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Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

A New Geometrical Form for Tin. Synthesis and Structure of the Spirocyclic Complex $[(CH_3)_4N][(C_7H_6S_2)_2SnCl]$ and the Related Monocyclic Derivative $[(C_2H_5)_4N][(C_7H_6S_2)Ph_2SnCl]$[1,2]

ARJUN C. SAU, ROBERTA O. DAY, and ROBERT R. HOLMES*

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The synthesis and X-ray structure of the tetramethylammonium chloride adduct of the spirobi(dithiolato)stannate(IV), $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$, (**2**), provide the first example of a tin compound having a discrete rectangular-pyramidal geometry. The synthesis and X-ray structure of the related monocyclic derivative $[(C_2H_5)_4N]^+[(C_7H_6S_2)Ph_2SnCl]^-$ (**4**) shows tin to possess a trigonal-bipyramidal geometry. **2** crystallizes in the monoclinic space group *Cc*, with $a = 14.126$ (4), $b = 11.485$ (6) Å, $c = 14.609$ (5) Å, $\beta = 100.37$ (3)°, and $Z = 4$. **4** crystallizes in the monoclinic space group $P2_1/c$, with $a = 12.344$ (4) Å, $b = 11.975$ (5) Å, $c = 19.120$ (5) Å, $\beta = 96.41$ (2)°, and $Z = 4$. Data for both compounds were collected on an Enraf-Nonius CAD 4 automated diffractometer out to a maximum $2\theta_{\mathrm{Mo}\,K\alpha}$ of 50°. The final conventional unweighted residuals were 0.039 and 0.048 for **2** and **4**, respectively. It is shown that the ^{119m}Sn Mössbauer quadrupole splitting parameter is useful in distinguishing the square (or rectangular) pyramid from the trigonal bipyramid. Comparison of pentacoordinated tin(IV) with pentacoordinated germanium(IV) and phosphorus shows that the known rectangular pyramids have spirocyclic systems as a common structural feature.

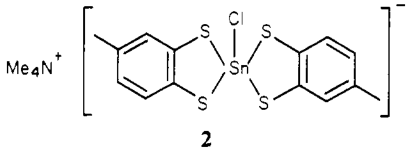
Introduction

The X-ray structures of most pentacoordinated tin compounds fall into one of three classes: (1) those that possess intermolecular tin–ligand bridge bonds, e.g., $(CH_3)_3SnCl$,[3] $(CH_3)_3SnF$,[4] $(CH_3)_2SnF_2$,[5] $(CH_3)_3SnOH$,[6] $(CH_3)_3SnOCH_3$,[7] and $(CH_3)_3SnON{=}C_6H_{10}$;[8] (2) those that are monomeric and possess intramolecular dative ligand–tin bonds, e.g., *o*-$(CH_3)_2NC_5H_4N{\rightarrow}Sn(Cl)Ph_3$,[2] $[(CH_3)_2N]_3PO{\rightarrow}Sn(Cl)Ph_3$,[2] $[(CH_3)_2N]_3PO{\rightarrow}Sn(Cl)(CH_3)_3$,[9] $(CH_3)_2(Cl)SnSCH_2CH_2NH_2$,[2] $Cl_3SnCH_2CH_2COOCH_3$,[10] $(CH_3)_2(Cl)Sn[S_2CN(CH_3)_2]$,[11] $Ph_2SnCl_2\cdot$(benzthiazole),[12] $Ph_3SnONPh(COPh)$,[13] and $(CH_3)_2Sn(Cl)SCH_2CH(NH_2)CO_2C_2H_5$;[14] (3) those that are anionic and contain five covalent bonds to tin, e.g., $[Ph_3PCH_2Ph][Bu_3SnCl_2]$,[15] $[Ph_3AsCH_2COPh][Ph_3SnCl_2]$,[15] $[(CH_3)_2SnCl(terpyridyl)][(CH_3)_2SnCl_3]$,[16a] $[Mo(\eta^5\text{-}C_5H_5)_3S_4][(CH_3)_3SnCl_2]$,[16b] and $[(CH_3)_3Sn\cdot 2(Me_2N)_3PO][(CH_3)_3SnBr_2]$.[9] The latter complex has a cation with two donor ligands forming dative bonds with tin.

The trigonal bipyramid is the basic structural representation for all members of these classes studied so far. For those derivatives which include ring formation, the ring spans apical–equatorial positions with the donor ligand occupying the apical coordination site. This same structural type is found from NMR studies[17] for related derivatives in solution. Predictions of geometry using Mössbauer data, in general, have been in agreement with the X-ray results.[18] The quadrupole splittings obtained from ^{119m}Sn spectra have proven most useful for this purpose. The values range from about 2–4 mm s^{-1} depending on the ligand arrangement and degree of distortion around the pentacoordinate tin atom in the solid state.

It is noted that the anionic tin complexes are isoelectric with phosphoranes. We have shown that spirocyclic phosphoranes form a continuous series of structures between the trigonal bipyramid and rectangular or square pyramid.[19-20] It seems likely that this also might be the case for main group 4 elements. Accordingly, we initiated a study to synthesize and determine the structure of spirocyclic derivatives of this class of elements.

Reported herein are the details of the preparation and X-ray study of the first tin compound having a discrete rectangular-pyramidal geometry.[21] The compound tetramethylammonium 2-chloro-5,5′-dimethyl-2,2′-spirobi(1,3,2-benzodithiastannole) (**2**) was formed by the reaction of bis(toluene-3,4-dithiolato)tin(IV), $Sn(TDT)_2$ (**1**), with 1 equiv of $(CH_3)_4N^+Cl^-$ in methyl cyanide at room temperature.



2

The structure of the monocyclic dithiastannate(IV) derivative **4**, $[(C_2H_5)_4N][(C_7H_6S_2)Ph_2SnCl]$, which offers an interesting comparison with **2**, also was determined by X-ray crystallography.

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It was prepared by treating diphenyl(toluene-3,4-dithiolato)tin, $(C_7H_6S_2)SnPh_2$ (**3**), with 1 equiv of $Et_4N^+Cl^-$ in methyl cyanide at 25 °C.

Experimental Section

^1H NMR spectra were recorded on a Varian Model A-60 NMR spectrometer at 60 MHz using 10% (w/v) solutions of the samples in appropriate solvents. Chemical shifts are reported in ppm relative to tetramethylsilane as internal standard.

Preparation of Compounds. Bis(toluene-3,4-dithiolato)tin(IV), $Sn(TDT)_2$ (1) (TDT = Toluene-3,4-dithiolato Anion, $(CH_3)C_6H_3S_2^{2-}$). Toluene-3,4-dithiol (1.1 g, 7.0 mmol) was added to a solution of $SnCl_4 \cdot 5H_2O$ (1.2 g, 3.5 mmol) in water (100 mL) at room temperature. On stirring the resulting heterogeneous reaction mixture vigorously, a flocculent red precipitate appeared. Stirring was continued for $^1/_2$ h to ensure completion of the reaction. The red precipitate was filtered under suction, washed three times with water, and air-dried to obtain an almost pure sample of bis(toluene-3,4-dithiolato)tin(IV) (**1**) (yield 1.4 g, 94.3%).

The use of a base (KOH or NaOEt) in the preparation of $Sn(TDT)_2$ from the reaction of $SnCl_4 \cdot 5H_2O$ with toluene-3,4-dithiol, as reported earlier,[22,23] leads to the formation of an alkali chloride as the byproduct, and hence further purification of $Sn(TDT)_2$ is demanded. Our present method of the preparation of $Sn(TDT)_2$ without the use of a base rules out the possibility of contamination of $Sn(TDT)_2$ by other solid byproducts as the hydrogen chloride formed in the reaction gets absorbed in the reaction medium (water).

Tetramethylammonium 2-Chloro-5,5′-dimethyl-2,2′-spirobi(1,3,2-benzodithiastannole), $[Me_4N][ClSn(TDT)_2]$ (2). Tetramethylammonium chloride (0.11 g, 1 mmol) was added to a suspension of bis(toluene-3,4-dithiolato)tin (IV) (**1**) (0.43 g, 1 mmol) in methyl cyanide (30 mL). The resulting heterogeneous reaction mixture was stirred magnetically at room temperature for 1 h to obtain a yellow solution containing traces of suspended material. Filtration of the solution followed by evaporation of solvent from the filtrate in vacuo gave a yellow crystalline residue which was dissolved in a minimum volume of boiling methyl cyanide. On cooling the solution to room temperature, yellow crystals of $[Me_4N][ClSn(TDT)_2]$ (**2**) deposited; mp 206–210 °C (yield 0.51 g, 95%). Anal. Calcd for $C_{18}H_{24}S_4NClSn$: C, 40.27; H, 4.47; N, 2.61. Found: C, 40.46; H, 4.61; N, 2.74. ^1H NMR spectrum (CD_3CN): δ 7.35 (m, 4 H, aromatic protons), 6.75 (m, 2 H, aromatic protons), 3.00 (s, 12 H, NCH_3 protons), 2.20 (s, 6 H, CH_3 groups of TDT groups).

Crystals suitable for X-ray crystallography were obtained by the recrystallization of $[Me_4N][ClSn(TDT)_2]$ (**2**) from methyl cyanide at 0 °C.

2,2-Diphenyl-5-methyl-1,3,2-benzodithiastannole, $Ph_2Sn(TDT)$ (3). This compound was prepared according to the method of Epstein and Straub[22] with specific modification for the isolation and purification of the compound as described below.

A solution of toluene-3,4-dithiol (0.78 g, 5 mmol) and potassium hydroxide (0.55 g, 10 mmol) in water (20 mL) was added to a suspension of diphenyltin dichloride (1.7 g, 5 mmol) in water (20 mL) dropwise under vigorous stirring over a period of 15 min. The white precipitate formed was extracted twice with ether (50 mL). The ether extract was dried over anhydrous sodium sulfate and filtered. Evaporation of solvent from the filtrate gave a white crystalline residue which was recrystallized from a mixture of benzene and hexane (1:3) to obtain white crystals of $Ph_2Sn(TDT)$ (**3**), mp 152–153 °C (lit.[22] mp 151–152 °C, lit.[23] mp 155 °C) (yield 2.07 g, 97%). ^1H NMR spectrum ($CDCl_3$): δ 7.4–8.0 (m, 12 H, 10 aromatic protons from two SnPh groups and 2 aromatic protons from the TDT), 6.8 (m, 1 H, aromatic proton from the TDT), 2.22 (s, 3 H, CH_3 protons).

Tetraethylammonium 2-Chloro-2,2-diphenyl-5-methyl-1,3,2-benzodithiastannole (4). Tetraethylammonium chloride (0.165 g, 1 mmol) was added to a solution of $Ph_2Sn(TDT)$ (**3**) (0.427 g, 1 mmol) in methyl cyanide (5 mL) at room temperature. The mixture was stirred for 5 min to obtain a clear solution. Ether was added dropwise to the solution under stirring till a turbidity persisted. The resulting solution was cooled at 0 °C overnight in a refrigerator to obtain very pale yellow crystals of $[Et_4N][Ph_2(Cl)Sn(TDT)]$ (**4**), mp 156–157 °C (yield 0.55 g, 93%). Anal. Calcd for $C_{27}H_{36}S_2NClSn$: C, 54.72; H, 6.12; N, 2.36. Found: C, 54.47; H, 6.17; N, 2.30. ^1H NMR spectrum (CD_3CN): δ 8.1 (m, 4 H, ortho protons of SnPh), 7.35 (m, 6 H, meta and para protons of SnPh), 7.30 (m, 2 H, aromatic protons of TDT group), 6.6 (m, 1 H, aromatic proton of TDT group), 3.0 (q, 8 H, NCH_2 protons), 2.15 (s, 3 H, CH_3 group of TDT), 1.05 (m, 12 H, $NCCH_3$ protons).

Space Group Determination and Data Collection for 2. A bright yellow somewhat irregular lath-shaped crystal having approximate dimensions of 0.13 × 0.17 × 0.35 mm was cut from a polycrystalline mass and sealed inside of a thin-walled glass capillary. Preliminary investigations using an Enraf-Nonius CAD 4 automated diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, 40 kV, 26 mA, takeoff angle = 3.1°, $\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) showed monoclinic ($2/m$) symmetry. From the observed extinctions hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, the space group was determined to be either $C2/c$ or Cc.

The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.08° \le \theta_{\text{Mo }K\bar{\alpha}} \le 14.06°$ and measured at an ambient laboratory temperature of 25 ± 2 °C are $a = 14.126$ (4) Å, $b = 11.485$ (6) Å, $c = 14.609$ (5) Å, and $\beta = 100.37$ (3)°. A unit cell content of four molecules gives a calculated volume of 23.3 Å^3/nonhydrogen atom, which falls in the range expected for such molecules. The assignment of $Z = 4$ was confirmed by successful solution refinement of the structure in the space group Cc (C_s^4, No. 9).[24]

Data were collected with use of the θ–2θ scan mode with a θ scan range of $(0.75 + 0.35 \tan \theta)°$ centered about the calculated Mo $K\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.65 to 4.0°/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is then given by $I = (\text{FF}/S)\,[P - 2(B_1 + B_2)]$, where P are the counts accumulated during the peak scan, B_1 and B_2 are the left and right background counts, S is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I{}^2 = (\text{FF}^2/S^2)\,[P + 4(B_1 + B_2)] + 0.002I^2$. A total of 2045 independent reflections ($+h,+k,\pm l$) having $2° \le 2\theta_{\text{Mo }K\bar{\alpha}} \le 50°$ was measured. Five standard reflections, monitored after every 12 000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\text{Mo }K\bar{\alpha}} = 1.56$ mm^{-1}), and the intensities were reduced to relative amplitudes by means of standard Lorentz and polarization corrections, including corrections for the monochromator.

Solution and Refinement for 2. Initial coordinates for the Sn atom were deduced from a Patterson synthesis, while initial coordinates for the remaining 24 independent nonhydrogen atoms were obtained by standard Fourier difference techniques. Isotropic unit-weighted full-matrix least-squares refinement[25] of the structural parameters for these 25 atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.059 and a weighted residual $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ of 0.066 for the 1284 reflections having $I \ge 2\sigma_I$.

Anisotropic refinement then gave $R = 0.038$ and $R_w = 0.051$. Since attempts to locate geometrically reasonable positions for the methyl hydrogen atoms on a difference Fourier synthesis calculated at this point proved unsuccessful, the methyl hydrogen atoms were omitted from the refinement. Coordinates for the six independent aromatic hydrogen atoms were calculated with use of a bond length of 0.98 Å. These were included in subsequent refinement as fixed isotropic contributions, but their positional parameters were updated as refinement converged. The last cycles of refinement, employing variable weights ($w^{1/2} = 2F_oLp/\sigma_I$) and including the high-angle data, led to the final values[26] of $R = 0.039$, $R_w = 0.055$ and GOF[27] = 1.514 for

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(25) The function minimized was $\sum w(|F_o| - |F_c|)^2$. The mean scattering factors were taken from: Reference 24, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Sn, Cl, and S were taken from: Reference 24, Vol. IV, 1974, pp 149–150.

(26) These results are for the configuration having the lowest R_w.

(27) GOF = goodness of fit = $\{\sum w(|F_o| - |F_c|)^2/(N_o - N_v)\}^{1/2}$, where N_o = the number of observations = 1775 and N_v = the number of variables = 224.

Table I. Atomic Coordinates in Crystalline $[(C_7H_6S_2)_2SnCl][NMe_4]$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	0[c]	2223.6 (6)	2500[c]
Cl	1298 (3)	854 (3)	2515 (3)
S1	368 (3)	3560 (3)	1293 (2)
S2	−1329 (3)	1509 (4)	1336 (2)
S1′	−797 (3)	1343 (4)	3695 (2)
S2′	594 (3)	3704 (3)	3667 (2)
C1	−312 (14)	2892 (15)	272 (13)
C2	−1001 (9)	2050 (11)	307 (9)
C3	−1497 (9)	1612 (13)	−532 (9)
C4	−1338 (10)	1966 (12)	−1399 (10)
C5	−637 (14)	2825 (16)	−1388 (13)
C6	−134 (10)	3286 (12)	−580 (10)
C7	−1887 (11)	1463 (15)	−2290 (9)
C1′	−133 (9)	1976 (10)	4707 (8)
C2′	457 (13)	2964 (13)	4689 (11)
C3′	930 (9)	3421 (12)	5539 (8)
C4′	886 (13)	2914 (14)	6379 (12)
C5′	310 (11)	1927 (13)	6383 (9)
C6′	−178 (9)	1454 (12)	5552 (9)
C7′	1422 (12)	3447 (18)	7283 (9)
N	−2466 (8)	4389 (12)	5076 (9)
CN1	−1929 (12)	4462 (19)	4295 (13)
CN2	−1819 (18)	4005 (33)	5920 (17)
CN3	−2703 (27)	5606 (25)	5300 (27)
CN4	−3300 (26)	3717 (41)	4849 (21)

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

the 1775 reflections having $I \geq 2\sigma_I$ and $2° \leq 2\theta_{\mathrm{Mo\,K\bar{\alpha}}} \leq 50°$. During the final cycle of refinement the largest shift in any parameter was 0.003 times its estimated standard deviation. The only peaks of any consequence on a final difference Fourier synthesis (0.55–0.71 e/Å^3) were in the immediate vicinity of the Sn atom.

Space Group Determination and Data Collection for 4. Experimental conditions were the same as described for **2** unless otherwise noted. A well-formed rhombohedral crystal having dimensions of 0.20 × 0.24 × 0.24 mm was glued to the interior of a thin-walled glass capillary which was then sealed. Preliminary diffractometric investigations indicated monoclinic ($2/m$) symmetry. From the observed extinctions $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, the space group was uniquely determined as $P2_1/c$ (C_{2h}^5, No. 14).[28] The lattice constants based on 25 reflections having $10.15° \leq \theta_{\mathrm{Mo\,K\bar{\alpha}}} \leq 13.74°$ are $a = 12.344$ (4) Å, $b = 11.975$ (5) Å, $c = 19.120$ (5) Å, and $\beta = 96.41$ (2)°. A unit cell volume of four molecules gives a calculated volume of 21.9 Å^3/nonhydrogen atom. The assignment of $Z = 4$ was confirmed by solution and refinement of the structure.

The scan range used for data collection was $(0.87 + 0.35 \tan\theta)°$, while the scan rates varied from 0.71 to 4.0°/min. A total of 4920 independent reflections was measured. No corrections were made for absorption ($\mu_{\mathrm{Mo\,K\bar{\alpha}}} = 1.17$ mm^{-1}).

Solution and Refinement for 4. Initial coordinates for the Sn atom were obtained from a Patterson synthesis, while initial coordinates for the remaining 31 independent nonhydrogen atoms were obtained by standard difference Fourier techniques. Unit-weighted isotropic refinement of the structural parameters for these 32 atoms and a scale factor led to $R = 0.069$ and $R_w = 0.076$ for the 2457 reflections having $I \geq 3\sigma_I$ and $(\sin\theta)/\lambda \leq 0.52$. Anisotropic refinement then gave $R = 0.049$ and $R_w = 0.057$ for the 2597 low-angle reflections having $I \geq 2\sigma_I$. A difference Fourier synthesis run at this point did not give geometrically reasonable coordinates for the methyl hydrogen atoms, and they were omitted from subsequent refinement. Initial coordinates for the remaining 21 independent hydrogen atoms were calculated with use of a C–H bond length of 0.98 Å. These were included in subsequent refinement as fixed isotropic contributions, but their positional parameters were updated as refinement converged. Refinement including the hydrogen atoms and using variable weights gave $R = 0.044$ and $R_w = 0.057$ for the low-angle data. Inclusion of the high-angle data in the refinement led to the final values of $R = 0.048$, $R_w = 0.059$, and GOF[29] = 1.50 for the 3438 reflections having $I \geq 2\sigma_I$ and $2° \leq 2\theta_{\mathrm{Mo\,K\bar{\alpha}}} \leq 50°$. During the final cycle of refinement the largest shift in any parameter was 0.04 times its estimated standard deviation. The only peaks of any consequence on a final Fourier difference synthesis (1.180 and 1.135 e/Å^3) were in the immediate vicinity of the Sn atom.

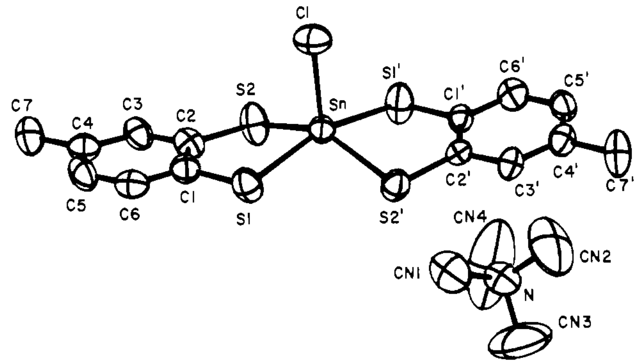

Figure 1. ORTEP plot of the complex $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$ (**2**), with thermal ellipsoids at the 50% probability level.

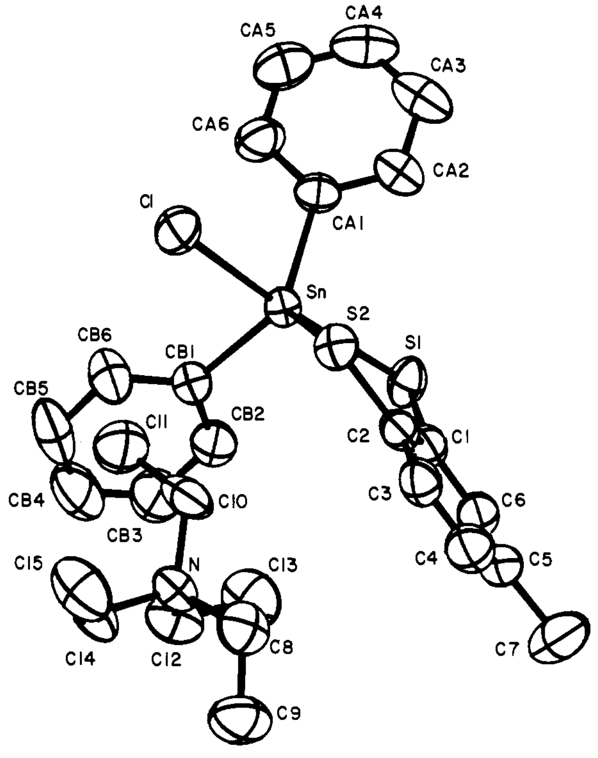

Figure 2. ORTEP plot of $[(C_2H_5)_4N]^+[(C_7H_6S_2)Ph_2SnCl]^-$ (**4**), with thermal ellipsoids at the 50% probability level.

Table II. Fixed Parameters for Hydrogen Atoms in Crystalline $[(C_7H_6S_2)_2SnCl][NMe_4]$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
H3	−1989	1016	−509
H5	−501	3112	−1983
H6	352	3890	−602
H3′	1309	4135	5532
H5′	248	1563	6977
H6′	−557	742	5566

[a] Isotropic thermal parameters were fixed at 5 Å^2. [b] Hydrogen atoms are named according to the carbon atom to which they are bonded.

Computations were done on a CDC Cyber-175 computer using LINEX, a modification of the Busing and Levy full-matrix least-squares program, ORFLS, Johnson's thermal ellipsoid plot program, ORTEP,

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(28) Reference 24, p 99.

(29) As defined in ref 27, but with $N_o = 3438$ and $N_v = 289$.

Table III. Atomic Coordinates in Crystalline $[(C_7H_6S_2)SnPh_2Cl][NEt_4]$ (4)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	−2893.6 (4)	5303.5 (4)	3295.4 (2)
Cl	−3407 (1)	3643 (1)	4059 (1)
S1	−1918 (1)	6751 (1)	2620 (1)
S2	−1244 (1)	4210 (2)	3232 (1)
N	−2177 (5)	1568 (5)	1263 (3)
C1	−982 (5)	5895 (6)	2250 (3)
C2	−690 (5)	4829 (6)	2511 (3)
C3	74 (6)	4211 (6)	2197 (4)
C4	570 (6)	4610 (7)	1643 (4)
C5	309 (6)	5670 (7)	1369 (4)
C6	−474 (6)	6277 (6)	1668 (4)
C7	896 (9)	6144 (8)	765 (5)
C8	−1037 (7)	1523 (8)	1056 (4)
C9	−914 (8)	1194 (9)	299 (5)
C10	−2098 (7)	1810 (7)	2051 (4)
C11	−3199 (8)	1855 (9)	2361 (5)
C12	−2840 (6)	2447 (7)	846 (4)
C13	−2423 (9)	3660 (7)	957 (5)
C14	−2763 (7)	471 (6)	1084 (5)
C15	−2202 (9)	−567 (7)	1456 (5)
CA1	−3037 (5)	6399 (6)	4172 (3)
CA2	−2220 (6)	7170 (6)	4371 (4)
CA3	−2314 (8)	7896 (7)	4941 (4)
CA4	−3231 (8)	7885 (8)	5283 (4)
CA5	−4043 (7)	7118 (8)	5093 (4)
CA6	−3943 (6)	6373 (7)	4536 (4)
CB1	−4250 (5)	5008 (6)	2514 (3)
CB2	−4398 (7)	5668 (8)	1910 (4)
CB3	−5251 (8)	5472 (10)	1381 (5)
CB4	−5924 (8)	4594 (10)	1425 (5)
CB5	−5822 (7)	3951 (8)	2015 (6)
CB6	−4990 (7)	4145 (7)	2568 (5)

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

Table IV. Fixed Parameters for Hydrogen Atoms in Crystalline $[(C_7H_6S_2)SnPh_2Cl][NEt_4]$ (4)[a]

atom type[b]	10^4x	10^4y	10^4z
H3	264	3463	2379
H4	1111	4150	1438
H6	−686	7009	1467
H81	−626	980	1364
H82	−714	2265	1135
H101	−1738	2534	2137
H102	−1655	1223	2298
H121	−3585	2417	977
H122	−2848	2267	346
H141	−2801	357	574
H142	−3502	528	1221
HA2	−1575	7207	4115
HA3	−1720	8416	5093
HA4	−3310	8420	5662
HA5	−4691	7093	5347
HA6	−4523	5827	4404
HB2	−3890	6284	1857
HB3	−5364	5978	975
HB4	−6482	4422	1035
HB5	−6339	3338	2056
HB6	−4932	3673	2990

[a] Isotropic thermal parameters were fixed at 6 Å^2. [b] Hydrogen atoms are named according to the carbon atom to which they are bonded, where H81 and H82 are bonded to C8, etc.

Table V. Bond Lengths (Å) and Bond Angles (Deg) for $[(C_7H_6S_2)_2SnCl][NMe_4]$ (2)[a]

type[b]	bond length	type	bond length
Sn–Cl	2.413 (4)	C6–C1	1.389 (24)
Sn–S1	2.463 (3)	C1′–C2′	1.411 (21)
Sn–S1′	2.458 (4)	C2′–C3′	1.402 (20)
Sn–S2	2.437 (4)	C3′–C4′	1.370 (22)
Sn–S2′	2.447 (3)	C4′–C5′	1.396 (23)
S1–C1	1.795 (19)	C5′–C6′	1.394 (20)
S1′–C1′	1.760 (12)	C6′–C1′	1.384 (17)
S2–C2	1.764 (13)	C4–C7	1.505 (20)
S2–C2′	1.759 (17)	C4′–C7′	1.528 (23)
C1–C2	1.379 (23)	N–CN1	1.482 (19)
C2–C3	1.392 (19)	N–CN2	1.465 (24)
C3–C4	1.386 (19)	N–CN3	1.488 (28)
C4–C5	1.396 (24)	N–CN4	1.398 (27)
C5–C6	1.370 (25)		

type	bond angle	type	bond angle
S1–Sn–S1′	161.3 (1)	C2–C3–C4	124.1 (13)
S2–Sn–S2′	147.6 (1)	C3–C4–C5	115.3 (14)
S1′–Sn–S2	87.9 (1)	C3–C4–C7	122.3 (14)
S1–Sn–S2′	88.6 (1)	C5–C4–C7	122.3 (14)
S1–Sn–S2	98.9 (1)	C4–C5–C6	122.7 (16)
S1′–Sn–S2′	106.4 (1)	C5–C6–C1	119.8 (15)
Cl–Sn–S1	98.9 (1)	S1′–C1′–C6′	117.9 (10)
Cl–Sn–S2	106.0 (1)	C2′–C1′–C6′	119.1 (12)
Cl–Sn–S1′	99.8 (2)	S2′–C2′–C3′	117.6 (12)
Cl–Sn–S2′	106.4 (1)	C1′–C2′–C3′	118.3 (14)
Sn–S1–C1	100.3 (6)	C2′–C3′–C4′	122.9 (14)
Sn–S2–C2	100.9 (4)	C3′–C4′–C5′	118.1 (15)
Sn–S1′–C1′	100.6 (4)	C3′–C4′–C7′	120.5 (15)
Sn–S2′–C2′	100.3 (5)	C5′–C4′–C7′	121.4 (15)
S1–C1–C2	123.0 (14)	C4′–C5′–C6′	120.6 (13)
S2–C2–C1	125.1 (12)	C5′–C6′–C1′	120.9 (12)
S1′–C1′–C2′	123.0 (10)	CN1–N–CN2	109.7 (14)
S2′–C2′–C1′	124.1 (11)	CN1–N–CN3	106.5 (18)
S1–C1–C6	116.7 (14)	CN1–N–CN4	112.0 (16)
C2–C1–C6	120.4 (16)	CN2–N–CN3	103.2 (22)
S2–C2–C3	117.1 (10)	CN2–N–CN4	113.9 (25)
C1–C2–C3	117.8 (13)	CN3–N–CN4	110.9 (26)

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

the Oak Ridge Fortran function and error program, ORFFE, Zalkin's Fourier program, FORDAP, and several locally written programs.

Results and Discussion

The molecular geometry and atom labeling scheme are shown for **2** in Figure 1 and for **4** in Figure 2. Atomic coordinates for **2** are given in Tables I and II; bond lengths and angles are presented in Table V. For **4**, the analogous information is given in Tables III, IV, and VI. For both compounds, anisotropic thermal parameters are provided as supplementary material.

The compounds **2** and **4** represent the first examples of anionic pentacoordinated tin complexes containing cyclic substituents. The molecular geometry of the anion of **2** most closely approximates the idealized rectangular pyramid (RP), where S1, S2, S1′, and S2′ form the basal plane and Cl occupies the apical position. The anion has approximate twofold symmetry, where the pseudo twofold axis is coincident with the Sn–Cl bond. In keeping with this twofold pseudo symmetry, the geometry of the anion lies on the coordinate connecting the idealized RP to an idealized trigonal bipyramid (TP) where S2, S2′, and Cl occupy equatorial positions and S1 and S1′ axial ones. In terms of this coordinate, the geometry of the anion is displaced 77.2% (76.9% using unit vectors)[19,20] from the TP towards the RP, where Cl is the pivotal atom in the Berry pseudorotation process.[30] The atoms Sn, Cl, S1, and S1′ are coplanar to within ±0.002 Å (plane I, Table VII), while the atoms Sn, Cl, S2, and S2′ are coplanar to within ±0.005 Å (plane II, Table VII). The dihedral angle between these planes is 89.1°, close to the 90° angle required by the local C_{2v} constraint of the Berry coordinate.

The molecular geometry of the anion of **4** most closely approximates an idealized TP, where CA1, CB1, and S2 are equatorially positioned and Cl and S1 are axial. On the basis

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Table VI. Bond Lengths (Å) and Bond Angles (Deg) for $[(C_7H_6S_2)SnPh_2Cl][NEt_4]$ (4)[a]

type[b]	bond length	type	bond length
Sn–S1	2.544 (2)	CA4–CA5	1.378 (12)
Sn–S2	2.436 (2)	CA5–CA6	1.405 (11)
Sn–Cl	2.588 (2)	CA6–CA1	1.382 (9)
Sn–CA1	2.152 (6)	CB1–CB2	1.393 (10)
Sn–CB1	2.146 (7)	CB2–CB3	1.397 (11)
S1–C1	1.752 (7)	CB3–CB4	1.349 (13)
S2–C2	1.769 (7)	CB4–CB5	1.360 (13)
C1–C2	1.402 (9)	CB5–CB6	1.409 (12)
C2–C3	1.387 (9)	CB6–CB1	1.391 (10)
C3–C4	1.369 (10)	N–C8	1.505 (9)
C4–C5	1.397 (11)	N–C10	1.526 (9)
C5–C6	1.384 (10)	N–C12	1.506 (9)
C6–C1	1.413 (4)	N–C14	1.521 (9)
C5–C7	1.537 (11)	C8–C9	1.523 (11)
CA1–CA2	1.389 (10)	C10–C11	1.543 (12)
CA2–CA3	1.409 (10)	C12–C13	1.548 (12)
CA3–CA4	1.369 (12)	C14–C15	1.555 (11)
type	**bond angle**	**type**	**bond angle**
S1–Sn–Cl	165.9 (1)	CA1–CA2–CA3	120.1 (7)
CA1–Sn–CB1	121.2 (3)	CA2–CA3–CA4	120.5 (8)
CA1–Sn–S2	120.6 (2)	CA3–CA4–CA5	119.8 (8)
CB1–Sn–S2	118.0 (2)	CA4–CA5–CA6	120.0 (7)
Cl–Sn–CA1	89.0 (2)	CA5–CA6–CA1	120.7 (8)
Cl–Sn–CB1	92.6 (2)	Sn–CB1–CB2	120.2 (5)
Cl–Sn–S2	82.7 (1)	Sn–CB1–CB6	122.5 (5)
S1–Sn–CA1	93.7 (2)	CB6–CB1–CB2	117.2 (7)
S1–Sn–CB1	97.8 (2)	CB1–CB2–CB3	121.6 (8)
S1–Sn–S2	84.0 (1)	CB2–CB3–CB4	120.4 (9)
Sn–S1–C1	100.2 (2)	CB3–CB4–CB5	119.5 (8)
Sn–S2–C2	102.2 (2)	CB4–CB5–CB6	121.5 (8)
S1–C1–C2	123.0 (5)	CB5–CB6–CB1	119.7 (8)
S2–C2–C1	123.5 (5)	C7–C5–C4	121.7 (8)
S1–C1–C6	119.9 (6)	C7–C5–C6	120.6 (7)
S2–C2–C3	117.0 (6)	C8–N–C10	107.9 (6)
C6–C1–C2	117.1 (6)	C8–N–C12	110.8 (6)
C1–C2–C3	119.5 (6)	C8–N–C14	110.2 (6)
C2–C3–C4	122.3 (7)	C10–N–C12	111.2 (6)
C3–C4–C5	120.2 (7)	C10–N–C14	111.2 (6)
C4–C5–C6	117.6 (7)	C12–N–C14	105.6 (6)
C5–C6–C1	123.2 (7)	N–C8–C9	117.0 (7)
Sn–CA1–CA2	119.9 (5)	N–C10–C11	115.1 (7)
Sn–CA1–CA6	121.3 (5)	N–C12–C13	114.3 (7)
CA6–CA1–CA2	118.8 (7)	N–C14–C15	114.3 (7)

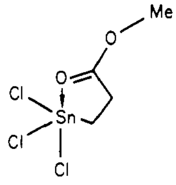
[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 2.

of the dihedral angle method, as applied to cyclic phosphoranes,[19,20] **4** is displaced 18.8% (14.1% using unit vectors) from the TP toward the RP. The Sn atom is displaced 0.074 Å out of the equatorial plane (plane III, Table VIII) in a direction away from the Cl atom. The latter observation may be a result of the geometrical constraints imposed by the bidentate ligand. The phenyl rings are tipped out of the equatorial plane. The dihedral angle between the least-squares mean plane through the phenyl ring and the equatorial plane is 46.9° for the A ring and 86.8° for the B ring.

The axial Sn–S1 bond length for **4**, 2.544 (2) Å, is approximately 0.1 Å longer than the equatorial Sn–S2 distance, 2.436 (2) Å, of the order expected for trigonal bipyramids. This compares with the unusually long axial Sn–S bond length, 2.79 (1) Å, found in the dithiocarbamate derivative, $(CH_3)_2Cl)Sn[S_2CN(CH_3)_2]$.[11] Here, however, the molecule belongs to the class containing a weak dative bond. For the spirocyclic tin complex **2**, the Sn–S bond lengths are much closer: two shorter ones, 2.437 (4) and 2.447 (3) Å, and two longer ones, 2.458 (4) and 2.463 (3) Å. This small difference is indicative of residual trigonal-bipyramidal character that was expressed by the 77% displacement toward the rectangular pyramid cited above and is in accord with the variation in the trans basal angles S2–Sn–S2′ = 147.6 (1)° and S1–Sn–S1′ = 161.3 (1)°, respectively. The kind of bond length alternation that is found in cyclic phosphoranes that have a trigonal-bipyramidal structure[31] also is present for the ring bonds in **4**, i.e., the S1–C1 bond length, 1.752 (2) Å, is shorter than the S2–C2 length 1.769 (7) Å.

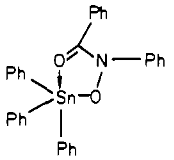
The shorter Sn–Cl bond in **2**, 2.413 (4) Å, compared to a Sn–Cl distance of 2.588 (2) Å in **4**, is representative of axial bond lengths in square pyramids relative to those in trigonal bipyramids.[32] Some Sn–Cl bond lengths for anionic pentacoordinated tin complexes are compared in Table IX. The axial Sn–Cl bonds in trigonal bipyramids range from 2.54–2.70 Å which is considerably longer than the axial Sn–Cl bond length (2.413 Å) in the rectangular-pyramidal complex **2**.

The quadrupole splitting parameter from ^{119m}Sn Mössbauer data[15,33] listed in Table IX for **4** is in the range[10,34] found for related dative bonded complexes of known structure[10,13] (**9** and **10**). By way of contrast, the quadrupole splitting values for the anionic complexes **7** and **8**, having the so-called trans geometry, are in the range[35] found for related geometries[36] containing intermolecular dative bridge bonds (**11** and **12**).



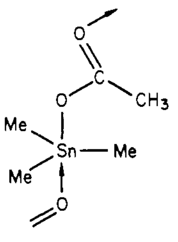
9[10]

QS = 2.18[10]



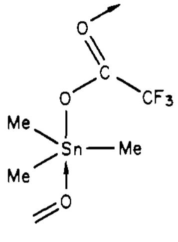
10[13]

QS = 1.94[34]



11[36]

QS = 3.43–3.68[35]



12[36]

QS = 4.22[35]

Theoretical calculations[8,37] of quadrupole splittings give agreement in showing considerably higher values for the trans geometry, **11** and **12**, compared to that for **9** and **10**. Clearly, the quadrupole spitting, 1.44 mm s^{-1}, observed for the rectangular-pyramidal geometry for complex **2**, is below the range for any of the trigonal-bipyramidal arrangements discussed above. Zuckerman and co-workers[33] have measured the quadrupole splitting for five other related anionic complexes we prepared $[(C_7H_6S_2)_2SnX]^-$, where the halogen and cation composition varied. The resultant values fell in the range 1.06–1.35 mm s^{-1}. Presumably, one now is in a position to use Mössbauer quadrupole splittings to readily decide the basic structural type for pentacoordinated tin species.

As found with phosphoranes,[19,20] and more recently with pentacoordinated germanium(IV),[38,39] the formation of a

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Table VII. Deviations (Å) from Some Least-Squares Mean Planes in $[(C_7H_6S_2)_2SnCl][NMe_4]$ (2)[a, b]

atoms	I	II	atoms	III	IV	atoms	V	VI
Sn	0.002	−0.005	C1	0.004	0.017	C1′	0.013	0.004
Cl	−0.000	0.001	C2	−0.000	0.018	C2′	−0.018	−0.017
S1	−0.001		C3	−0.003	0.003	C3′	0.011	0.021
S1′	−0.001		C4	−0.003	−0.005	C4′	−0.004	0.004
S2		0.002	C5	−0.001	−0.015	C5′	0.008	0.006
S2′		0.002	C6	−0.003	−0.006	C6′	−0.010	−0.020
			S1	(−0.025)	−0.000	S1′	(0.034)	−0.014
			S2	(−0.048)	−0.011	S2′	(−0.014)	−0.011
			Sn	(0.507)	(0.556)	Sn	(−0.682)	(−0.695)
			Cl	(2.912)	(2.960)	Cl	(−3.076)	(−3.090)

[a] Dihedral angles between planes I and II = 89.1°, planes III and V = 11.3°, and planes IV and VI = 11.5°. [b] Entries in parentheses are for atoms not included in the calculation of the plane.

Table VIII. Deviations (Å) from Some Least-Squares Mean Planes in $[(C_7H_6S_2)SnPh_2Cl][NEt_4]$ (4)[a, b]

atoms	I	II	III	IV	atoms	V	atoms	VI	atoms	VII	VIII
Sn	0.138	−0.055	(−0.074)	−0.072	CA1	−0.004	CB1	−0.012	CC1	0.006	−0.011
Cl	−0.048		(2.500)	0.042	CA2	−0.009	CB2	−0.006	CC2	0.004	−0.006
S1	−0.061		(−2.592)	0.040	CA3	0.017	CB3	0.024	CC3	−0.007	−0.004
S2		0.017	0.0	−0.010	CA4	−0.013	CB4	−0.025	CC4	0.000	0.011
CA1		0.021	0.0		CA5	0.000	CB5	0.005	CC5	0.010	0.014
CB1	−0.029	0.017	0.0		CA6	0.008	CB6	0.014	CC6	−0.014	−0.023
					Sn	(−0.063)		(−0.130)	S1	(0.052)	0.018
					Cl	(1.891)		(−0.169)	S2	(0.021)	0.002
									Sn	(−0.725)	(−0.766)
									Cl	(−1.135)	(−1.178)
									CA1	(0.623)	(0.565)
									CB1	(−2.803)	(−2.847)

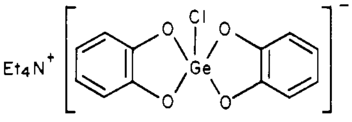
[a] Dihedral angles between planes I and II = 89.4°, planes II and V = 46.9°, planes II and VI = 86.7°, planes II and VIII = 76.9°, planes IV and VIII = 22.1°, planes III and V = 46.9°, planes III and VI = 86.8°, planes III and VIII = 76.9°, and planes VI and VIII = 85.2°. [b] Entries in parentheses are for atoms not included in the calculation of the plane.

Table IX. Tin(IV)-Chlorine Bond Lengths and ^{119}Sn Mössbauer Data for Anionic Pentacoordinated Complexes[a]

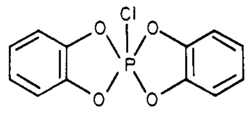
compd	QS[b]	ref	Sn–Cl, Å	ref
$[Me_4N][(C_7H_6S_2)_2SnCl]$ (**2**)	1.44	33	2.413 (4) ax	this study
$[Et_4N][(C_7H_6S_2)SnPh_2Cl]$ (**4**)	2.08	33	2.588 (2) ax	this study
$[Me_2SnCl(terpyridyl)][Me_2SnCl_3]$ (**5**)			2.32 eq, 2.54 ax	16a
$[Mo(\eta^5\text{-}C_5H_5)_3S_4][Me_3SnCl_2]$ (**6**)			2.572 (4) ax, 2.696 (3) ax	16b
$[Ph_3AsCH_2COPh][Ph_3SnCl_2]$ (**7**)	2.88	15	2.58 (1) ax, 2.60 (1) ax	15
$[Ph_3PCH_2Ph][Bu_3SnCl_2]$ (**8**)	3.41	15	2.573 (7) ax, 2.689 (6) ax	15

[a] All anions contain trigonal-bipyramidal tin except **2** which, as found in this study, is rectangular pyramidal. [b] Quadrupole splitting in mm s^{-1}.

square- or rectangular-pyramidal geometry for tin(IV) seems to require the presence of a spirocyclic unsaturated system when five-membered rings are involved. An additional requirement for the latter system is that like atoms are bonded to the central atom in any one ring.[20] The structures of **13**[38] and **14**[40] are 84% (91% based on unit vectors) and 72%, respectively, along the C_{2v} coordinate from the trigonal bipyramid toward the rectangular pyramid[20] and compare closely with that for the tin complex **2**. Examples[41] of square-pyramidal phosphoranes are known containing a more strained four-membered saturated ring in a spirocyclic system.[20,31] It is likely that pentacoordinate silicon(IV) may possess this geometrical arrangement. However, no examples have been reported.[42]



13[38]



14[40]

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 7910036) is greatly appreciated as is the generous allocation of computing time by the University of Massachusetts Computing Center.

Registry No. **1**, 13241-47-9; **2**, 76566-57-9; **3**, 4312-02-1; **4**, 78085-83-3.

Supplementary Material Available: Anisotropic thermal parameters (Tables A and B, respectively) and observed and calculated structure factor amplitudes for **2** and **4** (24 pages). Ordering information is given on any current masthead page.

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