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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XVII *. THE CRYSTAL AND MOLECULAR STRUCTURE OF PHENYLCHLOROBIS(DIETHYLDITHIOCARBAMATO)TIN(IV)

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Summary

The crystal structure of the title compound has been determined by single crystal X-ray diffraction from diffractometer data using Patterson and Fourier techniques. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in each unit cell of dimensions $a = 19.764(8)$, $b = 15.760(8)$, $c = 7.121(4)$ Å, $\beta = 93.7(1)^\circ$. The structure was refined by block-diagonal least squares methods to R 0.059 for 3022 observed reflections. The tin atoms are six-coordinated in a distorted octahedral fashion by the phenyl group, chlorine atom, and two chelating diethyldithiocarbamato residues, the phenyl group and chlorine atom occupying mutually *cis* positions (Sn—C 2.154(5); Sn—Cl 2.438(6), mean Sn—S 2.583(7) Å).

The structures of few monoorganotin(IV) derivatives have been determined. Methylstannane and the methyltin trihalides, MeSnX_3 X = Cl, Br, I, all possess tetrahedral structures in the vapour phase [2], whilst $[(\text{MeSn})_4\text{S}_6]$, which has an adamantane-type structure [3] and $[\text{PhCl}_2\text{SnFe}(\text{CO})_2(\text{C}_5\text{H}_5)]$ [4] both have four-coordinated tin in the crystal. However, in $[(\text{C}_{10}\text{H}_8\text{N}_2)(\text{CO})_3\text{MoClSnMeCl}_2]$ [5] and $[(\text{C}_4\text{H}_{10}\text{S}_2)(\text{CO})_3\text{WClSnMeCl}_2]$ [6] the coordination number at tin is raised to five by a chlorine atom which bridges both metals. Seven-coordination at tin is observed in $[\text{MeSn}(\text{NO}_3)_3]$ in which all three nitrate groups chelate the metal [7].

The reaction of $[\text{PhSnCl}_3]$ with potassium diethyldithiocarbamate in a 1 : 3

* For part XVI see ref. 1.

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molar ratio does not produce $[\text{PhSn}(\text{S}_2\text{CNET}_2)_3]$, instead $[\text{PhSnCl}(\text{S}_2\text{CNET}_2)_2]$ is obtained, and it is the structure of this latter derivative which is reported in this paper.

Experimental

Colourless crystals of $[\text{PhSnCl}(\text{S}_2\text{CNET}_2)_2]$ were obtained from the reaction of $[\text{PhSnCl}_3]$ (1 mol) and $[\text{KS}_2\text{CNET}_2]$ (3 mol) in methanol. Found: C, 36.42; H, 4.98; N, 5.22. $\text{C}_{16}\text{H}_{25}\text{ClN}_2\text{S}_4\text{Sn}$ calcd: C, 36.43; H, 4.78; N, 5.31%. A crystal of approximate dimensions $0.4 \times 0.3 \times 0.3 \text{ mm}^3$ was mounted directly on a fine glass fibre, and was used for both the cell data and the subsequent intensity data collection. Crystal Data: $\text{C}_{16}\text{H}_{25}\text{ClN}_2\text{S}_4\text{Sn}$, mol.wt. 527.5, $a = 19.764(8)$, $b = 15.760(8)$, $c = 7.121(4) \text{ \AA}$, $\beta = 93.7(1)^\circ$, $U = 2213.4 \text{ \AA}^3$, $Z = 4$, $F(000) = 1064$, Space group $P2_1/n$ by systematic absences ($h0l$ for $h + 1 = 2n + 1$ and OkO for $k = 2n + 1$).

The space group and initial cell parameters were determined from zero- and first-layer Weissenberg photographs obtained on an equi-inclination Weissenberg camera. The cell parameters were further refined and the intensities of 5894 reflections were measured (Mo- K_α radiation $\lambda = 0.7107 \text{ \AA}$, $2\theta < 70^\circ$) using a Siemens AED single crystal diffractometer. Reflections having $I < 2\sigma(I)$ were considered unobserved, reducing the number used to 3022. The intensities were corrected for Lorentz and polarization effects but none was applied for absorption because of the small size of the crystal.

TABLE 1
FINAL FRACTIONAL ATOMIC COORDINATES (estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Sn(1)	0.12254(2)	0.23327(3)	0.20913(7)
Cl(1)	0.2227(1)	0.2057(1)	0.0360(3)
S(1)	0.0774(1)	0.0852(1)	0.1270(3)
S(2)	0.1387(1)	0.1335(1)	0.4982(3)
S(3)	-0.0022(1)	0.2798(1)	0.2956(3)
S(4)	0.0588(1)	0.2934(1)	-0.0800(3)
N(1)	0.0857(4)	-0.0203(4)	0.4216(10)
N(2)	-0.0636(3)	0.3531(3)	-0.0198(8)
C(1)	0.0995(4)	0.0556(4)	0.3546(11)
C(2)	0.0095(3)	0.3137(4)	0.0552(10)
C(3)	0.0515(4)	-0.0858(4)	0.3003(13)
C(4)	0.1011(5)	-0.1348(5)	0.1922(12)
C(5)	0.1012(5)	-0.0455(6)	0.6337(14)
C(6)	0.1638(4)	-0.0871(5)	0.6405(14)
C(7)	-0.0711(4)	0.3780(5)	-0.2221(13)
C(8)	-0.0382(4)	0.4667(5)	-0.2519(11)
C(9)	-0.1206(4)	0.3763(4)	0.0967(10)
C(10)	-0.1751(4)	0.3094(7)	0.0823(15)
C(11)	0.1645(4)	0.3452(5)	0.3452(12)
C(12)	0.2007(5)	0.4035(6)	0.2420(14)
C(13)	0.2247(4)	0.4782(5)	0.3313(11)
C(14)	0.2125(6)	0.4939(9)	0.5185(17)
C(15)	0.1773(5)	0.4356(5)	0.6207(14)
C(16)	0.1534(5)	0.3602(6)	0.5307(17)

TABLE 2

FINAL ANISOTROPIC THERMAL PARAMETERS (estimated standard deviations in parentheses)^{a, b}

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	3.88(2)	3.20(1)	4.50(2)	0.13(2)	0.66(1)	0.02(2)
Cl	5.6(1)	5.9(1)	7.4(1)	1.2(1)	2.4(1)	-0.7(1)
S(1)	6.4(1)	3.5(1)	5.0(1)	-0.0(1)	-1.5(1)	-0.4(1)
S(2)	6.6(1)	3.6(1)	4.8(1)	-1.0(1)	-1.2(1)	0.2(1)
S(3)	4.2(1)	4.2(1)	4.4(1)	0.5(1)	1.1(1)	0.3(1)
S(4)	4.7(1)	5.1(1)	4.4(1)	1.1(1)	1.3(1)	0.9(1)
N(1)	7.6(4)	2.8(2)	7.1(4)	-1.9(2)	-0.6(3)	0.7(3)
N(2)	4.7(3)	3.5(2)	5.2(3)	0.6(2)	0.1(2)	0.1(2)
C(1)	5.0(3)	3.8(3)	5.2(4)	0.2(3)	-0.6(3)	-0.9(3)
C(2)	4.3(3)	2.7(3)	5.0(4)	-1.0(2)	1.2(3)	0.1(2)
C(3)	4.4(3)	3.4(3)	9.2(6)	-1.2(2)	-0.4(3)	-0.8(3)
C(4)	8.1(6)	5.1(4)	12.1(8)	-1.9(4)	-0.4(6)	-2.3(5)
C(5)	7.1(5)	4.9(4)	8.4(6)	-0.3(3)	0.1(4)	0.8(4)
C(6)	9.7(8)	13.6(10)	9.0(8)	2.4(7)	-0.3(6)	0.0(7)
C(7)	5.9(4)	4.6(3)	5.4(4)	0.8(3)	0.7(3)	0.4(3)
C(8)	8.3(4)	4.6(3)	5.4(4)	0.8(3)	0.7(3)	0.4(3)
C(9)	4.3(3)	5.2(4)	7.7(5)	1.7(3)	1.6(3)	-0.6(3)
C(10)	4.8(4)	9.9(7)	9.6(7)	1.4(4)	1.3(4)	-0.5(5)
C(11)	4.4(3)	3.3(3)	4.8(3)	-0.6(2)	0.6(3)	0.1(3)
C(12)	5.0(4)	3.8(3)	6.6(4)	-1.5(3)	0.8(3)	1.3(3)
C(13)	4.3(3)	4.9(4)	8.4(5)	-0.4(3)	1.0(3)	1.7(4)
C(14)	6.1(4)	3.5(3)	9.9(6)	-2.1(3)	0.5(4)	0.0(4)
C(15)	8.5(6)	5.4(4)	7.1(5)	-1.7(4)	1.1(4)	-1.2(4)
C(16)	7.6(5)	4.1(3)	5.6(4)	-0.3(3)	1.1(4)	0.1(3)

^a B_{ij} values as listed have been multiplied by 10^2 . ^b Of the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE 3

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (°) (estimated standard deviations in parentheses)

Atoms	Bond distances	Atoms	Bond distances
Sn(1)—Cl(1)	2.438(6)	C(13)—C(14)	1.39(2)
Sn(1)—S(1)	2.551(5)	C(14)—C(15)	1.39(2)
Sn(1)—S(2)	2.593(7)	C(15)—C(16)	1.42(2)
Sn(1)—S(3)	2.661(7)		
Sn(1)—S(4)	2.528(6)		
Sn(1)—C(11)	2.154(5)		
S(1)—C(1)	1.72(1)		
S(2)—C(1)	1.75(1)		
S(3)—C(2)	1.72(1)		
S(4)—C(2)	1.74(1)		
N(1)—C(1)	1.32(1)		
N(1)—C(3)	1.48(1)		
N(1)—C(5)	1.57(1)		
N(2)—C(2)	1.32(1)		
N(2)—C(7)	1.49(1)		
N(2)—C(9)	1.49(1)		
C(3)—C(4)	1.50(2)		
C(5)—C(6)	1.40(2)		
C(7)—C(8)	1.56(2)		
C(9)—C(10)	1.51(2)		
C(11)—C(12)	1.40(2)		
C(11)—C(16)	1.37(2)		
C(12)—C(13)	1.41(2)		

TABLE 3 (continued)

Atoms	Angles	Atoms	Angles
Cl(1)—Sn(1)—S(1)	90.3(3)	Cl(1)—Sn(1)—S(2)	103.4(3)
Cl(1)—Sn(1)—S(4)	91.9(4)	Cl(1)—Sn(1)—C(11)	94.0(3)
S(1)—Sn(1)—S(3)	89.1(3)	S(1)—Sn(1)—S(4)	90.5(4)
S(2)—Sn(1)—S(3)	94.2(4)	S(2)—Sn(1)—S(4)	154.6(4)
S(3)—Sn(1)—S(4)	69.1(3)	S(3)—Sn(1)—C(11)	91.0(3)
Sn(1)—S(1)—C(1)	88.2(4)	Sn(1)—S(2)—C(1)	86.2(5)
Sn(1)—S(4)—C(2)	88.9(4)	C(1)—N(1)—C(3)	121.1(6)
C(3)—N(1)—C(5)	115.9(5)	C(2)—N(2)—C(7)	122.8(7)
C(7)—N(2)—C(9)	116.3(5)	S(1)—C(1)—S(2)	116.0(8)
S(2)—C(1)—N(1)	121.2(6)	S(3)—C(2)—S(4)	116.8(8)
S(4)—C(2)—N(2)	120.0(6)	N(1)—C(3)—C(4)	111.7(9)
N(2)—C(7)—C(8)	110.5(7)	N(2)—C(9)—C(10)	110.7(8)
Sn(1)—C(11)—C(16)	119.5(7)	C(12)—C(11)—C(16)	120.7(8)
C(12)—C(13)—C(14)	120.5(7)	C(13)—C(14)—C(15)	120.6(9)
C(11)—C(16)—C(15)	120.7(8)	C(14)—C(15)—C(16)	118.8(9)
C(11)—C(12)—C(13)	118.7(8)	Sn(1)—C(11)—C(12)	119.7(6)
N(1)—C(5)—C(6)	105.6(8)	S(3)—C(2)—N(2)	123.2(7)
S(1)—C(1)—N(1)	122.7(7)	C(2)—N(2)—C(9)	120.9(9)
C(1)—N(1)—C(5)	122.9(9)	Sn(1)—S(3)—C(2)	85.0(6)
Cl(1)—Sn(1)—S(3)	161.0(4)	S(1)—Sn(1)—S(2)	69.6(4)
S(1)—Sn(1)—C(11)	166.2(5)	S(2)—Sn(1)—C(11)	96.6(4)
S(4)—Sn(1)—C(11)	102.5(5)		

Structure determination and refinement

A three-dimensional Patterson synthesis yielded the positions of the tin, sulphur and chlorine atoms and these were used to phase the initial structure factor calculation. A Fourier synthesis established the positions of the remaining non-hydrogen light atoms, which fitted the chemically expected model. Refinement using block-diagonal least-squares methods with all atoms anisotropic produced convergence at R 0.059 for the observed reflections (R 0.059 for the observed reflections (R 0.113 for all reflections). Positional and thermal parameters are listed in Tables 1 and 2, respectively. Intramolecular bond distances and angles are collected in Table 3. A list of the final observed and calculated structure factors can be obtained from the authors.

Discussion

Crystals of the title compound are composed of stacks of discrete molecules of $[\text{PhSnCl}(\text{S}_2\text{CNET}_2)_2]$ (Fig. 1). Individual molecules are six-coordinated in a slightly distorted octahedral fashion by the phenyl group, the chlorine atom, and the chelating dithiocarbamate residues, with the phenyl group and chlorine atom occupying mutually *cis* positions (Fig. 2). The tin—carbon bond distance, 2.154(5) Å, is identical to that in the bipyridyl complex of $[\text{Ph}_2\text{SnCl}_2]$, 2.152(8) Å [8], but shorter than that in $[\text{Ph}_2\text{Sn}(\text{S}_2\text{CNET}_2)_2]$ 2.18(2) Å [9]. However, the tin—chlorine distance is slightly shorter in the present case, 2.438(6) Å vs. 2.508(2) Å for $\text{Ph}_2\text{SnCl}_2 \cdot \text{bipy}$.

The two dithiocarbamate groups are not equivalent, that *trans* to the phenyl group chelating significantly more symmetrically (Sn—S 2.551(5), 2.593(7) Å) than that *trans* to the chlorine (Sn—S 2.528(6), 2.661(7) Å). All four tin—sul-

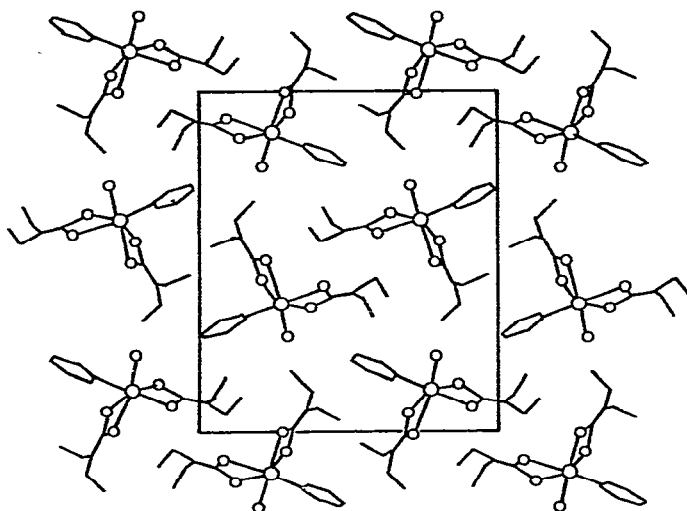


Fig. 1. Projection of the unit cell on to the *ab* plane.

phur band distances are longer than those observed in $[(\text{MeSn})_4\text{S}_6]$, 2.35 Å [3] and $[(\text{Ph}_2\text{SnS})_3]$ 2.42(2) Å [10], which may be regarded as normal single covalent bond distances. The dithiocarbamate ligand in both orthorhombic and monoclinic modifications of $[\text{Me}_3\text{SnS}_2\text{CNMe}_2]$ is essentially unidentate in character, the longer tin–sulphur distance being too long in each to be regarded as a bonding interaction [11,12] (Table 4). However, as organic groups attached to tin are replaced by more negative ligands, the shorter tin–sulphur distance

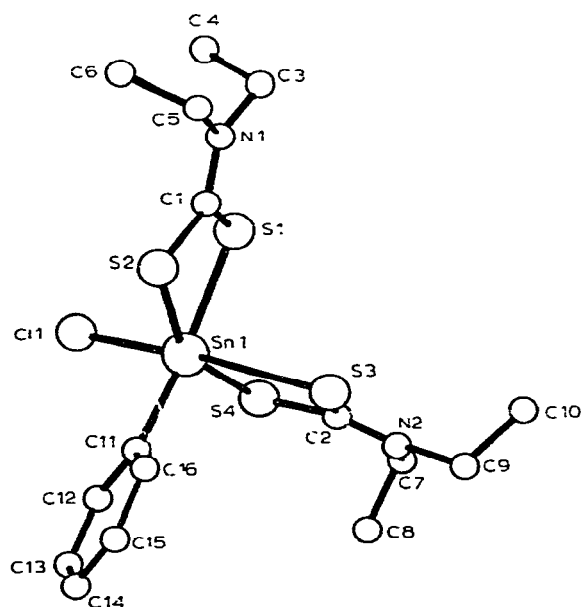


Fig. 2. View of the molecule showing the octahedral coordination and atomic numbering.

TABLE 4

COMPARISON OF VALENCE BOND DISTANCES (Å) AND ANGLES (°) IN DITHIOCARBAMATOTIN-(IV) COMPOUNDS

Compound	mean $r(\text{Sn}-\text{C})$	$r(\text{Sn}-\text{S})$	$r(\text{Sn} \cdots \text{S})$	$r(\text{Sn}-\text{Cl})$	C-Sn-C	Reference
$\text{Me}_3\text{SnS}_2\text{CNMe}_2$ (orthorhombic form)						
molecule 1	2.22(4)	2.47(1)	3.16(1)			11
molecule 2	2.21(4)	2.47(1)	3.33(1)			
$\text{Me}_3\text{SnS}_2\text{CNMe}_2$ (monoclinic form)	2.19(2)	2.47(1)	3.16(1)			12
$\text{Me}_2\text{ClSnS}_2\text{CNMe}_2$	2.19(5)	2.48(1)	2.79(1)	2.46(1)		14
$\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2$		2.511(8)	3.007(8)		136(1)	15
$\text{Ph}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$	2.18(2)	2.613(5)	2.637(5)		101.4(6)	9
		2.548(5)	2.790(6)			
$\text{PhClSn}(\text{S}_2\text{CNEt}_2)_2$	2.154(5)	2.551(5)	2.593(7)	2.438(6)	94.0(3)	This work
		2.528(6)	2.661(7)			
$\text{Sn}(\text{S}_2\text{CNEt}_2)_2$	unidentate:	2.503(7)				13
	bidentate:	2.531(7)	2.555(7)			

increases and the longer tin-sulphur interaction decreases, until near equality is reached in the two chelating dithiocarbamate residues in $[\text{Sn}(\text{S}_2\text{CNEt}_2)_4]$ [13] (Table 4). At the same time the tin-carbon bond distance decreases. In general, the structure of $[\text{PhSnCl}(\text{S}_2\text{CNEt}_2)_2]$ resembles that of $[\text{Ph}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2]$ [9], in which one phenyl group has been replaced by a chlorine atom.

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