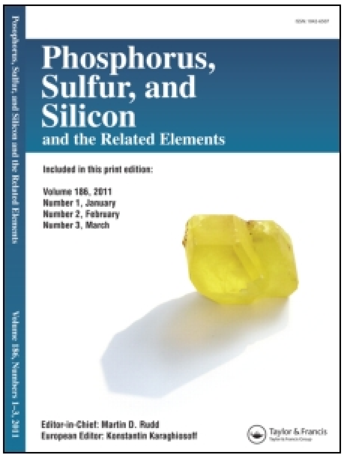

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DISTORTION COORDINATE FOR FIVE-COORDINATED TIN. A MODEL FOR NUCLEOPHILIC SUBSTITUTION. SYNTHESIS AND STRUCTURE OF HYPERVALENT ANIONIC (CYANOETHYLENEDITHIOLATO)STANNATES

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DISTORTION COORDINATE FOR FIVE-COORDINATED TIN. A MODEL FOR NUCLEOPHILIC SUBSTITUTION. SYNTHESIS AND STRUCTURE OF HYPERVALENT ANIONIC (CYANOETHYLENEDITHIOLATO)STANNATES[1,2]

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Reactions of Ph_3SnCl and $RSnCl_3$ (R = Me, *n*-Bu) with $R_4N^+Cl^-$ and disodium maleonitriledithiolate, $Na_2(mnt)$, yield the monostannole $[((CN)_2C_2S_2)SnPh_3][Me_4N]$ (**1**) and the new distannoles $[((CN)_2C_2S_2)_2SnR][Et_4N]$ [R = Me (**2**), *n*-Bu (**3**)]. X-ray analysis reveals the geometries of **1** as trigonal bipyramidal and **2** and **3** as square pyramidal. The tristannole $[((CN)_2C_2S_2)_3Sn][Et_4N][Na]$ (**4**) results from Sn—C bond cleavage of $PhSnCl_3$ in a hydrolysis reaction with $Na_2(mnt)$ and $Et_4N^+Cl^-$. The geometrical data on organotin complexes containing ring unsaturation, **1–3**, and related anionic five-coordinated tin compounds show that the distortion coordinate expressing solid-state nonrigidity is the Berry pseudorotational coordinate. As a result of this work, one is able for the first time to compare structural principles for five-coordinated compounds established for other main-group 14 and 15 elements. Their significance in reaction mechanisms is discussed. Stannole **1** crystallizes in the monoclinic space group *Cc* with a = 16.780 (3) Å, b = 9.433 (2) Å, c = 16.858 (3) Å, β = 96.85 (1)°, and Z = 4. Distannole **2** crystallizes in the monoclinic space group $P2_1/c$ with a = 14.997 (3) Å, b = 11.730 (3) Å, c = 14.167 (3) Å, β = 107.61 (2)°, and Z = 4. Distannole **3** crystallizes in the monoclinic space group $P2_1/m$ with a = 9.016 (2) Å, b = 10.906 (3) Å, c = 14.310 (2) Å, β = 98.35 (1)°, and Z = 2. Tristannole **4** crystallizes in the monoclinic space group $C2/c$ with a = 9.434 (2) Å, b = 25.123 (6) Å, c = 12.773 (1) Å, β = 101.76 (1)°, and Z = 4. The final conventional unweighted agreement factors were 0.024 (**1**), 0.041 (**2**), 0.038 (**3**), and 0.035 (**4**).

Relative to unsaturated cyclic derivatives of five-coordinated anionic tin(IV), previous studies have provided four examples containing a single ring component[4,5] and one example with two ring components[4,6] that have been characterized by X-ray analysis. These comprise the halodimethylstannoles $[(C_6H_4OS)SnMe_2F][Et_4N]$,[5] $[(C_6H_4CO_2S)SnMe_2Cl][Et_4N]$,[5] and $[(C_6H_4OS)SnMe_2I][Ph_4P]$,[5] the chlorodiphenylstannole $[(CH_3C_6H_3S_2)SnPh_2Cl][Et_4N]$,[4] and the chlorobis(dithiastannole) $[(CH_3C_6H_3S_2)_2SnCl][Me_4N]$.[4,6] The monocyclic stannoles have geometries approaching the trigonal bipyramid while the geometrical arrangement for the single bicyclic stannole is based on the square or rectangular pyramid. Other members belonging to these classes of substances have been synthesized.[5,7] The neutral derivative, tribenzyl(2-pyridinethiolato *N*-oxide)tin(IV), also has been found in a square-pyramidal geometry.[8]

The dicyanoethylene-1,2-dithiolate (mnt) ligand has been the subject of a number of studies leading to complexes with the main-group[4] elements, primarily germanium and tin.[9–11] Complexes formed in these studies from $SnCl_4$ or the appropri-

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ately substituted tin chloride are $[Sn(mnt)_3]^{2-}$, $[Sn(mnt)_2X_2]^{2-}$[9] (X = Cl, Br, I), $[R_3Sn(mnt)]^-$,[9b] and $[R_2Sn(mnt)X]^-$[11] (R = Me, Ph; X = halogen). Neutral complexes $R_2Sn(mnt)$ that probably exhibit intermolecular association were also formed.[10] The results of ^{119}Sn Mössbauer studies[11] in conjunction with ^1H NMR and IR data[9a,b] indicated that the dianionic complexes are octahedral and the halogen-containing monoanionic derivatives are five-coordinated. Mössbauer data[11,12] suggest monodentate coordination of the mnt unit in the monoanionic complexes, $[R_3Sn(mnt)]^-$ (R = Me, Ph), whereas ^1H NMR data[9b] leave open the question of whether the coordination at tin is four or five.

Of interest is the reaction of the mnt ligand with $MeSnCl_3$ and $PhSnCl_3$ in the presence of tetraalkylammonium chloride. Tin-carbon cleavage occurs, yielding $[Sn(mnt)_3]^{2-}$ or $[Sn(mnt)_2Cl_2]^{2-}$ salts,[9b] depending on the ligand to tin ratio at either room temperature or 0°C. Further, it is noted that no organo derivatives of the type $[(mnt)_2SnR]^-$ have been synthesized.

The present investigation was undertaken to explore the versatility of the mnt ligand in coordination to tin relative to the above classes of complexes and to obtain additional members of pentacoordinated tin derivatives possessing ring unsaturation. This work compliments studies in related papers[1b,13] on five-coordinated anionic tin complexes containing saturated and mixed-ligand systems. Synthesis and X-ray structural studies are reported in this work on $[((CN)_2C_2S_2)SnPh_3][Me_4N]$ (**1**), $[((CN)_2C_2S_2)_2SnMe][Et_4N]$ (**2**), $[((CN)_2C_2S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**3**), and $[((CN)_2C_2S_2)_3Sn][Et_4N][Na]$ (**4**). All of these derivatives contain the mnt ligand, and **2**–**4** represent newly synthesized substances. In addition, no detailed synthesis of **1** has previously been reported.[12] The availability of the structural data combined with that already known[1b,4–6,13] provides sufficient examples to discuss the distortion coordinate for five-coordinated tin and, for the first time, allows a comparison with structural principles established for other main-group 14 and 15 elements, i.e., Si,[14–17] Ge,[18,19] P,[20–22] As,[23,24] and Sb.[25,26] As a result of this work, the significance of these structural principles applied to reactive species postulated in nucleophilic substitution reactions is evaluated.

EXPERIMENTAL

All solvents either were used directly from freshly opened bottles or were dried prior to use. Acetonitrile was refluxed and distilled from phosphorus pentoxide. Diethyl ether was distilled from lithium aluminum hydride. Reagents, methyltin trichloride, phenyltin trichloride, and *n*-butyltin trichloride (Alfa) and triphenyltin chloride and tetramethylammonium bromide (Aldrich) were used as received. Disodium maleonitriledithiolate was synthesized according to a published procedure.[27]

^{119}Sn NMR spectra were recorded on a Varian X-L-300 instrument operating at 111.862 MHz under broad-band decoupling conditions. $Cr(acac)_3$ was used as a relaxing agent. Chemical shifts (δ) are reported with reference to tetramethyltin, and the standard convention (positive shifts downfield) is used. ^1H NMR were recorded on a Varian X-L-300 instrument operating at 300 MHz and referenced vs tetramethylsilane.

Synthesis. Tetramethylammonium Triphenyl(1,2-dicyanoethylene-1,2-dithiolato)stannate, $[((CN)_2C_2S_2)SnPh_3][Me_4N]$ (**1**). To a mixture of triphenyltin chloride (1.20 g, 3.1 mmol), disodium maleonitriledithiolate (0.58 g, 3.1 mmol), and tetramethylammonium bromide (0.48 g, 3.1 mmol) were added 20 mL of ethanol and 20 mL of methanol. The reaction mixture was stirred at room temperature for 30 min and filtered. A pale yellow precipitate (0.9 g) was obtained from the filtrate upon concentration. A second crop was obtained from the mother liquid (0.4 g); total yield 1.3 g (73.9%). It was recrystallized from a mixture of acetonitrile and ether (1:1) at 0°C to yield yellow crystals: mp 185–187°C; ^1H NMR (CD_3CN) 7.62 (m, ortho), 7.38 (m, meta and para), 3.11 (s, NCH_3); ^{119}Sn NMR

($CDCl_3/CH_3CN$, 1:1) − 173.80. Anal. Calcd for $C_{26}H_{27}N_3S_2Sn$: C, 55.34; H, 4.82. Found: C, 55.24; H, 5.00.

Tetraethylammonium Bis(dicyanoethylene-1,2-dithiolato)methylstannate, [((CN)$_2$C$_2$S$_2$)$_2$SnCH$_3$][Et$_4$N] (**2**). Tetraethylammonium chloride (0.2 g 1.67 mmol) was added to a solution of methyltin trichloride (0.40 g, 1.67 mmol) in acetone (10 mL) and the resultant mixture stirred under nitrogen for 0.5 h. Sodium *cis*-1,2-dicyano-1,2-ethylenedithiolate (0.59 g, 3.18 mmol) was added to the above solution and the resultant mixture heated to 50°C for 0.5 h. After filtering, the green solution was evaporated under vacuum to dryness. The dark green oil that formed was dissolved in 10 mL of acetone. The resultant mixture was treated with 10 mL of hexane and cooled to yield yellow crystals: yield 0.348 g (40%); mp 120–123°C; ^{1}H NMR (CD_3CN) 1.15 (t, 12 H), 3.15 (q, 8 H), 0.95 (s, 3 H). Anal. Calcd for $C_{17}H_{23}N_5S_4Sn$: C, 37.51; H, 4.25; N, 12.86. Found: C, 37.50; H, 4.36; N, 12.79. Crystals suitable for X-ray analysis were grown by the slow vapor diffusion of diethyl ether into a solution of the product in acetone.

Tetraethylammonium Bis(dicyanoethylene-1,2-dithiolato)-n-butylstannate, [((CN)$_2$C$_2$S$_2$)$_2$Sn(n-Bu)][Et$_4$N] (**3**). Tetraethylammonium chloride (0.55 g, 3.3 mmol) was added to a solution of *n*-butyltin trichloride (0.32 g, 2.3 mmol) in acetone (20 mL) and the resultant mixture stirred for 0.5 h under nitrogen. Addition of sodium *cis*-1,2-dicyano-1,2-ethylenedithiolate (0.72 g, 3.9 mmol) to the above mixture caused the immediate formation of white solid. The mixture was heated at 50°C for 0.5 h. After filtering, the light green solution was evaporated under vacuum to dryness. The oil that formed was dissolved in 5 mL of acetone, and the resultant mixture was treated with 15 mL of diethyl ether and cooled to yield yellow crystals: yield 0.45 g (39%); mp 92–93°C; ${}_1$H NMR (CD_3CN) 1.15 (m, 12 H), 3.1 (q, 8 H). Anal. Calcd for $C_{20}H_{29}N_5S_4Sn$: C, 40.95; H, 4.94; N, 11.94. Found: C, 40.84; H, 5.00; N, 11.96. Crystals suitable for X-ray analysis were grown from a mixture of acetone and ether (1:4).

Tetraethylammonium Sodium Tris(dicyanoethylene-1,2-dithiolato)stannate, [((CN)$_2$C$_2$S$_2$)$_3$Sn][Et$_4$N][Na] (**4**). Attempts to prepare an analogous compound with the phenyl group in the fifth position led to cleavage of the tin-carbon bond and formation of the dianion $[Sn(mnt)_3)]^{2-}$. The synthetic procedure used was similar to that for the methyl and *n*-butyl compounds, **2** and **3**, respectively. The reaction was carried out both at 50°C and at room temperature. Orange crystals were obtained by slow evaporation of a benzene solution of the product: yield 0.42 g (46%); mp > 240°C.

Crystallography. All X-ray crystallographic studies were done on an Enraf- Nonius CAD4 diffractometer with 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.[4]

Crystals were mounted in thin-walled glass capillaries that were sealed as a precaution against moisture sensitivity. Data were collected in the θ–2θ scan mode for $3° \leq 2\theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 50°$ for **1**, **3**, and **4** and $3° \leq 2\theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 43°$ for **2**. The structures were solved by Patterson and difference Fourier techniques and were refined by use of full-matrix least-squares procedures.[28]

X-ray Studies for [((CN$_2$)C$_2$S$_2$)SnPh$_3$][Me$_4$N] (**1**). The crystal used for the X-ray study was cut from a large yellow tabular crystal and was approximately a trigonal prism with a edge length of 0.48 mm and a height of 0.33 mm.

Crystal data: $[(N_2C_4S_2)SnPh_3][Me_4N]$ (**1**), monoclinic space group *Cc* [C_s^4-No. 9],[29] a = 16.780 (3) Å, b = 9.433 (2) Å, c = 16.858 (3) Å, β = 96.85 (1)°, Z = 4, $\mu_{\mathrm{Mo}\ K\bar{\alpha}}$ = 1.140 mm^{-1}. A total of 2319 independent reflections ($+h$, $+k$, $\pm l$) was measured. No corrections were made for absorption.

The 32 independent non-hydrogen atoms were refined anisotropically. The 15 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 0.95 Å. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[30] were R = 0.024 and R_w = 0.031 for the 2147 reflections having $I \geq 2\sigma_I$.

X-ray Studies for [((CN)$_2$C$_2$S$_2$)$_2$SnMe][Et$_4$N] (**2**). The crystal used for the X-ray study was cut from a larger yellow plate and had dimensions of 0.12 × 0.25 × 0.28 mm.

Crystal data: $[(N_2C_4S_2)_2SnMe][Et_4N]$ (**2**), monoclinic space group $P2_1/c$ [C_{2h}^5-No. 14],[31] a = 14.997 (3) Å, b = 11.730 (3) Å, c = 14.167 (3) Å, β = 107.61 (2)°, Z = 4, $\mu_{\mathrm{Mo}\ K\bar{\alpha}}$ = 1.431 mm^{-1}. A total of 2717 independent reflections ($+h$, $+k$, $\pm l$) was measured. No corrections were made for absorption.

The 27 independent non-hydrogen atoms were refined anisotropically. The eight independent methylene H atoms were treated as described for **1**. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[30] were $R = 0.041$ and $R_w = 0.049$ for the 2021 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $[((CN)_2C_2S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**3**). The crystal used for the X-ray study was cut from a larger yellow lath and had dimensions of 0.23 × 0.33 × 0.38 mm.

Crystal data: $[(N_2C_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**3**), monoclinic space group $P2_1/m$ [C^2_{2h}-No. 11],[32] $a = 9.016$ (2) Å, $b = 10.906$ (3) Å, $c = 14.310$ (2) Å, $\beta = 98.35$ (1)°, $Z = 2$, $\mu_{\text{Mo K}\bar{\alpha}} = 1.226\ \text{mm}^{-1}$. A total of 2577 independent reflections ($+h$, $+k$, $\pm l$) was measured. No corrections were made for absorption.

The terminal atom of the *n*-Bu group is disordered with respect to the mirror plane of the anion. This atom (C16) was refined isotropically in half-occupancy in a general position. Similarly, the methylene carbon atoms of the cation are disordered with respect to the mirror plane passing through the remaining five non-hydrogen atoms of the cation. These four atoms (C5-C8) were refined anisotropically in half-occupancy in general positions. The remaining 17 non-hydrogen atoms were refined anisotropically in full occupancy for their positions. The H atoms bonded to C13 were treated as described for **1**. The remaining H atoms were omitted from the refinement. The final agreement factors[30] were $R = 0.038$ and $R_w = 0.053$ for the 2167 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $[((CN)_2C_2S_2)_3Sn][Et_4N][Na]$ (**4**). The crystal used for the X-ray study was cut from an orange polycrystalline mass and had dimensions of 0.20 × 0.30 × 0.33 mm.

Crystal data: $[(N_2C_4S_2)_3Sn][Et_4N][Na]$ (**4**), monoclinic space group $C2/c$ [C^6_{2h}-No. 15],[33] $a = 9.434$ (2) Å, $b = 25.123$ (6) Å, $c = 12.773$ (1) Å, $\beta = 101.76$ (1)°, $Z = 4$, $\mu_{\text{Mo K}\bar{\alpha}} = 1.311\ \text{mm}^{-1}$. A total of 2610 independent reflections ($+h$, $+k$, $\pm l$) was measured. No corrections were made for absorption.

The 19 independent non-hydrogen atoms were refined anisotropically. The four independent methylene hydrogen atoms were treated as described for **1**. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[30] were $R = 0.035$ and $R_w = 0.049$ for the 2170 reflections having $I \geq 2\sigma_I$.

RESULTS

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

The basic structural representation for the monocyclic derivative **1** is trigonal bipyramidal (TBP), whereas that for the bicyclic derivatives **2** and **3** is square or rectangular pyramidal (RP) while **4** is octahedral.

DISCUSSION

Synthetic Aspects

Formation of cyclic stannoles **1–3** proceeded from the reaction of an organotin chloride, tetraalkylammonium halide, and disodium maleonitriledithiolate. For example, the syntheses of **2** and **3** are represented by eq 1.

$$\mathrm{RSnCl_3 + Et_4N^+Cl^- + 2Na_2[(CN)_2C_2S_2] \xrightarrow{(CH_3)_2CO} [((CN)_2C_2S_2)_2SnR][Et_4N] + 4NaCl} \quad (1)$$

$$R = \text{Me } (\mathbf{2}),\ n\text{-Bu } (\mathbf{3})$$

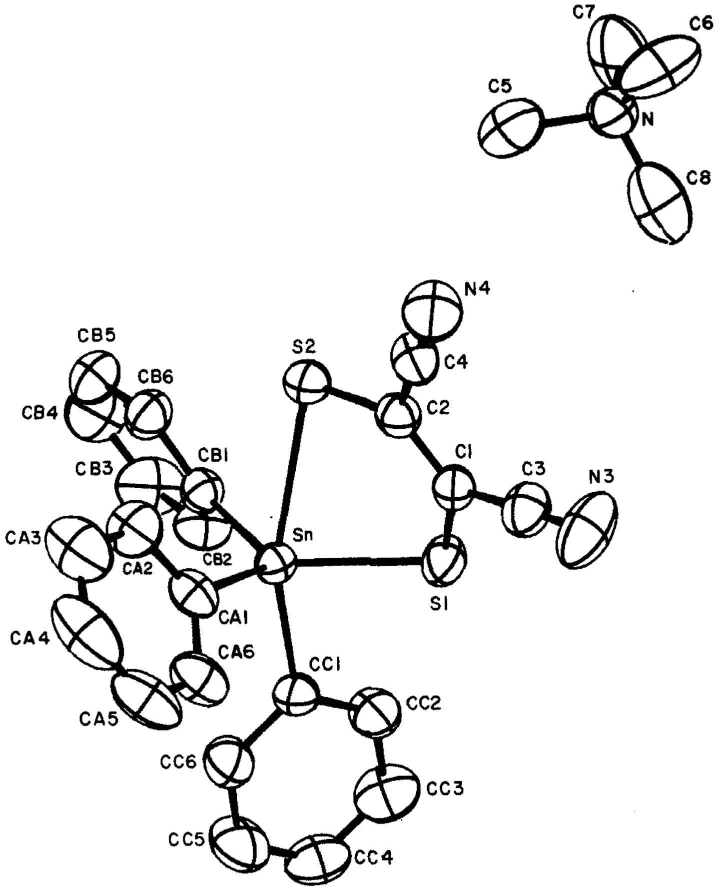


FIGURE 1 ORTEP plot of $[((CN)_2C_2S_2)SnPh_3][Me_4N]$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

Earlier, Bretschneider and Allen[9b] carried out this same reaction with monoalkyl and aryltin trichlorides at 0 °C and at room temperature in ethanolic solution. In all cases, they found that tin-carbon bond cleavage occurred, giving $[Sn(mnt)_3]^{2-}$ or $[Sn(mnt)_2Cl_2]^{2-}$ species depending on the ligand to tin ratio used, whereas our observations lead to the formation of the pentacoordinated structure for **2** with R = Me.

In agreement with the previous workers,[9b] tin-carbon bond cleavage evidently occurred with phenyltin trichloride as a reactant. Indications are that this process is activated by mnt.[9b,c] The product isolated, **4**, is most likely a result of the presence of adventitious water. Its formation is expressed by eq 2. It is known

$$PhSnCl_3 + Et_4N^+Cl^- + 3Na_2((CN)_2C_2S_2] + H_2O \rightarrow$$

$$\underset{\mathbf{4}}{[((CN)_2C_2S_2)_3Sn][Et_4N][Na]} + C_6H_6 + 4NaCl + NaOH \quad (2)$$

TABLE I

Atomic Coordinates in Crystalline$[((CN)_2C_2S_2)SnPh_3][Me_4N]$ (1)[a]

atom[b]	10^4x	10^4y	10^4z
Sn	0[c]	2180.5 (3)	2500[c]
S1	482 (1)	−318 (2)	2660 (1)
S2	1274 (1)	2348 (2)	3788 (1)
C1	802 (3)	−433 (5)	3676 (3)
C2	1131 (3)	647 (6)	4132 (6)
C3	698 (4)	−1784 (7)	4016 (4)
C4	1391 (4)	406 (7)	4959 (4)
N3	613 (6)	−2903 (6)	4254 (4)
N4	1633 (4)	177 (7)	5615 (3)
CA1	−832 (3)	2785 (6)	3322 (3)
CA2	−632 (6)	3829 (10)	3887 (5)
CA3	−1167 (5)	4270 (12)	4400 (4)
CA4	−1894 (5)	3602 (13)	4368 (4)
CA5	−2122 (4)	2544 (11)	3811 (5)
CA6	−1579 (4)	2153 (7)	3283 (4)
CB1	603 (3)	3950 (5)	2027 (3)
CB2	585 (5)	4076 (10)	1209 (5)
CB3	904 (5)	5259 (10)	873 (5)
CB4	1232 (4)	6338 (8)	1361 (5)
CB5	1251 (4)	6216 (7)	2175 (5)
CB6	953 (3)	5024 (6)	2517 (4)
CC1	−738 (3)	1484 (6)	1416 (3)
CC2	−483 (4)	441 (7)	922 (3)
CC3	−919 (5)	50 (9)	216 (4)
CC4	−1653 (5)	718 (9)	−27 (4)
CC5	−1917 (5)	1753 (9)	438 (4)
CC6	−1462 (6)	2129 (7)	1157 (6)
N1	3214 (3)	2050 (6)	2220 (3)
C5	2704 (5)	771 (9)	2382 (5)
C6	3487 (8)	2768 (12)	2990 (7)
C7	3906 (6)	1591 (13)	1795 (7)
C8	2724 (7)	3098 (12)	1695 (7)

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

TABLE II

Selected Bond Lengths (Å) and Bond Angles (deg) for $[((CN)_2C_2S_2)SnPh_3][Me_4N]$ (1)[a]

	Lengths		
Sn–S1	2.496 (2)	Sn–CA1	2.158 (5)
Sn–S2	2.864 (2)	Sn–CB1	2.154 (5)
Sn–C1	1.735 (5)	Sn–CC1	1.183 (5)
S2–C2	1.732 (6)		
	Angles		
S2–Sn–CC1	161.6 (2)	S2–Sn–S1	76.5 (1)
S1–Sn–CB1	127.7 (1)	S2–Sn–CB1	84.1 (1)
CA1–Sn–S1	114.0 (2)	CC1–Sn–S1	87.2 (2)
CA1–Sn–CB1	113.7 (2)	CC1–Sn–CB1	99.7 (2)
S2–Sn–CA1	88.8 (2)	CC1–Sn–CA1	105.8 (2)

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

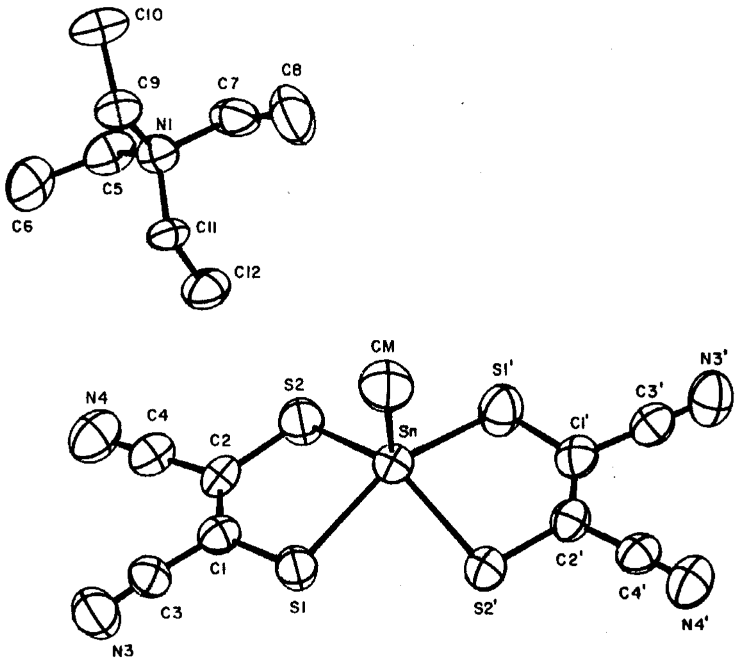


FIGURE 2 ORTEP plot of $[((CN)_2C_2S_2)_2SnMe][Et_4N]$ (**2**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity. Primed atoms are not symmetry related to unprimed ones.

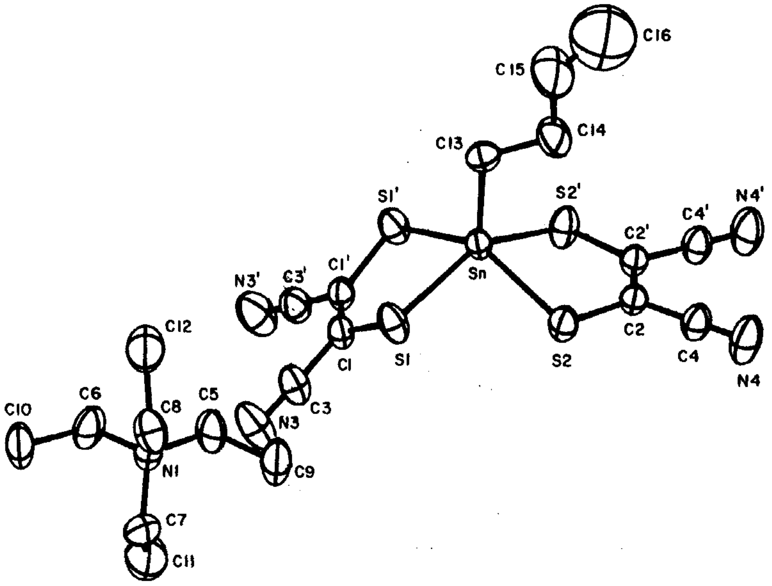


FIGURE 3 ORTEP plot of $[((CN)_2C_2S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**3**) with thermal ellipsoids at the 30% probability level. Primed atoms are mirror related (x, $\frac{1}{2} - y$, z) to unprimed ones. Only one of the two half-occupied positions is shown for the disordered atoms (C5-C8, C16). Hydrogen atoms are omitted for purposes of clarity.

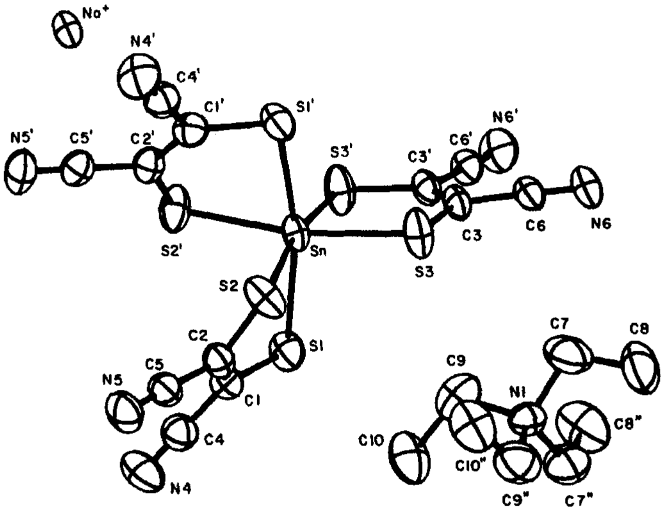


FIGURE 4 ORTEP plot of $[((CN)_2C_2S_2)_3Sn][Et_4N][Na]$ (4) with thermal ellipsoids at the 50% probability level. Primed $(-x, y, \frac{1}{2} - z)$ and double-primed $(1 - x, y, \frac{1}{2} - z)$ atoms are 2-fold related to unprimed ones. Hydrogen atoms are omitted for purposes of clarity.

TABLE III

Atomic Coordinates in Crystalline $[((CN)_2C_2S_2)_2SnMe][Et_4N]$ (2)[a]

atom[b]	10^4x	10^4y	10^4z
Sn	430.2 (4)	236.7 (5)	3272.6 (4)
S1	1911 (2)	-560 (2)	4445 (2)
S2	1155 (2)	2130 (2)	3761 (2)
S1′	-1146 (2)	1169 (2)	2971 (2)
S2′	-276 (2)	-1365 (2)	3942 (2)
CM	497 (7)	-159 (9)	1829 (7)
C1	2597 (6)	652 (7)	4662 (6)
C2	2305 (5)	1713 (7)	4382 (6)
C3	3553 (6)	469 (7)	5218 (7)
C4	2965 (6)	2624 (8)	4597 (7)
N3	4296 (6)	287 (7)	5687 (6)
N4	3514 (6)	3334 (7)	4748 (6)
C1′	-1790 (6)	-77 (7)	2944 (6)
C2′	-1440 (5)	-1098 (7)	3332 (6)
C3′	-2790 (7)	41 (7)	2490 (6)
C4′	-2053 (6)	-2055 (8)	3273 (6)
N3′	-3558 (6)	158 (7)	2153 (6)
N4′	-2507 (6)	-2844 (7)	3239 (6)
N1	-3687 (4)	3582 (5)	3801 (4)
C5	-4086 (7)	2545 (7)	3187 (7)
C6	-5111 (7)	2561 (8)	2697 (7)
C7	-2638 (6)	3378 (9)	4268 (7)
C8	-2104 (7)	4347 (11)	4895 (8)
C9	-4159 (6)	3789 (7)	4601 (6)
C10	-4092 (7)	2808 (8)	5309 (7)
C11	-3863 (5)	4641 (6)	3161 (5)
C12	-3459 (6)	4633 (8)	2311 (6)

[a] Numbers in parentheses are estimated standard deviations

[b] Atoms are labeled to agree with Figure 2.

TABLE IV

Selected Bond Lengths (Å) and Bond Angles (deg) for $[((CN)_2C_2S_2)_2SnMe][Et_4N]$ (2)[a]

	Lengths		
Sn–S1	2.517 (2)	Sn–S2	2.478 (2)
Sn–S1′	2.522 (2)	Sn–S2′	2.482 (2)
Sn–CM	2.130 (9)		
	Angles		
S1–Sn–S1′	150.2 (1)	CM–Sn–S1′	104.3 (3)
S2–Sn–S2′	140.7 (1)	S1–Sn–S2	85.6 (1)
CM–Sn–S2	108.6 (3)	S1′–Sn–S2′	84.6 (1)
CM–Sn–S2′	110.6 (3)	S1′–Sn–S2	88.2 (8)
CM–Sn–S1	105.3 (3)	S1–Sn–S2′	82.0 (1)

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

TABLE V

Atomic coordinates in Crystalline $[((CN)_2C_2S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (3)[a]

atom[b]	10^4x	10^4y	10^4z
Sn	575.6 (5)	2500[c]	4487.2 (3)
S1	1516 (2)	947 (1)	3413 (1)
S2	1342 (2)	953 (1)	5776 (1)
C1	2634 (5)	1881 (4)	2812 (3)
C2	1379 (5)	1877 (4)	6758 (3)
C3	3570 (6)	1232 (5)	2279 (4)
N3	4291 (8)	718 (5)	1826 (4)
C4	1417 (6)	1257 (4)	7638 (3)
N4	1416 (7)	759 (5)	8329 (3)
C5[d]	2352 (14)	−1759 (11)	974 (7)
C6[d]	2468 (16)	−1665 (10)	−721 (7)
C7[d]	3723 (14)	−3436 (12)	183 (9)
C8[d]	993 (13)	−3421 (11)	−35 (8)
C9	2484 (14)	−2500[c]	1901 (6)
C10	2318 (13)	−2500[c]	−1696 (6)
C11	5257 (13)	−2500[c]	422 (9)
C12	−457 (11)	−2500[c]	−293 (8)
N1	2394 (7)	−2500[c]	98 (4)
C13	−1826 (7)	2500[c]	4252 (5)
C14	−2446 (9)	2500[c]	5175 (6)
C15	−4207 (12)	2500[c]	4936 (11)
C16[d]	−4732 (42)	3073 (36)	5572 (21)
H13[e]	−2180[c]	1766[c]	3891[c]

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Fixed. [d] Half-occupancy. [e] B_{iso} was fixed at 5 Å^2.

that Sn—C(alkyl) bonds are more difficult to rupture than Sn—C(phenyl) bonds. Rigorous exclusion of moisture should yield the five-coordinated species $[(mnt)_2SnPh]^-$. However, this has not been tried.

This and an earlier[1b] paper have derivatives exhibiting only Sn—S bonding with cyclic compounds. A related paper[13] shows some five- and six-coordinated compounds formed from *o*-mercaptophenol. However, despite attempts to obtain penta

TABLE VI

Selected Bond Lengths (Å) and Bond Angles (deg) for $[((CN)_2C_2S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (3)[a]

	Lengths		
Sn–S1	2.516 (1)	Sn–C13	2.142 (7)
Sn–S2	2.521 (1)		
	Angles		
S1–Sn–S2′	144.8 (1)	S1–Sn–S2	85.2 (1)
S1–Sn–C13	109.1 (1)	S1–Sn–S1′	84.6 (1)
S2–Sn–C13	106.2 (1)	S2–Sn–S2′	85.2 (1)

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

TABLE VII

Atomic Coordinates in Crystalline $[((CN)_2C_2S_2)_3Sn][Et_4N][Na]$ (4)[a]

atom[b]	10^4x	10^4y	10^4z
Sn	0[c]	2079.4 (2)	2500[c]
S1	2248 (2)	1958.9 (5)	1708 (1)
S2	1301 (2)	1408.7 (6)	3850 (1)
S3	820 (2)	2813.3 (5)	3832 (1)
Na^+	5000[c]	0[c]	0[c]
C1	2613 (5)	1305 (2)	2121 (4)
C2	2229 (5)	1086 (2)	3001 (4)
C3	303 (5)	3366 (2)	3027 (4)
C4	3283 (6)	975 (2)	1441 (4)
C5	2563 (5)	536 (2)	3252 (4)
C6	569 (5)	3863 (2)	3580 (4)
N4	3809 (6)	712 (2)	912 (4)
N5	2827 (5)	105 (2)	3476 (4)
N6	789 (5)	4256 (2)	4029 (4)
C7	3953 (7)	4024 (3)	2974 (7)
C8	4721 (9)	4414 (3)	3838 (7)
C9	4074 (7)	3322 (3)	1636 (6)
C10	4983 (9)	2909 (3)	1149 (5)
N1	5000[c]	3671 (2)	2500[c]

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

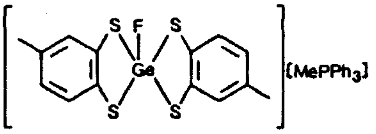
TABLE VIII

Selected Bond Lengths (Å) and Bond Angles (deg) for $[((CN)_2C_2S_2)_3Sn][Et_4NH][Na]$ (4)[a]

	Lengths		
Sn–S1	2.546 (2)	Sn–S3	2.521 (1)
Sn–S2	2.541 (1)		
	Angles		
S1–Sn–S1′	166.4 (1)	S1–Sn–S3	100.9 (1)
S2–Sn–S3′	169.2 (1)	S2–Sn–S2′	96.9 (1)
S1–Sn–S2	82.2 (1)	S1–Sn–S2′	88.7 (1)
S3–Sn–S3′	86.0 (1)	S2–Sn–S3	89.3 (1)
		S1–Sn–S3′	89.1 (1)

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

coordinated derivatives bearing only ring Sn—O coordination, no members were isolated. This contrasts with the predominant formation of ring Ge—O bonding in five-coordinated anionic germanates.[18,19,35,36] Again, despite attempts to prepare germanium derivatives with all ring Ge—S bonds, only one was isolated[34] and structurally characterized.[35] The preparation of $Ph_3Ge(mnt)^-$ is also known.[9b] The explanation for these observations is not firm. If steric effects inhibited the formation of Ge—S bonds in these complexes, one might expect tin to form both Sn—O and Sn—S bonds. Earlier, we commented that the less electronegative sulfur atoms renders germanium sufficiently less acidic such that it forms a five-coordinated complex only with the fluoride ion.[36] For tin of lower electronegativity than germanium, its acidity may be sufficiently enhanced when bonded to all sulfur atoms to readily add a variety of fifth groups. Replacing all sulfur atoms by oxygen atoms should lead to a further enhancement in acidity and render the formation of higher coordination numbers more favorable for tin, an occurrence readily accessible for tin compared to germanium. An example expressing this is reported elsewhere,[13] giving the dianionic tris(catecholate) $[(C_6H_4O_2)_3Sn][Et_4NH]_2$.



Structural Details

The geometry of the anion in **1** can be referred to a trigonal bipyramid (TBP) having S2 and CC1 in axial positions, with S1, CA1, and CB1 forming the equatorial plane. The difference between the Sn—S2 bond length of 2.864 (2) Å and the Sn—S1 bond length of 2.496 (2) Å is more pronounced than would be expected on the basis of axial vs equatorial distances. A typical range for Sn—S_{ax} bond lengths is 2.490–2.540 Å. However, the Sn—S2 bond length is far short of the van der Waals value of 4.0 Å and hence indicative of appreciable interaction. In this sense, the TBP structure is supported although Mössbauer data[11,12] indicate monodentate coordination of the mnt ligand in the solid state. The weaker nature of this bond is evident in some residual tetrahedral character at the tin atom. The tin atom is displaced 0.283 Å out of the plane defined by S1, CA1, and CB1 in a direction away from S2.

Retention of the solid-state structure of **1** in solution is supported by the high negative value of −173.8 ppm observed in the ^{119}Sn NMR spectrum. Chemical shifts for related four-coordinated tin compounds are considerably further downfield, e.g. 90.5 for Ph_3SnSMe and −70 to −61 for $Ph_3SnSC_6H_4(p\text{-}X)$ derivatives.[37] Additional evidence is supplied by the characteristic appearance of the low-field multiplet assignable to ortho protons, separated from a more intense high-field multiplet, assignable to the meta and para protons. Earlier we showed[38] that such enhanced multiplet separation was diagnostic of the presence of pentacoordination for main-group element compounds in solution.

The geometry about the Sn atom can alternatively be viewed as being displaced from a TBP toward a rectangular pyramid (RP) having CA1 in the apical position. By the dihedral angle method[39,40] with unit vectors to assess displacement, the geometry is displaced an average of 35.1% from the TBP toward the RP. This analysis has been applied to related derivatives of triphenyltin esters of benzoic acids.[41]

While **2** has no crystallographically imposed symmetry, the anion has a pseudo-2-fold axis coincident with the Sn—CM bond. To facilitate the inspection of this pseudosymmetry, atoms have been labeled so that primed ones go into unprimed ones with the same label by the pseudo-2-fold axis. The geometry about the tin atom lies on the coordinate connecting a TBP having S1 and S1′ in axial positions to an RP having CM in the apical position. By the dihedral angle method[39,40] with unit vectors to assess displacement, the geometry is 80.4% displaced from the TBP toward the RP and is therefore more rectangular pyramidal in nature.

The four sulfur atoms forming the basal plane are coplanar to within ±0.097 Å, with the tin atom displaced 0.738 Å out of this plane in a direction toward CM. Residual trigonal-bipyramidal character is evident in the Sn—S bond lengths. The Sn—S_{ax} bond lengths have an average value of 2.520 (2) Å, while the average value for Sn—S_{eq} bond lengths is 2.480 (2) Å.

Compound **3** has crystallographic C_s symmetry, with the tin atom and atoms C13–C15 of the butyl group lying on the mirror plane and the terminal atom of the butyl group, C16, disordered about the plane. The geometry about the tin atom is essentially rectangular pyramidal, with basal sulfur atoms and C13 of the butyl group in the apical position. The two trans basal angles are required by symmetry to be equal and have a value of 144.8°. Similarly, the four sulfur atoms are required by symmetry to be coplanar. The tin atom is displaced 0.762 Å from this basal plane in a direction toward the apical butyl group.

Deviations from the idealized RP geometry are very slight and do not conform to the C_{2v} constraints of the coordinate connecting the RP to the TBP, but rather reflect the C_s symmetry of the anion. In terms of the dihedral angle method with unit vectors, **3** is displaced an average of 96.7% from the TBP toward the RP.

For compound **4**, both the anion and the tetraethylammonium cation have crystallographic C_2 symmetry, while the sodium ion lies on a crystallographic inversion center. The geometry about the tin atom is distorted octahedral, where the largest deviation from the idealized geometry are probably caused by the constraints imposed by the five-member rings. The average Sn—S bond length for hexacoordinated **4** is 2.536 Å, which is 0.0269 Å longer than the average Sn—S bond lengths for the pentacoordinated molecules **2** and **3**.

Distortion Coordinate and Structural Comparisons

The geometries associated with stannoles **1–3** are in agreement with structural principles formulated for phosphoranes and found applicable to five-coordinated derivatives of other main-group **14** and **15** elements, i.e. Si,[14–17] Ge,[18,19] As,[23,24] and Sb.[25,26] The presence of one unsaturated five-membered ring normally gives TBP structures, as in **1**. The presence of two unsaturated five-membered rings containing like atoms bound to the central atom in each of the rings yields an RP, as apparent for **2** and **3**. The greater approach to the ideal RP for **3** compared to

2 is consistent with the criterion that the presence of a larger, less electronegative fifth ligand favors the formation of a RP.

Table IX summarizes structural data on anionic five-coordinated tin compounds obtained in the present study (**1–3**) and related work; those containing the ethanedithiolate ligand,[1b] $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**4**), $[(C_2H_4S_2)_2SnPh][Et_4N]$ (**5**), $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (**6**), and $[(C_2H_4S_2)_2SnSCH_2]_2[Et_3NH]_2$ (**7**); and those containing the toluene dithiolate ligand,[13] $[(MeC_6H_3S_2)_2SnBr][MePPh_3]\cdot 2C_6H_6$ (**8**), or the oxybenzenethiolate ligand,[13] $[(C_6H_4OS)_2SnCl][Et_4N]$ (**9**). In addition, the X-ray structures of the chlorodiphenylstannole[4] $[(CH_3C_6H_3S_2)SnPh_2Cl][Et_4N]$ (**10**) and the chlorobis(dithiastannole)[4,6] $[(CH_3C_6H_3S_2)_2SnCl][Me_4N]$ (**11**) have been reported by us. The availability of the structures of these ring-containing five-coordinated tin compounds provides a sufficient basis to establish the solid-state distortion coordinate.

A convenient measure of structural distortion for pentacoordinated molecules[39,40,42,43] is obtained by plotting the values of the trans basal angles θ_{15} and θ_{24} of the RP (which are axial and equatorial angles with reference to the TPB) vs the dihedral angle δ_{24}.[42] Figure 5 displays a θ vs δ_{24} graph for derivatives **1–11**, that have been structurally characterized by X-ray analysis. The lines shown are determined by the θ values of 120 and 180° for the ideal trigonal bipyramid, which has $\delta_{24} = 53.1°$, and the θ value of 150° for the "limiting" rectangular pyramid.[45] It is seen that the Berry coordinate[44] is well followed. A comparison of this type of plot for phosphoranes,[22,39,40] arsoranes,[23,24] stiboranes[26] and anionic five-coordinated silicon[15] and germanium[18] compounds indicates a similar scatter of points as well as a limiting rectangular pyramid with a trans basal θ angle near 150°.[46]

Earlier comparisons[36] indicated that anionic pentacoordinated germanium compounds should be more stereochemically nonrigid than analogous silicon derivatives and that related tin derivatives should be even more nonrigid than germanium species. A similar trend was found for the order of molecular nonrigidity of pentacoordinated derivatives in the group 15 series, i.e. Sb > As > P.[20,25] In view of the present work demonstrating that the distortion coordinate that exists for five-coordinated tin is the same as that found for five-coordinated derivatives of other group 14 and 15 elements and that this coordinate represents a low-energy path connecting trigonal bipyramids and square pyramids[47] (i.e. the Berry ligand-exchange process[44]), a firm basis has been formed to examine mechanistic features of nucleophilic substitution reactions. For example, many analogies exist between

TABLE IX

Axial and Equatorial Angles (θ, deg) and Dihedral Angles (δ, deg) for Pentacoordinated Anionic Tin Compounds

compd	anion	θ_{15}[a]	θ_{24}[a]	δ_{24}	% TBP → RP[b]	ref[c]
10	$(C_7H_6S_2)SnPh_2Cl$	165.9	121.2	44.1	14.1	4
6	$[(SCH_2CH_2S)Sn(Cl)CH_3]_2[SCH_2CH_2S]$	167.3	124.0	39.9	23.5	1b
7	$[(SCH_2CH_2S)_2Sn]_2[SCH_2CH_2S]$	169.0	130.9	35.5	33.6	1b
1	$((CN)_2C_2S_2)SnPh_3$	161.6	127.7	34.0	35.1	this work
9	$(C_6H_4OS)_2SnCl$	169.7	134.0	33.7	38.0	13
5	$(SCH_2CH_2S)_2SnC_6H_5$	159.2	137.6	20.9	60.2	1b
11	$(C_7H_6S_2)_2SnCl$	161.3	147.6	13.6	76.9	4, 6
4	$(SCH_2CH_2S)_2Sn(n\text{-}C_4H_9)$	153.5	142.3	10.9	78.7	1b
2	$((CN)_2C_2S_2)_2SnCH_3$	150.2	140.7	9.5	80.4	this work
8	$(C_7H_6S_2)_2SnBr$	155.7	152.0	3.7	94.2	13
3	$((CN)_2C_2S_2)_2Sn(n\text{-}C_4H_9)$	144.8	144.8	0	96.7	this work

[a] θ_{15} refers to the axial angle 1–Sn–5, and θ_{24} refers to the equatorial angle 2–Sn–4. The atom labeled 3 is the pivotal ligand in the angle-bending process. [b] Based on unit bond distances. [c] Referenced to X-ray studies.

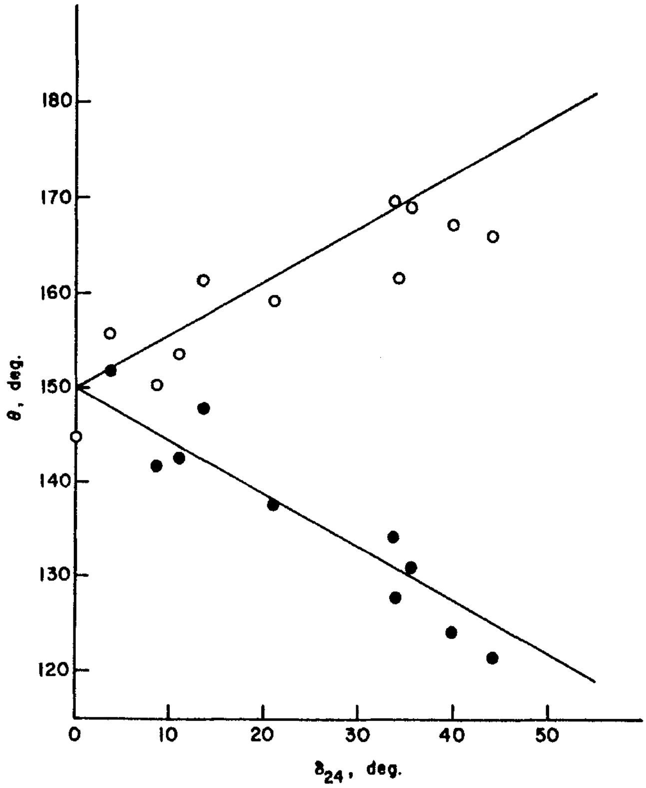


FIGURE 5 Variations of the axial angle θ_{15} (open circles) and equatorial angle θ_{24} (filled circles) vs the dihedral angle δ_{24} as structural distortion for pentacoordinated tin(IV) compounds listed in Table IX proceed along the Berry coordinate from a rectangular pyramid toward a trigonal bipyramid.

a variety of phosphorus and silicon displacement reactions,[48,49] yet no accord has been reached, at least in silicon chemistry,[47] on the basic displacement processes.

One implication of the present study is that either retention or racemization processes for chiral derivatives, proceeding by way of Berry pseudorotation in activated five-coordinated states, will be energetically more common relative to inversion processes as one goes to heavier elements in each of these series. This is a direct consequence of the ease of intramolecular ligand exchange implied in going down a series. In order to test the validity of this proposal, a common reaction must be sought applicable to each member of the series.

Conclusion

In general, solid-state five-coordinated tin structures lie along the Berry pseudorotational coordinate as an expression of their structural nonrigidity, similar to that found for other elements of groups 14 and 15 that have been studied. Implications are that in going down a particular family, nonrigid character increases, Sn > Ge > Si;[1b,36] Sb > As > P[25] as determined by the ease of structural distortion produced by a common substituent effect and the fact that pseudorotation for five-coordinated tin is in general a low-energy process. The role of five-coordinated tin in mechanisms of nucleophilic displacement reactions should be more readily defined by application of the structural principles herein summarized governing this state.

ACKNOWLEDGEMENT

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Registry No. **1**, 115162-45-3; **2**, 115162-50-0; **3**, 115162-47-5; **4**, 115162-48-6; Ph_3SnCl, 639-58-7; $PhSnCl_3$, 1124-19-2; $MeSnCl_3$, 993-16-8; (*n*-Bu)$SnCl_3$, 1118-46-3; disodium maleonitrile dithiolate, 5466-54-6.

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 S9–S11 for **4**) and thermal parameters and additional bond lengths and angles (Tables S7 and S8 for **3**) (11 pages); tables of observed and calculated structure factor amplitudes for **1–4** (32 pages). Ordering information is given on any current masthead page.

REFERENCES AND NOTES

(1) (a) Pentacoordinated Molecules. 74. (b) Part 73: Holmes, R. R.; Shafieezad, S.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1988**, *27*, 1232.

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

(3) This work represents in part of portion of: Shafieezad, S. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1986.

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

(5) Vollano, J. F.; Day, R. O.; Holmes, R. R. *Organometallics* **1984**, *3*, 750.

(6) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1264.

(7) Sau, A. C.; Holmes, R. R.; Molloy, K. C.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 1421.

(8) Ng, S. W.; Wei, C.; Das, V. G. K.; Mak, T. C. W. *J. Organomet. Chem.* **1987**, *334*, 283; *Ibid.* **1987**, *326*, C61.

(9) (a) Bretschneider, E. S.; Allen, C. W.; Waters, J. H. *J. Chem. Soc. A.* **1971**, 500. (b) Bretschneider, E. S.; Allen, C. W. *J. Organomet. Chem.* **1972**, *38*, 43. (c) Allen, C. W.; Lutes, D. E.; Durham, E. J.; Bretschneider, E. S. *Inorg. Chim. Acta* **1977**, *21*, 277.

(10) Bretschneider, E. S.; Allen, C. W. *Inorg. Chem.* **1973**, *12*, 623.

(11) Allen, C. W.; Brown, D. B. *Inorg. Chem.* **1974**, *13*, 2020.

(12) Petridis, D.; Fitzsimmons, B. W. *Inorg. Chim. Acta* **1974**, *11*, 105.

(13) Holmes, R. R.; Shafieezad, S.; Chandrasekhar, V.; Sau, A. C.; Holmes, J. M.; Day, R. O. *J. Am. Chem. Soc.* **1988**, *110*, 1168.

(14) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Harland, J. J.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 2016.

(15) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 2009.

(16) Holmes, R. R.; Day, R. O.; Harland, J. J.; Holmes, J. M. *Organometallics* **1984**, *3*, 347.

(17) Holmes, R. R.; Day, R. O.; Harland, J. J.; Sau, A. C.; Holmes, J. M. *Organometallics* **1984**, *3*, 341.

(18) Holmes, R. R.; Day, R. O.; Sau, A. C.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 600.

(19) Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutasse, C. A.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 607.

(20) Holmes, R. R. *Pentacoordinated Phosphorus*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980.

(21) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119, and references cited therein.

(22) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(23) Holmes, R. R.; Day, R. O.; Sau, A. C. *Organometallics* **1985**, *4*, 714.

(24) Poutasse, C. A.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Organometallics* **1985**, *4*, 708.

(25) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1987**, *26*, 157.

(26) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1987**, *26*, 163.

(27) Davidson, A.; Holm, R. H. *Inorg. Synth.* **1967**, *10*, 11.

(28) The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from Reference 29, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Sn, Na, and S were taken from the same source, pp 149–150.

(29) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 89.

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

(31) Reference 29, p 99.

(32) Reference 29, p 93.

(33) Reference 29, p 101.

(34) Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 4129.

(35) Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 281.

(36) Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutasse, C. A.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 193.

(37) Harris, R. K.; Kennedy, J. D.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: New York, 1978; Chapter 10, p 354.

(38) Sau, A. C.; Holmes, R. R. *J. Organomet. Chem.* **1981**, *217*, 157.

(39) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(40) Reference 20, p 34f.

(41) (a) Vollano, J. F.; Day, R. O.; Rau, D. N.; Chandrasekhar, V.; Holmes, R. R. *Inorg. Chem.* **1984**, *23*, 3153. (b) Swisher, R. G.; Vollano, J. F.; Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1984**, *23*, 3147.

(42) The latter angle is the dihedral angle formed between the planes of the TBP faces 124 and 245 that have the common equatorial edge 24 and is the one most intimately associated with the Berry exchange coordinate.[44] This dihedral angle has a value of 53.1° for an idealized TBP but becomes 0° as edge 24 disappears on forming the RP.

(43) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

(44) Berry, R. S. *J. Chem. Phys.* **1960**, *32, 933.*

(45) Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3745.

(46) In contrast, transition elements show a trans basal θ angle near 150° only for d^0, d^5 (high spin), and d^{10} configurations. For other d-orbital configurations, a range of θ values from 140 to 175° is encountered.[45]

(47) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686, 1692.

(48) Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265, and references cited therein.

(49) Corriu, R. J. P. *Phosphorus Sulfur* **1986**, *27*, 1, and references cited therein.