here which would give a dihydroxydistannoxane. The only example structurally characterized by X-ray diffraction was a low-temperature study of **4c**[10] which contains the relatively large protecting groups, Me_3SiCH_2, formed by hydrolysis of the corresponding diorganyltin dichloride with aqueous KOH in hot toluene. Finally, the formation of the diphenyltetrachlorostannate(IV) anion[23] may competitively occur by reaction of the base-hydrochloride and Ph_2SnCl_2 (eq 4).

This scheme is similar to the sequence formulated by Mufti and Poller[26] in their study of the hydrolysis of diisocyanates $R_2Sn(NCO)_2$ leading to polymeric tin oxides. In addition, the hydroxyhalide species $R_2SnX(OH)$ was postulated as a precursor to the formation of the dihalodistannoxane $R_2XSnOSnR_2X$. Although we found no evidence for the presence of $Ph_2SnCl(OH)$, considering the lability of this class of substances,[27] its formation as a transient species could take part in eq 2.

$$Ph_2SnCl_2\cdot\text{base} + H_2O \rightarrow Ph_2SnCl(OH) + HCl\cdot\text{base} \qquad (2a)$$

$$Ph_2SnCl_2\cdot\text{base} + Ph_2SnCl(OH) \rightarrow Ph_2ClSnOSnPh_2Cl + HCl\cdot\text{base} \qquad (2b)$$

Acknowledgment. The support of this research by the National Science Foundation (CHE8205411) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. 5, 89462-21-5; **6**, 89462-22-6; **7**, 89462-19-1; **8**, 89462-23-7; **9**, 89462-24-8; **10**, 89462-25-9; **11**, 89462-26-0; **12**, 89462-27-1; Ph_2SnCl_2, 1135-99-5.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes for 5 and 6, anisotropic thermal parameters for 5 (Table A), hydrogen atom parameters for 5 (Table B), anisotropic thermal parameters for 6 (Table C), hydrogen atom parameters for 6 (Table D), additional bond lengths and angles for 5 (Table E) and 6 (Table F), and deviations from least-squares mean planes for 5 (Table G) and 6 (Table H) (32 pages). Ordering information is given on any current masthead page.

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New Five-Coordinated Anionic Tin(IV) Complexes. Synthesis and Molecular Structure of Halodimethylstannoles Containing Rings with Mixed Ligands[1]

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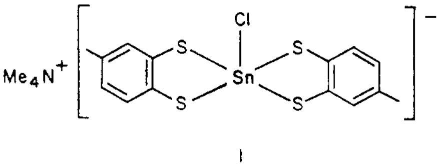
Received November 17, 1983

Anionic monocyclic five-coordinated stannoles $[(C_6H_4OS)SnMe_2X][Et_4N]$ (X = F, Cl, Br, I, **7**–**10**, respectively), $[(C_6H_4CO_2S)SnMe_2Cl][Et_4N]$ (**11**), and $[(C_6H_4OS)SnMe_2I][Ph_4P]$ (**12**), all containing ortho ligand attachments to tin, were prepared in acetonitrile solution by reacting the halide salt with the four-coordinated stannole precursor. X-ray analysis of the fluoro (**7**), chloro (**11**), and iodo (**12**) derivatives revealed trigonal-bipyramidal structures showing increasing distortion as the halogen size increases. The iodo compound forms a weakly coupled dimeric unit formed by intermolecular coordination of an oxygen atom. These structures represent the first examples of pentacoordinated anionic tin with ring systems containing mixed ligands attached to the tin center. This work reveals the close similarity in structural principles for five-coordinated anionic compounds of tin and silicon and the isoelectronic phosphoranes. **7** crystallizes in the orthorhombic space group *Pbca* with $a = 17.794$ (2) Å, $b = 12.060$ (2) Å, $c = 18.095$ (2) Å, and $Z = 8$. The structure was refined to $R = 0.043$ and $R_w = 0.060$. For **11**, the monoclinic space group $P2_1$ was obtained with $a = 8.971$ (2) Å, $b = 10.631$ (3) Å, $c = 11.949$ (2) Å, $\beta = 111.29$ (2)°, and $Z = 2$. The structure was refined to $R = 0.028$ and $R_w = 0.038$. The monoclinic space group $P2_1/n$ resulted for **12** with $a = 11.951$ (3) Å, $b = 13.169$ (3) Å, $c = 20.125$ (5) Å, $\beta = 106.03$ (2)°, and $Z = 4$. The structure refined to $R = 0.028$ and $R_w = 0.037$.

Introduction

Recently, we reported[3,4] the first tin compound having a discrete rectangular-pyramidal (RP) geometry, the spirocyclic complex $[Me_4N][(C_7H_6S_2)_2SnCl]$ (**1**). We also synthesized a number of similar anionic, spirocyclic derivatives, **2**–**5**.[5] From ^{119m}Sn Mossbauer data, the structures were indicated to be RP. Anionic tin complexes of this type are isoelectronic with pentacoordinated antimony derivatives.[6].



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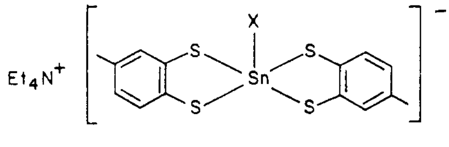

X = F, **2**; Cl, **3**; Br, **4**; I, **5**

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[1] Pentacoordinated Molecules. 53. Previous paper in the series: Vollano, J. F.; Day, R. O.; Holmes, R. R. *Organometallics*, preceding paper in this issue.

[2] This work represents a portion of the Ph.D. Thesis of J. F. Vollano, University of Massachusetts, Amherst.

[3] Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1264.

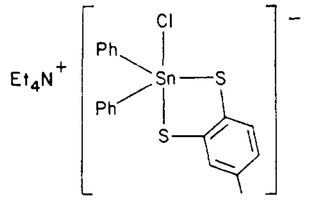
[4] Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

[5] Sau, A. C.; Holmes, R. R.; Molloy, K. C.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 1421.

[6] Holmes, R. R. "Progress in Inorganic Chemistry"; Lippard, S. J., Ed.; Wiley: New York; Vol. 32, in press.

It should be possible to compare structural principles found for pentacoordinated main group 5 compounds[7-9] with those for main group 4 anionic derivatives. However, little is known structurally for anionic tin members other than those that contain acyclic ligands. These include $[Ph_3PCH_2Ph][Bu_3SnCl_2]$,[10] $[Ph_3AsCH_2COPh][Ph_3SnCl_2]$,[10] $[(CH_3)_2SnCl(terpy)][(CH_3)_2SnCl_3]$,[11] $[Mo(\eta^5\text{-}C_5H_5)_3S_4][(CH_3)_3SnCl_2]$,[12] and $[(CH_3)_3,Sn\cdot 2(Me_2N)_3PO][(CH_3)_3,SnBr_2]$[13] (terpy = terpyridyl).

The only anionic derivative containing a cyclic substituent that has been structurally characterized by X-ray diffraction besides 1 is the related monocyclic derivative 6.[4] As expected, the structures[10-13] of the five-coordinated tin complexes containing acyclic ligands are trigonal bipyramidal (TBP). The monocyclic derivative 6 is somewhat more displaced from the ideal TBP.[4]



6

In order to build up the structural basis for comparison between main groups 4 and 5, we have embarked on a program to provide a range of structural types of anionic pentacoordinated derivatives of main group 4. In this paper, we report the synthesis of a series of halodimethylbenzoxathiastannoles, $[(C_6H_4OS)SnMe_2X][Et_4N]$ (X = F, Cl, Br, I, **7–10**, respectively), the chlorodimethyloxobenzoxathiastannin $[(C_6H_4CO_2S)SnMe_2Cl][Et_4N]$ (**11**), and the iodostannole, $[(C_6H_4OS)SnMe_2I][Ph_4P]$ (**12**). Structural characterization of the fluoro, chloro, and iodo derivatives, **7**, **11**, and **12**, respectively, by X-ray diffraction also is included.

Experimental Section

Synthesis. The starting materials were obtained from the following sources: tetraethylammonium halides from Eastman, tetraphenylphosphonium iodide from Alfa, thiosalicyclic acid and *o*-aminophenol from Aldrich, and dimethyltin oxide from ICN Pharmaceuticals.

2,2-Dimethyl-1,3,2-benzoxathiastannole was prepared by the reaction of *o*-mercaptophenol with dimethyltin oxide in refluxing benzene solution;[14a] *o*-mercaptophenol was prepared starting with *o*-aminophenol from a procedure by Greenwood and Stevenson.[14b]

Preparation of Tetraethylammonium 2-Fluoro-2,2-dimethyl-1,3,2λ⁶-benzoxathiastannolate (7). Tetraethylammonium fluoride dihydrate (0.289 g, 1.56 mmol) was added with stirring to a suspension of 2,2-dimethyl-1,3,2-benzoxathiastannole (0.427 g, 1.56 mmol) in acetonitrile. Immediate reaction took place with dissolution of the suspended material. After 10 min, the solution was evaporated, yielding a white crystalline solid. Recrystallization from hot acetonitrile gave white, needle-like crystals of $[(C_6H_4OS)SnMe_2F][Et_4N]$ (**7**); mp 143–144 °C (yield 0.47 g, 71%). Anal. Calcd for $C_{16}H_{30}NOSFSn$: C, 45.53; H, 7.11; N, 3.32. Found: C, 45.11; H, 7.47; N, 3.11.

Preparation of Chloro (8), Bromo (9), and Iodo (10) Derivatives of 2,2-Dimethyl-1,3,2-benzoxathiastannole. The synthesis of **8–10** was carried out following the same procedure that was used in the preparation of the fluoro derivative **7**. In each, a white solid formed. For $[(C_6H_4OS)SnMe_2Cl][Et_4N]$ (**8**): mp 101–102 °C (yield 64%). Anal. Calcd for $C_{16}H_{30}NOSClSn$: C, 43.82; H, 6.84; N, 3.19. Found: C, 43.75; H, 6.97; N, 3.00. For $[(C_6H_4OS)SnMe_2Br][Et_4N]$ (**9**): mp 116–117 °C (yield 73%). Anal. Calcd for $C_{16}H_{30}NOSBrSn$: C, 39.78; H, 6.22; N, 2.90. Found: C, 39.58; H, 6.50; N, 2.95. For $[(C_6H_4OS)SnMe_2I][Et_4N]$ (**10**): mp 142–143 °C. Anal. Calcd for $C_{16}H_{30}NOSISn$: C, 36.24; H, 5.66; N, 2.64. Found: C, 36.17; H, 5.71; N, 2.52.

Preparation of Tetraphenylphosphonium 2-Iodo-2,2-dimethyl-1,3,2λ⁶-benzoxathiastannolate (12). Tetraphenylphosphonium iodide (0.516 g, 1.10 mmol) was added to a suspension of 2,2-dimethyl-1,3,2-benzoxathiastannole (0.301 g, 1.10 mmol) in 25 mL of acetonitrile. The mixture was stirred for 10 min, causing dissolution. A white powder remained after evaporation of the solution. Recrystallization of the powder in benzene resulted in white crystals of $[(C_6H_4OS)SnMe_2I][Ph_4P]$ (**12**): mp 185–188 °C (yield 0.43 g, 53%). Anal. Calcd for $C_{32}H_{30}SOIPSn$: C, 51.98; H, 4.06. Found: C, 51.78; H, 3.90.

Preparation of Tetraethylammonium 2-Chloro-2,2-dimethyl-4-oxo-1,3,2λ⁶-benzoxathiastanninate (11). Thiosalicylic acid (3.14 g, 20.4 mmol) was added to a suspension of dimethyltin oxide (3.36 g, 20.4 mmol) in 100 mL of benzene. The reaction proceeded with refluxing at 80 °C for 3 h. During this time approximately 40 mL of benzene and some water byproduct were azeotropped off. A cream-colored solid of $(C_6H_4CO_2S)SnMe_2$ remained which was air-dried (yield, 5.60 g, 92%).

To a mixture of $(C_6H_4CO_2S)SnMe_2$ (1.32 g, 4.38 mmol) and tetraethylammonium chloride (0.724 g, 4.38 mmol) 40 mL of acetonitrile was added. The white solids dissolved and the reaction was allowed to proceed with stirring for 15 min. Upon evaporation of the solution, a white powder formed. Recrystallization from an acetone–benzene mixture gave crystalline $[(C_6H_4CO_2S)SnMe_2Cl][Et_4N]$ (**11**): mp 106–108 °C. Anal. Calcd for $C_{17}H_{30}NO_2SClSn$: C, 43.76; H, 6.44; N, 3.00. Found: C, 43.88; H, 6.41; N, 2.94.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[15] Crystals were mounted inside sealed thin-walled glass capillaries as a precaution against moisture sensitivity. Data were collected by using the θ–2θ scan mode for $2° \leq 2\theta(\text{Mo } K\bar{\alpha}) \leq 43°$. No corrections were made for absorption.

The structures were solved by using standard Patterson and difference Fourier techniques and were refined by full-matrix least-squares,[16] which was based on reflections having $I \geq 3\sigma_I$.

Crystal data for 7: $C_{16}H_{30}NOSFSn$, colorless crystal from acetonitrile (0.15 × 0.15 × 0.45 mm), uniquely determined orthorhombic space group *Pbca* [D_{2h}^{15}, No. 61],[17] $a = 17.794$ (2) Å, $b = 12.060$ (2) Å, $c = 18.095$ (2) Å, $Z = 8$, and $\mu(\text{Mo } K\bar{\alpha}) = 1.436$ mm^{-1}; 2225 independent reflections ($+h,+k,+l$) were measured. The 21 independent non-hydrogen atoms were refined anisotropically. The only methyl hydrogen atoms which could be located on a difference Fourier synthesis were those for C7. Coordinates for the methylene and aromatic hydrogen atoms were calculated. These 15 hydrogen atoms were included in the refinements as fixed isotropic scatterers. The calculated hydrogen atom coordinates were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The final agreement

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

(16) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_i$. Mean atomic scattering factors were taken from ref 17, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Sn, I, Cl, F, S, P, and O were taken from the same source, pp 149–150.

(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 150.

Table I. Atomic Coordinates in $[(C_6H_4OS)Sn(Me)_2F][Et_4N]$ (7)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	794.7 (3)	1674.9 (5)	956.4 (3)
S	1188 (1)	2911 (2)	1945 (1)
F	177 (3)	2993 (4)	594 (3)
O	1540 (3)	564 (5)	1521 (3)
N	4061 (4)	1737 (5)	1228 (4)
C7	1385 (5)	1557 (8)	−58 (6)
C8	−182 (5)	634 (8)	1099 (5)
C1	1727 (4)	1952 (6)	2448 (4)
C2	1835 (5)	852 (6)	2149 (5)
C3	2279 (5)	126 (7)	2574 (5)
C4	2591 (6)	425 (8)	3239 (5)
C5	2464 (6)	1465 (9)	3522 (5)
C6	2038 (5)	2239 (7)	3128 (5)
C1A	4906 (5)	1506 (8)	1188 (5)
C1B	5167 (6)	467 (8)	1604 (6)
C2A	3806 (5)	1962 (8)	2012 (5)
C2B	4155 (5)	2955 (9)	2396 (6)
C3A	3613 (5)	752 (7)	920 (5)
C3B	3777 (6)	439 (8)	129 (6)
C4A	3921 (6)	2777 (8)	733 (5)
C4B	3112 (6)	3110 (8)	692 (6)

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

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_6H_4OS)Sn(Me)_2F][Et_4N]$ (7)[a]

type[b]	length	type	angle
Sn-F	2.041 (5)	F-Sn-C8	93.3 (3)
Sn-O	2.145 (6)	F-Sn-C7	92.3 (3)
Sn-S	2.432 (2)	F-Sn-O	166.7 (2)
Sn-C8	2.159 (9)	F-Sn-S	85.1 (2)
Sn-C7	2.120 (10)	C7-Sn-C8	117.6 (4)
		C8-Sn-S	120.0 (3)
		C7-Sn-S	122.4 (3)
		C8-Sn-O	94.4 (3)
		C7-Sn-O	93.7 (3)
		S-Sn-O	81.6 (2)

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

factors[18] were $R = 0.043$ and $R_w = 0.060$ for 1642 reflections. A final difference Fourier showed a maximum density of 0.527 e/Å^3 in the vicinity of the tin atom.

Crystal data for 11: $C_{17}H_{30}NO_2SClSn$, colorless crystal from acetone–benzene, 0.20 × 0.25 × 0.10 mm, monoclinic space group $P2_1$ [C_2^2, No. 4],[19] $a = 8.971$ (2) Å, $b = 10.631$ (3) Å, $c = 11.949$ (2) Å, $\beta = 111.29(2)°$, $Z = 2$, and μ(Mo K$\bar{\alpha}$) = 1.438 mm^{-1}; 1303 independent reflections ($+h,+k,\pm l$) were measured. The 23 independent non-hydrogen atoms were refined anisotropically. Methyl hydrogen atoms were not included in the refinement. The 12 hydrogen atoms for which coordinates could be calculated were treated as for 7. The final agreement factors[20] were $R = 0.028$ and $R_w = 0.038$ for 1182 reflections. A final difference Fourier synthesis showed a maximum density of 0.438 e/Å^3.

Crystal data for 12: $C_{32}H_{30}SOIPSn$, colorless crystal from acetonitrile–benzene, 0.20 × 0.35 × 0.45 mm, monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [C_{2h}^5, No. 14][21]), $a = 11.951$ (3) Å, $b = 13.169$ (3) Å, $c = 20.125$ (5) Å, $\beta = 106.03(2)°$, Z = 4, and μ(MoK$\bar{\alpha}$) = 2.011 mm^{-1}; 3690 independent reflections ($+h,+k,\pm l$) were measured. The 37 independent non-hydrogen atoms were refined anisotropically. Coordinates for the six methyl hydrogen atoms were obtained from a difference Fourier synthesis. Coordinates for the remaining independent hydrogen atoms were calculated. These 30 hydrogen atoms were included in the refinement as described for 7. The final agreement factors were $R = 0.028$ and $R_w = 0.037$ for 2952 reflections. A final difference Fourier synthesis showed a maximum density of 0.810 e/Å^3 in the vicinity of the I atom.

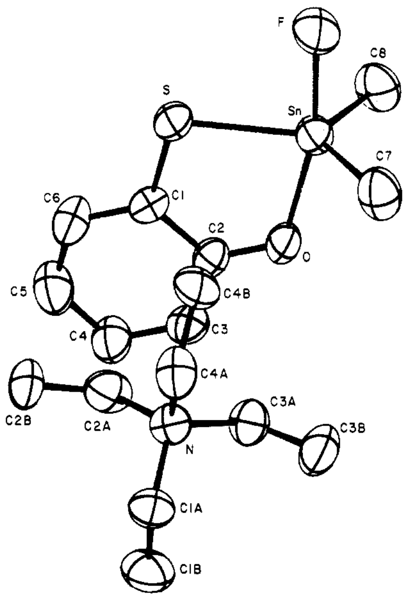

Figure 1. ORTEP plot of $[(C_6H_4OS)Sn(Me)_2F][Et_4N]$ (7) with thermal ellipsoids at the 50% probability level. H atoms have been omitted for purposes of clarity.

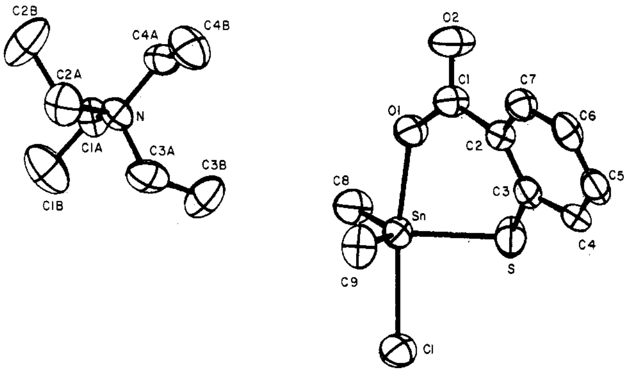

Figure 2. ORTEP plot of $[(C_6H_4CO_2S)Sn(Me)_2Cl][Et_4N]$ (11) with thermal ellipsoids at the 50% probability level. H atoms have been omitted for purposes of clarity.

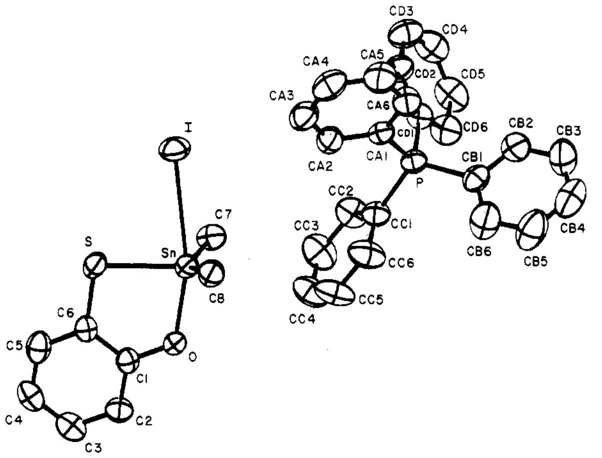

Figure 3. ORTEP plot of $[(C_6H_4OS)Sn(Me)_2I][Ph_4P]$ (12) with thermal ellipsoids at the 50% probability level. H atoms have been omitted for purposes of clarity.

Results

The atom labeling scheme for $[(C_6H_4OS)SnMe_2F][Et_4N]$ (7) is given in the ORTEP plot of Figure 1, while atomic coordinates are given in Table I. The corresponding in-

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(18) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.
(19) Reference 17, p 79.
(20) These values are for the configuration having the lowest R_w.
(21) Reference 17, p 99.

Table III. Atomic Coordinates in $[(C_6H_4CO_2S)Sn(Me)_2Cl][Et_4N]$ (11)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	9617.7 (7)	7500[c]	8044.2 (5)
Cl	8303 (4)	9041 (3)	6322 (2)
S	10534 (4)	6325 (3)	6680 (3)
O1	11053 (10)	6160 (8)	9402 (6)
C1	11293 (12)	4922 (10)	9328 (9)
O2	12200 (10)	4386 (7)	10208 (7)
C8	11189 (14)	8934 (12)	9085 (10)
C9	7447 (12)	6783 (11)	8134 (10)
C2	10531 (10)	4276 (9)	8186 (8)
C3	10170 (11)	4757 (10)	7044 (9)
C4	9524 (12)	3955 (11)	6045 (9)
C5	9232 (10)	2719 (11)	6202 (8)
C6	9534 (10)	2239 (9)	7330 (9)
C7	10213 (12)	2997 (9)	8320 (9)
N	5586 (9)	6686 (9)	12742 (7)
C1A	6523 (11)	7911 (9)	13078 (10)
C1B	5597 (19)	9131 (14)	12857 (16)
C2A	4472 (13)	6550 (14)	13429 (11)
C2B	5308 (16)	6482 (18)	14805 (11)
C3A	4538 (12)	6700 (12)	11427 (10)
C3B	5434 (15)	6847 (14)	10528 (10)
C4A	6767 (13)	5637 (11)	13036 (10)
C4B	6060 (17)	4351 (12)	12798 (13)

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

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_6H_4CO_2S)Sn(Me)_2Cl][Et_4N]$ (11)[a]

type[b]	length	type	angle
Sn-Cl	2.558 (3)	Cl-Sn-O1	170.7 (2)
Sn-C8	2.142 (12)	Cl-Sn-C8	91.5 (3)
Sn-C9	2.130 (10)	Cl-Sn-C9	96.1 (3)
Sn-O1	2.191 (7)	Cl-Sn-S	87.6 (1)
Sn-S	2.422 (3)	C8-Sn-S	116.5 (4)
		C9-Sn-S	112.9 (3)
		C8-Sn-C9	130.3 (4)
		O1-Sn-C8	87.0 (3)
		O1-Sn-C9	91.8 (4)
		O1-Sn-S	84.9 (2)

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

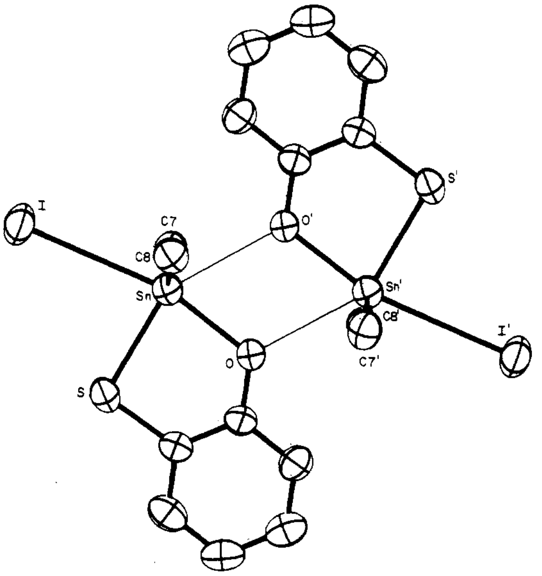

Figure 4. ORTEP plot of two symmetry related anions of **12**, showing the nature of the dimerization about an inversion center. Primed atoms are related to unprimed ones by $-x, -y, -z$. H atoms have been omitted for purposes of clarity.

Table V. Atomic Coordinates in $[(C_6H_4OS)Sn(Me)_2I][Ph_4P]$ (12)[a]

atom type[b]	10^4x	10^4y	10^4z
I	−3019.4 (3)	−1233.2 (3)	−2183.4 (2)
Sn	−1455.4 (3)	−373.9 (3)	−720.6 (2)
S	−3351 (1)	−5 (1)	−527 (1)
P	−2456 (1)	4729 (1)	1137 (1)
O	−843 (3)	324 (2)	261 (2)
C7	−1067 (5)	−1928 (4)	−473 (3)
C8	−1077 (4)	787 (4)	−1351 (3)
C1	−1606 (4)	603 (4)	607 (2)
C2	−1206 (4)	1027 (4)	1274 (2)
C3	−1981 (5)	1288 (4)	1642 (3)
C4	−3155 (5)	1132 (4)	1376 (3)
C5	−3560 (4)	745 (4)	708 (3)
C6	−2804 (4)	486 (3)	325 (2)
CA1	−1355 (4)	4120 (4)	1808 (2)
CA2	−362 (4)	3742 (4)	1663 (3)
CA3	520 (5)	3311 (5)	2191 (3)
CA4	402 (5)	3280 (5)	2844 (3)
CA5	−565 (5)	3664 (5)	2990 (3)
CA6	−1456 (5)	4080 (5)	2477 (3)
CB1	−3854 (4)	4472 (4)	1274 (3)
CB2	−4365 (5)	5179 (5)	1596 (3)
CB3	−5385 (6)	4943 (7)	1770 (4)
CB4	−5886 (5)	4013 (6)	1619 (4)
CB5	−5401 (6)	3322 (5)	1287 (4)
CB6	−4399 (6)	3547 (5)	1110 (4)
CC1	−2290 (4)	4274 (4)	328 (2)
CC2	−1905 (5)	4910 (4)	−109 (3)
CC3	−1692 (6)	4509 (5)	−702 (3)
CC4	−1853 (6)	3501 (5)	−861 (3)
CC5	−2226 (7)	2882 (5)	−433 (3)
CC6	−2435 (6)	3249 (5)	162 (3)
CD1	−2233 (4)	6079 (4)	1189 (3)
CD2	−1296 (5)	6482 (4)	1677 (3)
CD3	−1172 (5)	7540 (5)	1717 (3)
CD4	−1951 (6)	8155 (4)	1281 (3)
CD5	−2874 (6)	7750 (4)	785 (3)
CD6	−3082 (5)	6704 (4)	734 (3)

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

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_6H_4OS)Sn(Me)_2I][Ph_4P]$ (12)[a]

type[b]	length	type	angle
Sn-I	3.225 (1)	I-Sn-O	165.4 (1)
Sn-C7	2.127 (5)	I-Sn-C7	84.8 (1)
Sn-C8	2.114 (5)	I-Sn-C8	82.6 (1)
Sn-O	2.117 (3)	I-Sn-S	83.50 (4)
Sn-S	2.452 (2)	C7-Sn-C8	140.1 (2)
Sn-O'	2.646 (3)	C7-Sn-S	107.8 (1)
		C8-Sn-S	108.2 (1)
		O-Sn-S	82.1 (1)
		O-Sn-C7	101.7 (2)
		O-Sn-C8	99.8 (2)
		O'-Sn-S	148.8 (1)
		O'-Sn-O	67.1 (2)
		O'-Sn-C7	78.7 (2)
		O'-Sn-C8	79.6 (2)
		O'-Sn-I	127.7 (1)
		Sn-O-Sn'	113.3 (1)
		Sn'-O-C1	126.8 (3)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 3 and 4.

formation for $[(C_6H_4CO_2S)SnMe_2Cl][Et_4N]$ (11) and $[(C_6H_4OS)SnMe_2I][Ph_4P]$ (12) is given in Figure 2 and Table III and Figure 3 and Table V, respectively. Figure 4 illustrates the nature of the dimer formed for **12**. Selected bond lengths and angles are presented in Table II for **7**, Table IV for **11**, and Table VI for **12**. Anisotropic thermal parameters, fixed parameters for hydrogen atoms, additional bond lengths and angles, and deviations from least-squares mean planes are provided as supplementary material.

Discussion

Structures. Both the fluoro-containing benzoxathiastannole (7) and the chloro-containing oxobenzoxathiastannin (11) have pentacoordinated structures not too distorted from a trigonal bipyramid. The ring in each spans axial-equatorial positions with the more electronegative oxygen atom located axially. The other axial position is occupied by the halogen atom. The Sn atom is slightly displaced out of the equatorial plane (0.076 Å) *toward* the axial halogen atom (Table K) (supplementary material). In 7, the Sn atom is only 0.006 Å out-of-plane toward the halogen atom (Table J) (supplementary material).

The near trigonal-bipyramidal character is evident from the high planarity of the atoms in the equatorial (Sn, S, and methyl group carbon atoms) and axial (Sn, S, axial O, and halogen atoms) planes and their mutual orthogonality. For the fluoro derivative (7), the average deviations of the atoms from the equatorial and axial planes are ±0.003 and ±0.009 Å, respectively, with a dihedral angle of 90.0° between these two planes Table J). For 11, the average atom displacements are ±0.028 and ±0.044 Å, respectively, from the equatorial and axial planes with a dihedral angle of 89.6° between them (Table K). This same comparison for the iodobenzoxathiastannole (12) shows a poorer agreement with the TBP structure. Here, the average atom displacement from the equatorial and axial planes is ±0.089 and ±0.019 Å, respectively, although the angle between these planes is 89.9° (Table L). The lack of planarity of the equatorial atoms is caused by the large Sn atom displacement of 0.178 Å (Table L) (supplemental material) away from the axial iodine atom.

Actually, the structure of the iodo derivative (12) can be viewed as having trigonal-bipyramidal tin geometry distorted by the presence of an elongated Sn-I axial bond and a weak intermolecular Sn-O bond. The latter is formed via an inversion related oxygen atom, O′, producing a dimer in which the tin atom is six-coordinated (Figure 4).

As judged by comparison to the appropriate sums of covalent[22a] and van der Waals′ radii,[22b] these weaker bonding interactions are comparable in strength. The observed Sn-I distance of 3.225 (1) Å is 0.50 Å longer than the sum of the covalent radii of Sn and I (2.73 Å) and approximately 1.1 Å shorter than the corresponding van der Waals' sum (~4.3 Å). The observed Sn-O′ distance of 2.646 (3) Å is 0.59 Å longer than the covalent sum (2.06 Å) and approximately 0.7 Å less than the van der Waals' sum (~3.3 Å). The Sn_2O_2 ring system formed as a result of the weak dimeric association for the iodo derivative 12 (Figure 4) bears a loose relationship to the ladder structures observed for dimeric distannoxanes $(R_4Sn_2X_2O)_2$.[23] These compounds have Sn-O distances which fall in the range 2.0-2.2 Å, indicative of much stronger association. For the fluoro and chloro derivatives, 7 and 11, the intermolecular Sn-O contacts are all greater than 3.6 Å.

The most pronounced angular change for this series of halostannoles takes place in the CH_3-Sn-CH_3 equatorial angle. It increases from 117.6 (4)° for the fluoro derivative 7 to 130.3 (4)° for the chloro derivative 11 to 140.1(2)° for the iodo compound 12. This increase parallels both the increase in size of the axial halogen atom and the tendency for this bond to lengthen over single bond values. Whereas the Sn-F bond length in 7 of 2.041 (5) Å is equal to the sum of the covalent radii for Sn and F (2.04 Å) and the Sn-Cl bond length in 11 of 2.558 (3) Å is 0.17 Å longer than the covalent radii sum (2.39 Å), the Sn-I bond length, as previously discussed, is lengthened by 0.59 Å over the covalent radii sum. Since the axial halogen-Sn-ring oxygen atom bond angle is little changed in the series, 166.7 (2)° for 7, 170.7 (2)° for 11, and 165.4(1)° for 12, the increase in equatorial angle is consistent with either the steric size of the halogen or the increased Sn-X electron pair—Sn-Me electron pair repulsions expected from VSEPR theory[24] as the halogen electronegativity is reduced. An assist from the equatorial approach of the intermolecular O′ atom (Figure 4) in increasing the CH_3-Sn-CH_3 angle is expected for the iodo derivative 12.

Another feature worth noting is the similarity in the C-O bond lengths of the carboxylate portion of the ligand involved in ring formation for the chloro derivative, 11. The C1-O1 bond, which contains the oxygen atom coordinated to tin, has a length of 1.269 (13) Å. The C1-O2 bond length of 1.250 (12) Å is only slightly shorter, suggesting considerable charge delocalization in the carboxylate moiety.

The presence of the thiosalicylic acid ligand in 11 results in the formation of a six-membered ring in contrast to the fluoro- and iodostannoles, 7 and 12, respectively, which have five-membered rings. This accounts for the greater endocyclic angle at tin and a greater X-Sn-O axial bond angle in the chloro compound (11), 84.9 (2)° and 170.7 (2)°, respectively, compared with 81.6 (2)° and 166.7 (2)° for 7 and 82.1 (1)° and 165.4 (1) for 12 for these angles in the compounds containing the five-membered rings.

The greater conformational freedom associated with the six-membered ring in the chloro derivative (11) is expressed in the out-of-plane character of the benzene portion of the thiosalicylic acid ligand relative to the axial plane. The dihedral angle between the latter planes for 11, plane 1 (Sn, Cl, S, O1) and plane 3 (C2, C3, C4, C5, C6, C7) of Table K, is 49.9°, with the benzene ring tilted toward the equatorial carbon atom C9, as is evident in Figure 2. Dihedral angles between the two ring components for 7 and 12 are 6.0° and 4.9°, respectively. These angles are between planes 1 (C1, C2, C3, C4, C5, C6) and 2 (Sn, S, F, O) for 7 (Table J) and planes 3 (C1, C2, C3, C4, C5, C6) and 2 Sn, S, O, I) for 12 (Table L).

Structural Principles. All three halostannoles have trigonal-bipyramidal structures distorted along a coordinate in which an equatorial angular change takes place in a plane perpendicular to the plane of an axial angular change. The structural change is more so for the iodo derivative (12) (whose distortion is exagerated by the formation of a weakly coupled dimeric unit) compared to the fluoro (7) and chloro (11) compounds. This distortion as measured by the dihedral angle method[25,26] is about 11%, 19%, and 22% from the ideal TBP geometry based on unit bond distances. However, the structural displacement is not toward a square pyramid as defined by the Berry coordinate.[27] The axial and equatorial angles (using sulfur as the pivotal ligand in all cases) are in opposite directions for the fluoro compound from that expected for a pseudorotational motion while the chloro- and

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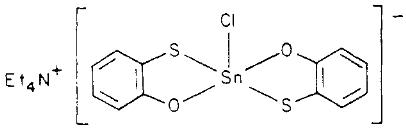
iodostannoles both show an opening of the equatorial and axial angles in the direction of what would be the pivotal sulfur atom. These structural displacements though are not unusual when near the trigonal bipyramid.[6]

The degree of distortion for **7** and **11** is comparable to that for the related chloro containing dithiastannole (**6**)[4] which is distorted 14.1% along the Berry coordinate toward the RP geometry. Analogous to the structural chemistry of phosphoranes,[28] placing one unsaturated, five-membered ring on the central atom in a five-coordinated environment whether the coordinating ring atoms are the same or not, yields a near trigonal-bipyramidal geometry. In contrast, there is a marked dependence on geometry when the ring atoms attached to the tin atom are the same or different if two five-membered, unsaturated rings are present in these anionic species.[7,9,29] For the anionic spirocyclic tin derivative (**1**) the structural displacement is 76.9% from the TBP toward the RP.[3,4] Preliminary data from a structural determination on the recently synthesized mixed-ligand spirocyclic stannole **13**[30] shows a geometry intermediate between the monocyclic (**11**) and spirocyclic (**1**) chloro derivatives and comparable with the analogous phosphorane (**14**)[31] which is 40% displaced toward the RP from the TBP along the Berry coordinate.



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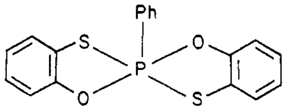

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One can conclude, on the basis of the limited sampling of pentacoordinated pntacoordinated anionic tin compounds studied so far, that structural principles for the tin derivatives closely follow those for phosphoranes.[7,9,29] In this connection, related studies on five-coordinated, anionic silicon compounds[32,33] which are isoelectronic with phosphoranes show a close similarity in structural principles controlling geometrical preference.[34] However, the comparison of the degree of molecular nonrigidity for pentacoordinated anionic tin and silicon species with the known fluxionaal character of phosphoranes[35] based on solution NMR studies has not been established to any degree.[36] The relative ease of geometrical distortion in the solid state with changes in ligand constitution for the five-coordinated tin and silicon[32,33] derivatives suggests that the occurrence of intramolecular ligand exchange in solution may prove general.

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Registry No. **7**, 89414-16-4; **8**, 89414-22-2; **9**, 89414-24-4; **10**, 89414-25-5; **11**, 89414-20-0; **12**, 89414-18-6; $(C_6H_4CO_2S)SnMe_2$, 69706-07-6; 2,2-dimethyl-1,3,2-benzoxathiastannole, 73217-01-3; thiosalicyclic acid, 147-93-3; dimethyltin oxide, 2273-45-2.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes for **7**, **11**, and **12**, anisotropic thermal parameters for **7** (Table A), hydrogen atom parameters for **7** (Table B), anisotropic thermal parameters for **11** (Table C), hydrogen atom parameters for **11** (Table D), anisotropic thermal parameters for **12** (Table E), hydrogen atom parameters for **12** (Table F), additional bond lengths and angles for **7** (Table G), **11** (Table H), and **12** (Table I), and deviations from least-squares mean planes for **7** (Table J), **11** (Table K), and **12** (Table L) (34 pages). Ordering information is given on any current masthead page.

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