μ-[*rac*-1,2-Bis(*n*-propylsulphinyl)ethylene]-(*O,O'*)-bis[chloro-*cis*-triphenyltin(IV)]

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Abstract. $C_{44}H_{46}Cl_2O_2S_2Sn_2$, $M_r = 979.26$, monoclinic, $P2_1/c$, $a = 10.366$ (2), $b = 15.155$ (3), $c = 16.057$ (4) Å, $\beta = 120.117$ (19)°, $U = 2181.96$ Å^3, $Z = 2$, $D_c = 1.49$ Mg m^{-3}, μ(Cu $K\alpha$) = 11.63 mm^{-1}. The structure was refined to an R of 0.037 for 1685 unique diffractometer data. The molecule lies on a crystallographic centre of symmetry situated at the centre of the C(4)—C(4') double bond of the bidentate disulphoxide ligand. This group is bonded to two symmetry-related Sn atoms to form a bridged species. The unique Sn atom exhibits a trigonal-bipyramidal coordination geometry, and is bonded to three phenyl groups in the equatorial plane and to a Cl and an O atom in the axial positions. The *n*-propyl substituent coordinated to the S atom is disordered.

Introduction. All the known crystal structures of complexes containing the Sn—O=S fragment involve only monosulphoxide ligands and show a coordination number of either six or seven around the Sn atom. These exhibit approximate octahedral (Abras, Filgueiras & Baba, 1982; Aslanov, Ionov, Attiya, Permin & Petrosyan, 1978; Pelizzi & Pelizzi, 1975) and pentagonal-bipyramidal (Coghi, Pelizzi & Pelizzi, 1976; Mangia, Pelizzi & Pelizzi, 1973) geometries, respectively. The structure of the title compound was determined in order to investigate the structure of a complex containing a bidentate sulphoxide ligand.

The title compound was prepared by refluxing Sn(C$_6$H$_5$)$_3$Cl and excess *rac*-(C$_3$H$_7$)SOCH$_2$OS(C$_3$H$_7$) in CHCl$_3$ for 2 h (Filgueiras, 1981). The mixture was evaporated to dryness under reduced pressure and the solid thus obtained recrystallized from propanone. Crystals were deposited as transparent rectangular blocks. 1972 intensities were recorded (3.0 < 2θ < 125.0°) on a Syntex *P*2$_1$, four-circle diffractometer, with graphite-monochromated Cu *K*α radiation and 96-step ω–2θ scans, from a crystal 0.29 × 0.25 × 0.13 mm. Lp corrections and semi-empirical absorption corrections based on a pseudo-ellipsoid model and 390 azimuthal scan data from 15 independent reflections were applied; transmission factors ranged from 0.534

to 0.919 for the full data set. Equivalent reflections were averaged to give 1685 unique observed intensities IF > 3σ(*F*)I. Cell dimensions were derived from the angular measurements of 15 strong reflections (45 < 2θ < 55°).

The Sn-atom position was determined from a Patterson synthesis, and the remaining non-hydrogen

Table 1. *Atomic coordinates* (×10⁴) *and isotropic temperature factors* (Å² × 10³)

For the anisotropically refined atoms (see text) the temperature factors listed are equivalent isotropic values, where $U_{eq} = \frac{1}{3}$ trace of the orthogonalized U matrix.

	x	*y*	*z*	U/U_{eq}
Sn(1)	5378 (1)	2532 (1)	1991 (1)	36 (3)
C(11)	3187 (10)	2607 (6)	1782 (8)	67 (5)
C(12)	1922 (11)	2423 (6)	897 (8)	74 (6)
C(13)	503 (11)	2466 (8)	781 (10)	87 (8)
C(14)	336 (14)	2669 (9)	1551 (13)	122 (11)
C(15)	1577 (16)	2804 (8)	2436 (12)	130 (11)
C(16)	2988 (12)	2789 (7)	2563 (9)	90 (8)
C(21)	5993 (8)	1638 (5)	1228 (6)	50 (5)
C(22)	6226 (9)	1921 (6)	493 (7)	64 (6)
C(23)	6718 (11)	1341 (7)	48 (7)	77 (7)
C(24)	6975 (11)	480 (8)	320 (7)	81 (7)
C(25)	6738 (12)	194 (7)	1056 (8)	89 (8)
C(26)	6280 (11)	768 (6)	1513 (7)	74 (6)
C(31)	6862 (10)	3601 (5)	2668 (6)	57 (6)
C(32)	6382 (12)	4436 (5)	2743 (7)	72 (7)
C(33)	7313 (14)	5118 (6)	3158 (8)	85 (8)
C(34)	8847 (15)	4987 (7)	3567 (8)	92 (9)
C(35)	9354 (12)	4151 (8)	3538 (9)	105 (9)
C(36)	8354 (11)	3472 (6)	3089 (7)	81 (7)
Cl(1)	6377 (3)	1641 (1)	3487 (2)	79 (1)
O(1)	4358 (6)	3430 (4)	529 (4)	82 (4)
S(1)	3465 (3)	4255 (2)	293 (2)	111 (2)
*C(1)	1995 (35)	4085 (27)	−1016 (12)	182 (6)
†C(1a)	1806 (34)	3948 (31)	−923 (19)	182 (6)
*C(2)	815 (37)	4826 (24)	−1435 (26)	182 (6)
†C(2a)	148 (37)	4213 (24)	−1422 (28)	182 (6)
*C(3)	−505 (33)	4868 (24)	−1254 (23)	182 (6)
†C(3a)	838 (46)	5075 (24)	−855 (28)	182 (6)
C(4)	4687 (15)	5155 (10)	249 (9)	135 (5)

* Occupancy 0.54 (2).

† Occupancy 0.46 (2).

atoms were found from subsequent electron-density difference syntheses. The n-propyl group is severely positionally disordered. The best model for the disorder consisted of two positions for the three C atoms, all assigned a common isotropic temperature factor, and the pairs of equivalent atoms having their occupancies set as k and $(1-k)$, respectively; k refined to 0·54 (2). The S—C and C—C distances were constrained to 1·90 (1) and 1·54 (1) Å. The structure was refined by blocked-full-matrix least squares with anisotropic thermal parameters assigned to the Sn, S, O, Cl and phenyl C atoms. H atoms were placed in idealized positions (C—H, 1·08 Å; C—C—H 120°) and constrained to ride on the relevant C atom; each set of ring H atoms was

assigned a common isotropic temperature factor. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed, with the weighting scheme $w = |\sigma^2(F) + 0\cdot0005|F|^2|^{-1}$ for the final stages. A final difference map showed no significant regions of electron density. The final $R = 0\cdot037$ and $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0\cdot040$. Atomic coordinates and isotropic or equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 1;* the atoms denoted '*a*' represent the second positions for the disordered atoms. Bond lengths and angles are in Tables 2 and 3 respectively.

Discussion. The crystal structure consists of discrete $[Sn(C_6H_5)_3Cl]_2\{rac-[(C_3H_7)SOCHCHSO(C_3H_7)]\}$ molecules separated by normal van der Waals distances (Fig. 1).

The molecular structure is illustrated in Fig. 2; only one orientation of the disordered n-propyl groups is shown, and the H atoms have been omitted for clarity. The Sn atom adopts trigonal-bipyramidal geometry with the three phenyl groups occupying the equatorial sites and a Cl and an O atom in the axial positions. The only significant difference between the title compound and other known complexes containing the Sn—O=S fragment is that the Sn—O distance is longer in this complex than in the octahedral species [2·273 (4)–2·368 (7) Å] (Aslanov *et al.*, 1978; Pelizzi & Pelizzi, 1975). However, the Sn—O distance in the title complex does lie in the range observed for pentagonal-bipyramidal complexes [2·17 (1)–2·50 (1) Å] (Coghi *et al.*, 1976; Mangia *et al.*, 1973). This is probably due to the spatial non-equivalence of the Sn bonds in this dsp^3

Table 2. Bond lengths (Å)

The atom designated as C(4') is related to C(4) by the operation $1 - x, 1 - y, -z$.

Sn(1)—C(11)	2·126 (11)	C(11)—C(12)	1·395 (11)
Sn(1)—C(21)	2·128 (10)	C(12)—C(13)	1·389 (18)
Sn(1)—C(31)	2·120 (7)	C(13)—C(14)	1·365 (27)
Sn(1)—Cl(1)	2·484 (2)	C(14)—C(15)	1·372 (19)
Sn(1)—O(1)	2·447 (6)	C(15)—C(16)	1·372 (23)
O(1)—S(1)	1·488 (6)	C(16)—C(11)	1·397 (20)
S(1)—C(1)	1·895 (18)	C(21)—C(22)	1·385 (16)
S(1)—C(1a)	1·901 (25)	C(22)—C(23)	1·383 (17)
S(1)—C(4)	1·887 (17)	C(23)—C(24)	1·359 (15)
C(1)—C(2)	1·544 (50)	C(24)—C(25)	1·390 (20)
C(1a)—C(2a)	1·541 (47)	C(25)—C(26)	1·368 (18)
C(2)—C(3)	1·536 (62)	C(26)—C(21)	1·379 (12)
C(2a)—C(3a)	1·547 (50)	C(31)—C(32)	1·389 (12)
C(4)—C(4')	1·344 (37)	C(32)—C(33)	1·341 (13)
		C(33)—C(34)	1·397 (19)
		C(34)—C(35)	1·380 (17)
		C(35)—C(36)	1·379 (14)
		C(36)—C(31)	1·356 (14)

Table 3. Bond angles (°)

C(4') is related to C(4) by the operation $1 - x, 1 - y, -z$.

C(11)—Sn(1)—C(21)	123·3 (3)	Sn(1)—C(11)—C(12)	122·2 (9)
C(11)—Sn(1)—C(31)	118·9 (4)	Sn(1)—C(11)—C(16)	119·7 (6)
C(11)—Sn(1)—Cl(1)	94·3 (3)	C(12)—C(11)—C(16)	117·9 (11)
C(11)—Sn(1)—O(1)	84·6 (3)	C(13)—C(12)—C(11)	121·1 (13)
C(21)—Sn(1)—C(31)	115·6 (4)	C(14)—C(13)—C(12)	119·8 (10)
C(21)—Sn(1)—Cl(1)	96·3 (2)	C(15)—C(14)—C(13)	119·5 (15)
C(21)—Sn(1)—O(1)	84·9 (3)	C(16)—C(15)—C(14)	121·8 (19)
C(31)—Sn(1)—Cl(1)	94·4 (2)	C(11)—C(15)—C(16)	119·7 (19)
C(31)—Sn(1)—O(1)	85·4 (3)	Sn(1)—C(21)—C(22)	121·6 (6)
Cl(1)—Sn(1)—O(1)	178·7 (2)	Sn(1)—C(21)—C(26)	119·7 (8)
Sn(1)—O(1)—S(1)	128·8 (5)	C(22)—C(21)—C(26)	118·6 (10)
O(1)—S(1)—C(1)	102·7 (12)	C(23)—C(22)—C(21)	120·6 (9)
O(1)—S(1)—C(1a)	100·5 (14)	C(24)—C(23)—C(22)	120·6 (12)
O(1)—S(1)—C(4)	105·9 (6)	C(25)—C(24)—C(23)	118·8 (12)
C(1)—S(1)—C(4)	103·8 (12)	C(26)—C(25)—C(24)	121·0 (10)
C(1a)—S(1)—C(4)	114·6 (14)	C(21)—C(26)—C(25)	120·3 (11)
S(1)—C(1)—C(2)	113·9 (24)	Sn(1)—C(31)—C(32)	122·8 (7)
S(1)—C(1a)—C(2a)	131·8 (30)	Sn(1)—C(31)—C(36)	120·0 (6)
C(1)—C(2)—C(3)	122·3 (33)	C(32)—C(31)—C(36)	117·2 (8)
C(1a)—C(2a)—C(3a)	81·3 (27)	C(33)—C(32)—C(31)	123·0 (11)
S(1)—C(4)—C(4')	107·6 (17)	C(34)—C(33)—C(32)	119·4 (10)
		C(35)—C(34)—C(33)	118·5 (10)
		C(36)—C(35)—C(34)	120·2 (11)
		C(31)—C(36)—C(35)	121·6 (10)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and associated parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36922 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
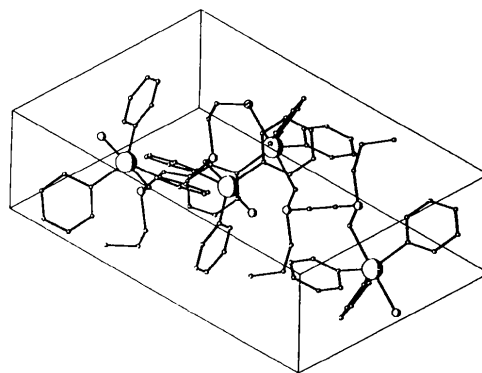

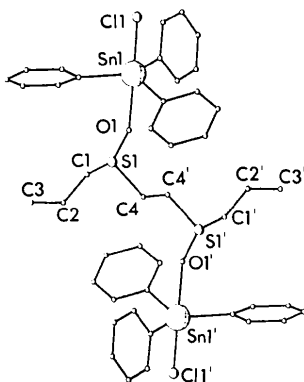Fig. 1. Unit-cell contents for $[Sn(C_6H_5)_3Cl]_2\{rac-[(C_3H_7)$-SOCHCHSO(C_3H_7)]\}$.

Fig. 2. The molecular structure of $[Sn(C_6H_5)_3Cl]_2\{rac-[(C_3H_7)SOCHCHSO(C_3H_7)]\}$; the atoms designated by a prime are related by the symmetry operation $1 - x, 1 - y, -z$.

species, which may be thought of as a linear combination of sp^2 and p_zd_z orbitals. The axial bonds will have greater p character on Sn and little s character, thereby increasing the Sn–O distance. The Sn–Cl bond shows no significant difference from the Sn–Cl distances in the octahedral complexes [2·474 (2) to 2·524 (4) Å] (Aslanov *et al.*, 1978; Pelizzi & Pelizzi, 1975), which are both *cis*-dichloro species with likely Cl···Cl interactions. The S–O bond length is indicative of multiple-bond character and the stereochemistry around the S atom is consistent with the

presence of a lone-pair of electrons on this atom. The C(4)–C(4′) bond length is close to the accepted value for a C–C double bond.

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Structure of Tris(di-*n*-propyldithiocarbamato)antimony(III)

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Abstract. $Sb(C_7H_{14}NS_2)_3$, $M_r = 650·72$, triclinic, $P\bar{1}$, $a = 14·501$ (4), $b = 11·653$ (3), $c = 9·891$ (1) Å, $\alpha = 103·45$ (1), $\beta = 97·03$ (1), $\gamma = 102·58$ (2)°, $Z = 2$, $V = 1559·94$ Å^3, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $F(000) = 672$, $D_c = 1·385$, $D_m = 1·35$ Mg m^{-3} (by flotation in KBr solution), m.p. $= 421$ K, $\mu = 1·26$ mm^{-1}; 2903 non-zero reflexions. The structure was solved by direct methods and refined by least-squares calculations to $R = 7·2\%$. The molecule consists of three asymmetrically bidentate ligands surrounding the central Sb atom in approximately C_s symmetry. There is a characteristic gap in the metal coordination due to a stereochemically active lone pair and the proximity of the inversion image of the molecule. An intermolecular Sb–S distance between these molecules is less than the sum, 3·80 Å, of the corresponding van der Waals radii, so that a weak intermolecular interaction takes place.

Introduction. In a recent paper (Kavounis, Kokkou, Rentzeperis & Karagiannidis, 1980) the structure of tris(1-pyrrolidinecarbodithioato)antimony(III) (TPCA) was reported. The present structure determination of the title compound (TDCA hereafter) is the second of a series of systematic investigations of dithiocarbamates.