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New Five- and Six-Coordinated Anionic Tin(IV) Complexes. Molecular Structure of Spirocyclic Stannates with Mixed Ligands[1,2]

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Abstract: The bromostannate $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (**1**) was formed by bromide addition to bis(toluene-3,4-dithiolato)tin. Mixed-ligand five-coordinated stannates $[(C_6H_4OS)_2SnX][Et_4N]$, where X = Cl (**2**) and F (**5**), respectively, resulted from the room-temperature reaction of tin tetraacetate, *o*-mercaptophenol, and tetraethylammonium halide. The six-coordinated stannate $[(C_6H_4OS)_3Sn]_2[H]_3[Et_4N]$ (**3**) resulted from hydrolytic cleavage of **5**. Similarly, $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (**4**) formed from the hydrolytic scission of the Sn–C(phenyl) bond in $[(C_6H_4O_2)_2SnPh][Et_3NH]$. The latter was prepared from phenylstannoic acid and catechol in the presence of Et_3N. These higher valent derivatives of tin are new substances. The X-ray analyses of **1**–**4** showed **1** as a square pyramid, **2** as a trigonal bipyramid, and **3** and **4** as distorted octahedra, with interesting hydrogen-bonding features. The high stability of tin–sulfur vs tin–oxygen bonding in ring-containing pentacoordinated anionic tin compounds in contrast to the opposite bonding effect with related germanium species correlates with the inherent higher acidity associated with the tin atom. Incorporating tin–oxygen bonds leads to the hexacoordinated stannates **3** and **4**. **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.886$ (3) Å, $b = 15.689$ (5) Å, $c = 28.291$ (7) Å, $\beta = 99.75$ (2)°, and $Z = 4$. **2** crystallizes in the monoclinic space group *Cc* with $a = 10.837$ (1) Å, $b = 12.982$ (1) Å, $c = 16.915$ (1) Å, $\beta = 102.06$ (1)°, and $Z = 4$. **3** crystallizes in the orthorhombic space group $Pbc2_1$ with $a = 12.759$ (1) Å, $b = 15.114$ (2) Å, $c = 23.526$ (4) Å, and $Z = 4$. **4** crystallizes in the orthorhombic space group *Fdd*2 with $a = 14.401$ (2) Å, $b = 32.708$ (5) Å, $c = 12.932$ (2) Å, and $Z = 8$. The final conventional unweighted agreement factors were 0.039 (**1**), 0.027 (**2**), 0.036 (**3**), and 0.029 (**4**).

Previous work[4,5] with five-coordinated spirocyclic anionic tin derivatives has provided one example containing a halogen atom in the fifth position, the spirobis(dithiastannole), $[(C_7H_6S_2)_2SnCl][Me_4N]$. Actually, it was the first example of a discrete square-pyramidal geometry isolated for tin(IV).[4] For pentacoordinated derivatives of anionic silicon[6-8] and germanium[9-11] of this class, a number of spirocyclic members with ring-containing oxygen, sulfur, carbon, and mixed oxygen–sulfur ligands have been synthesized and structurally characterized by X-ray diffraction. These are summarized in Table I, which shows their geometrical displacement from the trigonal bipyramid (TBP) to the rectangular pyramid (RP) as determined by application of the dihedral angle method[12,13] that we have commonly employed to measure structural distortions from polyhedral surfaces.

Table I. Structural Distortion for Cyclic Five-Coordinated Halogen-Containing Main-Group 4 Compounds

compd	TBP → RP,[a] %	ref
$[Et_4N][(C_6H_4OS)_2SnCl]$	38.0	this work
$[Me_4N][(C_7H_6S_2)_2SnCl]^d$	76.9	4, 5
$[MePPh_3][(C_7H_6S_2)_2SnBr]^d$	94.2	this work
$[Et_4N][(C_6H_4OS)_2GeBr]\cdot CH_3CN$	23.6, 26.2[b]	9
$[Et_4N][(C_6H_4OS)_2GeCl]$	34.2	9
$[Ph_3PMe][(C_7H_6S_2)_2GeF]\cdot CH_3CN^d$	40.3	10
$[Et_4N][(C_6H_4O_2)_2GeBr]$	70.4	9
$[Et_4N][(C_6H_4O_2)_2GeF]$	80.6	10
$[Et_4N][(C_6H_4O_2)_2GeCl]$	90.7	11
$[Et_3NH][(dtbc)_2GeOH]^c$	95.7	9
$[Et_4N][(C_6H_4O_2)_2SiF]$	68.7, 52.8[b]	6
$[Me_4N][(Me_4C_2O_2)_2SiF]$	53.6, 70.8[b]	8
$[(Me_2N)_3S][(C_6H_4(CF_3)_2CO)_2SiF]$	28.7, 25.4[b]	7

[a] The percent displacement from the ideal trigonal bipyramid toward the rectangular pyramid is calculated from unit bond distances on the basis of the dihedral angle method.[12] The θ value for the "ideal" rectangular pyramid used in the calculation of the percent displacement is 150°.[34] [b] Two independent molecules per unit cell. [c] The ligand dtbc is 3,5-di-*tert*-butylcatechol. [d] The ligand $C_7H_6S_2$ is toluene-3,4-dithiol.

The related papers in this series of investigations[14] centered on anionic derivatives possessing all ring Sn–S bonds, a prevalent feature for five-coordinated tin. Reported here are the synthesis and X-ray studies of two additional spirocyclic tin derivatives, with a halogen atom located at the fifth position, the bromostannate $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (**1**), incorporating the toluene-3,4-dithiol ligand, and the chlorostannate $[(C_6H_4OS)_2SnCl][Et_4N]$ (**2**), having the *o*-mercaptophenol ligand. Indicative of the hydrolytic instability of five-coordinated anionic tin compounds possessing ring Sn–O bonding, two six-coordinated dianionic stannates that resulted from attempts to obtain further spirocyclic derivatives are reported and their structures determined. These are the tris(1-hydroxybenzene-2-thiolato)stannate $[(C_6H_4OS)_3Sn]_2[H]_3[Et_4N]$ (**3**) and the tris(phenylene-1,2-di-

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(1) (a) Pentacoordinated Molecules. 70. (b) Part 69: Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 760–765.

(2) Presented in part at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 1986; paper INOR 220.

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oxy)stannate $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (**4**). In addition, the preparation of the fluorostannate $[(C_6H_4OS)_2SnF][Et_4N]$ (**5**) is given and provides the only example of pentacoordinated anionic tin exhibiting Sn–F bonding.

Experimental Section

All solvents (HPLC grade) were either used directly from freshly opened bottles or dried prior to use. Acetonitrile was refluxed and distilled from phosphorus pentoxide. Diethyl ether and benzene[15] were distilled from lithium aluminum hydride. Reagents were from commercial sources and were used without further purification.

Phenylstannoic acid was prepared by hydrolysis of phenyltin trichloride with potassium hydroxide.[16] *o*-Mercaptophenol was synthesized starting with *o*-aminophenol by a several-step synthesis proceeding to a diazonium salt by reaction with $NaNO_2$, formation of the ethyl xanthate, and $LiAlH_4$ reduction to the product. Tin tetraacetate was synthesized[17] from tin tetrachloride and ethanethiol and NH_3 in benzene[15] followed by reaction with anhydrous acetic acid.

Proton NMR spectra were obtained on Varian A-60 and 300-MHz Varian spectrometers and referenced versus tetramethylsilane. Melting points were obtained with a Uni-melt capillary melting point apparatus (Hoover) and were uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Syntheses. Methyltriphenylphosphonium Bis(4-methylbenzene-1,2-dithiolato)bromostannate, $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (1). To a solution of methyltriphenylphosphonium bromide (0.536 g, 1.5 mmol) in methyl cyanide (20 mL) was suspended bis(toluene-3,4-dithiolato)tin, $Sn(C_7H_6S_2)_2$ (0.634 g, 1.5 mmol), and the resulting mixture was stirred at room temperature for 0.5 h to obtain a dark yellow solution. Evaporation of solvent in vacuo gave a yellow crystalline residue, which was washed with water to remove any excess of $[MePPh_3][Br]$. The water-insoluble yellow precipitate was filtered under suction and air-dried. Recrystallization of the crude product from acetonitrile at 0 °C in a refrigerator gave pure $[(MeC_6H_3S_2)_2SnBr][MePPh_3]$: yield 1.05 g (89.7%); mp 153–154 °C. Crystals suitable for X-ray crystallography were grown by the recrystallization of a sample of $[BrSn(C_7H_6S_2)_2]$-$[MePPh_3]$ from a 1:1 mixture of acetonitrile and benzene[15] at 0 °C. The X-ray crystallographic studies showed that the sample of crystals thus obtained is a benzene solvate of the original complex having the composition $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (**1**).

Tetraethylammonium Bis(1-hydroxybenzene-2-thiolato)chlorostannate, $[(C_6H_4OS)_2SnCl][Et_4N]$ (2). Tin tetraacetate (0.5 g, 1.4 mmol) was stirred without dissolving in 10 mL of benzene[15] under nitrogen. The solution of *o*-mercaptophenol (0.34 g, 2.7 mmol) in benzene (10 mL) was added dropwise over 0.5 h. A clear yellow solution was obtained upon completion of the addition. Tetraethylammonium chloride (0.231 g, 1.4 mmol) in acetonitrile (30 mL) was added, and the solution was stirred for 0.5 h. After filtering, the volume was reduced to 10 mL by evaporation under vacuum, and the resultant mixture was treated with 10 mL of diethyl ether and cooled to yield yellow crystals: yield 0.45 g (51%); mp 168–173 °C; ^1H NMR (CD_3CN) 1.12 (t, 12 H), 3.08 (q, 8 H), 6.6–6.95 (br, 4 H), 7.2–7.45 (d, 4 H). Anal. Calcd for $C_{20}H_{28}O_2NS_2ClSn$: C, 45.11; H, 5.25; N, 2.29. Found: C, 44.25; H, 5.15; N, 2.64. Crystals suitable for X-ray structural analysis were grown by the slow vapor diffusion of ether into a solution of the product dissolved in acetonitrile.

Tetraethylammonium Bis(1-hydroxybenzene-2-thiolato)fluorostannate, $[(C_6H_4OS)_2SnF][Et_4N]$ (5), and Tetraethylammonium Trihydrogen Bis[tris(1-hydroxybenzene-2-thiolato)stannate] (3). Tin tetraacetate (0.25 g, 0.70 mmol) in 20 mL of chloroform was stirred under nitrogen. *o*-Mercaptophenol (0.25 g, 2.0 mmol) in chloroform (20 mL) was placed in a dropping funnel. Dropwise addition caused the immediate formation of a green solution. Tetraethylammonium fluoride dihydrate (0.134 g, 0.70 mmol) was added after the addition of *o*-mercaptophenol was completed. A yellow precipitate was formed that was filtered under suction and treated with water to dissolve unreacted tetraethylammonium fluoride. The crude product was dissolved in a mixture of acetonitrile and carbon tetrachloride (1:1) and cooled at 0 °C for several days to yield green crystals: yield 0.216 g (48.6%); mp 173–175 °C; ^1H NMR (CD_3CN) 1.1 (t, 12 H), 3.05 (q, 8 H), 6.5–6.85 (br, 4 H), 7.1–7.45 (d, 4 H). Anal. Calcd for $C_{20}H_{28}O_2NS_2FSn$: C, 46.53; H, 5.47; N, 2.71. Found: C, 46.34; H, 4.86; N, 2.79. Crystals were grown by the slow vapor diffusion of ether into a solution of the product in acetonitrile. X-ray analysis showed the formulation $[(C_6H_4OS)_3Sn][H]_3[Et_4N]$ (**3**), apparently formed in a hydrolysis reaction of **5**.

Bis(triethylammonium) tris(phenylene-1,2-dioxy)stannate, $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (4). To a suspension of phenylstannoic acid (1.02 g, 4.46 mmol) in acetonitrile (150 mL) were added catechol (0.98 g, 8.9 mmol), 2,2-dimethoxypropane (0.93 g, 8.9 mmol), and triethylamine (0.45 g, 4.5 mmol), and the reaction mixture was heated. As it warmed, the solution turned clear. Heating was continued under reflux for 12 h. Insoluble material was filtered off. Removal of solvent yielded a dark greenish precipitate, which did not redissolve easily. However, it was found to be soluble in a hot mixture of ethanol and isopropyl alcohol. This solution was heated with animal charcoal and filtered. A crystalline pale green material was obtained: yield 0.80 g (42%); mp 220 °C dec. Anal. Calcd for $C_{30}H_{44}N_2O_6Sn$: C, 55.66; H, 6.85; N, 4.33. Found: C, 55.66; H, 7.15; N, 4.32.

Because of the insolubility of this compound in common organic solvents, no NMR could be recorded.

Crystallography. All X-ray crystallographic studies were done with 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 ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[18] Crystals were mounted in thin-walled glass capillaries, which were sealed as a precaution against moisture. Data were collected with the θ–2θ scan mode for $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 45°$ for **1** and $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 50°$ for **2**–**4**. The structures were solved by use of Patterson and difference Fourier techniques and were refined by means of full-matrix least-squares procedures.[19]

X-ray Studies for $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (1). The crystal used for the X-ray study was cut from a bright yellow polycrystalline mass and had dimensions of 0.15 × 0.33 × 0.38 mm.

Crystal data: $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (1), monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [C_{2h}^5–No. 14][20]), $a = 9.886$ (3) Å, $b = 15.689$ (5) Å, $c = 28.291$ (7) Å, $\beta = 99.75$ (2)°, $Z = 4$, and $\mu_{Mo\,K\bar{\alpha}} = 1.813\ mm^{-1}$. A total of 5614 independent reflections ($+h$,$+k$,$\pm l$) was measured. No corrections were made for absorption.

The 52 independent non-hydrogen atoms were refined anisotropically. The 33 independent aromatic hydrogen atoms were included in the refinement as fixed isotropic scatterers, with calculated coordinates that were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[21] were $R = 0.039$ and $R_w = 0.055$ for the 4186 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $[(C_6H_4OS)_2SnCl][Et_4N]$ (2). The crystal used for the X-ray study was cut from a yellow polycrystalline mass and had dimensions of 0.20 × 0.25 × 0.38 mm.

Crystal data: $[(C_6H_4OS)_2SnCl][Et_4N]$ (2), monoclinic space group Cc [C_s^4–No. 9],[22] $a = 10.837$ (1) Å, $b = 12.982$ (1) Å, c = 16.915 (1) Å, $\beta = 102.06$ (1)°, $Z = 4$, and $\mu_{Mo\,K\bar{\alpha}} = 1.423\ mm^{-1}$. A total of 2027 independent reflections ($+h$,$+k$,$\pm l$) was measured. No corrections were made for absorption.

The 27 independent non-hydrogen atoms were refined anisotropically. The 16 independent aromatic and methylene hydrogen atoms were treated as described for **1**. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[21] were $R = 0.027$ and $R_w = 0.038$ for the 1921 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $[(C_6H_4OS)_3Sn]_2[H]_3[Et_4N]$ (3). The crystal used for the X-ray study was cut from a larger yellow brick-shaped crystal and was an approximate cube with an edge length of 0.30 mm.

Crystal data: $[(C_6H_4OS)_3Sn]_2[H]_3[Et_4N]$ (3), orthorhombic space group $Pbc2_1$ (alternate setting of $Pca2_1$ [C_{2v}^5–No. 29][23]), $a = 12.759$ (1) Å, $b = 15.114$ (2) Å, $c = 23.526$ (4) Å, $Z = 4$, and $\mu_{Mo\,K\bar{\alpha}} = 1.417\ mm^{-1}$. A total of 4087 independent reflections ($+h$,$+k$,$+l$) was measured. No corrections were made for absorption.

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(15) *Caution*! Benzene is a class A carcinogen and should be used in a hood equipped with a good exhaust system. All of our synthetic work is carried out under these conditions.

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(20) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(21) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. For compounds **2–4**, the values reported are for the configuration having the lowest R_w.

(22) Reference 20, p 89.

(23) Reference 20, p 115.

Table II. Atomic Coordinates in Crystalline $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (**1**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	−28.8 (4)	2473.8 (3)	1328.5 (1)
Br	124.8 (9)	3570.1 (5)	1990.7 (3)
S1	197 (2)	1154 (1)	1802 (1)
S2	−2491 (2)	2131 (1)	1141 (1)
S1′	−370 (2)	3332 (1)	590 (1)
S2′	2351 (2)	2287 (1)	1211 (1)
P	−2184 (2)	2806 (1)	3411 (1)
C1	−1497 (6)	1041 (3)	1905 (2)
C2	−2645 (6)	1440 (4)	1620 (2)
C3	−3956 (6)	1273 (4)	1721 (2)
C4	−4187 (6)	739 (4)	2087 (2)
C5	−3035 (7)	360 (4)	2369 (2)
C6	−1743 (6)	512 (4)	2281 (2)
C7	−5629 (7)	601 (5)	2194 (3)
C1′	1330 (6)	3430 (4)	477 (2)
C2′	2468 (6)	3015 (4)	745 (2)
C3′	3768 (6)	3148 (4)	625 (2)
C4′	3981 (7)	3651 (4)	245 (2)
C5′	2832 (7)	4044 (4)	−25 (2)
C6′	1548 (7)	3941 (4)	95 (2)
C7′	5384 (7)	3718 (5)	105 (3)
CM	−647 (7)	3018 (4)	3165 (2)
CA1	−3656 (7)	3123 (4)	2981 (2)
CA2	−3627 (8)	3007 (5)	2497 (3)
CA3	−4778 (11)	3227 (6)	2173 (3)
CA4	−5895 (9)	3562 (5)	2322 (3)
CA5	−5909 (8)	3707 (5)	2799 (4)
CA6	−4758 (7)	3496 (5)	3138 (3)
CB1	−2140 (6)	3424 (4)	3948 (2)
CB2	−2031 (7)	4303 (4)	3914 (2)
CB3	−1934 (8)	4788 (4)	4325 (3)
CB4	−1943 (9)	4406 (5)	4759 (3)
CB5	−2097 (9)	3534 (5)	4793 (2)
CB6	−2181 (8)	3048 (4)	4381 (2)
CC1	−2274 (6)	1689 (4)	3539 (2)
CC2	−1079 (6)	1191 (4)	3623 (3)
CC3	−1193 (7)	340 (4)	3715 (3)
CC4	−2429 (7)	−26 (4)	3739 (2)
CC5	−3604 (7)	460 (4)	3666 (3)
CC6	−3529 (6)	1312 (4)	3570 (2)
CD1	2819 (8)	2032 (5)	3657 (3)
CD2	2998 (8)	1546 (6)	4065 (3)
CD3	2847 (9)	694 (6)	4045 (3)
CD4	2496 (8)	312 (5)	3623 (4)
CD5	2303 (8)	766 (6)	3205 (3)
CD6	2461 (8)	1636 (6)	3222 (3)
CE1	1800 (9)	4357 (5)	4081 (3)
CE2	3046 (11)	4684 (6)	4060 (3)
CE3	4180 (10)	4400 (8)	4382 (4)
CE4	3999 (10)	3813 (7)	4729 (4)
CE5	2741 (10)	3506 (5)	4752 (3)
CE6	1650 (9)	3770 (5)	4432 (3)

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

The 59 independent non-hydrogen atoms were refined anisotropically. The 32 independent aromatic and methylene hydrogen atoms were treated as described for **1**. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[21] were $R = 0.036$ and $R_w = 0.049$ for the 3362 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (4). The colorless crystal used for the X-ray study was cut from a polycrystalline mass, which appeared gray-green in bulk, and had dimensions of 0.25 × 0.28 × 0.35 mm.

Crystal data: $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (**4**), orthorhombic space group $Fdd2$ [C_{2v}^{19}-No. 43],[24] $a = 14.401$ (2) Å, $b = 32.708$ (5) Å, $c = 12.932$ (2) Å, $Z = 8$, and $\mu_{Mo\,K\alpha} = 0.891$ mm^{-1}. A total of 1478 independent reflections ($+h,+k,+l$) was measured. No corrections were made for absorption.

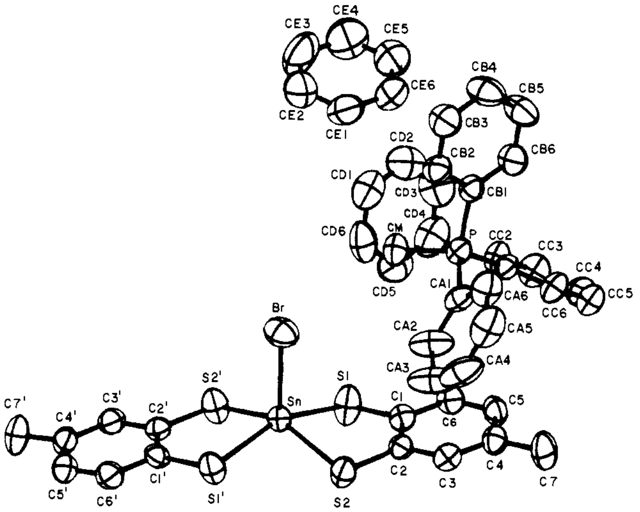

Figure 1. ORTEP plot of $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (**1**), with thermal ellipsoids at the 50% probability level. Primed atoms are not symmetry related to unprimed ones. Hydrogen atoms are omitted for purposes of clarity.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (**1**)[a]

type[b]	length	type[b]	length
Sn–S1	2.456 (2)	Sn–S2′	2.449 (2)
Sn–S1′	2.461 (2)	Sn–Br	2.529 (1)
Sn–S2	2.462 (2)		
type	**angle**	**type**	**angle**
S1–Sn–S1′	155.68 (7)	Br–Sn–S2′	104.07 (6)
S2–Sn–S2′	151.96 (7)	S1–Sn–S2	85.90 (6)
Br–Sn–S1	100.44 (6)	S1′–Sn–S2′	86.97 (6)
Br–Sn–S1′	103.85 (6)	S1–Sn–S2′	88.41 (6)
Br–Sn–S2	103.95 (5)	S1′–Sn–S2	87.03 (6)

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

Table IV. Atomic Coordinates in Crystalline $[(C_6H_4OS)_2SnCl][Et_4N]$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	0[c]	2613.4 (3)	2500[c]
Cl	−1126 (2)	3805 (2)	3134 (2)
S1	−838 (2)	2469 (2)	1075 (1)
S1′	1695 (2)	1791 (2)	3418 (1)
O1	1198 (5)	3691 (5)	2188 (3)
O1′	−1050 (4)	1353 (4)	2693 (3)
C1	997 (6)	3983 (5)	1405 (4)
C2	103 (7)	3487 (5)	803 (4)
C3	−67 (8)	3793 (6)	3 (4)
C4	652 (9)	4570 (7)	−209 (5)
C5	1560 (8)	5062 (6)	381 (5)
C6	1722 (6)	4782 (5)	1173 (4)
C1′	−522 (6)	707 (5)	3300 (4)
C2′	742 (6)	794 (5)	3695 (4)
C3′	1255 (8)	111 (7)	4301 (5)
C4′	525 (10)	−660 (7)	4526 (6)
C5′	−723 (9)	−754 (6)	4142 (5)
C6′	−1260 (7)	−72 (5)	3527 (4)
N	−5225 (5)	2579 (4)	1566 (4)
C7	−5024 (10)	2442 (5)	702 (5)
C8	−6079 (13)	2880 (10)	49 (6)
C9	−6433 (7)	2054 (7)	1660 (6)
C10	−6489 (11)	900 (8)	1474 (9)
C11	−5346 (7)	3715 (5)	1738 (5)
C12	−4233 (9)	4386 (6)	1664 (7)
C13	−4089 (7)	2134 (6)	2132 (5)
C14	−4125 (14)	2172 (11)	3007 (7)

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

The 20 independent non-hydrogen atoms were refined anisotropically. The 13 independent hydrogen atoms with calculable coordinates were treated as described for **1**, with the N–H bond length fixed at 0.90 Å. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[21] were $R = 0.029$ and $R_w = 0.038$ for the 1274 reflections having $I \geq 2\sigma_I$.

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[24] Reference 20, p 129.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) in $[(C_6H_4OS)_2SnCl][Et_4N]$ (**2**)[a]

type[b]	length	type[b]	length
Sn–Cl	2.362 (3)	O1–C1	1.350 (8)
Sn–O1	2.051 (5)	O1′–C1′	1.357 (8)
Sn–O1′	2.058 (5)	S1–C2	1.787 (8)
Sn–S1	2.400 (2)	S1′–C2′	1.779 (7)
Sn–S1′	2.394 (2)		
type	**angle**	**type**	**angle**
O1–Sn–O1′	169.7 (3)	S1–Sn–S1′	134.00 (9)
O1–Sn–S1	85.5 (2)	S1–Sn–Cl	112.6 (9)
O1–Sn–S1′	91.7 (2)	S1′–Sn–Cl	113.4 (1)
O1–Sn–Cl	94.9 (2)	Sn–S1′–C2′	94.9 (2)
O1′–Sn–S1	89.5 (2)	Sn–S1–C2	94.8 (2)
O1′–Sn–S1′	85.3 (1)	Sn–O1′–C1′	116.9 (4)
O1′–Sn–Cl	95.4 (2)	Sn–O1–C1	117.6 (4)

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

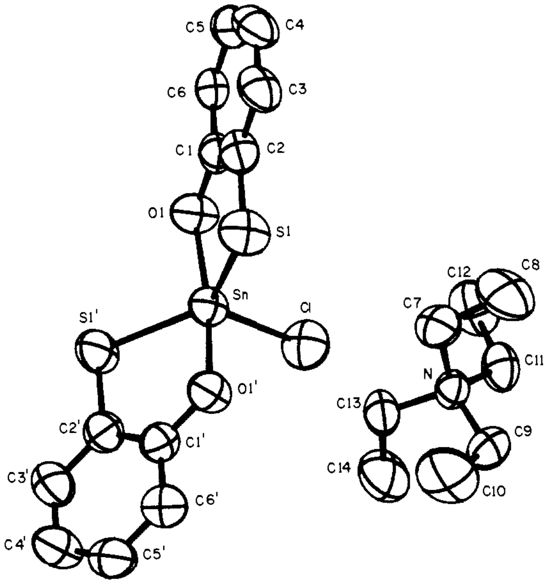


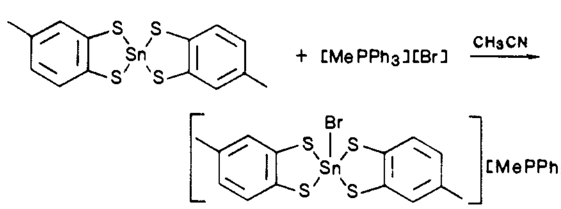
Figure 2. ORTEP plot of $[(C_6H_4OS)_2SnCl][Et_4N]$ (**2**), with thermal ellipsoids at the 50% probability level. Primed atoms are not symmetry related to unprimed ones. Hydrogen atoms are omitted for purposes of clarity.

Results

The atom-labeling scheme for **1** is shown in the ORTEP plot of Figure 1. Atomic coordinates are given in Table II, and selected bond lengths and angles are given in Table III. The corresponding information for **2–4** is given in Figures 2–4 and in Tables IV–IX. Thermal parameters, hydrogen atom parameters, and additional bond lengths and angles for all four compounds are provided as supplementary material.

Discussion

Syntheses. A variety of synthetic procedures were attempted to obtain five-coordinated spirocyclic anionic derivatives where the rings provided mixed-ligand attachments to tin. Although the spirocyclic bromostannate **1** readily formed in high yield from the addition of bromide to bis(toluene-3,4-dithiolato)tin (eq 1),



(1)

1

a similar preparation starting with *o*-mercaptophenol proved unsatisfactory. The formation of bis(toluene-3,4-dithiolato)tin results from the room-temperature reaction of $SnCl_4 \cdot 5H_2O$ with toluene-3,4-dithiol in aqueous solution.[5] In related germanium chemistry, mercaptophenol reacts smoothly with germanium tetrachloride in benzene solution to form the bis(mercaptophenolate) salt[9] (eq 2). The latter undergoes halide addition with relative ease with all of the halides.[9] With the use of $SnCl_4 \cdot 5H_2O$ in place of $GeCl_4$, mercaptophenol failed to yield the corresponding mixed-ligand bis(mercaptophenolate). Instead, a more complex reaction seemed to ensue.[25]

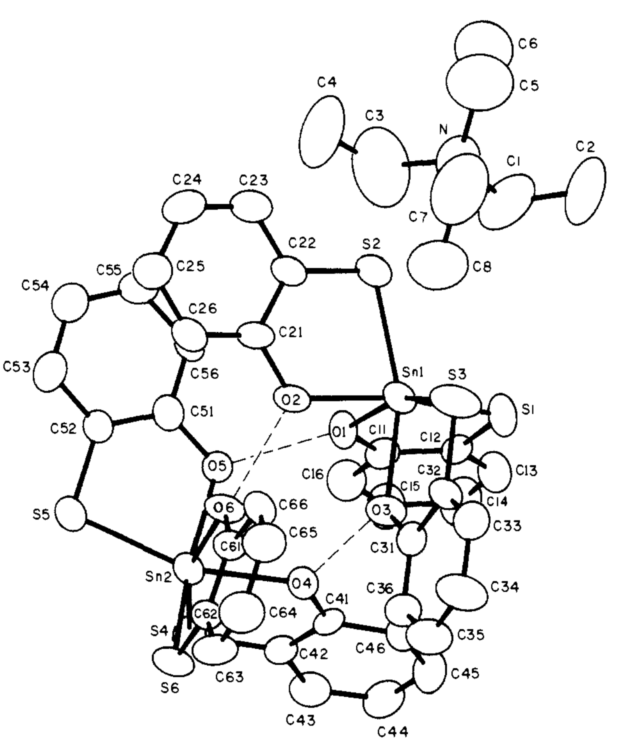


Figure 3. ORTEP plot of $[(C_6H_4OS)_3Sn]_2[H]_3[Et_4N]$ (**3**), with thermal ellipsoids at the 50% probability level. The proton–oxygen atom interactions are indicated by dashed lines. Hydrogen atoms are omitted for purposes of clarity.

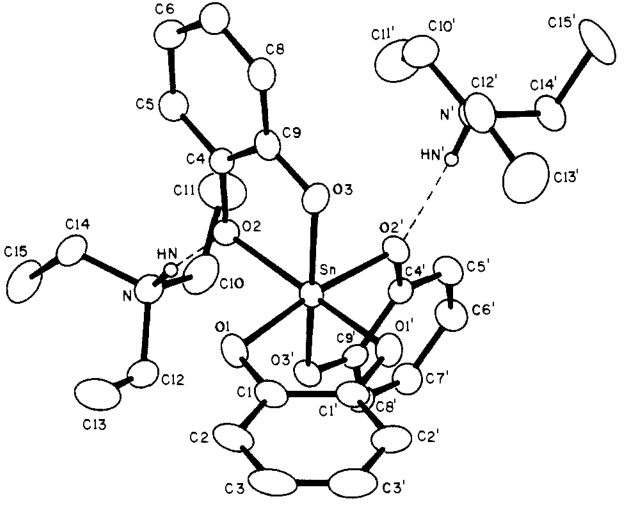
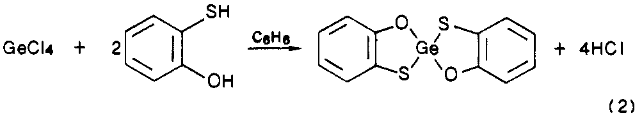


Figure 4. ORTEP plot of $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (**4**), with thermal ellipsoids at the 50% probability level. Primed atoms are 2-fold-related (–*x*, –*y*, *z*) to unprimed ones. Hydrogen-bonding interactions are shown as dashed lines. The remaining hydrogen atoms have been omitted for purposes of clarity.



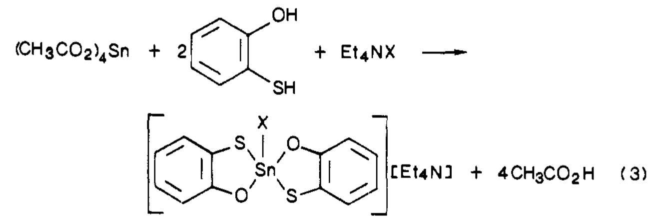
(2)

Table VI. Atomic Coordinates in Crystalline $[(C_6H_4OS)_3Sn]_2[Et_4N][H]_3$ (**3**)[a]

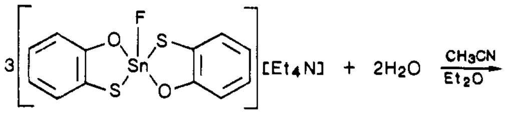
atom type[b]	10^4x	10^4y	10^4z
Sn1	2547.7 (5)	−148.0 (4)	2500[c]
Sn2	2577.3 (5)	2751.1 (4)	1371.6 (4)
S1	1485 (2)	−1340 (2)	2148 (1)
S2	4239 (2)	−850 (2)	2686 (1)
S3	1873 (3)	−59 (2)	3502 (1)
S4	1923 (2)	2662 (2)	401 (1)
S5	4292 (2)	3420 (2)	1200 (1)
S6	1565 (2)	3969 (2)	1772 (1)
O1	2796 (5)	128 (4)	1645 (3)
O2	3485 (5)	1033 (4)	2591 (3)
O3	1352 (5)	873 (4)	2400 (3)
O4	1370 (5)	1763 (4)	1511 (3)
O5	3527 (5)	1546 (4)	1313 (3)
O6	2836 (5)	2466 (5)	2270 (3)
C11	2224 (7)	−347 (6)	1248 (4)
C12	1592 (6)	−1049 (6)	1429 (4)
C13	1043 (9)	−1514 (7)	1034 (5)
C14	1082 (10)	−1294 (9)	458 (6)
C15	1710 (9)	−580 (8)	278 (5)
C16	2309 (8)	−116 (7)	682 (5)
C21	4528 (7)	984 (6)	2754 (4)
C22	4975 (8)	130 (6)	2818 (4)
C23	6053 (8)	76 (7)	2960 (5)
C24	6634 (8)	830 (8)	3029 (5)
C25	6168 (8)	1653 (7)	2957 (5)
C26	5114 (9)	1726 (6)	2831 (5)
C31	727 (8)	1145 (6)	2851 (4)
C32	891 (8)	751 (6)	3378 (4)
C33	277 (10)	1018 (8)	3834 (5)
C34	−467 (10)	1664 (9)	3752 (5)
C35	−624 (10)	2035 (8)	3228 (5)
C36	−19 (8)	1782 (7)	2771 (5)
C41	747 (7)	1525 (6)	1071 (4)
C42	922 (7)	1896 (6)	516 (4)
C43	259 (9)	1633 (7)	73 (5)
C44	−524 (9)	1000 (8)	160 (5)
C45	−672 (10)	635 (8)	701 (6)
C46	−60 (8)	913 (7)	1151 (5)
C51	4596 (7)	1629 (6)	1360 (4)
C52	5062 (6)	2461 (6)	1317 (4)
C53	6128 (7)	2530 (7)	1361 (4)
C54	6741 (8)	1796 (7)	1464 (5)
C55	6301 (8)	976 (7)	1502 (5)
C56	5208 (8)	885 (6)	1455 (4)
C61	2298 (7)	2980 (6)	2660 (4)
C62	1717 (7)	3697 (6)	2485 (5)
C63	1170 (8)	4185 (8)	2902 (5)
C64	1292 (10)	3957 (8)	3461 (6)
C65	1881 (10)	3251 (8)	3639 (5)
C66	2385 (7)	2743 (6)	3241 (5)
N	4530 (9)	−1407 (8)	4593 (4)
C1	3647 (11)	−1784 (14)	4254 (8)
C2	3025 (13)	−2471 (14)	4604 (11)
C3	5176 (21)	−771 (15)	4234 (8)
C4	6083 (14)	−297 (14)	4462 (8)
C5	5210 (18)	−2146 (15)	4818 (9)
C6	5636 (14)	−2794 (12)	4340 (8)
C7	4100 (16)	−842 (16)	5086 (7)
C8	3426 (14)	−91 (12)	4909 (9)

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

In a subsequent method, recorded here, to obtain mixed-ligand species, we found that tin tetraacetate when reacted with mercaptophenol followed by halide addition yielded the chlorostannate **2** and fluorostannate **5** according to eq 3. We were unable to isolate the bis(1-hydroxybenzene-2-thiolato)stannate, as it formed a light-sensitive solution, which, upon evaporation, led to decomposition. The fluoro derivative **5** itself is not very stable. Upon recrystallization, crystals of the hexacoordinated salt **3** were isolated, indicative of the hydrolytic cleavage expressed by eq 4.

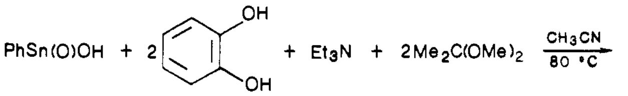


X = Cl (**2**), F (**5**)



$[(C_6H_4OS)_3Sn]_2[H]_3[Et_4N] + 2Et_4NF + SnO_2 + HF$ (4)

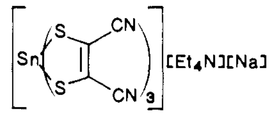
The reaction of phenylstannoic acid with catechol in the presence of triethylamine and 2,2-dimethoxypropane was anticipated to proceed according to eq 5 to give the phenyl bis(catecholate) salt. However, the product isolated, **4**, from the reaction with adventitious water (eq 6) indicates the instability of five-coordinated tin-containing oxygen ligand ring systems and the ease of cleavage of Sn–C(phenyl) bonds. Instead of eq 6, we can write the formation of **4** directly from phenylstannoic acid in terms of eq 7. The isolation of a six-coordinated tin compound via a Sn–C bond scission is not uncommon. In the previous paper in this series,[14a] the formation of the tris(cyanoethylenethiolato) complex **6** follows a similar hydrolytic course from $PhSnCl_3$.



$[(C_6H_4O_2)_2SnPh][Et_3NH] + 4MeOH + 2Me_2CO$ (5)

$$3[(C_6H_4O_2)_2SnPh][Et_3NH] + Et_3N + 2H_2O \rightarrow \underset{\mathbf{4}}{2[(C_6H_4O_2)_3Sn][Et_3NH]_2} + 3C_6H_6 + SnO_2 \quad (6)$$

$$3PhSn(O)OH + 6C_6H_4(OH)_2 + 4Et_3N + 6Me_2C(OMe)_2 + 2H_2O \xrightarrow[80\ ^\circ C]{CH_3CN} 2[(C_6H_4O_2)_3Sn][Et_3NH]_2 + 3C_6H_6 + SnO_2 + 12MeOH + 6Me_2CO \quad (7)$$



6

The formation and structural characterization of **4**, **3**, and **6** encompass a series of hexacoordinated tin compounds containing unsaturated ring systems providing OO, OS, and SS bonding to tin, respectively. It is interesting that the formation of this series was achievable, whereas a similar series did not form for pentacoordinated tin(IV) for lack of synthesis of the member providing ring OO to tin coordination.

The latter observation of bonding in these series lends support to the assertion presented in earlier work[9,14a] that the reduced electronegativity for tin relative to germanium gives tin a proper balance to form ring tin–sulfur bonds in five-coordinated anionic species, whereas germanium prefers germanium–oxygen ring bonding. Increasing the tin acidity by replacing ring sulfur atoms with oxygen atoms was suggested to bring higher coordination numbers into favorable competition.

In this regard, if a saturated ring system is used in place of an unsaturated ring system, the acidity of tin should be reduced with the accompanying result that five-coordination should be favored once again for ring systems providing all tin–sulfur bonding. This agrees with the ready formation of five-coordinated ethanedithiolate tin complexes reported elsewhere.[14b]

Structural Details. The pentacoordinated anions in compounds **1** and **2** have a pseudo-2-fold axis coincident with the tin–halogen

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(25) Shafieezad, S., unpublished observations.

Table VII. Selected Bond Lengths (Å), Bond Angles (deg), and Nonbonded Distances in $[(C_6H_4OS)_3Sn]_2[H]_3[Et_4N]$ (3)[a]

type[b]	length	type[b]	length
Sn1–O1	2.147 (7)	Sn2–O4	2.171 (6)
Sn1–O2	2.153 (6)	Sn2–O5	2.192 (6)
Sn1–O3	2.191 (7)	Sn2–O6	2.181 (7)
Sn1–S1	2.428 (3)	Sn2–S4	2.436 (3)
Sn1–S2	2.433 (3)	Sn2–S5	2.444 (3)
Sn1–S3	2.447 (3)	Sn2–S6	2.438 (3)
O1–C11	1.39 (1)	O4–C41	1.35 (1)
O2–C21	1.39 (1)	O5–C51	1.37 (1)
O3–C31	1.39 (1)	O6–C61	1.38 (1)
S1–C12	1.75 (1)	S4–C42	1.74 (1)
S2–C22	1.78 (1)	S5–C52	1.77 (1)
S3–C32	1.78 (1)	S6–C62	1.74 (1)
type	**angle**	**type**	**angle**
O1–Sn1–O2	79.7 (3)	O4–Sn2–O5	80.2 (2)
O1–Sn1–O3	80.2 (3)	O4–Sn2–O6	79.9 (3)
O1–Sn1–S1	82.4 (2)	O4–Sn2–S4	81.9 (2)
O1–Sn1–S2	95.7 (2)	O4–Sn2–S5	160.9 (2)
O1–Sn1–S3	161.3 (2)	O4–Sn2–S6	94.9 (2)
O2–Sn1–O3	79.2 (3)	O5–Sn2–O6	79.3 (3)
O2–Sn1–S1	161.8 (2)	O5–Sn2–S4	94.8 (2)
O2–Sn1–S2	81.9 (2)	O5–Sn2–S5	80.7 (2)
O2–Sn1–S3	95.0 (2)	O5–Sn2–S6	160.8 (2)
O3–Sn1–S1	94.7 (2)	O6–Sn2–S4	161.6 (2)
O3–Sn1–S2	161.1 (2)	O6–Sn2–S5	96.1 (2)
O3–Sn1–S3	81.2 (2)	O6–Sn2–S6	81.7 (2)
S1–Sn1–S2	103.2 (1)	S4–Sn2–S5	100.1 (1)
S1–Sn1–S3	101.0 (1)	S4–Sn2–S6	102.9 (1)
S2–Sn1–S3	101.3 (1)	S5–Sn2–S6	103.1 (1)
Sn1–O1–C11	118.4 (6)	Sn2–O4–C41	119.0 (5)
Sn1–S1–C12	97.3 (3)	Sn2–S4–C42	98.2 (3)
Sn1–O2–C21	120.5 (5)	Sn2–O5–C51	117.9 (5)
Sn1–S2–C22	97.5 (3)	Sn2–S5–C52	97.6 (3)
Sn1–O3–C31	120.1 (6)	Sn2–O6–C61	117.2 (6)
Sn1–S3–C32	97.6 (4)	Sn2–S6–C62	97.8 (3)
type	**distance**	**type**	**distance**
O1–O5	2.465 (9)	O3–O4	2.486 (8)
O2–O6	2.440 (9)		

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

Table VIII. Atomic Coordinates in Crystalline $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (4)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	0[c]	0[c]	0[c]
O1	397 (4)	378 (2)	−1184 (4)
O2	303 (3)	443 (1)	1111 (4)
O3	−1308 (3)	240 (1)	170 (4)
C1	206 (4)	201 (2)	−2107 (5)
C2	390 (5)	390 (3)	−3037 (6)
C3	197 (5)	198 (3)	−3962 (6)
C4	−496 (4)	631 (2)	1430 (5)
C5	−510 (4)	917 (2)	2227 (5)
C6	−1338 (4)	1103 (2)	2507 (6)
C7	−2160 (5)	1006 (2)	1995 (7)
C8	−2132 (5)	722 (2)	1198 (6)
C9	−1333 (4)	529 (2)	911 (5)
N	2107 (4)	535 (2)	1934 (5)
C10	2192 (6)	209 (2)	2750 (7)
C11	1405 (8)	240 (3)	3523 (8)
C12	2784 (5)	437 (2)	1064 (8)
C13	2689 (8)	726 (4)	162 (9)
C14	2232 (5)	967 (2)	2355 (8)
C15	3219 (6)	1048 (3)	2774 (11)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 4. [c] Fixed.

Table IX. Selected Bond Lengths (Å) and Bond Angles (deg) in $[(C_6H_4O_2)_3Sn][Et_3NH]_2$ (4)[a]

type[b]	length	type[b]	length
Sn–O1	2.049 (5)	Sn–O2	2.086 (4)
Sn–O3	2.052 (4)	HN···O2	1.927
type	**angle**	**type**	**angle**
O1–Sn–O2′	172.6 (3)	O2–Sn–O3′	90.0 (2)
O3–Sn–O3′	167.7 (3)	O2–Sn–O2′	93.0 (3)
O1–Sn–O2	92.1 (2)	O1–Sn–O1′	83.3 (3)
O1–Sn–O3	96.1 (2)	O2–Sn–O3	81.5 (2)
O1–Sn–O3′	93.1 (2)	N–HN···O2	175.0

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

bond. To facilitate the examination of this pseudosymmetry, atoms have been labeled so that primed ones go into unprimed ones with the same name by the pseudo-2-fold axis.

The geometry about the tin atom in **1** is essentially rectangular pyramidal with four basal sulfur atoms and the bromine atom in the apical position. The geometry about the tin atom in **2** lies on the coordinate connecting a trigonal bipyramid with oxygen atoms in the axial positions to a rectangular pyramid with an apical chlorine atom. When the dihedral method is used with unit vectors to access displacement,[12,13] the geometry is displaced 38.0% from the TBP toward the RP. Thus **2** is more nearly trigonal bipyramidal. For the rectangular-pyramidal **1**, the analogous displacement averages 94.2% (Table I).

Compound **3** crystallizes with two crystallographically independent, but nearly identical, hexacoordinated tin moities. The isomeric form that is present has all oxygen atoms cis to one another. The geometry about the tin atoms is distorted octahedral, with the distortion due in part to the constraints imposed by the five-membered rings. The constrained endocyclic O–Sn–S bond angles range from 80.7 (2)° to 82.4 (2)°, compared to the idealized value of 90°. A second distortion is apparent in the unconstrained exocyclic bond angles. The O–Sn–O bond angles range from 79.2 (3)° to 80.2 (3)° while the S–Sn–S bond angles, which range from 100.1 (1)° to 103.2 (1)°, are considerably larger. For each tin center, the plane defined by the three oxygen atoms is nearly parallel to the plane defined by the three sulfur atoms (dihedral angles of 0.5° and 0.7°).

The two independent tin anions are associated in the solid in such a way that the aforementioned planes from both centers are also parallel (dihedral angles ranging from 0.4° to 0.7°). The two three-atom oxygen planes are stacked together in a staggered fashion with a rotation of about 37° out of an eclipsed configuration. This arrangement causes three surprisingly short intermolecular O–O distances indicated by the dashed lines in Figure 3. These distances of 2.440 (9), 2.465 (9), and 2.486 (8) Å are less than the van der Waals sum of 2.8 Å and are comparable to the O–O distances found for the very short O–H–O bonds in acid salts of carboxylic acids, which are believed to be symmetric.[26] For purposes of electrical neutrality, four cations are required for each two of the formulated dianions. The X-ray results showed only one Et_4N^+ cation for two anions and gave no indication of possible protonated oxygen atoms. It seems reasonable to conclude that the three protons that are required to maintain electrical neutrality are involved in strong and possibly symmetric hydrogen-bonding interactions, which lead to the formation of the observed dimeric species.

While the dimer has no crystallographic symmetry, its approximate symmetry is D_3, with both of the tin atoms lying on the 3-fold axis. In the event that the hydrogen atoms are truly centered, each of the three protons would lie on one of the 2-fold axes. Such symmetry is believed to favor the formation of symmetric hydrogen bonds.

The anion in compound **4** has crystallographic C_2 symmetry, with the amino hydrogen atoms of a pair of 2-fold-related triethyl ammonium ions forming hydrogen bonds to the symmetry-related O2 and O2′. The geometry about the tin atom is distorted octahedral, where the distortions are due at least in part to the constraints imposed by the five-membered rings. The constrained endocyclic O–Sn–O bond angles range from 81.5 (2)° to 83.3 (3)° while the cis exocyclic O–Sn–O bond angles range from 90.0 (2)°

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(26) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968; p 181.

Table X. Average Sn–O and Sn–S Bond Lengths (Å) for the Cyclic Stannates **1**–**4**

compd	coord no.	Sn–S[a]	Sn–O[a]	Sn–O[b]
1	5	2.457 (2)		
2	5	2.397 (2)	2.054 (5)	
3	6	2.436 (3)		2.164 (7)
4	6		2.051 (5)	2.086 (4)

[a] Non-hydrogen bonded. [b] Hydrogen bonded.

to 96.1 (2)°. Evidence of the hydrogen-bonding interaction is found in the Sn–O2 bond length of 2.086 (4) Å, which is somewhat lengthened compared to the Sn–O1 and Sn–O3 bonds, with lengths of 2.049 (5) and 2.052 (4) Å, respectively.

A comparison of average values of Sn–S and hydrogen-bonded and non-hydrogen-bonded Sn–O bond lengths (Table X) shows that hydrogen bonding produces the most pronounced lengthening effect in **3**. The latter has O–H–O hydrogen bonding compared to the apparently weaker interaction N–H–O in **4**. No bond length effect is discernible accompanying the change in coordination number encountered between **1**–**2** and **3**–**4**.

Structural Comparisons. The spirocyclic stannates **1** and **2** give the expected structures. The general rule for five-coordinated anionic tin,[14] as with related germanium[9,27,28] and silicon[29-32] derivatives and the isoelectronic phosphoranes,[33,34] arsoranes,[35,36] and stiboranes,[37,38] is that wherever two unsaturated five-membered rings are present containing like atoms in each ring system bonded to the central atom, the resulting structure is rectangular pyramidal. Introduction of dissimilar bonding ring atoms, as in **2**, allows the apicophilicity rule[39,40] to take preference over the ring-strain effect[41] and causes structural displacement back to the inherently more stable trigonal bipyramid. The operation of these effects are apparent in examination of the data in Table I.

Conclusion. Ring-containing pentacoordinated anionic tin complexes prefer Sn–S to Sn–O bonding. The tendency to form M–O bonding in such systems increases from tin to germanium to silicon. For pentacoordinated anionic silicon(IV), no examples of ring Si–S bonding are known.[29-32] The special stability of ring Sn–S bonding in these compounds is attributed to a proper balance of the effects of low tin atom electronegativity vs the tendency of tin to increase its coordination number. Increased tin acidity provided by Sn–O bonds appears to favor the formation of hexacoordinated species.

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Supplementary Material Available: Thermal parameters, hydrogen atom parameters, and additional bond lengths and angles (Tables S1–S3, respectively, for **1**, Tables S4–S6 for **2**, Tables S7–S9 for **3**, and Tables S10–S12 for **4**) (18 pages); listings of observed and calculated structure factor amplitudes for **1**–**4** (37 pages). Ordering information is given on any current masthead page.

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Hydrolysis Reactions Leading to Ring-Containing Hexacoordinated Distannoxanes. Tin–Sulfur vs Tin–Oxygen Bonding[1,2]

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Abstract: Hydrolysis reactions employing $SnCl_4 \cdot 5H_2O$ with either disodium mercaptoethanolate or disodium dimercaptomaleonitrile in the presence of Et_4NCl yield the new distannates $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (**2**) and $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (**3**), respectively, possessing the four-membered Sn_2O_2 ring unit in cyclized hexacoordinated tin products. Their formation most likely proceeds via five-coordinated spirocyclic intermediates in which the integrity of the tin–sulfur bonding system is maintained as the distannoxane rings form. In agreement with previous results, the formation of tin–oxygen bonding is conducive in stabilizing tin(IV) in the dianionic hexacoordinated state while tin–sulfur bonding is preferred over tin–oxygen bonding in pentacoordinated anionic tin species. Hydrolysis of *n*-butyltin trichloride leads to the distannate $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (**1**), whose structure again contains hexacoordinated tin atoms in a Sn_2O_2 ring arrangement. **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.047$ (1) Å, $b = 25.090$ (6) Å, $c = 6.556$ (1) Å, $\beta = 107.16$ (1)°, and $Z = 2$. **2** crystallizes in the monoclinic space gruop $P2_1/n$ with $a = 12.522$ (2) Å, $b = 8.808$ (1) Å, $c = 26.000$ (2) Å, $\beta = 104.32$ (1)°, and $Z = 4$. **3** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.841$ (2) Å, $b = 11.201$ (2) Å, $c = 11.932$ (2) Å, $\alpha = 65.39$ (1)°, $\beta = 76.01$ (1)°, $\gamma = 80.17$ (1)°, and $Z = 1$. The final conventional unweighted agreement factors were 0.037 (**1**), 0.034 (**2**), and 0.032 (**3**).

The ready formation of the four-membered cyclic distannoxane unit, Sn_2O_2, in hydrolysis reactions of mono- and diorganotin compounds is well-known. As early as 1858 Strecker[4] formed $IEt_2SnOSnEt_2I$ by heating diethyltin oxide with diethyltin diiodide.

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