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Synthesis of 2-chloro-2-n-butyl-1,3-dithia-2-stannacyclopentane and the crystal structure of its 1,10-phenanthroline complex

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Abstract

2-Chloro-2-n-butyl-1,3-dithia-2-stannacyclopentane has been prepared and the structure of its 1,10-phenanthroline complex, $C_{18}H_{21}ClN_2S_2Sn$, has been determined by an X-ray diffraction study. The geometrical parameters indicate a distorted octahedral structure about the tin atom. The chlorine atom is *trans* to one nitrogen of the ligand in axial position, and the sulphur atoms, the carbon bonded to the tin and the other nitrogen form the equatorial plane. The SnS_2C_2 ring adopts an envelope form. No intermolecular contacts are observed.

Introduction

The dithiaorganostannolanes $SnR_2[S(CH_2)_nS]$ ($n = 2, 3$), have received attention because of their coordinating and structural properties in addition to their application as stabilizers of plastics [1]. They are monomeric in solution, with a tetrahedral arrangement about the tin [2–5]. In the solid, intermolecular $S \cdots Sn$ contacts link the molecules in a linear chain containing five-coordinate tin, reflecting the ability of tin to increase its coordination number [6,7]. This property has been previously exploited in the preparation of the complexes of dimethyl- and diphenyl-tin dithiolates with pyridine and 1,10-phenanthroline [8] and with dimethylsulphoxide [3]. As a part of a study on the coordination of organotin derivatives with N-donor ligands [9,10], we have examined dithiaorganostannolanes of the type $SnClR(SCH_2CH_2S)$. The replacement of an alkyl group by a chlorine on the tin should significantly increase the acceptor ability of the metal centre.

We report here the preparation and characterization of 2-chloro-2-n-butyl-1,3-dithia-2-stanna-cyclopentane and the crystal structure of its complex with 1,10-phenanthroline. Both compounds are new.

Table 1

Structure determination summary

<i>Crystal data</i>	
Empirical formula	$C_{18}H_{21}N_2S_2ClSn$
Color; habit	Pale yellow; parallelepiped
Crystal size (mm)	$0.20 \times 0.08 \times 0.24$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimension	$a = 8.696(2) \text{ \AA}$ $b = 21.897(9) \text{ \AA}$ $c = 10.468(3) \text{ \AA}$ $\beta = 98.27(2)^\circ$
Volume	$1972.3(1.1) \text{ \AA}^3$
Z	4
Formula weight	483.5
Density (calc.)	1.63 Mg/m^3
Absorption coefficient	1.64 mm^{-1}
$F(000)$	968
<i>Data collection</i>	
Diffractometer used	Siemens R3m/V
Radiation	Mo- K_α ($\lambda = 0.71073 \text{ \AA}$)
Temperature (K)	295
Monochromator	Highly oriented graphite crystal
2θ Range	3.0 to 50.0°
Scan type	$\omega-2\theta$
Scan speed	Variable; 1.50 to $14.65^\circ/\text{min}$ in ω
Scan range (ω)	1.2°
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	2 measured every 100 reflections
Index ranges	$-11 < h < 11$, $0 < k < 27$, $0 < l < 13$
Reflections collected	3810
Independent reflections	3494
Observed reflections	2793 ($F > 5.0\sigma(F)$)
<i>Solution and refinement</i>	
System used	Siemens SHELXTL PLUS (Release 4.1)
Solution	Heavy-atom methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\sum w(F_o - F_c)^2$
Hydrogen atoms	Riding model, common isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.001F^2$
Number of parameters refined	218
Final R indices (obs. data)	$R = 4.13\%$, $wR = 5.45\%$
R indices (all data)	$R = 6.56\%$, $wR = 7.56\%$
Goodness-of-fit	1.52
Data-to-parameter ratio	13:1
Largest difference peak	0.82 e \AA^{-3} (0.93 \AA for from Sn)
Largest difference hole	-1.8 e \AA^{-3}

Experimental

Commercial n-butyltin trichloride was distilled immediately before use. Ethane-1,2-dithiol and all other chemicals were used as supplied. NMR spectra were recorded on a Jeol FX 90Q spectrometer at 27°C.

2-Chloro-2-n-butyl-1,3-dithia-2-stanna-cyclopentane (I)

A solution of 3.4 g (0.012 mol) of n-butyltin trichloride in 20 ml of water was slowly added with stirring to an aqueous solution containing a molar proportion (1 ml, 1.13 g) of ethanedithiol and a two-molar proportion (0.96 g, 0.024 mol) of sodium hydroxide. The preparation of the solutions and mixing were carried out under nitrogen. After 2 h ca. 30 ml of dichloromethane were added and the mixture was stirred overnight. The clear layers formed were separated. The aqueous solution was extracted three times with 10 ml of dichloromethane. The combined organic solutions were evaporated and a colorless oil was recovered (2.4 g, 66% yield). Selected IR absorption maxima (liquid film, Perkin-Elmer 599B spectrophotometer) are: 595 and 530 (Sn-C stretching), 380, 340 and 330 (Sn-S and Sn-Cl stretching) cm^{-1} . NMR (deuteriochloroform solution): $\delta(^{119}\text{Sn})$: 184 ppm (relative to tetramethyltin); $\delta(^{13}\text{C})$: 35.64 (ethanedithiol carbons), 29.01, 27.58, 25.95, and 13.40 (butyl carbons) ppm; $\delta(^1\text{H})$, ethanedithiol protons): 3.19 ppm (relative to tetramethylsilane).

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^2$)

	x	y	z	U^a
Sn	2011(0)	1022(0)	2940(1)	4.1
Cl	-516(2)	1437(1)	3450(2)	7.6
S(1)	2983(2)	427(1)	4888(1)	5.5
S(2)	842(1)	89(1)	1945(1)	4.9
N(1)	4109(4)	813(2)	1764(4)	4.8
N(2)	1397(5)	1374(2)	752(4)	5.6
C(1)	2374(7)	-330(3)	4316(5)	6.2
C(2)	831(7)	-332(3)	3427(5)	6.5
C(3)	3178(7)	1875(3)	3459(7)	7.3
C(4)	4737(8)	1797(3)	4373(8)	8.4
C(5)	5378(10)	2363(4)	5039(9)	10.3
C(6)	6800(10)	2256(5)	5951(9)	11.3
C(7)	5419(5)	549(3)	2273(6)	6.3
C(8)	6625(6)	447(3)	1574(9)	8.5
C(9)	6477(9)	608(3)	325(11)	10.2
C(10)	5106(9)	875(3)	-262(7)	7.9
C(11)	3923(6)	982(2)	512(5)	5.3
C(12)	2488(7)	1267(3)	-35(5)	5.5
C(13)	63(7)	1638(3)	257(7)	8.1
C(14)	-246(12)	1815(4)	-1018(10)	10.8
C(15)	796(15)	1724(4)	-1806(8)	11.4
C(16)	2229(11)	1440(3)	-1357(5)	8.6
C(17)	3374(19)	1318(5)	-2114(8)	13.3
C(18)	4739(18)	1065(4)	-1633(11)	13.3

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected bond lengths (Å) and angles (°)

Sn-Cl	2.505(2)	C(1)-C(2)	1.52(1)
Sn-S(1)	2.464(2)	C(3)-C(4)	1.55(1)
Sn-S(2)	2.448(2)	C(4)-C(5)	1.49(1)
Sn-C(3)	2.158(6)	C(5)-C(6)	1.47(1)
Sn-N(1)	2.388(4)	N(1)-C(7)	1.32(1)
Sn-N(2)	2.403(4)	N(1)-C(11)	1.35(1)
S(1)-C(1)	1.814(6)	N(2)-C(12)	1.36(1)
S(2)-C(2)	1.804(6)	N(2)-C(13)	1.33(1)
		C(11)-C(12)	1.44(1)
Cl-Sn-S(1)	102.9(1)	N(1)-Sn-C(3)	85.9(2)
Cl-Sn-S(2)	94.0(1)	N(2)-Sn-C(3)	89.7(2)
Cl-Sn-N(1)	159.7(1)	Sn-S(1)-C(1)	99.3(2)
Cl-Sn-N(2)	90.3(1)	S(1)-C(1)-C(2)	113.3(4)
Cl-Sn-C(3)	91.6(2)	C(1)-C(2)-S(2)	114.3(4)
S(1)-Sn-S(2)	89.0(1)	C(2)-S(2)-Sn	96.5(2)
S(1)-Sn-N(1)	97.4(1)	Sn-N(1)-C(11)	117.1(3)
S(1)-Sn-N(2)	163.9(1)	N(1)-C(11)-C(12)	118.8(5)
S(1)-Sn-C(3)	99.0(2)	C(11)-C(12)-N(2)	118.3(5)
S(2)-Sn-N(1)	85.5(1)	C(12)-N(2)-Sn	116.3(3)
S(2)-Sn-N(2)	80.8(1)	Sn-C(3)-C(4)	113.4(4)
S(2)-Sn-C(3)	169.0(2)	C(3)-C(4)-C(5)	115.5(6)
N(1)-Sn-N(2)	69.6(1)	C(4)-C(5)-C(6)	113.3(7)

2-Chloro-2-n-butyl-1,3-dithia-2-[1,10-phenanthroline]stannacyclopentane

Solutions of equimolar amounts of I and anhydrous 1,10-phenanthroline in dichloromethane were mixed, giving a yellow solution. This was evaporated and the residual solid was recrystallized from a chloroform/n-hexane mixture (m.p. 166 °C; C, 44.62; H, 4.68; Cl, 8.66; N, 5.20; C₁₈H₂₁ClN₂S₂Sn calc.: C, 44.70; H, 4.37; Cl, 7.33; N, 5.79%).

Crystallography

Crystals of good quality were obtained by cooling of a methanol solution of the complex. Details of the crystal data, measurement of intensity, and data processing are summarized in Table 1. Fractional atomic coordinates and thermal parameters are given in Table 2, and selected bond lengths and angles in Table 3. A table of hydrogen atom coordinates and a list of observed and calculated structure factors are available from the authors.

Discussion

IR and NMR assignments were based on those previously reported for similar compounds [2,3,5,11,12]. The NMR chemical shifts of I are very close to those previously found for the corresponding dialkylstannadithiacyclopentanes [3,5,11,12]. In particular the replacement of an alkyl group by a chlorine atom is not expected to increase further the nuclear deshielding of the tin bonded to two electronegative atoms [11]. Thus the ¹¹⁹Sn chemical shift may be compared with those for the corresponding dialkyltin derivatives, and similarly considered as indicating for this compound a monomeric structure involving dithiastannolane rings rather than a

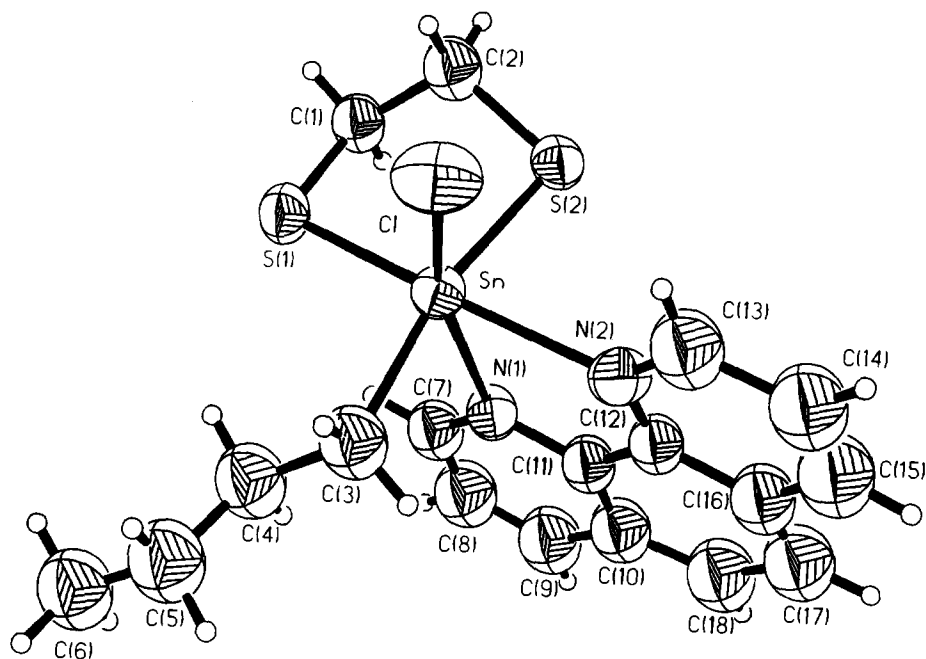


Fig. 1. Drawing of the complex with thermal ellipsoid at the 50% level. H atoms are represented by spheres of arbitrary size.

polymeric open chain. This was confirmed by the determination of the crystal structure of the complex formed between this species and 1,10-phenanthroline.

The molecular geometry and the atom numbering of this complex are shown in Fig. 1. The structure consists of discrete molecules. The internal geometrical

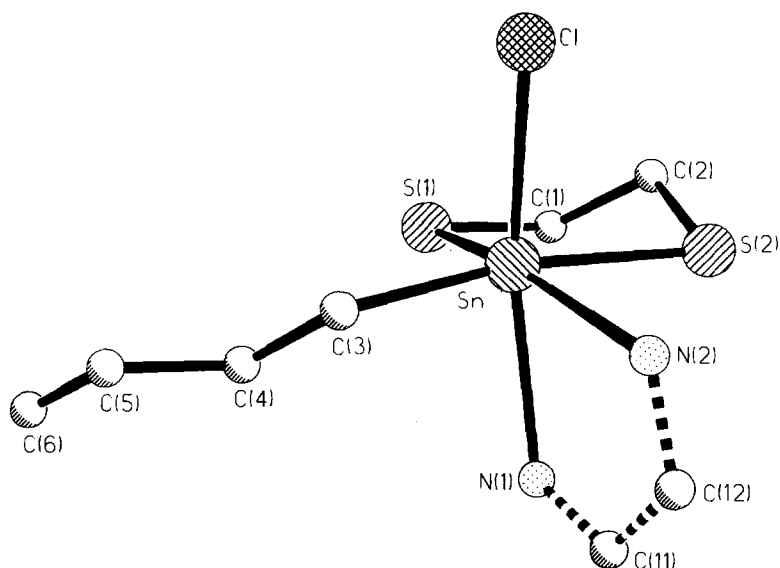


Fig. 2. Coordination about Sn with schematic representation of the 1,10-phenanthroline ligand.

parameters indicate a distorted octahedral geometry about the tin. The two sulphur atoms of the dithiolate group, together with the C(3) atom of the butyl group and the N(2) donor atom of the phenanthroline ligand, form the equatorial plane, and the chlorine and the N(1) atoms are *trans* to each other in axial positions. The

Table 4

i. Deviations (Å) of atom from various least-squares planes (distances marked with an asterisk (*) were excluded from the plane's calculation)

Atom	Plane(1)	Plane(2)	Plane(3)	Plane(4)
Sn	-0.20 *	-0.05 *	0.00	0.51 *
Cl	-2.69 *	0.06 *		
S(1)	0.06	-0.53 *	0.00	1.98 *
S(2)	-0.07	-2.45 *	0.00	0.69 *
N(1)	-2.12 *	-0.03		
N(2)	0.08	0.01	0.51 *	-1.21 *
C(1)			0.14 *	
C(2)			-0.60 *	
C(3)	-0.07		0.28 *	0.00
C(4)				0.00
C(5)				0.00
C(6)				0.08 *
C(7)		-0.03		
C(8)		0.01		
C(9)		0.03		
C(10)		0.01		
C(11)		0.00		
C(12)		0.00		
C(13)		0.01		
C(14)		0.01		
C(15)		0.00		
C(16)		-0.01		
C(17)		-0.03		
C(18)		0.00		

ii. Dihedral angles (°)

(1)-(2)	90.5	(2)-(3)	86.3
(1)-(3)	6.9	(2)-(4)	102.5
(1)-(4)	137.4	(3)-(4)	143.9

iii. Selected torsion angles (°)

Sn-S(1)-C(1)-C(2)	-35.7	Sn-N(1)-C(11)-C(12)	-0.7
S(1)-C(1)-C(2)-S(2)	62.8	N(1)-C(11)-C(12)-N(2)	2.3
C(1)-C(2)-S(2)-Sn	-49.7	C(11)-C(12)-N(2)-Sn	-2.7
C(2)-S(2)-Sn-S(1)	19.7	C(12)-N(2)-Sn-N(1)	1.7
S(2)-Sn-S(1)-C(1)	4.6	N(2)-Sn-N(1)-C(11)	-0.5

iv. Intramolecular contacts (Å) in the octahedral environment around tin

Cl...S(1)	3.88	N(1)...N(2)	2.73
Cl...S(2)	3.62	N(1)...C(3)	3.10
Cl...N(2)	3.48	S(1)...S(2)	3.44
Cl...C(3)	3.35	S(2)...N(2)	3.15
N(1)...S(1)	3.64	N(2)...C(3)	3.22
N(1)...S(2)	3.28	C(3)...S(1)	3.52

complexation of the tin with the bidentate N ligand prevents the potentially short intermolecular Sn...S contacts observed in the structure of 2,2-dimethyl-1,3-dithia-2-stannacyclopentane [6,7].

Distortions from the ideal Sn-centered octahedron (Fig. 2) result in (i) the Sn atom lying out of the mean equatorial plane by 0.20 Å towards the chloride ligand (Table 4); (ii) a non-linear Cl–Sn–N(1) axis of 159.7(1)° accompanied by S(1)–Sn–N(2) and S(2)–Sn–C(3) angles of 163.9(1) and 169.0(2)°, respectively; (iii) significant deviation (ca. 0.07 Å) of the S₂NC set atoms defining the “equatorial” plane; (iv) the N(1)...N(2) distance is 2.73 Å, and consequently the N(1)–Sn–N(2) “bite” angle (69.6°) is narrower than the S(1)–Sn–S(2) one (89.0°).

The 1,10-phenanthroline ligand overall is planar and lies normal (90.5°) to the equatorial plane, while the five-membered SnS₂C₂ ring has an envelope form with C(2) displaced by 0.69 Å above the mean plane of the other four atoms, as found in dimethyltin ethanedithiolate [6,7]. The butyl chain arrangement is fully extended and shows a rather short (1.47 Å) bond distance involving two atoms with high thermal motion. The bond lengths and angles do not differ significantly from the expected values [13]. In particular the Sn–C bond length [2.158(6) Å] is within the range normally found for Sn–alkyl bonds; the Sn–S bonds [2.464(2) and 2.448(2) Å] are in agreement with a covalent radii sum of 2.44 Å [14] and with a number of values reported for organotin thiolates [6,7,13,15]. The Sn–N bond distances are comparable with those found in the octahedral complexes 1,10-phenanthroline-dichlorodi-n-butyltin [16] and 2,2'-dipyridyldichlorodiphenyltin [17].

References

- 1 H. Schumann, I. Schumann-Ruidisch and M. Schmidt, in A.K. Sawyer, *Organotin Compounds*, Vol. 2, Marcel Dekker, New York, 1971.
- 2 R.C. Poller and J.A. Spillman, *J. Chem. Soc. A*, (1966) 958 and 1024.
- 3 J.D. Kennedy, W. McFarlane and G.S. Pyne, *Bull. Soc. Chim. Belg.*, 84 (1975) 289.
- 4 B. Mathiasch, *Z. Anorg. Allg. Chem.*, 425 (1976) 249.
- 5 E.W. Abel, S.K. Bhargava, K.G. Orrel and V. Šik, *J. Chem. Soc., Dalton Trans.*, (1982) 2073.
- 6 M. Drager, *Z. Anorg. Allg. Chem.*, 477 (1981) 154.
- 7 A.S. Secco and J. Trotter, *Acta Crystallogr., Sect. C*, 39 (1983) 451.
- 8 L.M. Epstein and D.K. Straub, *Inorg. Chem.*, 4 (1965) 1551.
- 9 V. Peruzzo, G. Plazzogna and G. Valle, *J. Organomet. Chem.*, 375 (1989) 167.
- 10 R. Graziani, V. Peruzzo, G. Plazzogna and U. Casellato, *J. Organomet. Chem.*, 396 (1990) 19.
- 11 W. McFarlane, J.C. Maire and M. Delmas, *J. Chem. Soc., Dalton Trans.*, (1972) 1862.
- 12 G. Domazetis, R.J. Magee and B.D. James, *J. Inorg. Nucl. Chem.*, 43 (1981) 1351.
- 13 J.A. Zubieta and J.J. Zuckermann, *Prog. Inorg. Chem.*, 24 (1978) 251.
- 14 L. Pauling, *The Nature of the Chemical Bond*, 3rd. ed., 1960, Cornell University Press, Ithaca, p. 224.
- 15 P.B. Bates, M.B. Hursthouse, A.G. Davies and S.D. Slater, *J. Organomet. Chem.*, 325 (1987) 129.
- 16 P. Ganis, V. Peruzzo and G. Valle, *J. Organomet. Chem.*, 256 (1983) 245.
- 17 P.G. Harrison, T.J. King and A. Richards, *J. Chem. Soc., Dalton Trans.*, (1972) 281.