (3)	5.4 (2)	C71	0.284 (1)	–0.088 (1)	0.1170 (7)	13.7 (7)
O2	0.0557 (6)	0.1512 (5)	0.2937 (3)	6.1 (2)	C81	–0.115 (1)	0.345 (1)	0.1124 (6)	8.0 (5)
O3	0.2560 (6)	0.1817 (6)	0.2617 (4)	7.3 (3)	C91	–0.211 (1)	0.552 (1)	0.818 (8)	13.1 (6)
O4	0.1946 (6)	0.1014 (6)	0.1864 (4)	7.4 (3)	C101	0.148 (1)	0.536 (1)	0.0830 (7)	9.9 (6)
O5	–0.0305 (5)	0.3918 (5)	0.2221 (3)	5.5 (2)	C201	–0.017 (1)	0.051 (1)	0.2175 (6)	9.8 (5)
O11	–0.0062 (7)	0.5818 (6)	0.1866 (4)	7.9 (3)	C301	0.112 (1)	0.2192 (9)	0.3872 (6)	8.1 (4)
O12	–0.1753 (6)	0.5616 (6)	0.2502 (4)	7.6 (3)	C401	0.416 (1)	0.129 (1)	0.1415 (8)	11.2 (6)
O21	0.0421 (5)	–0.0449 (5)	0.3349 (3)	5.9 (2)	C501	–0.337 (1)	0.465 (1)	0.3055 (7)	10.0 (6)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 1–3. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

–508.0 (t, $^2J(Sn\text{–}O\text{–}P)$ = 159.5 Hz). Anal. Calcd for $C_{66}H_{96}O_{10}ClP_3Sn_3$: C, 51.68; H, 6.26. Found: C, 51.49; H, 6.37.

X-ray Experimental Section

All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation ($\lambda(K\bar{\alpha})$ = 0.710 73 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental procedures have been described previously.[14] Crystals were mounted in thin-walled glass capillaries which were sealed. Data were collected using the θ–2θ scan mode. The structures were solved by use of Patterson and difference Fourier techniques and were refined by full-matrix least-squares.[15] All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data for compounds **1**–**3** are summarized in Table I.

X-ray Study for 1. The colorless crystal which was used for the X-ray study was cut from a polycrystalline mass of laths and had dimensions of 0.13 × 0.38 × 0.38 mm. A total of 10 284 independent reflections were measured ($+h, \pm k, \pm l$; $3° \leq 2\theta_{\text{MoK}\bar{\alpha}} \leq 41°$). An empirical absorption correction based on ψ scans was applied (from 0.80 to 1.00 on I).

Pendant carbon atoms of the *n*-Bu groups and of the cyclohexyl groups were, in general, poorly defined and these atoms were included in the refinement as isotropic scatterers. The remaining non-hydrogen atoms were refined anisotropically. There appeared to be serious disorder in atoms C202–C204 of the *n*-Bu group which contains C201. Atom C204 was omitted from the refinement, while C202 and C203 were included in positions with half-occupancy. Hydrogen atoms were omitted from the refinement. The final refinement was based on 7200 reflections with $I \geq 3\sigma_I$.

X-ray Study for 2. The colorless irregular crystal which was used for the study was cut from a flattened chunk to approximate dimensions of 0.33 × 0.43 × 0.45 mm. A total of 5891 independent reflections was

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(14) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(15) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

Table III. Selected Distances (Å) and Angles (deg) for $[(n\text{-BuSn(OH)O}_2\text{P(cyc)}_2)_3\text{O}][(n\text{-BuSnCl}_2\text{O}_2\text{P(cyc)}_2)_2\text{OH}]$ (**1**)[a]

			Bond Distances				
Sn1–O5	2.078 (7)	Sn3–O22	2.110 (8)	Sn2–O4	2.144 (8)	Sn4–C401	2.14 (2)
Sn1–Cl1	2.484 (4)	Sn3–O31	2.120 (8)	Sn2–O21	2.092 (7)	Sn5–O5	2.141 (6)
Sn1–Cl2	2.490 (4)	Sn3–C301	2.16 (2)	Sn2–O42	2.123 (8)	Sn5–Cl3	2.446 (4)
Sn1–O11	2.082 (9)	Sn4–O1	2.083 (7)	Sn2–C20–1	2.18 (2)	Sn5–Cl4	2.458 (5)
Sn1–O52	2.06 (1)	Sn4–O3	2.16 (1)	Sn3–O1	2.068 (8)	Sn5–O12	2.074 (9)
Sn1–C101	2.15 (1)	Sn4–O4	2.10 (1)	Sn3–O2	2.142 (9)	Sn5–O51	2.10 (1)
Sn2–O1	2.046 (9)	Sn4–O32	2.06 (1)	Sn3–O3	2.125 (8)	Sn5–C501	2.13 (1)
Sn2–O2	2.136 (9)	Sn4–O41	2.11 (1)	O3–Cl1	3.212 (8)	O4–Cl2	3.049 (8)
			Bond Angles				
O5–Sn1–Cl1	83.0 (3)	O4–Sn2–O21	163.0 (4)	O2–Sn2–O42	160.9 (4)	O1–Sn4–O4	76.8 (3)
O5–Sn1–Cl2	86.8 (2)	O4–Sn2–O42	85.3 (3)	O2–Sn2–C201	105.3 (5)	O1–Sn4–O32	86.7 (3)
O5–Sn1–O11	88.0 (3)	O4–Sn2–C201	97.8 (5)	O1–Sn4–O41	85.9 (3)	Cl3–Sn5–Cl4	89.6 (2)
O5–Sn1–O52	83.1 (3)	O21–Sn2–O42	92.2 (3)	O1–Sn4–C401	175.8 (5)	Cl3–Sn5–O12	170.5 (2)
O5–Sn1–C101	173.8 (5)	O21–Sn2–C201	99.2 (4)	O3–Sn4–O4	93.3 (4)	Cl3–Sn5–O51	90.1 (3)
Cl1–Sn1–Cl2	90.4 (1)	O42–Sn2–C201	93.6 (5)	O3–Sn4–O32	85.3 (4)	Cl3–Sn5–C501	98.0 (5)
Cl1–Sn1–O11	89.8 (3)	O1–Sn3–O2	75.3 (3)	O3–Sn4–O41	161.5 (3)	Cl4–Sn5–O12	93.3 (3)
Cl1–Sn1–O52	166.4 (2)	O1–Sn3–O3	77.0 (3)	O3–Sn4–C401	103.1 (6)	Cl4–Sn5–O51	166.1 (2)
Cl1–Sn1–C101	102.9 (5)	O1–Sn3–O22	86.6 (3)	O4–Sn4–O32	163.3 (3)	Cl4–Sn5–C501	101.7 (6)
Cl2–Sn1–O11	174.8 (3)	O1–Sn3–O31	85.2 (4)	O4–Sn4–O41	85.5 (4)	O12–Sn5–O51	84.9 (4)
Cl2–Sn1–O52	89.3 (3)	O1–Sn3–C301	177.3 (5)	O4–Sn4–C401	99.3 (6)	O12–Sn5–C501	90.3 (5)
Cl2–Sn1–C101	94.9 (5)	O2–Sn3–O3	88.2 (3)	O32–Sn4–O41	90.6 (4)	O51–Sn5–C501	92.1 (6)
O11–Sn1–O52	89.3 (4)	O2–Sn5–O22	89.1 (3)	O32–Sn4–C401	97.3 (6)	Sn2–O1–Sn3	106.2 (3)
O11–Sn1–C101	90.1 (5)	O2–Sn3–O31	160.5 (3)	O41–Sn4–C401	95.4 (6)	Sn2–O1–Sn4	104.8 (3)
O52–Sn1–C101	90.7 (5)	O2–Sn3–C301	102.0 (5)	O5–Sn5–Cl3	85.3 (2)	Sn3–O1–Sn4	105.5 (1)
O1–Sn2–O2	75.9 (3)	O3–Sn3–O22	163.6 (4)	O5–Sn5–Cl4	82.2 (2)	Sn2–O2–Sn3	100.5 (3)
O1–Sn2–O4	76.5 (3)	O3–Sn3–O31	86.7 (3)	O5–Sn5–O12	86.2 (3)	Sn3–O3–Sn4	100.7 (4)
O1–Sn2–O21	86.5 (3)	O3–Sn3–C301	102.9 (4)	O5–Sn5–O51	83.9 (3)	Sn2–O4–Sn4	101.0 (4)
O1–Sn2–O42	85.1 (3)	O22–Sn3–O31	90.5 (3)	O5–Sn5–C501	174.9 (5)	Sn1–O5–Sn5	137.8 (3)
O1–Sn2–C201	174.2 (4)	O22–Sn3–C301	93.5 (4)	Sn2–O4–Cl2	125.5 (3)	Sn3–O3–Cl1	116.6 (3)
O2–Sn2–O4	89.2 (3)	O31–Sn3–C301	97.5 (5)	Sn4–O4–Cl2	114.2 (4)	Sn4–O3–Cl1	130.0 (4)
O2–Sn2–O21	87.7 (3)	O1–Sn4–O3	75.9 (3)				

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figures 1–3.

$$5n\text{-BuSn(OH)}_2\text{Cl} + 5\text{cyc}_2\text{PO}_2\text{H} \rightarrow \underset{\mathbf{1}}{[(n\text{-BuSn(OH)O}_2\text{Pcyc}_2)_3\text{O}][(n\text{-BuSnCl}_2\text{O}_2\text{Pcyc}_2)_2\text{OH}]} + 5\text{H}_2\text{O} + \text{HCl} \quad (1)$$

$$6n\text{-BuSn(OH)}_2\text{Cl} + 6(t\text{-Bu})_2\text{PO}_2\text{H} \rightarrow \underset{\mathbf{2}}{[(n\text{-BuSn(OH)O}_2\text{P}(t\text{-Bu})_2)_4\text{O}_2][\text{H}][\text{Cl}][(n\text{-BuSn- (OH)ClO}_2\text{P}(t\text{-Bu})_2)]_2} + 4\text{H}_2\text{O} + 3\text{HCl} \quad (2)$$

$$4n\text{-BuSn(OH)}_2\text{Cl} + 6\ \text{Ph}_2\text{PO}_2\text{H} + 2\text{CH}_2\text{Cl}_2 \rightarrow \underset{\mathbf{3}}{[(\text{n-Bu})_2\text{Sn}_2\text{Cl}_2(\text{OH})(\text{O}_2\text{PPh}_2)_3]_2\cdot 2\text{CH}_2\text{Cl}_2} + 6\text{H}_2\text{O} \quad (3)$$

$$3n\text{-BuSn(OH)}_2\text{Cl} + 3\text{Mes}_2\text{PO}_2\text{H} \rightarrow \underset{\mathbf{4}}{[(\text{n-BuSn(OH)O}_2\text{PMes}_2)_3\text{O}]\text{Cl}} + 2\text{H}_2\text{O} + 2\text{HCl} \quad (4)$$

measured (+*h*, ±*k*, ±*l*; 3° ≤ $2\theta_{\text{MoK}\bar{\alpha}}$ ≤ 42°). An empirical absorption correction based on ψ scans was applied (from 0.90 to 1.00 on *I*).

As in the case of **1**, pendant carbon atoms were refined isotropically with the remaining non-hydrogen atoms anisotropic. Positions could not be found for 12 of the *n*-Bu group carbon atoms. These atoms, as well as all hydrogen atoms, were omitted from the refinement. The final refinement was based on the 5535 independent reflections with $I \geq 2\sigma_I$.

X-ray Study for 3. The colorless crystal which was used for the study was cut from a larger nearly cubic chunk and had approximate dimensions of 0.33 × 0.35 × 0.35 mm. A total of 5789 independent reflections was measured (+*h*, +*k*, +*l*; 3° ≤ $2\theta_{\text{MoK}\bar{\alpha}}$ ≤ 43°). No corrections were made for absorption.

The pendant carbon atoms of a *n*-butyl group which was disordered (C2A, C2B, C3, C4) and the atoms of the solvent of crystallization (C9, C13, and C14) were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the phenyl groups were included as isotropic scatterers in ideal positions. The remaining hydrogen atoms were omitted from the refinement. The final refinement was based on the 4036 reflections with $I \geq 3\sigma_I$.

Results

Selected coordinates for compound **1** are given in Table II while selected distances and angles are given in Table III. The molecular geometry is illustrated in Figures 1–3. The corresponding information is given in Tables IV and V and in Figures 4–6 for **2** and in Tables VI and VII and Figures 7 and 8 for **3**. Complete tables of coordinates and distances and angles as well as anisotropic thermal parameters for all three compounds are provided as supplementary material.

Discussion

Syntheses. It is interesting that the use of the common reagent *n*-$\text{BuSn(OH)}_2\text{Cl}$ leads to the formation of such a large variety of organooxotin clusters merely by altering the phosphinic acid employed in the reaction. It becomes more understandable when viewed in the context of previously formed tin clusters. This topic will be discussed after details of the solid- and solution-state structural features of **1**–**3** are presented in the following sections.

Compounds **1**–**3** were all formed in yields between 20 and 25%, while the mesityl phosphinate derivative **4** was obtained in a 56% yield. The reactions leading to their formation are illustrated in eqs 1–4. These are condensation reactions with different amounts of chlorine atoms being retained in the products.

Structural Aspects. X-ray analysis shows that in clusters **1**–**3** all of the tin centers are hexacoordinate with approximately octahedral ligand atom geometry, and in contrast to related

Table IV. Selected Atomic Coordinates in Crystalline $[(n\text{-BuSn(OH)O}_2\text{P}(t\text{-Bu})_2)_4\text{O}_2][\text{H}^+][\text{Cl}^-][(n\text{-BuSn(OH)ClO}_2\text{P}(t\text{-Bu})_2]_2$ (**2**)

atom[b]	x	y	z	B_{equiv},[c] Å^2	atom[b]	x	y	z	B_{equiv},[c] Å^2
Sn1	0.800	1.058	1.014	4.71 (3)	O31	1.206 (1)	0.940 (1)	1.1092 (7)	6.7 (4)
Sn2	1.0263 (1)	0.85146 (9)	0.93760 (8)	4.63 (3)	O32	1.056 (1)	1.0731 (9)	1.1640 (8)	5.8 (3)
Sn3	1.2038 (1)	0.94288 (9)	0.98370 (8)	4.56 (3)	O41	0.830 (1)	1.1867 (9)	1.1608 (8)	5.6 (3)
Sn4	0.9751 (1)	1.14296 (9)	1.06692 (8)	4.57 (3)	O42	0.6954 (9)	1.1249 (9)	1.1125 (8)	5.4 (3)
Sn5	1.2017 (1)	1.2746 (1)	0.48782 (9)	4.80 (3)	O51	1.3117 (9)	1.3514 (9)	0.5087 (8)	5.0 (3)
Sn6	1.0234 (1)	1.4507 (1)	0.56479 (9)	5.40 (4)	O52	1.172 (1)	1.4918 (9)	0.5669 (8)	5.6 (3)
Cl1	1.0662 (6)	1.1545 (5)	0.7906 (4)	7.9 (2)	O61	0.918 (1)	1.378 (1)	0.5358 (9)	6.0 (4)
Cl5	1.2932 (5)	1.2986 (5)	0.3336 (4)	7.8 (2)	O62	1.057 (1)	1.2421 (9)	0.4745 (8)	5.5 (3)
Cl6	0.9731 (6)	1.6117 (5)	0.4748 (6)	9.5 (2)	C11	0.753 (2)	0.745 (2)	1.193 (2)	8.2 (8)
P1	0.7713 (5)	0.8132 (4)	1.0749 (5)	6.5 (2)	C15	0.681 (2)	0.784 (2)	1.026 (2)	9.5 (9)
P2	1.2465 (5)	0.7024 (4)	0.9899 (3)	5.2 (1)	C21	1.353 (2)	0.668 (2)	0.896 (1)	7.2 (6)
P3	1.1538 (4)	0.9961 (4)	1.1805 (3)	6.3 (1)	C25	1.241 (2)	0.608 (2)	1.094 (1)	6.5 (6)
P4	0.7089 (4)	1.1780 (4)	1.1737 (4)	5.8 (1)	C31	1.104 (2)	0.909 (2)	1.287 (1)	7.2 (7)
P5	1.2910 (4)	1.4432 (4)	0.5412 (3)	5.6 (1)	C35	1.263 (2)	1.071 (2)	1.169 (1)	9.2 (6)
P6	0.9392 (4)	1.2921 (4)	0.4946 (3)	5.3 (1)	C41	0.656 (1)	1.106 (2)	1.285 (1)	6.1 (6)
O1	0.919 (1)	0.9876 (9)	0.9212 (7)	5.1 (3)	C45	0.644 (2)	1.301 (2)	1.147 (2)	9.5 (8)
O2	1.165 (1)	0.9331 (9)	0.8695 (8)	5.2 (3)	C51	1.368 (2)	1.534 (2)	0.452 (2)	7.5 (7)
O3	1.1149 (9)	1.0871 (8)	0.9743 (8)	5.1 (3)	C55	1.333 (2)	1.399 (2)	0.647 (1)	8.1 (7)
O4	0.887 (1)	1.1856 (9)	0.9649 (8)	5.5 (3)	C61	0.904 (2)	1.336 (2)	0.383 (1)	7.5 (7)
O5	1.1252 (9)	1.4184 (8)	0.4512 (8)	4.6 (3)	C65	0.8[illegible]5 (2)	1.193 (2)	0.577 (2)	7.3 (7)
O6	1.097 (1)	1.3064 (9)	0.6040 (8)	5.8 (4)	C101	0.686 (2)	1.118 (2)	0.931 (1)	7.0 (6)
O7	1.0587 (9)	0.8846 (8)	1.0373 (7)	4.5 (3)	C201	1.106 (2)	0.808 (2)	0.825 (1)	8.1 (8)
O8	0.9056 (8)	1.0189 (8)	1.0877 (7)	4.1 (3)	C301	1.360 (1)	0.996 (2)	0.914 (1)	6.1 (6)
O11	0.740 (1)	0.9182 (9)	1.0760 (9)	6.2 (4)	C401	1.022 (2)	1.287 (2)	1.039 (2)	6.9 (7)
O12	0.891 (1)	0.788 (1)	1.027 (1)	7.1 (4)	C501	1.273 (3)	1.130 (2)	0.550 (2)	11 (1)
O21	1.141 (1)	0.7199 (9)	0.9682 (8)	5.6 (3)	C601	0.915 (4)	1.460 (2)	0.699 (2)	13 (1)
O22	1.279 (1)	0.7950 (9)	0.9985 (8)	5.5 (3)					

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 4–6. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

compounds that have been reported previously,[4] these derivatives all have chlorine incorporated in some part of the structure. In doing so, some surprising features arise. It will be noted in the description to follow that it was not possible to locate hydrogen atoms experimentally. Therefore the presence of hydrogen is inferred from the arrangements of the non-hydrogen atoms and from the requirements of electrical neutrality.

Cluster **1** incorporating dicyclohexylphosphinate consists of the previously observed oxygen-capped cationic cluster type (Figure 1), which has been found in the presence of simple non-tin-containing anions[5-7] and a new structural form serving as the anion (Figure 2).

All three hexacoordinate tin atoms are equivalent in the cation. The tin atoms are connected pairwise by both a phosphinate bridge and a hydroxyl bridge, while the unique tricoordinate capping oxygen atom joins all three tin centers. The same holds true for the anion, which has two chemically equivalent hexacoordinate tin atoms. There are two phosphinate bridges and one hydroxyl bridge between the two tin centers. The presence of a hydroxyl bridge rather than an oxo bridge is required to maintain electrical neutrality of the compound overall. In the solid state, the relative orientation of the cation–anion pairs (Figure 3) suggests hydrogen-bonding interactions between hydroxyl hydrogen atoms of the cation and chlorine atoms of the anion. Relevant distances are O4–Cl2 = 3.049 (8) Å and O3–Cl1 = 3.212 (8) Å, where the Sn–O–Cl angles at O3 and O4 are consistent with hydroxyl hydrogen atoms which are roughly directed toward the adjacent chlorine atom.

Cluster **2**, prepared from di-*tert*-butylphosphinic acid, is extremely unusual in that it crystallizes in the rare space group *P*1 and is formally a cocrystalline species which contains two distinct compounds. The univalent cation in the first of these compounds is the protonated "crown" cluster (Figure 4) while the accompanying anion is a simple chloride ion. This cluster has been seen before with the di-*tert*-butylphosphinate anion.[8] In the crown, the four hexacoordinate tin atoms are chemically equivalent. They are connected pairwise by a phosphinate bridge and a hydroxyl bridge (O1–O4). In addition there are two alternating oxo bridges (O7 and O8) which form two four-membered Sn–O–Sn–O rings. Thus, while the four tin atoms are chemically equivalent there are two chemically distinct types of phosphorus atoms. The species thus far described would be neutral. Both the apparently unnecessary deformation of the framework which brings O7 and O8 into close proximity (2.58 (1) Å) and the need for a proton to main electrical neutrality overall suggest a hydrogen bonding interaction in which the proton is placed, perhaps symmetrically, between O7 and O8. With the addition of this proton, the crown cluster is a cationic species.

The second distinct compound which is present in crystals of **2** is a new neutral chlorine containing dimer (Figure 5). In this compound, the two equivalent hexacoordinate tin atoms are bridged by two hydroxyl groups forming a four-membered Sn–O–SnO ring. In addition the tin atoms are connected by two identical phosphinate bridges. This dimer is similar to the "butterfly" cluster $[n\text{-BuSn(OH)(O}_2\text{P(cyc)}_2)_2]_2$[6] (A), reported earlier. There are two differences. In the earlier butterfly cluster, the chlorine atoms of **2** are replaced by "dangling" phosphinate groups and the molecules are centrosymmetric dimers. In the present structure, the chlorine atoms have a "syn" disposition which is not consistent with C_i symmetry.

The relative orientations of the protonated crown cation, the chloride anion and the neutral dimer are shown in Figure 6. In this "side" view of the crown, the jagged nature of the eight-membered Sn_4O_4 ring which gives it its name is apparent. The chloride ion is "sandwiched" in between the other two species and is roughly equidistant from the four hydroxyl oxygen atoms, O1–O4, of the cation (3.11 (1)–3.19 (1) Å) as well as the hydroxyl oxygen atom, O6, of the dimer (3.13 (1) Å). Both the Cl–O distances and the Sn–O–Cl angles are consistent with O–H- - -Cl hydrogen-bonding interactions.

Cluster **3** is a chlorine-containing centrosymmetric dimer containing four tin centers (Figures 7 and 8) of two types as well as two types of phosphorus atoms in the molecule. Each central–terminal pair of tin atoms is joined by two bridging phosphinate groups and one bridging hydroxyl group, while the halves of the dimer are connected by a pair of phosphinate bridges between the two equivalent central tin atoms. The bridging hydroxyl group is trans to the *n*-Bu group for both types of tin centers. Except for this latter feature, the basic framework of the molecule is very

Table V. Selected Distances (Å) and Angles (deg) for $[(n\text{-BuSn(OH)O}_2\text{P}(t\text{-Bu})_2)_4\text{O}_2][\text{H}^+][\text{Cl}^-][(n\text{-BuSn(OH)ClO}_2\text{P}(t\text{-Bu})_2]_2$ (**2**)

Bond Distances

Sn1–O1	2.13 (1)	Sn4–O32	2.07 (1)	Sn2–C201	2.19 (3)	Sn6–O6	2.07 (1)
Sn1–O4	2.16 (1)	Sn4–O41	2.14 (1)	Sn3–O2	2.16 (1)	Sn6–O52	2.16 (2)
Sn1–O8	2.01 (1)	Sn4–C401	2.15 (2)	Sn3–O3	2.12 (1)	Sn6–O61	2.14 (2)
Sn1–O11	2.14 (1)	Sn5–C15	2.390 (6)	Sn3–O7	2.05 (1)	Sn6–C601	2.24 (3)
Sn1–O42	2.10 (1)	Sn5–O5	2.08 (1)	Sn3–O22	2.10 (1)	Cl1–O6	3.13 (1)
Sn1–C101	2.19 (2)	Sn5–O6	2.09 (1)	Sn3–O31	2.07 (1)	Cl1–O1	3.19 (1)
Sn2–O1	2.13 (1)	Sn5–O51	2.15 (1)	Sn3–C301	2.16 (2)	Cl1–O2	3.18 (1)
Sn2–O2	2.16 (1)	Sn5–O62	2.13 (1)	Sn4–O3	2.15 (1)	Cl1–O3	3.11 (2)
Sn2–O7	2.04 (1)	Sn5–C501	2.15 (2)	Sn4–O4	2.19 (1)	Cl1–O4	3.16 (1)
Sn2–O12	2.08 (1)	Sn6–C16	2.402 (7)	Sn4–O8	2.06 (1)	O7–O8	2.58 (1)
Sn2–O21	2.17 (1)	Sn6–O5	2.04 (1)				

Bond Angles

O1–Sn1–O4	90.8 (5)	O7–Sn2–O12	90.1 (6)	O4–Sn4–O32	168.2 (6)	C16–Sn6–O5	87.6 (3)
O1–Sn1–O8	87.9 (5)	O7–Sn2–O21	83.4 (5)	O4–Sn4–O41	90.7 (5)	C16–Sn6–O6	162.0 (4)
O1–Sn1–O11	86.5 (5)	O7–Sn2–C201	172.0 (7)	O4–Sn4–C401	95.5 (8)	C16–Sn6–O52	92.8 (4)
O1–Sn1–O42	173.7 (5)	O12–Sn2–O21	94.3 (5)	O8–Sn4–O32	92.6 (5)	C16–Sn6–O61	94.8 (4)
O1–Sn1–C101	95.0 (6)	O12–Sn2–C201	95.4 (8)	O8–Sn4–O41	86.3 (5)	C16–Sn6–C601	101.1 (8)
O4–Sn1–O8	78.0 (5)	O21–Sn2–C201	90.4 (8)	O8–Sn4–C401	170.0 (7)	O5–Sn6–O6	74.4 (4)
O4–Sn1–O11	167.7 (5)	O2–Sn3–O3	91.2 (5)	O32–Sn4–O41	92.5 (5)	O5–Sn6–O52	80.9 (5)
O4–Sn1–O42	87.3 (5)	O2–Sn3–O7	76.7 (5)	O32–Sn4–C401	96.0 (8)	O5–Sn6–O61	80.7 (5)
O4–Sn1–C101	96.4 (7)	O2–Sn3–O22	88.0 (5)	O41–Sn4–C401	88.2 (7)	O5–Sn6–C601	171.0 (8)
O8–Sn1–O11	89.9 (5)	O2–Sn3–O31	166.5 (5)	C15–Sn5–O5	85.5 (3)	O6–Sn6–O52	84.7 (5)
O8–Sn1–O42	85.8 (5)	O2–Sn3–C301	96.7 (7)	C15–Sn5–O6	158.9 (4)	O6–Sn6–O61	82.3 (6)
O8–Sn1–C101	173.7 (7)	O3–Sn3–O7	89.1 (4)	C15–Sn5–O51	93.3 (3)	O6–Sn6–C601	96.9 (8)
O11–Sn1–O42	94.0 (5)	O3–Sn3–O22	175.1 (5)	C15–Sn5–O62	93.3 (4)	O52–Sn6–O61	159.8 (5)
O11–Sn1–C101	95.8 (7)	O3–Sn3–O31	88.0 (5)	C15–Sn5–C501	104.3 (9)	O52–Sn6–C601	101 (1)
O42–Sn1–C101	91.2 (6)	O3–Sn3–C301	94.3 (6)	O5–Sn5–O6	73.4 (4)	O61–Sn6–C601	96 (1)
O1–Sn2–O2	89.6 (4)	O7–Sn3–O22	86.0 (4)	O5–Sn5–O51	81.5 (4)	Sn1–O1–Sn2	132.4 (5)
O1–Sn2–O7	88.5 (5)	O7–Sn3–O31	89.8 (5)	O5–Sn5–O62	81.0 (5)	Sn2–O2–Sn3	98.7 (4)
O1–Sn2–O12	86.3 (5)	O7–Sn3–C301	172.7 (8)	O5–Sn5–C501	169 (1)	Sn3–O3–Sn4	130.6 (5)
O1–Sn2–O21	171.8 (6)	O22–Sn3–O31	91.6 (5)	O6–Sn5–O51	84.1 (5)	Sn1–O4–Sn4	97.1 (4)
O1–Sn2–C201	97.7 (8)	O22–Sn3–C301	90.6 (6)	O6–Sn5–O62	83.3 (6)	Sn5–O5–Sn6	106.8 (5)
O2–Sn2–O7	76.8 (5)	O31–Sn3–C301	96.8 (8)	O6–Sn5–C501	96.7 (9)	Sn1–O8–Sn4	106.9 (4)
O2–Sn2–O12	166.4 (6)	O3–Sn4–O4	88.1 (5)	Sn5–O6–Sn6	105.3 (5)	Sn2–O7–Sn3	106.6 (4)
O2–Sn2–O21	88.0 (4)	O3–Sn4–O8	88.5 (1)	Sn2–O1–Cl1	106.5 (4)	Sn4–O3–Cl1	107.8 (5)
O2–Sn2–C201	98.1 (7)	O3–Sn4–O32	87.7 (5)	Sn1–O1–Cl1	104.9 (5)	Sn3–O3–Cl1	105.9 (5)
O3–Sn4–O41	174.8 (5)	O51–Sn5–O62	160.8 (4)	Sn2–O2–Cl1	105.9 (4)	Sn1–O4–Cl1	105.1 (5)
O3–Sn4–C401	96.9 (6)	O51–Sn5–C501	94 (1)	Sn3–O2–Cl1	102.8 (5)	Sn4–O4–Cl1	105.3 (5)
O4–Sn4–O8	76.2 (4)	O62–Sn5–C501	102 (1)	Sn5–O6–Cl1	123.6 (5)	Sn6–O6–Cl1	131.1 (5)

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figures 4–6.

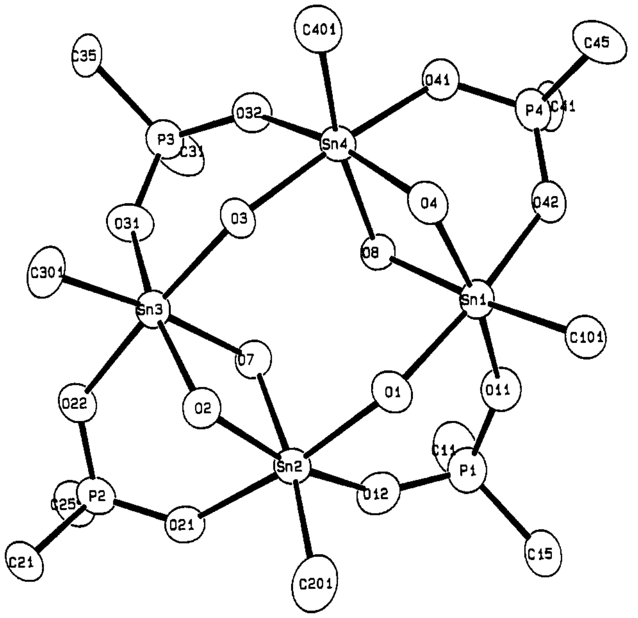


Figure 4. ORTEP plot of the tetranuclear "crown" cluster in $[(n\text{-BuSn(OH)O}_2\text{P-}t\text{-Bu}_2)_4\text{O}_2][\text{H}^+][\text{Cl}^-][n\text{-BuSn(OH)ClO}_2\text{P-}t\text{-Bu}_2]_2$ (**2**), with thermal ellipsoids at the 30% probability level. Pendant atoms of the *n*-Bu groups (bound to C101, C201, C301, and C401) and of the *t*-Bu groups (bound to C11, C15, C21, C25, C31, C35, C41, and C45) are omitted for clarity.

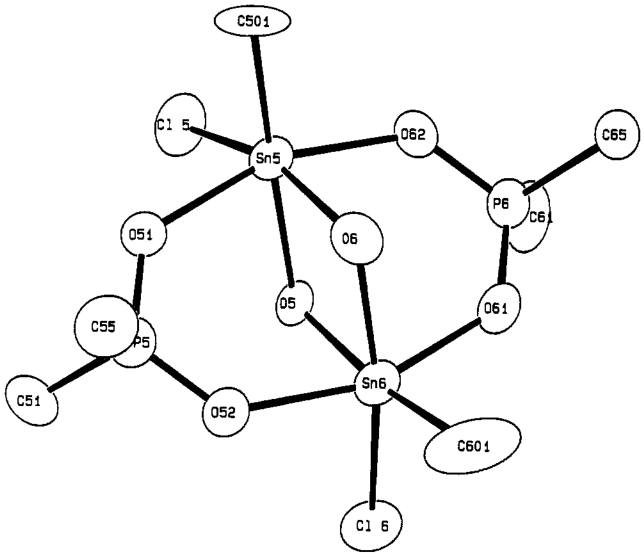


Figure 5. ORTEP plot of the neutral dimer in $[(n\text{-BuSn(OH)O}_2\text{P-}t\text{-Bu}_2)_4\text{O}_2][\text{H}^+][\text{Cl}^-][n\text{-BuSn(OH)ClO}_2\text{P-}t\text{-Bu}_2]_2$ (**2**), with thermal ellipsoids at the 30% probability level. Pendant atoms of the *n*-Bu groups (bound to C501 and C601) and of the *t*-Bu groups (bound to C51, C55, C61, and C65) are omitted for clarity.

similar to that found in $[(n\text{-Bu})_2\text{Sn}_2(\text{OSPPh}_2)_2(\text{OH})(\text{O}_2\text{PPh}_2)_3]_2 \cdot 8\text{C}_6\text{H}_6$ (**B**)[8] in which the monodentate thiophosphinate groups replace the chlorine atoms in **3**, but in which the *n*-Bu groups on the terminal tin atoms in **B** are cis rather than trans to the bridging hydroxyl group as found in **3**.

It is interesting to note the structural similarity between the anion in **1** and the asymmetric unit in the dimer in **3**. If O11 and

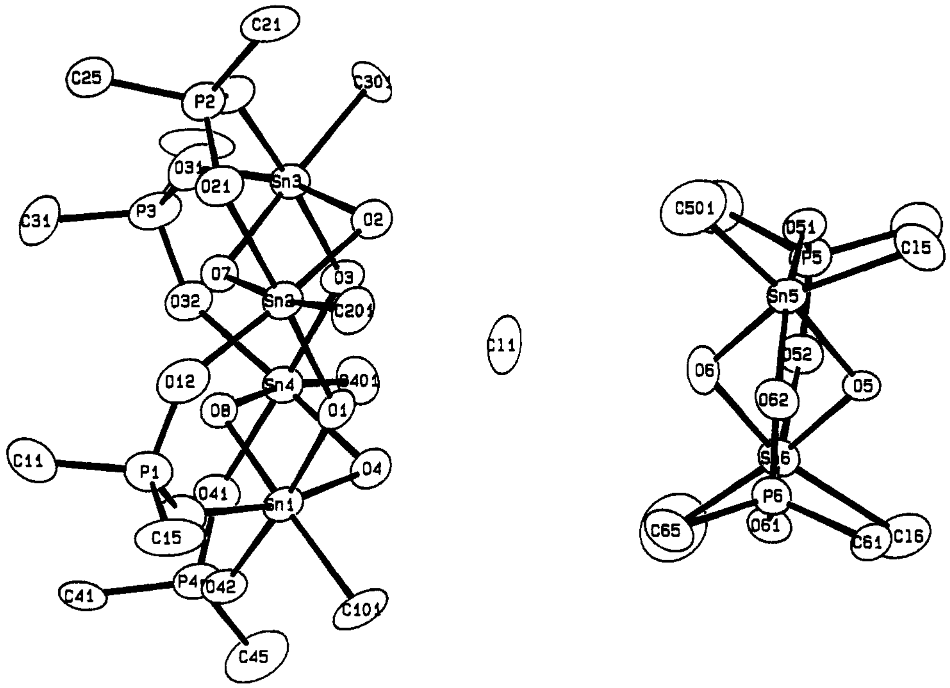


Figure 6. ORTEP plot showing the relative orientation of the fragments of the asymmetric unit in $[(n\text{-BuSn(OH)O}_2\text{P-}t\text{-Bu}_2)_4\text{O}_2][\text{H}^+][\text{Cl}^-][n\text{-BuSn(OH)ClO}_2\text{P-}t\text{-Bu}_2]_2$ (**2**).

Table VI. Selected Atomic Coordinates in Crystalline $[(n\text{-Bu})_2\text{Sn}_2\text{Cl}_2(\text{OH})(\text{O}_2\text{PPh}_2)_3]_2\cdot 2\text{CH}_2\text{Cl}_2$ (**3**)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
Sn1	0.01675 (3)	0.01002 (3)	0.10081 (2)	2.96 (1)
Sn2	0.06851 (3)	0.22524 (4)	0.14509 (3)	3.74 (1)
Cl1	0.1510 (1)	0.2357 (2)	0.0885 (1)	5.29 (7)
Cl2	0.0139 (1)	0.3142 (2)	0.0889 (1)	4.98 (6)
P1	−0.0906 (1)	0.0397 (2)	0.01278 (9)	3.01 (5)
P2	−0.0426 (1)	0.1218 (2)	0.19548 (9)	3.45 (5)
P3	0.1251 (1)	0.0420 (2)	0.1813 (1)	3.58 (6)
O1	0.0434 (3)	0.1295 (3)	0.0950 (2)	3.0 (1)
O11	−0.0538 (2)	0.0523 (4)	0.0598 (2)	3.5 (1)
O12	−0.0616 (3)	−0.0062 (4)	−0.0303 (2)	3.6 (1)
O21	−0.0218 (3)	0.0446 (3)	0.1699 (2)	3.5 (1)
O22	−0.0081 (3)	0.1969 (4)	0.1825 (3)	4.2 (1)
O31	0.0927 (3)	−0.0082 (4)	0.1420 (2)	3.8 (1)
O32	0.1076 (3)	0.1288 (4)	0.1867 (2)	4.1 (1)
C1	−0.0043 (4)	−0.1130 (6)	0.1033 (5)	4.9 (3)
C5	0.0935 (5)	0.3112 (6)	0.2030 (4)	5.6 (3)
C11	−0.1122 (4)	0.1377 (6)	−0.0080 (3)	3.5 (2)
C21	−0.1525 (4)	−0.0143 (5)	0.0302 (4)	3.6 (2)
C31	−0.0415 (4)	0.1053 (6)	0.2642 (4)	3.8 (2)
C41	−0.1153 (4)	0.1414 (6)	0.1779 (4)	4.2 (2)
C51	0.1180 (4)	−0.0040 (5)	0.2434 (4)	4.0 (2)
C61	0.1981 (4)	0.0358 (6)	0.1629 (4)	4.2 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 7 and 8. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VII. Selected Distances (Å) and Angles (deg) for $[(n\text{-Bu})_2\text{Sn}_2\text{Cl}_2(\text{OH})(\text{O}_2\text{PPh}_2)_3]_2\cdot 2\text{CH}_2\text{Cl}_2$ (**3**)[a]

	Bond Distances		
Sn1–O1	2.087 (5)	Sn2–Cl2	2.441 (3)
Sn1–O11	2.093 (6)	Sn2–O1	2.136 (5)
Sn1–O12	2.111 (6)	Sn2–O22	2.102 (7)
Sn1–O21	2.087 (6)	Sn2–O32	2.140 (6)
Sn1–O31	2.105 (6)	Sn2–C5	2.15 (1)
Sn1–C1	2.10 (1)	Sn2–Cl1	2.440 (3)
	Bond Angles		
O1–Sn1–O11	83.3 (2)	Cl1–Sn2–O1	84.7 (2)
O1–Sn1–O12	79.4 (2)	Cl1–Sn2–O22	167.6 (2)
O1–Sn1–O21	86.1 (2)	Cl1–Sn2–O32	90.8 (2)
O1–Sn1–O31	85.3 (2)	Cl1–Sn2–C5	98.9 (3)
O1–Sn1–C1	175.4 (3)	Cl2–Sn2–O1	86.7 (2)
O11–Sn1–O12	88.1 (2)	Cl2–Sn2–O22	87.6 (2)
O11–Sn1–O21	89.9 (2)	Cl2–Sn2–O32	168.8 (2)
O11–Sn1–O31	168.5 (2)	Cl2–Sn2–C5	99.1 (3)
O11–Sn1–C1	98.9 (3)	O1–Sn2–O22	82.9 (2)
O12–Sn1–O21	165.4 (2)	O1–Sn2–O32	82.5 (2)
O12–Sn1–O31	90.5 (2)	O1–Sn2–C5	173.1 (3)
O12–Sn1–C1	96.6 (3)	O22–Sn2–O32	88.3 (2)
O21–Sn1–O31	88.5 (2)	O22–Sn2–C5	93.5 (4)
O21–Sn1–C1	97.9 (3)	O32–Sn2–C5	91.5 (3)
O31–Sn1–C1	92.5 (3)	Sn1–O1–Sn2	138.3 (3)
Cl1–Sn2–Cl2	91.0 (1)		

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figures 7 and 8.

O12 of the phosphinate ligands in **3** are replaced by chlorine ligand atoms, then the anion in **1** results.

NMR Data. ^{119}Sn and ^{31}P NMR spectra of **1** and **2** were recorded in C_6D_6 solution, whereas $CDCl_3$ was the solvent for **3** and **4**. For **1** and **2** difficulty was experienced in obtaining reproducible ^{119}Sn and ^{31}P NMR spectra. For **1** in $CDCl_3$, the anionic portion of the compound apparently undergoes fast exchange at 20 °C as noted by the fact that resonances attributable to it are not seen in either the ^{119}Sn or ^{31}P NMR spectra. Also, there is a significant shift with time in the ^{119}Sn NMR resonance associated with the cationic portion. Most likely, the presence of adventious moisture is responsible.

When the ^{119}Sn NMR spectrum for **2** was recorded in $CDCl_3$, the signal due to the dimer portion of the molecule was not observed, possibly because of some kind of exchange phenomenon. However, the crown portion could easily be seen as a doublet of doublets centered at −535.69 ppm (^2J(Sn–O–P) = 149.7, 192.8 Hz). The latter spectral data agrees favorably with that obtained in $CDCl_3$ for the crown portion of **2**. Similarly the ^{31}P NMR pattern in $CDCl_3$ for **2** corresponded only to the crown portion. In both **1** and **2**, it is the chlorine-containing portions which indicate exchange behavior, thus implicating rupture of Sn–Cl bonds as the cause. This difficulty is not experienced in recording NMR spectra for either **3** or **4** in $CDCl_3$ solution. Organotin derivative **4** consists of an O-capped cluster void of chlorine. The extended structure for **3** contains chlorine atoms but has the least bulky phosphinate substituents, phenyl, compared to cyclohexyl and *tert*-butyl groups for **1** and **2**, respectively.

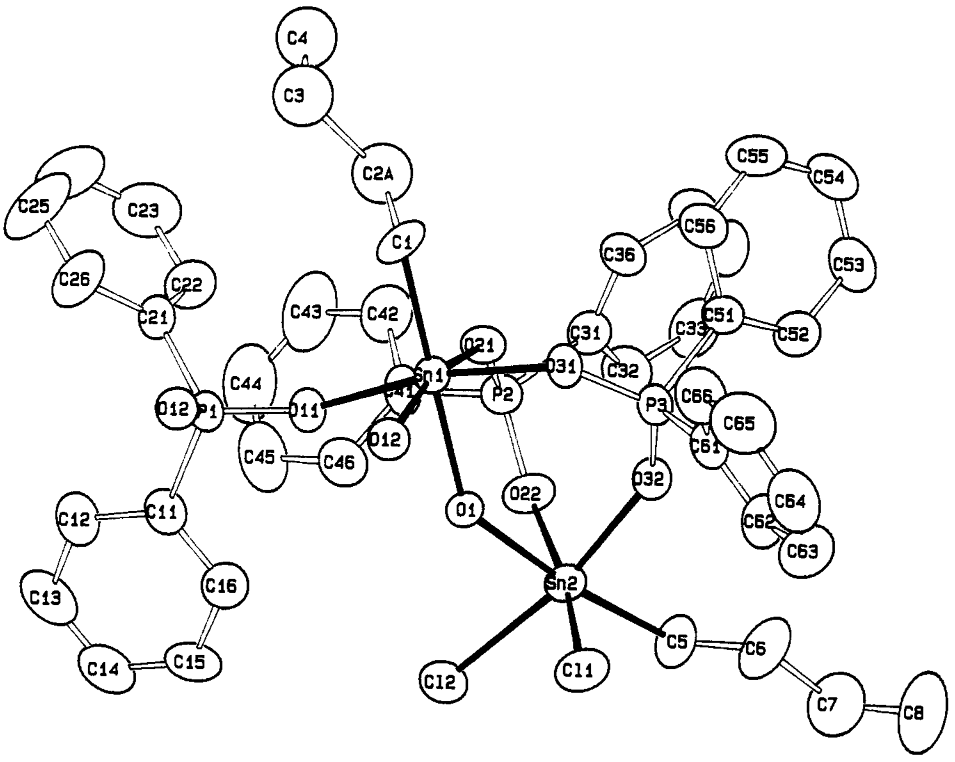


Figure 7. ORTEP plot showing the asymmetric unit for $[n\text{-Bu}_2\text{Sn}_2\text{Cl}_2(\text{OH})(\text{O}_2\text{PPh}_2)_3]_2{\cdot}2\text{CH}_2\text{Cl}_2$ (3), with thermal ellipsoids at the 40% probability level. A symmetry related O12 $(-x, -y, -z)$ is shown to complete the coordination of Sn1. The methylene chloride of solvation and phenyl group hydrogen atoms are omitted for clarity.

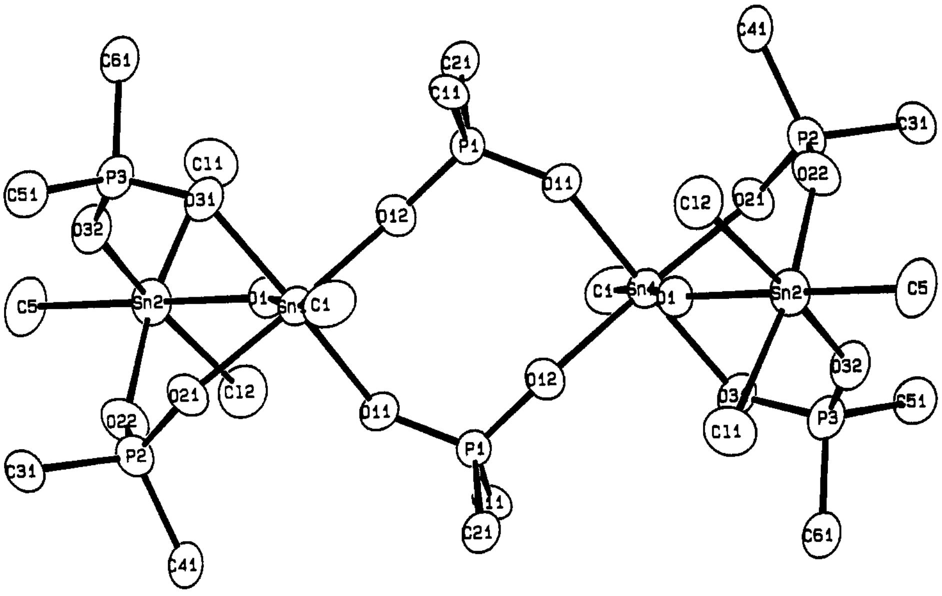


Figure 8. ORTEP plot showing the framework of the centrosymmetric dimer in $[n\text{-Bu}_2\text{Sn}_2\text{Cl}_2(\text{OH})(\text{O}_2\text{PPh}_2)_3]_2{\cdot}2\text{CH}_2\text{Cl}_2$ (3). Thermal ellipsoids are at the 40% probability level. Atoms with the same label are inversion related $(-x, -y, -z)$.

Analysis of the NMR data for **1–4** supports retention of the structural types in solution that were established by X-ray analysis in the solid state. The ^{119}Sn NMR spectrum for **1** shows a triplet at −517.29 ppm (^2J(Sn–O–P) = 136.0 Hz0 and an additional triplet of the same intensity at −525.81 ppm (^2J(Sn–O–P) = 209.1 Hz). The former resonance is assigned to the O-capped cation and the latter to the anion on the basis of previous ^{119}Sn chemical shift and coupling constant data for other O-capped clusters,[5-7] particularly the ^2J(Sn–O–P) coupling constants. Previous ^{119}Sn chemical shifts and ^2J coupling constants for O-capped clusters average near 500 ppm and 132 Hz, respectively. For the mesityl O-capped cluster **4**, the comparative values are −508.0 ppm and 159.5 Hz. The ^{31}P NMR spectrum of **1** reveals two signals in the ratio of 3:2, each with tin satellite structure. Consistent with the ratio of phosphorus atoms in the two portions of **1**, the higher intensity signal at 55.48 ppm is assigned to the O-capped cation and the lower intensity one at 50.89 ppm to the anionic unit. Here the ^2J coupling constants confirm the assignments made for the ^{119}Sn resonances. Both the ^{119}Sn and ^{31}P spectra show the presence of the respective equivalent atoms in each of the two components of **1** consistent with that found in the X-ray structure.

The ^{119}Sn NMR spectrum of **2** also indicates equivalent tin atoms in both the crown and butterfly (dinuclear tin) species that make up its composition. A ^{119}Sn signal at −533.2 ppm (^2J(Sn–O–P) = 148.4 and 191.4 Hz) appearing as a doublet of doublets as expected for two kinds of phosphorus atoms is assigned to the crown part of **2** while a broad signal at −499.0 ppm is assigned

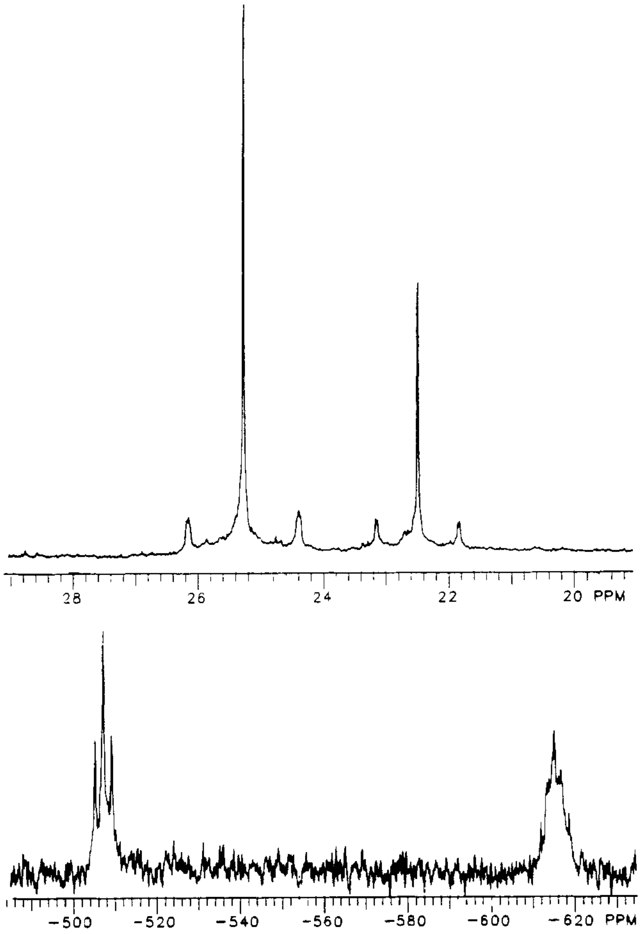


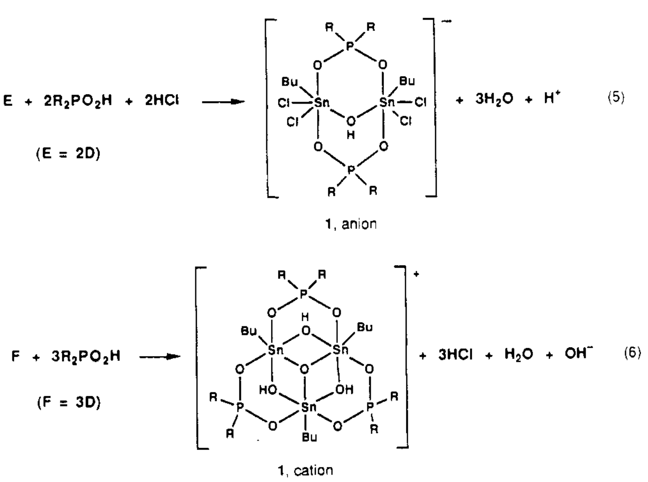
Figure 9. ^{31}P (upper) and ^{119}Sn (lower) NMR spectra of [n-$Bu_2Sn_2Cl_2(OH)(O_2PPh_2)_3]_2 \cdot 2CH_2Cl_2$ (**3**) in $CDCl_3$.

to the dinuclear tin species. A related cluster, [(n-$BuSn(OH)O_2P(t\text{-}Bu)_2)_4O_2$][H][$O_2P(t\text{-}Bu)_2$][8] (C), containing the same crown portion as **2**, has a similar ^{119}Sn spectrum with a signal at -535.3 ppm (dd, ^2J(Sn-O-P) = 145 and 181 Hz). The ^{31}P NMR spectra of **2** and the previous crown cluster, C, also are very similar, each showing two closely spaced signals with tin satellites as expected for the presence of two pairs of phosphorus atoms in different environments in the crown portion. The ^{31}P NMR signals for **2** at 59.40 and 59.55 ppm with Sn-O-P coupling constants of 147.0 and 183.0 Hz compare with shifts for C of 58.54 and 58.56 ppm and average Sn-O-P couplings of 140.6 and 186.3 Hz. An additional ^{31}P signal at 64.0 ppm is in the range found for the related butterfly form, A,[6] at 56.02 ppm.

The extended cluster, **3**, like the closely-related composition B,[8] has two pairs of tin atoms which differ from each other, a central pair and a terminal pair. Figure 9 displays ^{31}P and ^{119}Sn NMR spectra for **3**. The two ^{119}Sn signals of equal intensity, consistent with the solid-state structure, are assigned by comparison of coupling constants with that obtained in the ^{31}P spectrum. The latter shows two signals with tin satellites where the higher field peak for **3** at 25.27 ppm (^2J(Sn-O-P) = 213.2 Hz) has half the intensity of the peak at 22.49 ppm (^2J(Sn-O-P) = 162.2, 155.3 Hz). As a consequence, the ^{119}Sn signal at -507.39 ppm (^2J(Sn-O-P) = 222.8 Hz) is assigned to the terminal tin atoms and the ^{119}Sn signal at -615.36 ppm appearing as a multiplet is assigned to the central tins. These compare with ^{119}Sn signals of -575.0 and -614.0 ppm for B,[8] which has a more complex ^{31}P spectrum due to the presence of both phosphinate and thiophosphinate ligands of different types.

The ^{119}Sn and ^{31}P spectra of **4** are entirely consistent with its composition indicating the formation of an oxygen-capped cluster. One ^{119}Sn resonance is present with a characteristic ^2J(Sn-O-P) triplet pattern associated with the attachment of two phosphinate units to each equivalent tin atom. As expected for this type of cationic cluster[5-7] with chloride as the anion, only one ^{31}P signal is present.

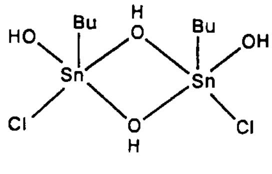
Scheme I[a]

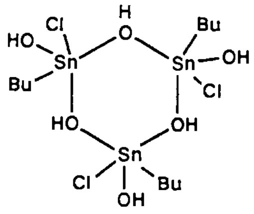


[a] R = cyc.

Finally, the ^1H NMR spectra obtained on all these compositions, **1-4**, give signals assignable to the different types of alkyl and aromatic functions consistent with the structural representations supported by the more diagnostic ^{119}Sn and ^{31}P data. However, only in the case of **1** was a signal assignable to a hydroxyl proton, 6.13 ppm. It is assumed that proton exchange prevented its observance in the other cluster formations.

Cluster Formation Schemes. Feasible reaction schemes leading to the formation of **1-3** possessing different structures but originating from the common reactant n-$BuSn(OH)_2Cl$ (D) are suggested by reaction of feasible dimer and trimer forms of D with phosphinates in condensation and rearrangement reactions. Earlier work on structures of compositions related to reactant D, in particular [n-$BuSn(OH)Cl_2(OH_2)]_2$[16] which has a hydroxy-bridged dimeric structure, suggest that D most likely possesses a dimeric structure, E. A water molecule may occupy a coordination site to give the tin(IV) its usual hexacoordinated state. If we invoke the formation of the corresponding trimeric arrangement, F, as a reaction intermediate, plausible reaction schemes for the formation of **1-3** may be rationally developed.


E


F

Using the E and F formulations of the reactant D, the formation of cluster 1 is readily visualized to result in Scheme I according to eqs 5 and 6. The sum of eqs 5 and 6 corresponds to eq 1 governing the reaction stoichiometry for the preparation of **1**.

The crown cluster-chloro butterfly pair comprising **2** may be considered to originate from the bridged form E of the reactant D. Scheme II illustrates the possible formation of both components of **2** by this route. The summation of reactions 7-9 is the stoichiometry expressed in eq 2 for the formation of **2**.

The formation of the extended cluster **3** may follow the course outlined for the route leading to the anion of **1** given in eq 5. As noted earlier, formal replacement of the two central phosphinates

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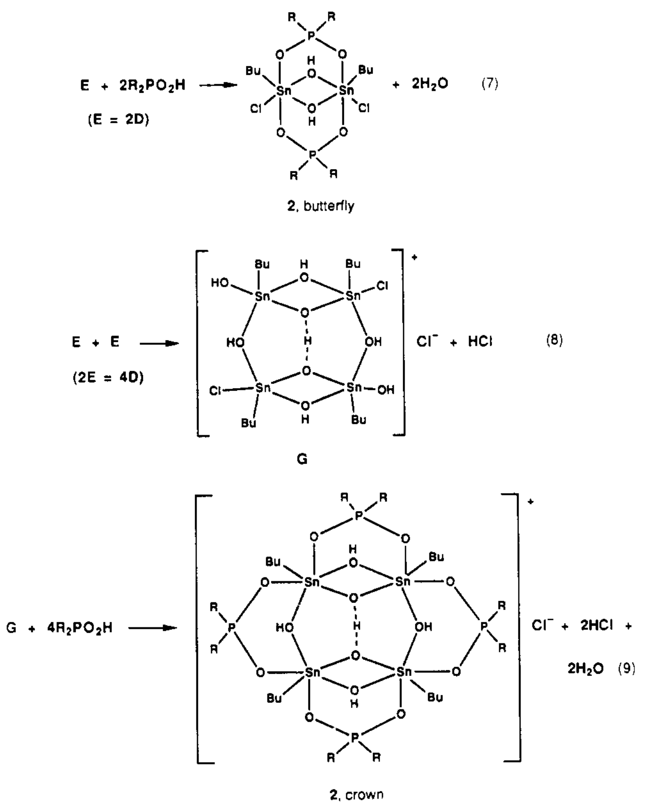
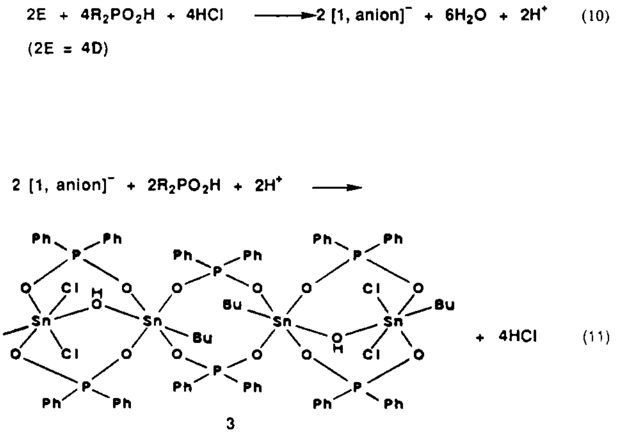
[16] Holmes, R. R.; Shafeizad, S.; Chandrasekhar, V.; Holmes, J. M.; Day, R. O. *J. Am. Chem. Soc.* **1988**, *110*, 1174-1180.

Scheme II[a]



[a] R = *t*-Bu.

Scheme III[a]



[a] R = Ph.

of **3** by four chlorine atoms results in two anions of **1**. Hence, a suggested route for the formation of **3** starts with the latter anion and proceeds simply as indicated in eqs 10 and 11 of Scheme III. Addition of eqs 10 and 11 is the stoichiometry expressed in eq 3 for the formation of **3**.

The formation of clusters **1**–**3** with varied structures resulting from the reaction of phosphinic acids with the common reagent *n*-BuSn(OH)$_2$Cl has a basis in previous work. Known O-capped cationic structures similar to that present in **1** have been formed with the phosphinic acids R$_2$PO$_2$H where R = cyclohexyl,[6] benzyl,[6] and phenyl,[7] and with diphenylphosphoric acid, (PhO)$_2$PO$_2$H.[5] This structural type is more prevalent than most other cluster structural types and can be prepared by hydrolysis reactions of other cluster forms, e.g., from the butterfly R = cyclohexyl and from the cube (R = benzyl).[6] Previously two crown clusters have been prepared[8] both involving (*t*-Bu)$_2$PO$_2$H. Formulation C,[8] referred to earlier, and [(MeSn(O)O$_2$P(*t*-Bu)$_2$)(MeSn(OH)(OMe)O$_2$P(*t*-Bu)$_2$]$_2$[H][O$_2$P(*t*-Bu)$_2$]·4MeOH·2H$_2$O (H),[8] both incorporating the di-*tert*-butylphosphinate ligand, are the only examples of structures containing the cationic crown structure similar to that in the cationic portion of **2**. It is noted that formulation of the cationic crown cluster in C and **2** are the same. Only one other cluster structure analogous to the extended form in **3** has been reported, B[8] referred to above. It like **3** results from use of Ph$_2$PO$_2$H. Also one other "butterfly" structure, A,[6] is known, but in this case, the formulation is based on dicyclohexyl phosphinic acid rather than the di-*tert*-butylphosphinate present as the other neutral component in the complex cluster **2**.

Overall their is a remarkable similarity in the phosphinic acids that yield the various cluster components in **1**–**3** and in analogous clusters that have been prepared in other ways. For example, the cationic portion of the crown cluster represented in **2** has been prepared by three other routes;[8] i.e., B was prepared by one in which *n*-BuSn(O)OH acid is condensed with the phosphinic acid (*t*-Bu)$_2$PO$_2$H, a second in which *n*-BuSnCl$_3$ was reacted in a hydrolysis reaction with the silver salt of the phosphinic acid, and a third preparation wherein the prismane [*n*-BuSn(O)O$_2$CMe]$_6$ underwent hydrolysis with the displacement of the acetate ligand by the phosphinate group. This suggests that a special stability is imparted to the crown cluster when the bulky *t*-Bu groups are present. Their presence also apparently is sufficient to stabilize the chlorobutterfly cluster found in **2**.

Similarly, the extended cluster present in **3** and B[8] incorporates the least sterically demanding phosphinate, Ph$_2$PO$_2^-$, as a ligand. As pointed out above, this cluster type is closely related to the new anionic form in **1** containing dicyclohexylphosphinate groups in place of the diphenylphosphinates. The cyclohexyl group, intermediate in steric properties between phenyl and *tert*-butyl and present in the O-capped cationic portion of **1**, may serve to stabilize the anion of **1** containing this group.

In conclusion, one may expect to form other new kinds of oxotin cluster formulations based on reactions of *n*-BuSn(OH)$_2$Cl (which appears to be a versatile reagent) and variations of the type of phosphorus acid used in the synthesis. It remains to ascertain the precise role steric effects play in controlling cluster formation.

Acknowledgment. We gratefully acknowledge financial support by the National Science Foundation (Grant CHE 8504737) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and additional bond lengths and angles for **1**–**3** (Tables S1–S3 for **1**, Tables S4–S6 for **2**, and Tables S7–S9 for **3**) and in addition hydrogen atom parameters (Table S10) for **3** (44 pages). Ordering information is given on any current masthead page.