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Intramolecularly Formed Pentacoordinated Structures of Triphenyltin Esters of Salicylic Acid, *o*-Anisic Acid, and *p*-Methylthiobenzoic acid[1,2]

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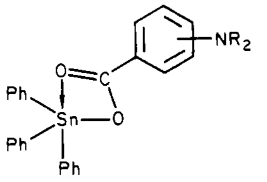
Triphenyltin esters were formed by the reaction of bis(triphenyltin) oxide with salicylic acid, *o*-anisic acid, and *p*-methylthiobenzoic acid, **6–8**, respectively. X-ray analysis revealed pentacoordinated structures containing Ph$_3$Sn coordinated to the carboxylate group for **7** and **8**. The structural distortion for each is a displacement from the tetrahedron toward a trigonal bipyramid. For **6**, the structure contains an intramolecular oxygen atom interaction, in addition to hydrogen-bonding effects, with a resultant geometry close to tetrahedral. Infrared data confirm that carboxylate coordination occurs in solution. Factors influencing the appearance of the discrete five-coordinated form **6–8** relative to five-coordinated tin in a chain arrangement for related derivatives is discussed. For **6**, the monoclinic space group $P2_1/c$ ($Z = 4$) was obtained with a = 13.318 (6) Å, b = 12.113 (2) Å, c = 14.590 (4) Å, and β = 116.47 (3)°. Refinement gave $R = 0.022$ and $R_w = 0.032$. **7** crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$) with a = 10.632 (2) Å, b = 11.452 (2) Å, c = 11.719 (2) Å, α = 62.86 (2)°, β = 71.95 (2)°, and γ = 62.31 (2)°. Refinement gave $R = 0.024$ and $R_w = 0.041$. For **8**, the triclinic space group $P\bar{1}$ resulted with a = 8.814 (1) Å, b = 9.816 (1) Å, c = 14.430 (3) Å, α = 89.39 (1)°, β = 80.19 (1)°, and γ = 68.89 (1)°. Refinement gave $R = 0.025$ and $R_w = 0.040$.

Introduction

To aid in understanding the biochemical action of triorganotin derivatives, it is felt that the coordination chemistry of tin(IV) toward O-, S-, and N-containing ligands requires further exploration. In the previous paper,[1] we have contrasted the role of oxygen and nitrogen atoms as ligands by examining the interaction of triphenyltin with anthranilic acid, its N-methylated derivative, and the paraamino isomer. The resultant complexes have the general representation **1a–c**, respectively, where R = H or CH$_3$. A five-coordinated tin atom is present as a result of intramolecular chelation.



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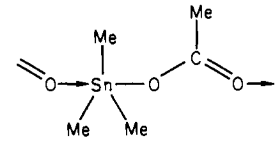
This discrete molecular formulation **1** contrasts with the chain polymeric, structure **2** found for trimethyltin acetate[4] formed by intermolecular chelation of the carboxylate groups.



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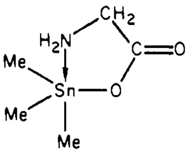
Trimethyltin hydroxide[5] and triphenyltin hydroxide[6] among others have this chain polymeric arrangement as well, with the most electronegative atoms appearing at the axial sites of a trigonal bipyramid. Trimethyltin glycinate Me$_3$Sn(O$_2$CCH$_2$NH$_2$) has the chain structure,[7] but the axial positions are occupied by only one of the carboxylate oxygen atoms and the less electronegative nitrogen atom. For the triphenyltin esters of the anthranilic acid analogues (**1**),[1] it is reasonable that the four-membered ring spans the axial–equatorial positions, leaving one of the less electronegative groups at the other axial position of a trigonal bipyramid.

The observance of the chain structure for trimethyltin glycinate[7] implies that the unobserved conformations **3** and **4** are less stable, in addition to the chain **2** containing the



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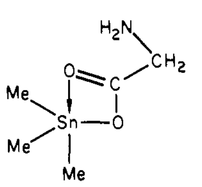

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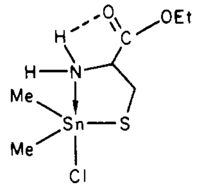
coordinating carboxylate groups. X-ray analysis of (ethyl L-cysteinato-*S*,*N*)chlorodimethyltin reveals a structure, **5**,[8]



5

analogous to **3** but containing the more electronegative axial chlorine atom. Obviously, several factors contribute in determining the relative stability of the chain polymer vs. the discrete molecular structural representations of intramolecularly bound, five-coordinated tin(IV) derivatives.

Poder and Sams[9] have shown, for example, that trimethyltin carboxylates in the chain polymeric arrangement experience an increasing difference between the two Sn–O bond lengths as the acidity of the carboxylic acid increases. In agreement, Chih and Penfold[4] found a 0.28 (2) Å difference between the

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[1] Pentacoordinated Molecules. 57. Part 56: Swisher, R. G.; Vollano, J. F.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* preceding paper in this issue.

[2] Presented in part at the Fourth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin, and Lead, Montreal, Quebec, Canada, Aug 8–11, 1983; see Abstract P2.

[3] Represents in part material from; Vollano, J. F. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1982.

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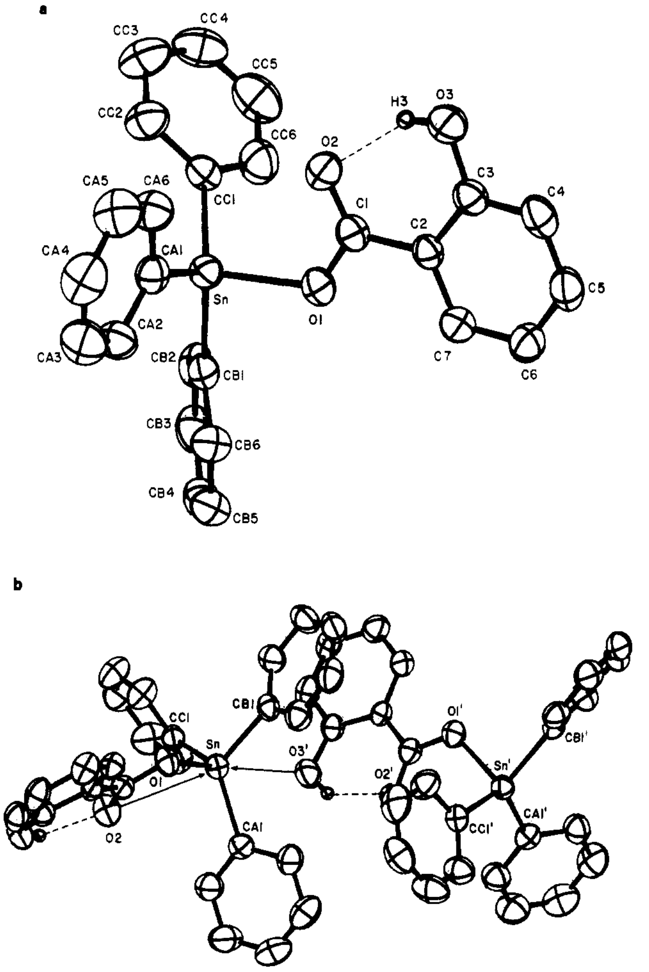

Figure 1. ORTEP plot of $Ph_3Sn[o\text{-}(OH)C_6H_4CO_2]$ (**6**) with thermal ellipsoids shown at the 50% probability level. The hydroxyl hydrogen atom is shown as a sphere of arbitrary radius. The remaining hydrogen atoms have been omitted for purposes of clarity. (b) ORTEP plot of **6**, including a *C*-glide related molecule (prime, x, $^1/_2 - y$, $^1/_2 + z$) to show the full coordination sphere of the Sn atom.

two Sn–O bond lengths in the chain polymeric structure of the trimethyltin trifluoroacetate. This compares with a 0.186 (5) Å difference in trimethyltin acetate. The respective pK values are 0.23 and 4.75. The structural representation **1** normally has one considerably longer Sn–O bond length than observed for Sn–O bonds in the chain structure **2**.[10,11] As an additional factor, hydrogen bonding, which is present in many of the triorganotin derivatives under discussion, also shows an influence by lengthening the tin–ligand bond for affected ligands.[10,11]

In the present study, we report the interaction of triphenyltin oxide with salicylic acid, *o*-anisic acid, *p*-methylthiobenzoic acid, and thiosalicylic acid. The structures of the resultant esters for the first three acids were determined by X-ray crystallography. To establish conformational changes between the solid and solution states, infrared and NMR measurements were performed. These substances form a related series to the anthranilic acid analogues studied in the preceding paper,[1] and this represents the first comprehensive structural study of a series of (benzoato)triphenyltin derivatives. The results illustrate the competitive role of biologically interesting ligands, O, S, and N in forming pentacoordinated tin structures.

Experimental Section

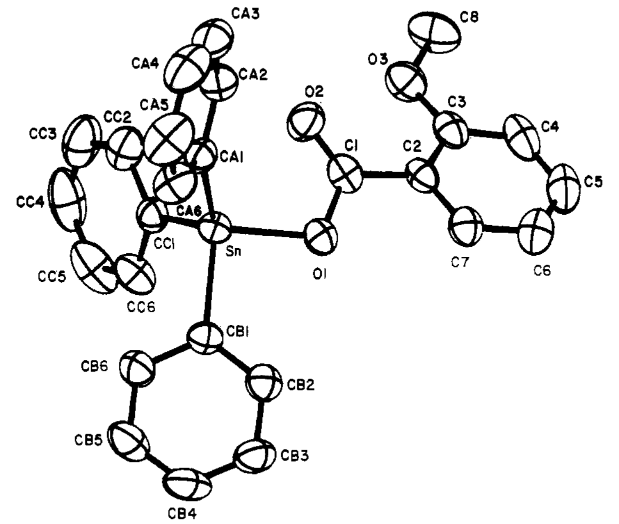

Figure 2. ORTEP plot of $Ph_3Sn[o\text{-}(CH_3O)C_6H_4CO_2]$ (**7**) with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

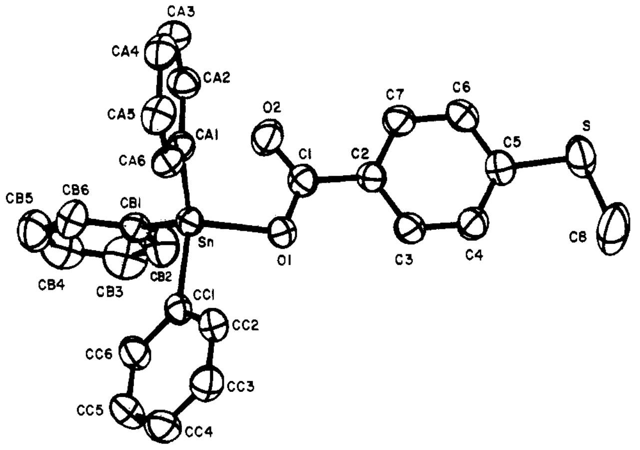

Figure 3. ORTEP plot of $Ph_3Sn[p\text{-}(CH_3S)C_6H_4CO_2]$ (**8**) with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

Proton NMR spectra were recorded on a Perkin-Elmer Model R12A NMR spectrometer at 60 MHz. Chemical shifts were measured in ppm relative to tetramethylsilane as an internal standard. The infrared spectra were recorded by using KBr windows on a Perkin-Elmer Model 180 spectrometer.

Synthesis. The triphenyltin esters of benzoic acid derivatives were prepared according to a procedure that Khoo and Smith[12] used to prepare the related esters of *o*- and *p*-aminobenzoic acids. The method consisted of reacting bis(triphenyltin)oxide with the appropriate benzoic acid derivative in refluxing benzene. Representative preparations are given in detail. Data on the other two esters that were synthesized also are given. These represent new triphenyltin ester dervatives for **6**–**8**. Compound **9** appears to be a polymeric diphenyltin ester of thiosalicylic acid.

Preparation of (*o*-Hydroxybenzoato)triphenyltin, $Ph_3Sn[o\text{-}(OH)C_6H_4CO_2]$ (6). Bis(triphenyltin) oxide (1.0 g, 1.4 mmol) was added to benzene (50 mL) with stirring. To this solution was added salicylic acid (0.386 g, 2.80 mmol). The mixture was heated to 80 °C and allowed to reflux for 30 min. The benzene–water byproduct was allowed to distill over into a Dean–Stark collector until 10 mL of solution was left. After the remaining solvent was evaporated, a clear oil was left. The oil was dissolved in 2 mL of diethyl ether. Hexane (25 mL) was added to the solution. The solution was placed in a refrigerator overnight. White crystals formed: mp 123–124 °C; yield 1.20 g (88%). Anal. Calcd for $C_{25}H_{20}O_3Sn$: C, 61.64; H, 4.11. Found: C, 61.88; H, 4.09.

Data on (*o*-Methoxybenzoato)triphenyltin, $Ph_3Sn[o\text{-}(CH_3O)C_6H_4CO_2]$ (7). A white crystalline product resulted by re-

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Table I. Atomic Coordinates in Crystalline $Ph_3Sn[o\text{-}(OH)C_6H_4CO_2]$ (6)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn	2224.5 (1)	2216.3 (1)	442.3 (1)
O1	2871 (2)	3406 (1)	−179 (1)
O2	1525 (2)	3070 (2)	−1740 (2)
O3	1459 (2)	4204 (2)	−3274 (1)
C1	2335 (2)	3621 (2)	−1153 (2)
C2	2738 (2)	4585 (2)	−1514 (2)
C3	2251 (2)	4857 (2)	−2553 (2)
C4	2598 (3)	5799 (2)	−2876 (2)
C5	3445 (3)	6440 (2)	−2179 (2)
C6	3961 (3)	6170 (2)	−1155 (2)
C7	3603 (2)	5254 (2)	−826 (2)
CA1	732 (2)	2972 (2)	309 (2)
CA2	704 (3)	3488 (3)	1154 (2)
CA3	−271 (3)	4006 (3)	1055 (3)
CA4	−1213 (3)	3995 (3)	133 (3)
CA5	−1198 (3)	3469 (3)	−701 (3)
CA6	−232 (3)	2969 (3)	−617 (2)
CB1	3667 (2)	2250 (2)	1892 (2)
CB2	4372 (2)	1341 (2)	2217 (2)
CB3	5324 (3)	1346 (3)	3152 (2)
CB4	5591 (3)	2262 (3)	3771 (2)
CB5	4902 (3)	3178 (3)	3463 (2)
CB6	3940 (3)	3183 (3)	2528 (2)
CC1	2171 (2)	739 (2)	−360 (2)
CC2	1300 (3)	0 (3)	−640 (2)
CC3	1312 (3)	−998 (3)	−1121 (3)
CC4	2187 (3)	−1230 (3)	−1337 (3)
CC5	3053 (3)	−504 (4)	−1067 (3)
CC6	3055 (3)	482 (3)	−570 (3)
H3	1219 (30)	3770 (30)	−3029 (30)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

Table II. Atomic Coordinates in Crystalline $Ph_3Sn[o\text{-}(CH_3O)C_6H_4CO_2]$ (7)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn	2407 (2)	−1442.2 (2)	1861.7 (2)
O1	918 (3)	−2300 (3)	2270 (3)
O2	2829 (3)	−4281 (3)	2692 (3)
O3	1988 (3)	−6496 (3)	4406 (3)
C1	1549 (4)	−3695 (4)	2637 (3)
C2	544 (4)	−4397 (4)	2940 (3)
C3	771 (4)	−5778 (4)	3837 (4)
C4	−259 (5)	−6340 (5)	4131 (4)
C5	−1474 (5)	−5531 (6)	3512 (5)
C6	−1670 (5)	−4195 (5)	2598 (5)
C7	−695 (4)	−3621 (4)	2336 (4)
C8	2271 (6)	−7953 (5)	5323 (5)
CA1	3927 (4)	−1800 (4)	255 (4)
CA2	4847 (5)	−3145 (5)	246 (5)
CA3	5750 (5)	−3312 (6)	−860 (5)
CA4	5764 (5)	−2140 (7)	−1953 (5)
CA5	4901 (6)	−822 (6)	−1952 (4)
CA6	3978 (5)	−636 (5)	−864 (4)
CB1	882 (4)	693 (4)	1348 (3)
CB2	1242 (5)	1744 (4)	1295 (4)
CB3	250 (5)	3114 (4)	1077 (5)
CB4	−1104 (5)	3458 (4)	893 (5)
CB5	−1494 (4)	2452 (5)	927 (4)
CB6	−496 (4)	1069 (4)	1144 (4)
CC1	3105 (4)	−1958 (4)	3601 (4)
CC2	4424 (5)	−3010 (5)	3952 (4)
CC3	4899 (6)	−3301 (6)	5070 (5)
CC4	4061 (7)	−2568 (6)	5843 (5)
CC5	2727 (7)	−1511 (5)	5515 (5)
CC6	2285 (5)	−1202 (4)	4384 (4)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 2.

Table III. Atomic Coordinates in Crystalline $Ph_3Sn[p\text{-}(CH_3S)C_6H_4CO_2]$ (8)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn	1108.5 (2)	−1615.5 (2)	1716.2 (1)
S	5629 (1)	−8410 (1)	5371 (1)
O1	2753 (2)	−3140 (2)	2410 (1)
O2	570 (3)	−2461 (3)	3553 (2)
C1	2000 (4)	−3283 (3)	3249 (2)
C2	2950 (4)	−4506 (3)	3785 (2)
C3	4590 (4)	−5346 (4)	3441 (2)
C4	5431 (4)	−6513 (4)	3915 (2)
C5	4665 (4)	−6899 (3)	4732 (2)
C6	3011 (4)	−6040 (4)	5093 (2)
C7	2178 (4)	−4858 (4)	4623 (2)
C8	7602 (7)	−9344 (6)	4635 (4)
CA1	−831 (4)	−2357 (3)	1563 (2)
CA2	−2115 (4)	−2277 (4)	2291 (2)
CA3	−3397 (4)	−2696 (4)	2124 (3)
CA4	−3402 (4)	−3195 (4)	1249 (3)
CA5	−2116 (4)	−3297 (4)	514 (3)
CA6	−847 (4)	−2872 (4)	674 (2)
CB1	659 (4)	509 (3)	2288 (2)
CB2	1600 (5)	723 (4)	2902 (3)
CB3	1440 (6)	2125 (5)	3181 (3)
CB4	320 (6)	3320 (5)	2853 (3)
CB5	−622 (6)	3132 (4)	2231 (3)
CB6	−462 (4)	1725 (4)	1956 (3)
CC1	2706 (4)	−1891 (3)	386 (2)
CC2	3432 (4)	−3229 (3)	−127 (2)
CC3	4519 (5)	−3393 (4)	−966 (2)
CC4	4864 (5)	−2189 (4)	−1325 (3)
CC5	4159 (5)	−874 (4)	−837 (3)
CC6	3076 (4)	−708 (4)	16 (2)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 3.

Table IV. Selected Distances (Å) and Angles (deg) for $Ph_3Sn[o\text{-}(OH)C_6H_4CO_2]$ (6)[a,b]

Distances			
Sn–O1	2.083 (2)	C1–O1	1.301 (3)
Sn–O2	3.071 (2)	C1–O2	1.232 (3)
Sn–CB1	2.132 (3)	C3–O3	1.362 (3)
Sn–CA1	2.117 (3)	O3–H3	0.78 (4)
Sn–CC1	2.122 (3)	O2···H3	1.93 (4)
C1–C2	1.478 (4)	Sn–O3[c]	3.035 (2)
Angles			
O1–Sn–CB1	93.1 (1)	O1–C1–C2	116.0 (2)
O1–Sn–CA1	102.4 (1)	O2–C1–C2	121.6 (2)
O1–Sn–CC1	105.2 (1)	O1–C1–O2	122.4 (3)
CB1–Sn–CA1	118.5 (1)	C1–C2–C7	121.0 (2)
CB1–Sn–CC1	110.9 (1)	C1–C2–C3	120.4 (2)
CA1–Sn–CC1	121.0 (1)	O3–C3–C2	121.8 (2)
O2–Sn–O1	46.3 (1)	O3–C3–C4	118.4 (2)
O2–Sn–CB1	138.1 (1)	C3–O3–H3	112 (3)
O2–Sn–CA1	85.4 (1)	C3–O3–Sn[d]	116.6 (1)
O2–Sn–CC1	105.2 (1)	H3–O3–Sn[d]	103 (3)
O3[c]–Sn–O1	168.2 (1)	O3–H3···O2	142 (3)
O3[c]–Sn–O2	143.2 (1)	C1–O2···H3	100 (1)
O3[c]–Sn–CB1	78.5 (1)		
O3[c]–Sn–CA1	75.0 (1)		
O3[c]–Sn–CC1	85.7 (1)		
Sn–O1–C1	118.8 (2)		
Sn–O2–C1	72.2 (2)		

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I. [c] $x, \frac{1}{2}-y, \frac{1}{2}+z$. [d] $x, \frac{1}{2}-y, z-\frac{1}{2}$.

crystallization of the initially formed oil from a diethyl ether–hexane solution that was refrigerated overnight: mp 107–108 °C; yield 0.99 g (71%). Anal. Calcd for $C_{26}H_{22}O_3Sn$: C, 62.31; H, 4.39. Found: C, 62.25; H, 4.45.

Data on (*p*-(Methylthio)benzoato)triphenyltin, $Ph_3Sn[p\text{-}(CH_3S)C_6H_4CO_2]$ (8). Clear crystals resulted from the initially formed oily product by recrystallization from a minimal amount of benzene solution to which hexane was added to the cloud point. After the mixture was allowed to stand at room temperature for 3 days, the crystals formed: mp 141–143 °C; yield 0.823 g (50%). Anal. Calcd

Table V. Selected Distances (Å) and Angles (deg) for $Ph_3Sn[o\text{-}(CH_3O)C_6H_4CO_2]$ (7)[a]

Distances

Sn-O1	2.054 (3)	C1-O1	1.321 (5)
Sn-O2	2.781 (3)	C1-O2	1.214 (5)
Sn-CB1	2.130 (4)	C3-O3	1.357 (5)
Sn-CC1	2.122 (4)	O3-C8	1.459 (5)
Sn-CA1	2.131 (4)		
C1-C2	1.488 (6)		

Angles

O1-Sn-CB1	94.4 (1)	O1-C1-C2	113.3 (3)
O1-Sn-CC1	109.6 (1)	O2-C1-C2	126.3 (3)
O1-Sn-CA1	111.2 (1)	O1-C1-O2	120.3 (3)
CB1-Sn-CC1	106.9 (1)	C1-C2-C7	118.4 (3)
CB1-Sn-CA1	111.8 (1)	C1-C2-C3	122.6 (4)
CC1-Sn-CA1	119.9 (1)	O3-C3-C2	117.2 (3)
O2-Sn-O1	51.5 (1)	O3-C3-C4	123.3 (4)
O2-Sn-CB1	145.9 (1)	C3-O3-C8	118.4 (4)
O2-Sn-CC1	87.9 (1)		
O2-Sn-CA1	84.8 (1)		
Sn-O1-C1	110.1 (2)		
Sn-O2-C1	78.2 (2)		

[a] See footnotes *a* and *b* of Table II.

for $C_{26}H_{22}O_2SSn$: C, 60.38; H, 4.26; S, 6.19. Found: C, 60.90; H, 4.29; S, 6.43.

Preparation of (*o*-Thiobenzoato)diphenyltin, $Ph_2Sn[o\text{-}(S)C_6H_4CO_2]$ (9). Bis(triphenyltin) oxide (1.0 g, 1.4 mmol) was dissolved in benzene (50 mL). Next, thiosalicylic acid (0.43 g, 2.8 mmol) was added. After the mixture was heated for 20 min at 80 °C with stirring, all the solid dissolved. The reaction was allowed to reflux for an additional 30 min, after which the benzene–water byproduct was distilled off until approximately 25 mL of solution remained. At this point, a white powdery solid formed. The solid was filtered, washed with benzene, and air-dried. The solid did not dissolve in acetonitrile, diethyl ether, or acetone but did dissolve in dimethyl sulfoxide; mp >260 °C. Anal. Calcd for $C_{19}H_{14}O_2SSn$: C, 53.68; H, 3.30; S, 7.54. Found: C, 53.92; H, 3.32; S, 7.71.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[13]

Crystals of all three compounds were colorless and were cut from polycrystalline masses. They were mounted in thin-walled glass capillaries, which were sealed as a precaution against moisture sensitivity.

X-ray Crystallographic Study for $Ph_3Sn[o\text{-}(OH)C_6H_4CO_2]$ (6). Crystal Data for $C_{25}H_{20}O_3Sn$ (6): Crystal dimensions approximately spherical, diameter 0.38 mm; uniquely determined monoclinic space group $P2_1/c$ [C_{2h}^5-No.14],[14] $a = 13.318$ (6) Å, $b = 12.113$ (2) Å, $c = 14.590$ (4) Å, $\beta = 116.47$ (3)°, $Z = 4$, $\mu_{Mo\,K\bar{\alpha}} = 1.25$ mm^{-1}. A total of 3714 independent reflections ($+h,+k,\pm l$) was measured by using the θ–2θ scan mode for $2° \le 2\theta_{Mo\,K\bar{\alpha}} \le 50°$. No corrections were made for absorption.

The structure was solved by using standard Patterson and difference-Fourier techniques and was refined by full-matrix least squares.[15] The 29 independent non-hydrogen atoms were refined anisotropically. The hydroxyl hydrogen atom was located on a difference-Fourier map and was refined isotropically. The 19 independent phenyl hydrogen atoms were treated as fixed isotropic scatters, with calculated coordinates that were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The final agreement factors[16] were $R = 0.022$ and $R_w = 0.032$ for the 3218 reflections having $I \ge 2\sigma_I$. A final difference-Fourier synthesis showed a maximum density of 0.312 e/Å^3.

Table VI. Selected Distances (Å) and Angles (deg) for $Ph_3Sn[p\text{-}(CH_3S)C_6H_4CO_2]$ (8)[a]

Distances

Sn-O1	2.060 (2)	C1-O1	1.310 (4)
Sn-O2	2.783 (3)	C1-O2	1.232 (4)
Sn-CC1	2.135 (3)	C5-S	1.762 (3)
Sn-CB1	2.126 (3)	S-C8	1.799 (5)
Sn-CA1	2.128 (3)		
C1-C2	1.488 (4)		

Angles

O1-Sn-CC1	97.6 (1)	O1-C1-C2	116.2 (3)
O1-Sn-CB1	108.9 (1)	O2-C1-C2	123.0 (3)
O1-Sn-CA1	108.9 (1)	O1-C1-O2	120.7 (3)
CC1-Sn-CB1	107.0 (1)	C1-C2-C7	120.1 (3)
CC1-Sn-CA1	108.8 (1)	C1-C2-C3	121.0 (3)
CB1-Sn-CA1	122.7 (1)	S-C5-C4	124.2 (3)
O2-Sn-O1	51.7 (1)	S-C5-C6	117.1 (2)
O2-Sn-CC1	149.2 (1)	C5-S-C8	104.2 (2)
O2-Sn-CB1	88.0 (1)		
O2-Sn-CA1	83.3 (1)		
Sn-O1-C1	109.7 (2)		
Sn-O2-C1	77.5 (2)		

[a] See footnotes *a* and *b* of Table III.

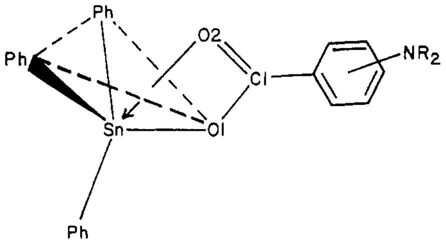

Figure 4. Schematic representation of the structural form assumed by **6–8**.

X-ray Crystallographic Study for $Ph_3Sn[o\text{-}(CH_3O)C_6H_4CO_2]$ (7). Crystal Data for $C_{26}H_{22}O_3Sn$ (7): Crystal dimensions 0.18 × 0.23 × 0.35 mm, triclinic space group $P\bar{1}$ [C_i^1-No. 2],[17] $a = 10.632$ (2) Å, $b = 11.452$ (2) Å, $c = 11.719$ (2) Å, $\alpha = 62.86$ (2)°, $\beta = 71.95$ (2)°, $\gamma = 62.31$ (2)°, $Z = 2$, $\mu_{Mo\,K\bar{\alpha}} = 1.18$ mm^{-1}. A total of 2569 independent reflections ($+h,\pm k,\pm l$) was measured by using the θ–2θ scan mode for $2° \le 2\theta_{Mo\,K\bar{\alpha}} \le 43°$. No corrections were made for absorption.

The structure was solved and refined by using the techniques that were applied for **6** (30 non-hydrogen atoms anisotropic, 19 phenyl hydrogen atoms fixed isotropic). The three independent methyl hydrogen atoms were not included in the refinement. The final agreement factors were $R = 0.024$ and $R_w = 0.041$ for the 2364 reflections having $I \ge 2\sigma_I$. A final difference-Fourier synthesis showed a maximum density of 0.534 e/Å^3.

X-ray Crystallographic Study for $Ph_3Sn[p\text{-}(CH_3S)C_6H_4CO_2]$ (8). Crystal Data for $C_{26}H_{22}O_2SSn$ (8): Crystal dimensions 0.30 × 0.25 × 0.23 mm, triclinic space group $P\bar{1}$ [C_i^1-No. 2],[17] $a = 8.814$ (1) Å, $b = 9.816$ (1) Å, $c = 14.430$ (3) Å, $\alpha = 89.39$ (1)°, $\beta = 80.19$ (1)°, $\gamma = 68.89$ (1)°, $Z = 2$, $\mu_{Mo\,K\bar{\alpha}} = 1.23$ mm^{-1}. A total of 4037 independent reflections ($+h,\pm k,\pm l$) was measured by using the θ–2θ scan mode for $2° \le 2\theta_{Mo\,K\bar{\alpha}} \le 50°$. No corrections were made for absorption.

The structure was solved and refined by using the techniques that were applied for **7** (30 non-hydrogen atoms anisotropic, 19 phenyl hydrogen atoms fixed isotropic, 3 methyl hydrogen atoms not included). The final agreement factors were $R = 0.025$ and $R_w = 0.040$ for the 3712 reflections having $I \ge 2\sigma_I$. A final difference-Fourier synthesis showed a maximum density of 0.450 e/Å^3.

Results

The atom-labeling schemes for **6–8** are shown in the ORTEP plots of Figures 1a–3, respectively. Atomic coordinates are listed in Tables I–III. Selected bond lengths and angles for the three compounds are given in Tables IV–VI. NMR and

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

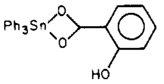
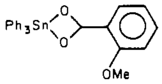
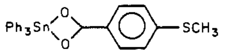
(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

(15) The function minimized was $\sum w(|F_0| - |F_c|)^2$, where $w^{1/2} = 2F_0Lp/\sigma_I$. Mean atomic scattering factors were taken from: Reference 14, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Sn, S, and O were taken from: Reference 14, 1974; Vol. IV, pp 149–150.

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

(17) Reference 14, p 75.

Table VII. Proton NMR and Infrared Data on Ph_3Sn Esters

		^1H NMR[a] (δ ±0.05)		infrared, cm^{-1}		
no.	compd	aromatic	$S-CH_3$ or $O-CH_3$	Nujol	CCl_4	assgnt[b]
6		7.80[c] (m, 6 H) 7.45 (m, 9 H) 6.95 (m, 4 H)		1630	1630	C=O (st)
7		7.80 (m, 6 H) 7.40 (m, 9 H) 6.95 (m, 4 H)	3.85 (s, 3 H)	1630	1628	C=O (st)
8		8.05 (m, 4 H) 7.80 (m, 6 H) 7.40 (m, 9 H)	2.46 (s, 3 H)	1625	1628	C=O (st)

[a] The NMR spectra were all recorded in CCl_4 solution with Me_4Si as the internal reference. [b] The carbonyl stretches for the free acids are 1660, 1665, and 1670 cm^{-1} for **6**–**8**, respectively. [c] Center of a multiplet.

Table VIII. Bond Parameters for the Triphenyltin Benzoates Showing Distortion Toward the Trigonal Bipyramid

	6	7	8
ax C_{Ph}	CB1	CB1	CC1
av atom displcmnt from ax plane, Sn,O1,O2,C_{Ph}/Å	±0.107	±0.002	±0.021
dihedral angle between ax and eq planes/deg	89.8	87.4	87.8
Δ(ax–eq) Sn–C bond dist/Å	+0.012 (3)	+0.003 (4)	+0.008 (3)
Sn atom displcmnt from plane of eq C atoms/Å	0.693	0.542	0.544
O2–Sn–C_{ax}/deg	138.1 (1)	145.9 (1)	149.2 (1)
sum of eq angles at Sn/deg	328.6	340.7	340.5

infrared data are listed in Table VII. Anisotropic thermal parameters, additional bond lengths and angles, and deviations from some least-squares mean planes are provided as supplementary material.

Discussion

Structural Aspects. The basic structure of triphenyltin benzoate esters, **6**–**8**, results from a distortion from tetrahedral geometry induced by the approach of an oxygen atom, O2, of the carboxylate group at a tetrahedral face opposite one of the tin phenyl groups. The distortion is toward a trigonal bipyramid that contains O2 and the latter phenyl group at axial sites (Figure 4). The axial Sn–O2 lengths are considerably longer than the equatorial Sn–O1 bond length (Tables IV–VI). Tin-119m Mössbauer data give quadrupolar splittings for **7** and **8** that are consistent with the presence of five-coordinated tin in this structural representation.[18]

For **6**, there is an additional weak bonding interaction to the tin atom involving O3 from a *C*-glide related molecule, Sn–O3′ = 3.035 (2) Å (see Figure 1b), in which O3 approaches the tetrahedral face opposite that approached by O2, Sn–O2 = 3.071 (2) Å, and having the edge defined by CA1 and CC1 in common.

Some measures of distortion indicate that the trigonal bipyramid is being approached. These are given in Table VIII. For example, the average deviation of the atoms from the axial plane, Sn,O1,O2,C_{ax}, ranges between ±0.002 and ±0.107 Å, with the salicylate derivative **6** showing the least atom deviation. Also, the dihedral angle between the axial plane and the equatorial plane, defined by O1 and the carbon atoms of the other two phenyl groups, is close to 90° as expected for the formation of a trigonal bipyramid. However, the displacement of the tin atom from the equatorial plane (toward the axial C_{Ph} atom) varies from 0.542 Å for **7** to 0.544 Å for **8** to 0.693 Å for **6**, indicating that the degree of distortion from the tetrahedron is modest. The out-of-plane displacement of the tin atom for a tetrahedron having bond lengths of 2.1 Å, i.e., the average value of the tin–ligand bond lengths in these structures, is 0.73 Å.

Making use of the latter value, percentage displacements toward the trigonal bipyramid from the tetrahedron may be calculated on the basis of the distance of the tin atom from the equatorial plane. Using a linear relation, values of 5.1%, 25.8%, and 25.5% result for **6**–**8**, respectively.

The small degree of trigonal-bipyramidal character for **6** is no doubt aided by the placement of the intermolecular oxygen atom O3′ close to the tin atom. In fact, the sum of the equatorial angles at tin for the salicylate **6** (328.6°) is almost the same as for the tetrahedron, 328.40°. For **7** and **8**, lacking any intermolecular interactions, this sums are 340.7 and 340.5°, respectively.

Consistent with the greater displacement of **7** and **8** toward the trigonal bipyramid, the O2–Sn–C_{ax} angles are larger, 145.9 (1) and 149.2 (1)°, respectively, compared with 138.1 (1)° for **6** (Table VIII), and the Sn–O2 axial bond lengths are shorter for **7** and **8**, 2.781 (3) and 2.783 (3) Å, respectively, compared to that for **6**, 3.071 (2) Å. The intramolecular hydrogen bond formed from the orthohydroxy group of salicylic acid [O2- - -H3 = 1.93 (4) Å] contributes in causing the longer Sn–O2 bond length in **6** (Figure 1). The atoms of the resultant six-membered ring are coplanar to within ±0.062 Å. A similar hydrogen-bonded situation exists in the structure of the salicylaldehyde adduct with Me_2SnCl_2.[19] For **7** and **8**, there were no Sn–E (E = O, S) intermolecular contacts up to 4.0 Å.

For the anisic acid derivative **7**, deviations from coplanarity of the Sn–methoxybenzoate system appear to be due to crowding between the ortho methoxy oxygen atom, O3, and the carbonyl oxygen atom, O2. These atoms are separated by a distance of 2.760 (4) Å, as compared to the van der Waals sum of 3.0 Å.[20]

The atoms of the methoxyphenyl system, C2, C3, C4, C5, C6, C7, O3, and C8 are coplanar to within ±0.024 Å, while the atoms Sn, O1, C1, and O2 are coplanar to within ±0.000 Å. The dihedral angle between these planes is 27.7° and corresponds primarily to a rotation about the C1–C2 bond. In the absence of such a rotation, crowding between O3 and O2 would be severe.

Solution Structure. Examination of the infrared spectra of the triphenyltin benzoates **6**–**8** in Nujol mull and in CCl_4 (Table VII) revealed very similar carbonyl stretching frequencies, about 1625–1630 cm^{-1}, shifted to lower frequencies relative to those of the uncomplexed acids (1660–1670 cm^{-1}). The latter shift that is indicative in itself[21] of carbonyl group coordination coupled with the X-ray data indicates a lack of evidence for nitrogen to tin coordination in solution. Nitro-

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(18) Smith, P. J., personal communication.

(19) Cunningham, D.; Douek, I.; Frazer, M. J.; McPartlin, M.; Matthews, J. D. *J. Organomet. Chem.* **1975**, *90*, C23.

(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(21) Bellamy, L. J.; Branch, R. F. *J. Chem. Soc.* **1954**, 4491.

Table IX. Tin Donor Bond Parameters for Pentacoordinated Derivatives Containing the R_3Sn Group (R = Me, Ph)

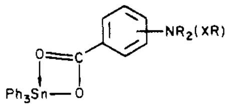
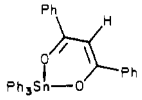
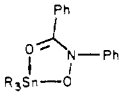
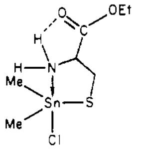
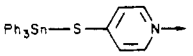
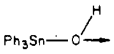
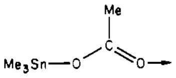
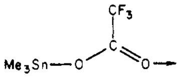
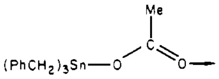
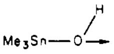
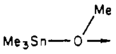
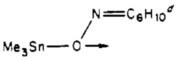
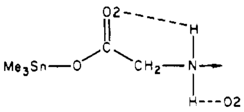
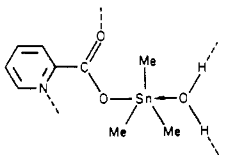
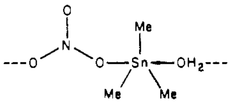
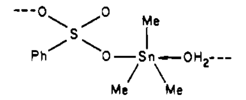
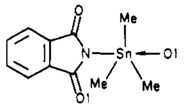
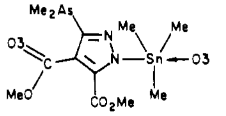
no.	structure	ref	bond lengths, Å		Δ,[a] Å	bond angle, deg X-Sn-X'
			Sn-X	Sn-X'		
Discrete Forms						
						
1a	$NR_2 = o\text{-}NH_2$	1	2.043 (3)	2.823 (3)	0.780	146.6 (1)
1b	$NR_2 = o\text{-}NMe_2$	1	2.115 (6)	2.564 (7)	0.449	143.7 (3)
1c	$NR_2 = p\text{-}NH_2$	1	2.072 (2)	2.629 (2)	0.557	151.3 (1)
6	XR = *o*-OH	this work	2.083 (2)	3.071 (2)	0.988	138.1 (1)
7	XR = *o*-OMe	this work	2.054 (3)	2.781 (3)	0.727	145.9 (1)
8	XR = *p*-SMe	this work	2.060 (2)	2.783 (3)	0.723	149.2 (1)
10		22	2.094 (7)	2.276 (7)	0.182	163.7 (2)
11	 a, R = Ph	23	2.091 (5)	2.308 (4)	0.217	157.2 (2)
	b, R = Me[b]	24	2.152 (6)	2.263 (6)	0.111	151.9 (5)
			2.064 (6)	2.392 (6)	0.328	157.8 (3)
12		8	2.413 (2)	2.434 (12)		166.9 (3)
Chain Forms						
13		25	2.576 (7)	2.62 (2)		172.1 (5)
14		6	2.197 (5)	2.255 (5)	0.058	177.6 (3)
15	$Ph_3Sn\text{-}NCO\rightarrow$	26	2.122 (3)	2.807 (5)		178 (2)
16	$Ph_3Sn\text{-}NCS\rightarrow$	27	2.22 (5)[c]	2.92 (1)[c]		175 (3)[c]
2		4	2.205 (3)	2.391 (4)	0.186	171.6 (1)
17		4	2.177 (14)	2.458 (15)	0.281	174.8 (5)
18		28	2.14 (2)	2.65 (2)	0.51	168.6 (8)
19		5, 29	2.15 (8)	2.15 (5)	0.0	178 (2)
20		30	2.20 (2)	2.26 (2)	0.06	172.4 (7)
21		31	2.190 (3)	2.481 (3)	0.291	174.9 (1)
22	$Me_3Sn\text{-}NCS\rightarrow$	32	2.15 (6)	3.13 (2)		173 (5)
23		7	2.14 (3)	2.53 (3)		159.8
Other Planar Me_3Sn Forms						
24[e]		33	2.18 (2)[c]	2.43 (3)[c]	0.25	174.6 (9)[c]
25[f]		34	2.22 (3)	2.47 (2)	0.25	169.3 (8)

Table IX (*Continued*)

no.	structure	ref	bond lengths, Å		Δ,[a] Å	bond angle, deg X-Sn-X'
			Sn-X	Sn-X'		
			Discrete Forms			
26[f]		35	2.34 (1)	2.30 (1)	0.04	176.2 (3)
27[g]		36	2.17 (2)	2.90 (4)		177 (1)
28		37	2.18 (1)	3.32 (1)		

[a] The value of Δ is equal to (Sn-X) - (Sn-X'). [b] Two independent molecules per unit cell. [c] Four independent molecules per unit cell. Mean values are listed. [d] C_6H_{10} is a cyclohexyl group. [e] Three-dimensional hydrogen-bonded network. [f] Hydrogen-bonded chains. [g] A tetrameric arrangement results in the form of a square.

gen–ligand coordination in related triorganotin *o*- and *p*-aminobenzoates was suggested on the basis of their infrared spectra.[12] However, as we have shown,[1] this is not the case. In the present study, retention of the solid-state structure in solution for **6–8** also is supported.

In our attempt to prepare an analogous derivative to **6–8** with (*o*-thiobenzoato)triphenyltin **9**, a relatively insoluble white powdery solid resulted that had a high melting point compared to **6–8**, >260 °C, and an elemental analysis indicating the loss of a benzene molecule. The lack of an S–H stretch in the infrared spectrum and its inferred polymeric nature suggest intermolecular Sn–S coordination.

Structural Implications. As stated in the Introduction, the chain structure **2**, which has been observed primarily with the Me_3Sn group, contrasts with the discrete five-coordinated form **1**, which we have observed in benzoates containing the Ph_3Sn group. Summarized in Table IX are bond parameter data on some related molecules[1,4–8,22–37] of each of these structural types.

One observes that the discrete forms **10–12** have Sn–O axial–equatorial bond length differences that vary with ring size. For the benzoates containing four-membered rings **1a–c**, **6–8**, the range is 0.45–0.99 Å, while the five-membered ring containing derivatives **11a,b** show values centered at 0.22 Å with a variation between 0.11 and 0.33 Å. For the only member containing a six-membered ring, **10**, the bond length difference is 0.18 Å. The Sn–O bond length differences for comparable compounds, **2**, **4**, **17–21**, possessing the chain structure **2**, is in the range or a little lower for that seen in the discrete form containing the less strained five- and six-membered rings

Consistent with structural principles for pentacoordinated compounds,[38,39] the location of the less electronegative methyl group at an axial site of a trigonal bipyramid disfavors structure **1** for derivatives containing the Me_3Sn group relative to those that have the Ph_3Sn group. The greater electronegativity of the phenyl group,[40] comparable to that of a chlorine atom, results in the chain form **2** being disfavored since placement of more electronegative phenyl groups equatorially relative to methyl groups is required. From structural data accumulated so far, the relative ligand electronegativity appears to be an important factor in determining whether the discrete structural form **1** or the chain form **2** is observed. The axial tin–ligand bond lengths in both forms **1** and **2** are subject to variations depending on substituent electronegativity, ring strain, hydrogen bond, and steric interactions. These features are evident in some of the structures in Table IX.

The formation of the interesting chain structure for trimethyltin glycinate (**23**)[7] having oxygen and nitrogen atoms situated axially in preference to the chain form **2**, exhibiting only oxygen attachment, most likely is aided by the presence of hydrogen bonding. The latter serves to enhance the donor character of the nitrogen atom at the expense of oxygen. This reduced coordination ability is apparent in several of the benzoate derivatives of triphenyltin in our studies, **1a**[1] and **6**. In structures **24–26**, hydrogen bonding enhances the donor properties of the water molecule. Substantiation for the hydrogen-bonding effect is found in the anthranilate, $Me_3Sn[o\text{-}(H_2N)C_6H_4CO_2]$, which shows a chain structure analogous to **23**.[41] This contrasts to $Me_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$, lacking hydrogen bonding, which has the chain form **2**.[41]

The existence of the trimethyltin derivative **11b**[24] in the discrete form **1**, which is a rare appearance for the trimethyltin moiety in this five-coordinate geometry instead of **2**, probably results from the added stability received through chelation in forming an unstrained five-membered ring. In general, for the triphenyltin group, when small-membered ring formation is not possible, as in **13–16**, the chain arrangement **2** results.

From the above, a delicate balance between the discrete and chain forms, **1** and **2**, is implied. By suitable variation of factors controlling stability, it should be possible to obtain the chain form for a triphenyltin benozate derivative. Future

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studies centered on this problem no doubt will make this structural variation a reality.

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Registry No. **6**, 24379-26-8; **7**, 91266-58-9; **8**, 91266-59-0; **9**, 91266-60-3; bis(triphenyltin) oxide, 1262-21-1; salicylic acid, 69-72-7; *o*-anisic acid, 579-75-9; *p*-(methylthio)benzoic acid, 13205-48-6; thiosalicylic acid, 147-93-3.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters (Tables A–C), hydrogen atom parameters (Tables D–F), additional bond lengths and angles (Tables G–I), and deviations from least-squares mean planes (Tables J–L) for **6**–**8** (47 pages). Ordering information is given on any current masthead page.

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Structural Studies of Salts of Cis and Trans μ-Fluoro-Bridged Polymers of GeF_5^- and of the GeF_5^- Monomer

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$XeF_5^+GeF_5^-$ is orthorhombic, and at 20 °C a_0 = 7.119 (2) Å, b_0 = 12.986 (4) Å, c_0 = 7.398 (1) Å, and V = 683.9 (5) Å^3; Z = 4, and the space group is *Pmnb* (a nonstandard setting of *Pnma*, No. 62). From 437 independent X-ray diffraction data, the structure was refined to a weighted R of 0.018 (unweighted R = 0.021) with a standard deviation in an observation of unit weight of 0.725. The structure contains infinite chains of GeF_6 octahedra sharing trans vertices. The XeF_5 cations are arranged alternately to left and right along the chain such that each cation approaches symmetrically two of the μ-fluoro-bridged GeF_6 units. The nonbridging GeF_4 units are planar and approximately square, with Ge–F = 1.75 (2) Å. The μ-bridging Ge–F distance is 1.890 (1) Å. $ClO_2^+GeF_5^-$ is orthorhombic, and at −105 ± 10 °C a_0 = 14.648 (2) Å, b_0 = 7.576 (1) Å, c_0 = 8.894 (2) Å, and V = 987.0 (4) Å^3; Z = 8, and the space group is $C222_1$ (No. 20). From 645 independent X-ray diffraction intensity data, refinement led to convergence with a weighted R factor of 0.068 (unweighted R = 0.059) and a standard deviation in an observation of unit weight of 3.938. In the structure, infinite chains of approximately octahedral GeF_6 units are joined by sharing cis vertices. This is an infinite helix having all Ge atoms of the chain nearly coplanar. The nonbridging Ge–F distances are in two sets, the shorter (Ge–F = 1.737 (4) and 1.728 (3) Å) being cis to the bridging Ge–F bonds and the longer (Ge–F = 1.776 (3) and 1.768 (3) Å) being trans to the Ge–F bridging. The two μ-bridging Ge–F distances are not significantly different, at 1.887 (1) Å. The anion chains are held together by interactions with the cations. There are two crystallographically distinguishable ClO_2^+ units. Each lies on a twofold axis, and the closest cation to anion contacts (Cl1–F1 = 2.539 (3) Å; Cl2–F4 = 2.625 (3) Å) involve approach of F to Cl normal to the ClO_2 triangle. Infrared and Raman spectra of the $XeF_5^+GeF_5^-$ and $ClO_2^+GeF_5^-$ salts have been assigned. Similarities of the vibrational spectra of the latter to the spectra of the O_2^+ salt indicate that the same anion occurs in both. The vibrational data show that a third oligomeric form of the anion must occur in the NO_2^+, NF_4^+, and SF_3^+ salts. The tetrabutylammonium salt contains a monomeric anion of approximately D_{3h} symmetry.

Introduction

The GeF_5^- anion is stabilized by a variety of cations including some of high electron affinity.[1–4] To date such salts have been characterized by their vibrational spectra. Those studies [2–4] have indicated that monomeric and oligomeric forms of the anion can occur. A need for detailed structural information for lattice energy evaluations, based upon the method of Bertaut[5] as modified by Templeton,[6] prompted the structural work reported in this paper. Salts were selected for those studies for which thermodynamic data, to complete the Born–Haber cycles, were accessible. The lattice energy evaluations and fluoride ion affinities derived by using them are given in the accompanying paper.[7] The present studies include the crystal and molecular structures and vibrational spectra of the previously known compound[1] $XeF_6{\cdot}GeF_4$ (for which X-ray structural work[8–11] had suggested the formulation $XeF_5^+GeF_5^-$) and similar studies of the new compound $ClO_2^+GeF_5^-$. The present crystallographic studies have provided a basis for the assignment of the structural form present in other salts.

Experimental Section

Apparatus and Materials. A Monel vacuum line was used. It was equipped with stainless-steel or Monel 1KS4 Kel-F tipped Whitey valves and a Monel Acco Helicoid pressure gauge (0–1400 torr ± 0.3%). Reaction vessels were made from $^1/_4$- or $^3/_8$-in. Teflon-FEP tubing (Penntube Plastics Co.) sealed at one end and degassed for several hours at 65–70 °C. A J-Y Ramanor spectrometer with a double holographic grafting monochromator, using either argon (514 or 488 nm) or krypton (647 nm) laser excitation, provided the Raman spectra. Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer using an airtight Kel-F sample cell with AgCl windows cut from a 1 mm thick sheet (Harshaw Chemical Co., Solon, OH). X-ray powder diffraction patterns were obtained from a General Electric Co. precision camera (circumference 45 cm), with a Ni-filtered Cu K$\bar{\alpha}$ source.

GeF_4 was made from GeO_2 powder (Alfa Inorganics, 99.995%) and F_2 in a Monel bomb at 250 °C. It was purified by trap to trap distillation. XeF_6 was prepared by heating a F_2/Xe mixture (10/1 mole ratio) at 300 °C in a Monel bomb previously passivated with F_2. The small quantities of XeF_4 and $XeOF_4$ also formed were

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