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Square-Pyramidal and Trigonal-Bipyramidal Anionic (Ethanedithiolato)stannates. Binuclear Centers with Tin-Sulfur Bonding[1,2]

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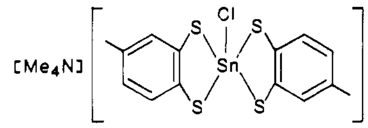
The first anionic five-coordinated tin compounds containing saturated rings were formed from the reaction of $RSnCl_3$ and $Et_4N^+Cl^-$ with sodium ethane-1,2-dithiolate and from the partial hydrolysis of bis(ethane-1,2-dithiolato)tin in the presence of an amine base. The reactions yielded the new stannates, $[(C_2H_4S_2)_2SnR][Et_4N]$, where R = *n*-Bu (**1**) and Ph (**2**), and the new distannates $[(C_2H_4S_2)R(Cl)SnSCH_2]_2[Et_4N]_2$, where R = Me (**3**) and *n*-Bu (**5**), and $[(C_2H_4S_2)_2SnSCH_2]_2[BH]_2$, where B = Et_3N (**4**) and Dabco (**6**). Mechanistic considerations suggest that binuclear tin structural representations similar to that found for **3** may enter as intermediates on the way to formation of the mononuclear representations, **1** and **2**. X-ray analysis showed the geometry of **1** and **2** is best described in terms of distortions from a square or rectangular pyramid, while the geometry in **3** and **4** more closely approaches a trigonal bipyramid. The appearance of the square-pyramidal forms **1** and **2** possessing saturated bicyclic ring systems is indicative of the relative ease of distortion for five-coordinated tin compared to related silicon and arsenic compounds. Stannate **1** crystallizes in the orthorhombic space group $Pbc2_1$ with a = 12.132 (4) Å, b = 12.386 (4) Å, c = 15.344 (2) Å, and Z = 4. Stannate **2** crystallizes in the orthorhombic space group $Aba2$ with a = 12.932 (3) Å, b = 11.282 (3) Å, c = 15.577 (5) Å, and Z = 4. Distannate **3** crystallizes in the monoclinic space group $P2_1/n$ with a = 8.436 (2) Å, b = 17.961 (5) Å, c = 13.004 (4) Å, β = 95.61 (2)°, and Z = 2. Distannate **4** crystallizes in the triclinic space group $P\bar{1}$ with a = 8.638 (3) Å, b = 10.095 (3) Å, c = 12.538 (3) Å, α = 69.35 (2)°, β = 76.08 (2)°, γ = 69.40 (3)°, and Z = 1. The final conventional unweighted agreement factors were 0.036 (**1**), 0.040 (**2**), 0.036 (**3**), and 0.039 (**4**).

Introduction

Previous work on pentacoordinated tin compounds has revealed compounds that contain intermolecular tin-ligand bonds, e.g. $(CH_3)_3SnCl$,[4] those that are monomeric and possess intramolecular dative ligand-tin bonds, e.g. $[(CH_3)_2N]_3PO \rightarrow Sn(Cl)Ph_3Me$,[5] and those that are anionic and contain five covalent bonds to tin, e.g. $[Ph_3PCH_2Ph][Bu_3SnCl_2]$.[6] A summary of most examples of these classes has been given earlier.[7] X-ray investigations have shown that the trigonal bipyramid is the basic structural representation for all members of these classes studied so far with one exception. We reported the synthesis and X-ray study of the first tin compound having a discrete square-pyramidal geometry. The compound was a spirocyclic derivative that resulted from the reaction of bis(toluene-3,4-dithiolato)tin(IV) with $(CH_3)_4N^+Cl^-$ at room temperature.



Anionic derivatives such as these are isoelectronic with five-coordinated antimony compounds. Recently, we reported[9,10] the synthesis and X-ray analysis of a range of organostiboranes with geometries forming a sequence from trigonal bipyramidal to square pyramidal. Earlier, we have explored the five-coordinated state for other members of groups 4 and 5, i.e., Si,[11-14] Ge,[15,16] P,[17,18] and As.[19,20] In each series of compounds studied, we have found that, for cyclic ligand components, the normally less stable square-pyramidal structure can be formed.

It is of interest to extend the work to related tin(IV) chemistry to ascertain the degree of correspondence in structural principles between elements in the same periodic family as well as their isoelectronic congeners. This paper concentrates on tin-sulfur compounds that contain saturated rings and thus provides the first examples of pentacoordinated tin derivatives of this class. The synthesis and X-ray characterization of the bicyclic (ethanedithiolato)stannates $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**1**), $[(C_2H_4S_2)_2SnPh][Et_4N]$ (**2**), $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (**3**), and $[(C_2H_4S_2)_2SnSCH_2]_2[Et_3NH]_2$ (**4**) are reported here. The latter two five-coordinated derivatives provide unique examples containing binuclear tin centers.

Interestingly, **3** results from the same type of synthetic procedure as that used for the formation of **1** and **2**, i.e., the reaction of either the alkyl- or aryltin trichloride with $Et_4N^+Cl^-$ and sodium ethane-1,2-dithiolate. Compound **4** forms as a partial hydrolysis product of bis(ethane-1,2-dithiolato)tin with Et_3N. Also synthesized, but not structurally characterized by X-ray crystallography, are the butyl derivative, analogous to **3**, $[(C_2H_4S_2)\text{-}n\text{-}Bu(Cl)SnSCH_2]_2$ (**5**) and the Dabco salt, analogous to **4**, $[(C_2H_4S_2)_2SnSCH_2]_2[N(C_2H_4)_3NH]_2$ (**6**).

Experimental Section

All solvents were either used directly from freshly opened bottles or dried prior to use. Acetonitrile was refluxed and distilled over phosphorus pentoxide. Diethyl ether was distilled over lithium aluminum hydride. Methyltin trichloride, phenyltin trichloride, *n*-butyltin trichloride, and ethanedithiol were from Alfa and were used without further purification.

Proton NMR spectra were obtained on Varian A-60 and 300-MHz Varian spectrometers and referenced versus tetramethylsilane. Tin-119 NMR spectra were recorded on the 300-MHz unit and referenced vs tetramethyltin. Melting points were obtained with a Hoover Uni-Melt capillary melting point apparatus and were uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

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(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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Syntheses. Tetraethylammonium Bis(ethane-1,2-dithiolato)-*n*-butylstannate, $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (1). Tetraethylammonium chloride (0.717 g, 4.33 mmol) was stirred without dissolving in 30 mL of acetone under nitrogen. *n*-Butyltin trichloride (1.07 g, 3.99 mmol) was added, and a clear solution formed upon stirring at room temperature for 0.5 h. Sodium ethanedithiolate (0.707 g, 5.12 mmol), which was prepared by mixing sodium and ethanedithiol in methanol, was placed in a dropping funnel. Dropwise addition caused the immediate formation of a white solid. After the addition was completed, the mixture was heated at 50 °C for 3 h and stirred at room temperature overnight, during which time it turned yellow. After filtering, the solvent was removed under vacuum to yield a yellow oil. The yellow oil was dissolved in 10 mL of acetonitrile, and the resulting mixture was treated with 40 mL of ether and cooled to 7 °C for several weeks to yield colorless crystals: yield 1.78 g (91.0%); mp 126–129 °C. ^1H NMR (CD_3CN): 0.9 (m, 9 H), 1.4 (t, 12 H), 2.65 (s, 8 H), 3.2 ppm (q, 8 H). Anal. Calcd for $C_{16}H_{37}NS_4Sn$: C, 39.18; H, 7.57; N, 2.85. Found: C, 39.29; H, 7.61; N, 2.94. Crystals suitable for X-ray analysis were grown from a mixture of acetonitrile and ether (1:4) at 0 °C.

Tetraethylammonium Bis(ethane-1,2-dithiolato)phenylstannate, $[(C_2H_4S_2)_2SnC_6H_5][Et_4N]$ (2). Tetraethylammonium chloride (1.30 g, 7.85 mmol) was stirred without dissolving in 30 mL of acetone under nitrogen. Phenyltin trichloride (2.27 g, 7.51 mmol) was added, and a clear solution was obtained upon stirring at 24 °C for 0.5 h. Sodium ethanedithiolate (2.1 g, 15.20 mmol), which was prepared by mixing sodium and ethanedithiol in methanol, was placed in a dropping funnel. Dropwise addition caused immediate formation of a white solid. The mixture was heated at 50 °C for 1 h after the addition was completed. The solvent was removed, and the solid was treated with water to dissolve sodium chloride. The remaining solid was dissolved in a minimum amount of hot acetonitrile. Colorless crystals were deposited upon cooling to room temperature: yield 2.8 g (73.0%); mp 165–165.5 °C. ^1H NMR (CD_3CN): 1.15 (t, 12 H), 3.10 (q, 8 H), 2.75 (s, 8 H), 7.35–8.05 ppm (m, 5 H). ^{119}Sn NMR (CH_3CN): −82.4 ppm. Anal. Calcd for $C_{18}H_{33}NS_4Sn$: C, 42.39; H, 6.47; N, 2.75. Found: C, 42.71; H, 6.54; N, 2.71.

Bis(tetraethylammonium) (*μ*-Ethane-1,2-dithiolato-*S*,*S*′)bis(chloro-*n*-butyl(ethane-1,2-dithiolato)stannate), $[(C_2H_4S_2)\text{-}n\text{-}Bu(Cl)SnSCH_2]_2[Et_4N]_2$ (5). To a solution of *n*-butyltin trichloride (0.265 g, 0.988 mmol) in acetone (30 mL) was added tetraethylammonium chloride (0.179 g, 1.08 mmol). The reaction mixture was stirred for 0.5 h at room temperature. Sodium ethanedithiolate (0.30 g, 2.17 mmol), which was prepared by mixing sodium and ethanedithiol in methanol, was placed in a dropping funnel. Dropwise addition caused immediate formation of a white solid. The mixture was heated at 50 °C for 3 h after the addition was completed. After filtering, the colorless solution was evaporated under vacuum to dryness. The colorless oil that formed was dissolved in 5 mL of acetonitrile. The resultant mixture was treated with 15 mL of diethyl ether and cooled to 0 °C. Colorless needlelike crystals formed: yield 1.00 g (86%); mp 91–92 °C. ^1H NMR (CD_3CN): 1.15 (m, 24 H), 2.6 (s, 12 H), 3.1 ppm (q, 16 H). Anal. Calcd for $C_{30}H_{70}Cl_2N_2S_6Sn_2$: C, 37.50; H, 7.35; N, 2.92. Found: C, 37.58; H, 7.08; N, 2.95.

Bis(tetraethylammonium) (*μ*-Ethane-1,2-dithiolato-*S*,*S*′)bis(chloromethyl(ethane-1,2-dithiolato)stannate), $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (3). To a solution of methyltin trichloride (0.613 g, 2.55 mmol) in acetone (20 mL) was added tetraethylammonium chloride (0.613 g, 3.70 mmol), and the mixture was stirred for 0.5 h at room temperature. Sodium ethanedithiolate (0.60 g, 4.34 mmol), which was prepared freshly by mixing sodium and ethanedithiol in methanol, was placed in a dropping funnel. Dropwise addition caused immediate formation of a white solid. The reaction mixture was heated at 50 °C for 2 h after the addition was completed. After filtering, the colorless solution was evaporated under vacuum, and the colorless oil that formed was dissolved in acetonitrile. Ether was added to induce crystallization. White needlelike crystals were deposited: yield 1.00 g (91%); mp 155–156 °C. ^1H NMR (CD_3CN): 0.95 (s, 6 H), 1.2 (t, 24 H), 2.7 (s, 12 H), 3.2 ppm (q, 16 H). ^{119}Sn NMR (CH_3CN): −52.3 ppm. Anal. Calcd for $C_{24}H_{58}Cl_2N_2S_6Sn_2$: C, 32.93; H, 6.67; N, 3.19; Cl, 8.09. Found: C, 33.01; H, 6.56; N, 3.22; Cl, 8.42.

Bis(triethylammonium)(*μ*-Ethane-1,2-dithiolato-*S*,*S*′)tetrakis(ethane-1,2-dithiolato)distannate, $[(C_2H_4S_2)_2SnSCH_2]_2[Et_3NH]_2$ (4). Bis(ethane-1,2-dithiolato)tin (1.0 g, 3.30 mmol) was dissolved in 40 mL of boiling chloroform under nitrogen. Triethylamine (0.46 mL, 6.37 mmol) was added, and the reaction mixture was stirred and refluxed for 3 h. The reaction mixture was allowed to stand at room temperature for 24 h. A mixture of insoluble and crystalline material was formed. Colorless crystals that melted at 129–131 °C were separated by hand from the insoluble material (mp > 240 °C): yield 0.50 g (50%); mp 129–131 °C. ^1H NMR (Me_2SO): 1.2 (t, 18 H), 2.8 (s, 20 H), 3.1 ppm (q, 12 H). ^{119}Sn NMR (CH_3CN): −14.8 ppm. Anal. Calcd for $C_{22}H_{52}N_2S_{10}Sn_2$: C, 29.20; H, 5.75; N, 3.10. Found: C, 28.87; H, 5.62; N, 3.02.

Bis(1-azonia-4-azabicyclo[2.2.2]octane) (*μ*-Ethane-1,2-dithiolato-*S*,*S*′)bis(bis(ethane-1,2-dithiolato)stannate), $[(C_2H_4S_2)_2SnSCH_2]_2[N(C_2H_4)_3NH]_2$ (6). Bis(ethane-1,2-dithiolato)tin (0.630 g, 2.08 mmol) was dissolved in 50 mL of boiling chloroform under nitrogen. 1,4-Diazabicyclo[2.2.2]octane (Dabco) (0.23 g, 2.05 mmol) was added, and the reaction mixture was stirred and refluxed for 3 h. After filtering, the colorless solution was evaporated under vacuum, and the colorless oil that formed was dissolved in a minimum amount of chloroform. Ether was added to induce crystallization. White needlelike crystals were deposited: yield 0.40 g (62%); mp 193–195 °C. Anal. Calcd for $C_{22}H_{46}N_4S_{10}Sn_2$: C, 28.57; H, 4.98; N, 6.06. Found: C, 28.69; H, 4.94; N, 6.26. Crystals suitable for X-ray structural analysis were grown by the slow vapor diffusion of ether into a solution of the product dissolved in chloroform.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[21]

Crystals were mounted inside thin-walled glass capillaries that were sealed as a precaution against moisture sensitivity. Data were collected by using the θ–2θ scan mode for $3° \le 2\theta_{Mo\,K\bar{\alpha}} \le 50°$ for **1**, **3**, and **4** and $3° \le 2\theta_{Mo\,K\bar{\alpha}} \le 55°$ for **2**. The structures were solved by using Patterson and difference Fourier techniques and were refined by using full-matrix least squares.[22]

X-ray Studies for $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (1). The colorless crystal used for the X-ray study was cut from a polycrystalline mass and had approximate dimensions of 0.25 × 0.28 × 0.35 mm.

Crystal Data: $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**1**), orthorhombic, space group $Pbc2_1$ (alternate setting of $Pca2_1$ [C_{2v}^5–No. 29][23]), $a = 12.132$ (4) Å, $b = 12.386$ (4) Å, $c = 15.344$ (2) Å, $Z = 4$, and $\mu_{Mo\,K\bar{\alpha}} = 1.458$ mm^{-1}. A total of 2113 independent reflections ($+h,+k,+l$) were measured. No corrections were made for absorption.

The 22 independent non-hydrogen atoms were refined anisotropically. The 22 independent methylene 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[24] were $R = 0.036$ and $R_w = 0.047$ for the 1560 reflections having $I \ge 2\sigma_I$.

X-ray Studies for $[(C_2H_4S_2)_2SnPh][Et_4N]$ (2). Crystals of **2** are colorless chunky triangular tabs. The crystal used for the X-ray study was cut to approximate dimensions of 0.18 × 0.30 × 0.35 mm.

Crystal Data: $[(C_2H_4S_2)_2SnPh][Et_4N]$ (**2**), orthorhombic, space group $Aba2$ [C_{2v}^{17}–No. 41],[25] $a = 12.932$ (3) Å, $b = 11.282$ (3) Å, $c = 15.577$ (5) Å, $Z = 4$, and $\mu_{Mo\,K\bar{\alpha}} = 1.481$ mm^{-1}. A total of 1355 independent reflections ($+h,+k,+l$) were measured. No corrections were made for absorption.

The 14 independent non-hydrogen atoms were refined anisotropically. The 11 independent hydrogen atoms with calculable coordinates were treated as described for **1**. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors were $R = 0.040$ and $R_w = 0.074$ for the 899 reflections having $I \ge 2\sigma_I$.

X-ray Studies for $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (3). The colorless crystal used for the X-ray study was cut from a hemispherical cluster of small laths and had approximate dimensions of 0.20 × 0.25 × 0.40 mm.

Crystal Data: $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (**3**), monoclinic, space group $P2_1/n$ (alternate setting of $P2_1/c$ C_{2h}^5–No. 14][26]), $a = 8.436$ (2) Å, $b = 17.961$ (5) Å, $c = 13.004$ (4) Å, $\beta = 95.61$ (2)°, $Z = 2$, and $\mu_{Mo\,K\bar{\alpha}} = 1.737$ mm^{-1}. A total of 3440 independent reflections ($+h,+k,\pm l$) were measured. No corrections were made for absorption.

The 18 independent non-hydrogen atoms were refined anisotropically. The 14 independent methylene hydrogen atoms were treated as described for **1**. Coordinates for the 15 independent methyl hydrogen atoms were obtained from a difference Fourier synthesis, and these atoms were included in the refinement as fixed isotropic scatterers. The final agree-

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

(22) The function minimized was $\sum w(|F_0| - |F_c|)^2$, where $w^{1/2} = 2F_0Lp/\sigma_I$. Mean atomic scattering factors were taken from: Reference 23, Vol. IV, 1974; pp 72–98. Real and imaginary dispersion corrections for Sn, S, and Cl were taken from the same source, pp 149–150.

(23) *International Tables for -ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 115.

(24) $R = \sum||F_0| - |F_c||/\sum|F_0|$ and $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$. For **1** and **2**, these values are for the configuration having the lowest R_w.

(25) Reference 23, p 127.

(26) Reference 23, p 99.

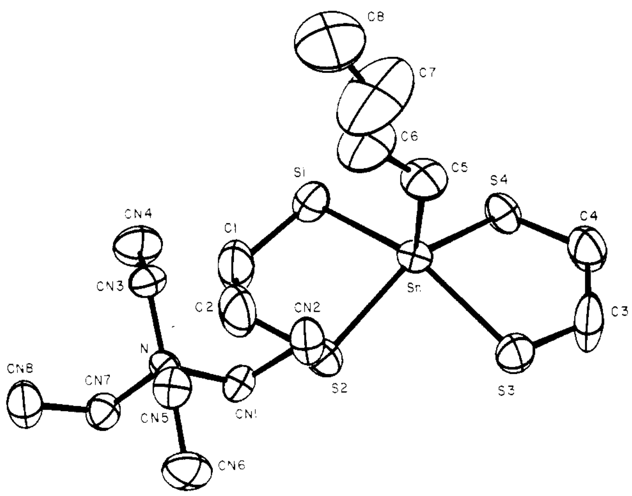

Figure 1. ORTEP plot of $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

Table I. Atomic Coordinates in Crystalline $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**1**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	2559.3 (3)	371.3 (4)	2500[c]
S1	2556 (2)	−1638 (2)	2761 (2)
S2	594 (2)	311 (3)	2910 (3)
S3	2489 (2)	2315 (3)	2989 (3)
S4	4444 (2)	362 (2)	3127 (3)
C1	1112 (12)	−1828 (11)	2974 (13)
C2	350 (11)	−1116 (12)	2772 (15)
C3	3883 (12)	2480 (13)	3362 (13)
C4	4698 (10)	1762 (11)	3089 (15)
C5	2702 (12)	542 (14)	1100 (10)
C6	2269 (19)	−137 (21)	570 (13)
C7	2323 (30)	63 (32)	−396 (17)
C8	2270 (23)	−716 (35)	−956 (22)
N	−2581 (6)	231 (7)	744 (7)
CN1	−1743 (9)	874 (8)	1284 (7)
CN2	−913 (11)	1496 (11)	740 (10)
CN3	−2022 (9)	−541 (10)	104 (9)
CN4	−1308 (11)	−1387 (11)	527 (11)
CN5	−3238 (9)	994 (8)	169 (8)
CN6	−3920 (11)	1837 (11)	647 (10)
CN7	−3333 (9)	−352 (8)	1373 (8)
CN8	−4245 (11)	−1029 (11)	986 (11)

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

ment factors were $R = 0.036$ and $R_w = 0.045$ for the 2652 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $[(C_2H_4S_2)_2SnSCH_2]_2[Et_3NH]_2$ (4). The colorless crystal used for the X-ray study was cut from a polycrystalline mass and had approximate dimensions of 0.13 × 0.20 × 0.20 mm.

Crystal Data: $[(C_2H_4S_2)_2SnSCH_2]_2[Et_3NH]_2$ (**4**), triclinic, space group $P\bar{1}$ [C_i^1-No. 2],[27] $a = 8.638$ (3) Å, $b = 10.095$ (3) Å, $c = 12.538$ (3) Å, $\alpha = 69.35$ (2)°, $\beta = 76.08$ (2)°, $\gamma = 69.40$ (3)°, $Z = 1$, and $\mu_{\text{Mo K}\bar{\alpha}} = 1.864$ mm^{-1}. A total of 3326 independent reflections ($+h,\pm k,\pm l$) were measured. No corrections were made for absorption.

The 18 independent non-hydrogen atoms were refined anisotropically, while the N–H hydrogen atoms were refined isotropically. The 16 independent methylene hydrogen atoms were treated as described for **1**. The hydrogen atoms of the methyl groups were omitted from the refinement. The final agreement factors were $R = 0.039$ and $R_w = 0.053$ for the 2790 reflections having $I \geq 2\sigma_I$.

The identity of the Dabco analogue of **4**, i.e., $[(C_2H_4S_2)_2SnSCH_2]_2[N(C_2H_4)_3NH]_2$ (**6**), has been established by preliminary X-ray results.[28] The complete refinement was abandoned since the structure of **4** had been completed.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_2H_4S_2)_2Sn(n\text{-}Bu)][Et_4N]$ (**1**)[a]

Sn–S1	2.521 (3)	Sn–S2	2.467 (3)
Sn–S3	2.523 (3)	Sn–S4	2.480 (3)
Sn–C5	2.17 (2)		
S1–Sn–S3	153.5 (1)	C5–Sn–S1	104.7 (5)
S2–Sn–S4	142.3 (2)	C5–Sn–S2	109.4 (4)
S1–Sn–S2	85.9 (1)	C5–Sn–S3	101.8 (5)
S3–Sn–S4	85.4 (1)	C5–Sn–S4	108.2 (4)
S1–Sn–S4	96.3 (1)	S2–Sn–S3	85.4 (1)

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

Table III. Atomic Coordinates in Crystalline $[(C_2H_4S_2)_2SnPh][NEt_4]$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	0[c]	0[c]	0[c]
S1	1925 (3)	2 (4)	−293 (3)
S2	−1 (4)	−2043 (3)	−574 (3)
N	0[c]	0[c]	−3237 (14)
CP1	0[c]	0[c]	1395 (13)
CP4	0[c]	0[c]	3149 (26)
CP2	900 (13)	−197 (13)	1835 (11)
CP3	911 (18)	−198 (18)	2726 (13)
C1	2109 (15)	−1560 (18)	−442 (17)
C2	1338 (25)	−2298 (17)	−768 (24)
C3	751 (13)	636 (13)	−2657 (12)
C4	1565 (17)	1400 (18)	−3114 (17)
C5	569 (13)	−847 (13)	−3824 (11)
C6	1128 (15)	−1839 (15)	−3374 (15)

[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 $[(C_2H_4S_2)_2SnPh][Et_4N]$ (**2**)[a]

Sn–S1	2.530 (4)	Sn–CP1	2.17 (2)
Sn–S2	2.472 (4)		
S1–Sn–S1′	159.2 (2)	S1–Sn–CP1	100.4 (1)
S2–Sn–S2′	137.6 (2)	S1–Sn–S2	86.3 (1)
S2–Sn–CP1	111.2 (1)	S1′–Sn–S2	86.2 (1)

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

Table V. Atomic Coordinates in Crystalline $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (**3**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	769.5 (4)	547.6 (2)	2413.6 (3)
Cl	508 (2)	1979 (1)	2009 (1)
S1	1665 (2)	−753 (1)	2858 (1)
S2	3110 (2)	682 (1)	1491 (1)
S3	562 (2)	1026 (1)	4141 (1)
CM	−1459 (7)	314 (4)	1547 (5)
C1	3615 (9)	−709 (4)	2406 (6)
C2	3774 (8)	−281 (4)	1463 (6)
C3	752 (5)	229 (3)	5021 (4)
N	−4207 (4)	2305 (2)	3805 (3)
C4	−3802 (6)	1763 (3)	4685 (4)
C5	−4657 (7)	1028 (3)	4582 (5)
C6	−3610 (6)	1987 (3)	2835 (4)
C7	−3851 (9)	2495 (4)	1905 (5)
C8	−6007 (5)	2416 (3)	3609 (4)
C9	−6802 (6)	2685 (3)	4516 (4)
C10	−3421 (6)	3045 (3)	4096 (4)
C11	−1620 (6)	3041 (4)	4165 (5)

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

Results

The atom-labeling scheme and the molecular geometry of **1** are shown in Figure 1. Atomic coordinates are given in Table I, and selected bond lengths and angles are given in Table II. The

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(27) Reference 23, p 75.

(28) Space group $P2_1/n$, $a = 12.570$ (2) Å, $b = 8.036$ (1) Å, $c = 17.851$ (3) Å, $\beta = 93.82$ (1)°, $Z = 2$. Like **4**, the dimer has crystallographic C_i symmetry with hydrogen bonding from the cations to the anion.

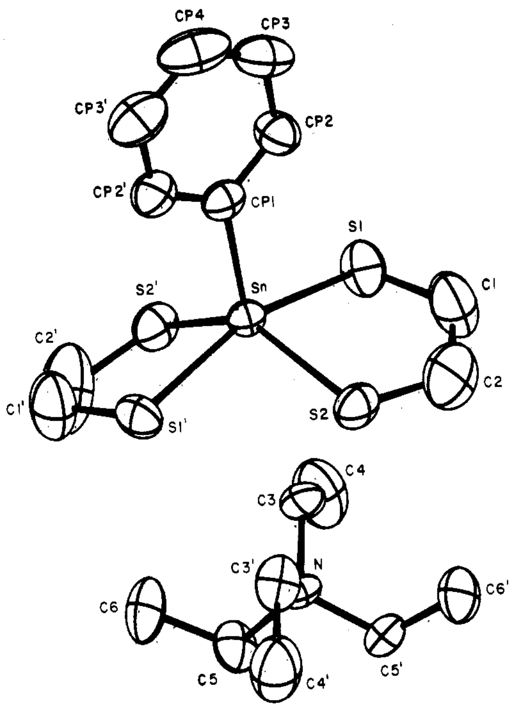


Figure 2. ORTEP plot of $[(C_2H_4S_2)_2SnPh][Et_4N]$ (**2**) with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by $-x, -y, z$. Hydrogen atoms are omitted for purposes of clarity.

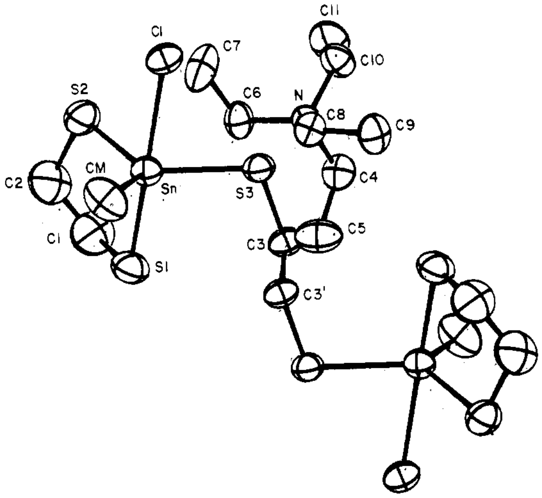


Figure 3. ORTEP plot of $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (**3**) with thermal ellipsoids at the 50% probability level. Primed or unlabeled atoms are related to unprimed labeled ones by $-x, -y, 1 - z$. A symmetry-related cation and all hydrogen atoms are omitted for purposes of clarity.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_2H_4S_2)Me(Cl)SnSCH_2]_2[Et_4N]_2$ (**3**)[a]

Sn–S1	2.506 (2)	Sn–Cl	2.629 (2)
Sn–S2	2.420 (2)	Sn–CM	2.137 (6)
Sn–S3	2.427 (2)		
Cl–Sn–S1	167.3 (1)	Cl–Sn–S2	82.0 (1)
S2–Sn–S3	124.0 (1)	Cl–Sn–S3	80.0 (1)
CM–Sn–S2	118.5 (2)	S1–Sn–S2	88.0 (1)
CM–Sn–S3	114.7 (2)	S1–Sn–S3	99.4 (1)
Cl–Sn–CM	92.0 (2)	S1–Sn–CM	99.7 (2)

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

analogous information for **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

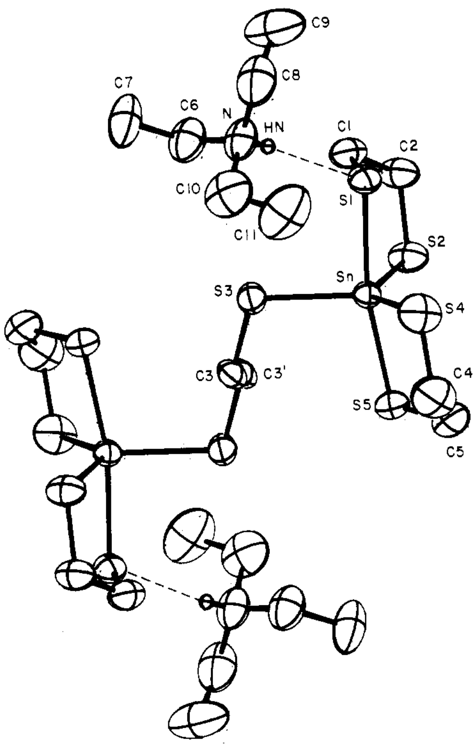


Figure 4. ORTEP plot of $[(C_2H_4S_2)_2SnCH_2]_2[Et_3NH]_2$ (**4**) with thermal ellipsoids at the 50% probability level. Primed or unlabeled atoms are related to unprimed labeled ones by $1 - x, -y, 1 - z$. Hydrogen atoms, except for HN, are omitted for purposes of clarity. Hydrogen-bonding interactions are shown as dashed lines.

Table VII. Atomic Coordinates in Crystalline $[(C_2H_4S_2)_2SnSCH_2][Et_3NH]_2$ (**4**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	3679.6 (5)	583.0 (4)	2348.1 (3)
S1	645 (2)	1645 (2)	2001 (1)
S2	3177 (2)	−1841 (2)	2976 (2)
S3	3024 (2)	1633 (2)	3943 (1)
S4	4317 (3)	2166 (2)	440 (2)
S5	6730 (2)	−654 (2)	2376 (2)
C1	3 (8)	202 (8)	3164 (6)
C2	936 (8)	−1338 (8)	3021 (7)
C3	4909 (8)	787 (7)	4657 (5)
C4	6557 (12)	1658 (13)	319 (7)
C5	7377 (10)	35 (12)	853 (7)
N	−1322 (8)	4575 (7)	2783 (5)
C6	−1573 (11)	4093 (9)	4064 (7)
C7	−2519 (13)	5352 (10)	4578 (7)
C8	−2769 (13)	5298 (10)	2178 (2)
C9	−3902 (11)	4271 (11)	2488 (12)
C10	−97 (13)	5537 (12)	2384 (10)
C11	670 (15)	5769 (12)	1159 (10)
HN	−946 (94)	3931 (83)	2620 (62)

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

Table VIII. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(C_2H_4S_2)_2SnSCH_2]_2[Et_3NH]_2$ (**4**)[a]

Sn–S1	2.540 (2)	Sn–S3	2.444 (2)
Sn–S5	2.490 (2)	S1–HN	2.52 (7)
Sn–S2	2.454 (2)	N–HN	0.70 (7)
Sn–S4	2.423 (2)	N- - -S1	3.210 (6)
S1–Sn–S5	168.95 (5)	S1–Sn–S2	85.52 (6)
S2–Sn–S4	130.86 (8)	S1–Sn–S4	86.78 (7)
S3–Sn–S2	111.49 (7)	S5–Sn–S2	90.19 (6)
S3–Sn–S4	117.03 (7)	S5–Sn–S4	88.35 (7)
S1–Sn–S3	90.43 (6)	N–HN–S1	175 (8)
S5–Sn–S3	100.61 (6)		

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

provided as supplementary material.

Discussion

Synthetic Aspects. The ethanedithiolates **1**–**6** represent the first anionic five-coordinated compounds of tin containing ring saturation. The synthetic procedure employed in forming the bicyclic derivatives **1** and **2** follows the reaction sequence displayed in eq 1 and 2.

$$\mathrm{RSnCl_3 + Et_4NCl \xrightarrow{(CH_3)_2CO} \underset{\text{not isolated}}{[RSnCl_4][Et_4N]}} \qquad (1)$$

$$\mathrm{[RSnCl_4][Et_4N] + 2Na_2(SCH_2CH_2S) \xrightarrow[(CH_3)_2CO]{MeOH} [(C_2H_4S_2)_2SnR][Et_4N] + 4NaCl} \qquad (2)$$

$$\mathrm{R} = n\text{-Bu } (\mathbf{1}),\ \mathrm{Ph}\ (\mathbf{2})$$

The first step is suggested by the solution of $Et_4N^+Cl^-$ in the presence of $RSnCl_3$ and the lack of its solution in the absence of $RSnCl_3$. It is found that this reaction proceeds more rapidly with R = Ph than with R = *n*-Bu.

When the same reaction procedure is used with $MeSnCl_3$, the binuclear tin species **3** is formed. Assuming the same initial formation of $[MeSnCl_4][Et_4N]$ in acetone solution, the subsequent reaction corresponds to that in eq 3.

$$\mathrm{2[RSnCl_4][Et_4N] + 3Na_2(SCH_2CH_2S) \xrightarrow[(CH_3)_2CO]{MeOH} [(C_2H_4S_2)R(Cl)SnSCH_2]_2[Et_4N]_2 + 6NaCl} \qquad (3)$$

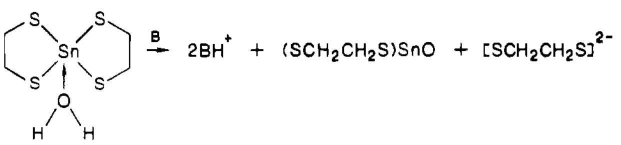
$$\mathrm{R} = \mathrm{Me}\ (\mathbf{3}),\ n\text{-Bu}\ (\mathbf{5})$$

Somewhat surprisingly, *n*-$BuSnCl_3$ reacts with sodium ethane-1,2-dithiolate by the latter route, giving the binuclear tin derivative **5** in addition to its reaction yielding the mononuclear stannate **1**. From the experimental details, it appears that a shorter reaction time favors the formation of the dinuclear tin product. The latter is consistent with the reaction stoichiometries showing that 2 mol of sodium dithiolate/mol of $RSnCl_3$ is required to form the mononuclear reaction product (eq 2), whereas this mole ratio is only 1.5 to form the binuclear derivative (eq 3). However, increasing the reaction time when $MeSnCl_3$ was used as the starting reagent failed to yield a mononuclear product. Independent of the reaction time, only the binuclear product, **3**, was isolated. Even so, the formation of binuclear tin species, like **3**, provides a plausible reaction path leading to the bicyclic stannates **1** and **2**.

The cyclic distannates **4** and **6** are similar to **3**. These form presumably as partial hydrolysis products of the interaction of bis(ethane-1,2-dithiolato)tin with an amine according to eq 4. One might speculate that nucleophilic attack by H_2O at tin accompanied by proton abstraction by the base present could provide a source of the dithiolate anion, e.g. by eq 5. The addition of dithiolate to cause coupling of the two tin centers then is envisioned to complete the reaction (eq 6). The (dithiolato)tin oxide formed is most likely a polymeric species. However, no characterization of this material was obtained.

$$\mathrm{3Sn(SCH_2CH_2)_2 + 2B + H_2O \xrightarrow{CHCl_3} [(C_2H_4S_2)_2SnSCH_2]_2[BH]_2 + (1/}n\mathrm{)\underset{\text{not isolated}}{[(SCH_2CH_2S)SnO]_}}{}_{n} \qquad (4)$$

$$\mathrm{B} = \mathrm{Et_3N}\ (\mathbf{4}),\ \text{Dabco}\ (\mathbf{6})$$



(5)

$$\mathrm{2Sn(SCH_2CH_2S)_2 + [SCH_2CH_2S]^{2-} + 2BH^+ \rightarrow [(C_2H_4S_2)_2SnSCH_2]_2[BH]_2} \qquad (6)$$

Structural Details. As outlined below, the geometry in **1** and **2** is more nearly rectangular pyramidal, while the geometry in **3** and **4** more closely approaches the trigonal bipyramid.

Compound **2** has crystallographic C_2 symmetry with Sn, CP1, and CP4 of the anion and N of the cation lying on a 2-fold axis. The anions of the binuclear compounds **3** and **4** have crystallographic C_i symmetry, each with an inversion center lying on the C3–C3′ bond of the bridging ethanedithiolate ligand.

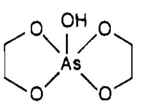
The geometry about the Sn atom in all four compounds lies on the coordinate connecting an ideal trigonal bipyramid (TBP) with an ideal rectangular pyramid (RP). From the dihedral angle method[29,30] with unit vectors to assess displacement, **1** is displaced 78.7% from a TBP having S1 and S3 in axial positions toward an RP with C5 in the apical position, **2** is displaced 60.2% from a TBP having S1 and S1′ in axial positions toward an RP with CP1 in the apical position, **3** is displaced 23.5% from a TBP having S1 and C1 in axial positions toward an RP with CM in the apical position, and **4** is displaced 33.6% from a TBP having S1 and S5 in axial positions toward the RP with S3 in the apical position.

Residual trigonal-bipyramidal character is apparent in all four compounds in that the $Sn-S_{ax}$ (ax = axial) bonds are longer than the $Sn-S_{eq}$ (eq = equatorial) bonds. The average (over all four compounds) $Sn-S_{ax}$ bond length is 2.518 (3) Å with a range of 2.490 (2)–2.540 (2) Å, while the average $Sn-S_{eq}$ bond length is 2.448 (3) Å with a range of 2.420 (2)–2.480 (3) Å.

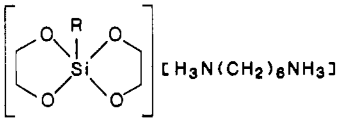
The longest of the $Sn-S_{ax}$ bond lengths is the Sn–S1 bond in compound **4**, which has a length of 2.540 (2) Å as compared to the other $Sn-S_{ax}$ bond in **4**, with a value of 2.490 (2) Å. The hydrogen atom of the cation is involved in a hydrogen bond to S1 (H–S1 = 2.52 (7) Å, as compared to the van der Waals sum of 3.05 Å; N–HN–S1 and 175 (8)°). The lengthening of the Sn–S1 bond is typical for ligand atoms involved in hydrogen bonds, as we have observed with other anionic pentacoordinated compounds, particularly those of silicon[12] and germanium.[16]

Solution ^{119}Sn NMR data on **2**–**4** show single resonances in the range −15 to −82 ppm. This range is consistent with the presence of five-coordinate tin centers and thus indicates that no drastic change in the coordination geometry occurs between the solid and solution states for these tin–sulfur compounds. Four-coordinate compounds containing multiple tin–sulfur bonds, e.g. $MeSn(SMe)_3$ and $PhSn(SMe)_3$, have ^{119}Sn chemical shift values considerably downfield, at +167 and +107 ppm, respectively.[31] Other related examples are $(MeS)_4Sn$, which has a ^{119}Sn resonance at +160 ppm, and $(Me_2SnCl)_2S$, with a value at +144 ppm.[31]

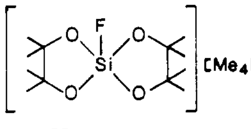
Structural Comparisons. The presence of one or two saturated five-membered ring systems in a five-coordinated compound of groups 4[11-16] or 5[17,32] usually leads to a trigonal-bipyramidal geometry as represented by the structures of **3** and **4**. The following exceptions show either strong hydrogen bonding, **7**–**9**,[14,33,34] or lattice effects, **10**,[35] which are conductive to influencing structural distortions toward the square pyramid. The percentages shown in parentheses are structural displacements, TBP → RP.



7[33] (58.6%)



R = Me (**8**)[34] (53.3%), Ph (**9**)[14] (72.1%)



10[35] (53.6%, 70.8%)

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The unusual aspect of the present structural determinations then is the formation of the geometries for **1** and **2**, displaced toward the square or rectangular pyramid 78.7% and 60.2%, respectively. In these cases, no hydrogen bonding is present and lattice effects are not indicated to be important. For example, only one type of molecule per unit cell is found for each, while the fluorosilicate, **10**, shows two types of molecules per unit cell. Hence, we take the observed geometries of **1** and **2** as evidence supporting the ease of structural distortion in going down the periodic series from Si to Ge to Sn. VSEPR theory[36] supports this trend in that the larger, less electrongative central atom of a five-coordinated species would suffer decreased electron bond-pair repulsion. This effect favors the displacement toward the inherently less stable RP. The greater RP character for the *n*-butyl derivative, **1**, over the phenyl derivative, **2**, follows the observation that the presence of larger, less electronegative groups in the fifth position causes displacement toward the square pyramid.[17,32] These same tendencies were found to operate in the group 5 series, where molecular nonrigidity increased in the order P < As < Sb.[9,10]

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Registry No. **1**, 113161-03-8; **2**, 113161-05-0; **3**, 113161-07-2; **4**, 113161-09-4; **5**, 113161-11-8; **6**, 113216-79-8; *n*-butyltin trichloride, 1118-46-3; sodium ethanedithiolate, 23851-16-3; phenyltin trichloride, 1124-19-2; methyltin trichloride, 993-16-8; bis(ethane-1,2-dithiolato)tin, 176-56-7.

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**) and deviations from least-squares mean planes (Tables S13–S16, for **1–4**, respectively) (10 pages); tables of calculated and observed structure factors for **1–4** (31 pages). Ordering information is given on any current masthead page.

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Pyrazine and Pyridine Complexes of Copper(II) Trifluoromethanesulfonate. Crystal Structure of Tetrakis(pyridine)bis(trifluoromethanesulfonato-*O*)copper(II) and Magnetic Exchange in (Pyrazine)bis(trifluoromethanesulfonato-*O*)copper(II)

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Received October 30, 1987

Copper(II) trifluoromethanesulfonate reacts with excess pyridine or pyrazine to yield complexes of compositions $Cu(py)_4(CF_3SO_3)_2$ and $Cu(pyz)_4(CF_3SO_3)_2{\cdot}H_2O$. Crystals of $Cu(py)_4(CF_3SO_3)_2$ are orthorhombic, of space group *Pbcn*, with $a = 10.5618$ (7) Å, $b = 16.287$ (1) Å, $c = 16.830$ (2) Å, $Z = 4$, and $R = R_w = 0.046$ for 1130 reflections with $I \geqslant 2\sigma(I)$. The *trans*-$Cu(py)_4(CF_3SO_3)_2$ molecule has crystallographic C_2 symmetry. The coordination about Cu is tetragonally distorted pseudooctahedral with mean Cu–N = 2.035 Å and Cu–O = 2.425 (4) Å. An analogous structure with trans-axially coordinated anions and equatorially bound monodentate pyrazine ligands is proposed for $Cu(pyz)_4(CF_3SO_3)_2{\cdot}H_2O$. Thermolysis of this latter compound at 87 °C yields $Cu(pyz)(CF_3SO_3)_2$, and spectroscopic studies on this material support a sheet structure in which chains of copper atoms, doubly bridged by bidentate sulfonate groups, are cross-linked by bidentate bridging pyrazine ligands. Magnetic susceptibility studies (100–4.2 K) reveal antiferromagnetic behavior with a maximum in the susceptibility at ~7 K. Exchange coupling is considered to take place primarily via the bridging pyrazine groups; analysis of the magnetic data according to a Heisenberg linear-chain model yields best fit values of $J = -3.78$ cm^{-1} and $g = 2.08$.

Introduction

Several transition-metal complexes containing the coordinated trifluoromethanesulfonate (triflate) ligand have been synthesized in recent years;[1-3] interest in the molecular and electronic structures of these compounds, as well as in their potential as inorganic synthons, stems from the low basicity of the $CF_3SO_3^-$ anion and hence from its expected poor coordinating ability.[1] We report here the synthesis and characterization of 1,4-diazine (pyrazine, pyz) and azine (pyridine, py) complexes of copper(II) trifluoromethanesulfonate.[4] $Cu(pyz)_4(CF_3SO_3)_2{\cdot}H_2O$ and $Cu(py)_4(CF_3SO_3)_2$ were obtained by reaction of copper(II) trifluoromethanesulfonate with an excess of the appropriate base in methanol. The pyridine complex was obtained in crystalline form, and because of the relative paucity of structural data on transition-metal complexes containing coordinated triflate,[1] a single-crystal X-ray study was undertaken on this compound. Thermolysis of the tetrakis(pyrazine) complex gave $Cu(pyz)(CF_3SO_3)_2$; this compound is of particular interest because of the opportunity for pyrazine bridging as in the nitrate[5] and hexafluoroacetylacetonate[6] analogues and the consequent possibility of magnetic exchange between metal centers. Exchange was observed previously for the nitrate but not for the hexafluoroacetylacetonate.

Experimental Section

Synthesis. Tetrakis(pyridine)bis(trifluoromethanesulfonato-*O*)copper(II), $Cu(py)_4(CF_3SO_3)_2$. Copper(II) trifluoromethanesulfonate[4] (0.994 g, 2.75 mmol) was dissolved in hot methanol (11 mL). An excess of pyridine (5 mL, 62 mmol) was added dropwise, whereupon an intensely blue solution formed. On cooling, a blue crystalline solid resulted, which was isolated by filtration. The product was recrystallized from a solution of pyridine in methanol (1:4 v/v) and isolated in 82% yield. Anal. Calcd for $CuC_{22}H_{20}N_4F_6S_2O_6$: C, 38.97; H, 2.97; N, 8.26. Found: C, 38.99; H, 2.97; N, 8.29.

Tetrakis(pyrazine)bis(trifluoromethanesulfonato-*O*)copper(II) Hydrate, $Cu(pyz)_4(CF_3SO_3)_2{\cdot}H_2O$. Copper(II) trifluoromethanesulfonate (0.565 g, 1.55 mmol) was dissolved in hot methanol (3 mL). The copper(II) solution was then added to a hot solution of pyrazine (1.781 g, 22.3 mmol) dissolved in methanol (5 mL). A dark blue solution resulted, and after a period of 30 min, a blue crystalline solid formed; the product was isolated by filtration in 92% yield. Anal. Calcd for $CuC_{18}H_{18}N_8F_6S_2O_7$: C, 30.88; H, 2.59; N, 16.01. Found: C, 30.65; H, 2.57; N, 15.75.

(Pyrazine)bis(trifluoromethanesulfonato-*O*)copper(II), $Cu(pyz)(CF_3SO_3)_2$. When $Cu(pyz)_4(CF_3SO_3)_2{\cdot}H_2O$ was heated in an Aberhalden drying pistol at a temperature of 87 °C in the presence of phos-

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