

Fig. 2. The molecular structure of $[\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}]_2\{\text{rac}-[(\text{C}_3\text{H}_7)\text{SOCHCHSO}(\text{C}_3\text{H}_7)]\}$; 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 $p_z d_z$ 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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References

- ABRAS, A., FILGUEIRAS, C. A. L. & BABA, J. M. K. (1982). *J. Inorg. Nucl. Chem.* In the press.
- ASLANOV, L. A., IONOV, V. N., ATTIYA, V. M., PERMIN, A. B. & PETROSYAN, V. S. (1978). *Zh. Strukt. Khim.* **19**, 109–115.
- COGHI, L., PELIZZI, C. & PELIZZI, G. (1976). *J. Organomet. Chem.* **114**, 53–65.
- FILGUEIRAS, C. A. L. (1981). Unpublished results.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MANGIA, A., PELIZZI, C. & PELIZZI, G. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2557–2561.
- PELIZZI, C. & PELIZZI, G. (1975). *Gazz. Chim. Ital.* **105**, 1187–1197.
- SHELDRICK, G. M. (1976). *SHELX 76*. A program for crystal structure determination. Univ. of Cambridge, England.

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

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Abstract. $\text{Sb}(\text{C}_7\text{H}_{14}\text{NS}_2)_3$, $M_r = 650.72$, 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)°, $Z = 2$, $V = 1559.94$ Å³, $\lambda(\text{Mo } K\alpha) = 0.71069$ 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_3 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-pyrrolidinedithioato)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.

Yellow prismatic crystals of TDCA were obtained from CCl_4 /petroleum ether. Diffraction data were recorded from a crystal $0.35 \times 0.15 \times 0.14$ mm with a computer-controlled Philips PW 1100 diffractometer. With Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) the cell parameters were determined from the θ angles of 200 strong reflexions with large θ values measured on the diffractometer with the least-squares program *PARAM* (Stewart, Kruger, Ammon, Dickinson & Hall, 1976). Intensity statistics indicated the space group *P1*, which was confirmed by the final structure. Data were collected with a scintillation counter in the θ - 2θ scan mode. Of 5474 unique reflexions with $3 \leq \theta \leq 25^\circ$, 2903 with $I > 2\sigma(I)$ were considered observed and used for the structure analysis. Data reduction was carried out using the program *DATRED* (Main, 1970).

The structure was solved by direct methods with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The phases of 300 reflexions with $E > 1.66$ were determined and on the resulting *E* map it was possible to locate unambiguously nine of the 31 non-H atoms in the asymmetric unit. The remaining atoms were located by means of a Fourier synthesis.

The structure was refined by full-matrix least-squares calculations with *XRAY* (Stewart *et al.*, 1976). The atomic scattering factors and anomalous-dispersion corrections for Sb and S were taken from *International Tables for X-ray Crystallography* (1974). The weighting scheme was $w = 1/[A + B\sigma^2(F_o)]$ with $A = 8$, $B = 0.9$.

After several cycles of isotropic and anisotropic refinement the structure practically converged. But, whereas all the other distances were normal, that of the terminal C atom in one of the six propyl groups, C(21) in Fig. 1, was unacceptably short [C(20)–C(21) = 1.02 Å]. Since the very high temperature factors of this atom and of its neighbor, C(20), indicated a possible disorder, a careful examination of this site was carried

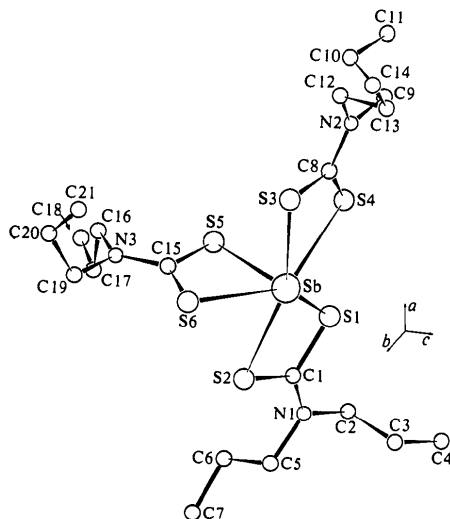


Fig. 1. Clinographic projection of the TDCA molecule.

out by means of difference Fourier syntheses and site-occupation analysis. However, no unambiguous results could be obtained. C(21) was therefore placed at its expected distance of 1.54 Å along the C(20)–C(21) direction and kept fixed there during the subsequent refinement cycles. To avoid unrealistic changes in the C(19)–C(20) and C(20)–C(21) distances, atoms C(19) and C(20) were also kept fixed at their positions obtained during the last least-squares cycle.

A difference Fourier synthesis revealed most of the H atoms. All of them were then included in the refinement cycles with isotropic temperature coefficients equal to those of the C atoms to which they are bonded but their parameters were not refined. The *R* factor converged to 7.2% ($R_w = 7.2\%$) (average shift/error < 0.08).

The final positional and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1. Interatomic distances and bond angles are given in Tables 2 and 3 respectively.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, C–H bond distances and various least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36908 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors for the non-H atoms

Here and throughout this paper e.s.d.'s are given in parentheses and refer to the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^* (Å ²)
Sb(1)	0.1210 (1)	−0.0993 (1)	−0.0029 (1)	3.9
S(1)	0.0191 (3)	−0.3080 (3)	0.0347 (4)	4.8
S(2)	−0.0681 (3)	−0.1746 (3)	−0.1425 (4)	4.8
S(3)	0.3164 (3)	0.0410 (4)	0.0605 (5)	5.8
S(4)	0.2535 (3)	−0.2009 (3)	0.1130 (4)	5.0
S(5)	0.1558 (3)	−0.2096 (3)	−0.2276 (4)	5.3
S(6)	0.1182 (3)	0.0328 (3)	−0.2083 (4)	6.0
N(1)	−0.1692 (8)	−0.3560 (10)	−0.0545 (14)	5.4
N(2)	0.4346 (8)	−0.0677 (11)	0.1830 (12)	5.5
N(3)	0.1396 (9)	−0.1172 (11)	−0.4470 (11)	5.6
C(1)	−0.0832 (9)	−0.2859 (11)	−0.0563 (13)	3.9
C(2)	−0.1831 (11)	−0.4477 (13)	0.0258 (22)	7.0
C(3)	−0.2096 (14)	−0.3911 (16)	0.1713 (22)	8.2
C(4)	−0.2301 (18)	−0.4887 (21)	0.2515 (29)	13.5
C(5)	−0.2574 (11)	−0.3387 (15)	−0.1343 (21)	7.0
C(6)	−0.2873 (15)	−0.4257 (21)	−0.2853 (27)	10.0
C(7)	−0.3806 (17)	−0.4076 (26)	−0.3600 (32)	13.9
C(8)	0.3428 (9)	−0.0734 (12)	0.1244 (13)	4.4
C(9)	0.4607 (11)	−0.1658 (17)	0.2347 (19)	7.2
C(10)	0.4954 (16)	−0.2517 (21)	0.1173 (29)	11.6
C(11)	0.5156 (21)	−0.3528 (32)	0.1718 (38)	15.9
C(12)	0.5120 (11)	0.0419 (16)	0.1987 (18)	6.3
C(13)	0.5265 (13)	0.1337 (20)	0.3446 (21)	8.3
C(14)	0.5965 (15)	0.2509 (23)	0.3601 (27)	10.6
C(15)	0.1370 (10)	−0.0939 (13)	−0.3073 (13)	5.0
C(16)	0.1462 (12)	−0.2370 (13)	−0.5319 (14)	5.8
C(17)	0.0506 (12)	−0.3281 (16)	−0.5841 (16)	6.2
C(18)	0.0635 (16)	−0.4526 (17)	−0.6584 (20)	9.0
C(19)	0.1227 (17)	−0.0248 (19)	−0.5224 (19)	7.7
C(20)	0.2132 (33)	0.0529 (46)	−0.5579 (39)	20.1
C(21)	0.2958	0.1072	−0.4294	22.6

* $B_{eq} = \frac{1}{3} \pi^2 \text{trace } \bar{U}$.

Table 2. *Interatomic distances* (Å)

Sb—S(1)	2.688 (4)	S(3)—C(8)	1.70 (2)
S(2)	2.767 (4)	S(4)—C(8)	1.72 (1)
S(3)	2.857 (4)	C(8)—N(2)	1.37 (2)
S(4)	2.737 (5)	N(2)—C(9)	1.46 (3)
S(5)	2.465 (4)	C(9)—C(10)	1.56 (3)
S(6)	2.822 (5)	C(10)—C(11)	1.47 (5)
		N(2)—C(12)	1.47 (2)
S(1)—C(1)	1.74 (1)	C(12)—C(13)	1.54 (3)
S(2)—C(1)	1.70 (2)	C(13)—C(14)	1.48 (3)
C(1)—N(1)	1.34 (2)		
N(1)—C(2)	1.47 (3)	S(5)—C(15)	1.77 (2)
C(2)—C(3)	1.57 (3)	S(6)—C(15)	1.67 (2)
C(3)—C(4)	1.53 (4)	C(15)—N(3)	1.35 (2)
N(1)—C(5)	1.50 (2)	N(3)—C(16)	1.48 (2)
C(5)—C(6)	1.55 (3)	C(16)—C(17)	1.50 (2)
C(6)—C(7)	1.54 (4)	C(17)—C(18)	1.53 (3)
		N(3)—C(19)	1.49 (1)
		C(19)—C(20)	1.55 (5)
		C(20)—C(21)	1.54

Table 3. *Bond angles* (°)

S(1)—Sb—S(2)	65.3 (0.1)	Sb—S(3)—C(8)	86.4 (0.4)
S(3)	138.0 (0.1)	Sb—S(4)—C(8)	89.9 (0.5)
S(4)	74.4 (0.1)	S(3)—C(8)—S(4)	119.9 (0.8)
S(5)	91.4 (0.1)	S(3)—C(8)—N(2)	121.5 (1.0)
S(6)	137.8 (0.1)	S(4)—C(8)—N(2)	118.6 (1.2)
S(2)—Sb—S(3)	155.7 (0.1)	C(8)—N(2)—C(9)	123.1 (1.2)
S(4)	137.6 (0.1)	C(8)—N(2)—C(12)	119.9 (1.4)
S(5)	84.8 (0.1)	C(9)—N(2)—C(12)	116.9 (1.2)
S(6)	76.1 (0.1)	N(2)—C(9)—C(10)	110.2 (1.7)
S(3)—Sb—S(4)	63.7 (0.1)	C(9)—C(10)—C(11)	108.1 (2.4)
S(5)	87.5 (0.1)	N(2)—C(12)—C(13)	111.7 (1.5)
S(6)	79.6 (0.1)	C(12)—C(13)—C(14)	113.8 (1.9)
S(4)—Sb—S(5)	83.2 (0.1)		
S(6)	134.1 (0.1)	Sb—S(5)—C(15)	91.2 (0.5)
S(5)—Sb—S(6)	67.7 (0.1)	Sb—S(6)—C(15)	81.6 (0.5)
Sb—S(1)—C(1)	88.8 (0.5)	S(5)—C(15)—S(6)	119.1 (0.8)
Sb—S(2)—C(1)	87.0 (0.5)	S(5)—C(15)—N(3)	115.5 (1.1)
S(1)—C(1)—S(2)	117.7 (0.8)	S(6)—C(15)—N(3)	125.4 (1.3)
S(1)—C(1)—N(1)	118.9 (1.1)	C(15)—N(3)—C(16)	122.5 (1.3)
S(2)—C(1)—N(1)	123.4 (1.2)	C(15)—N(3)—C(19)	118.7 (1.1)
C(1)—N(1)—C(2)	123.7 (1.3)	C(16)—N(3)—C(19)	118.3 (0.9)
C(1)—N(1)—C(5)	119.2 (1.4)	N(3)—C(16)—C(17)	113.1 (1.5)
C(2)—N(1)—C(5)	117.1 (1.2)	C(16)—C(17)—C(18)	110.4 (1.6)
N(1)—C(2)—C(3)	109.4 (1.3)	N(3)—C(19)—C(20)	115.8 (0.5)
C(2)—C(3)—C(4)	109.5 (1.7)	C(19)—C(20)—C(21)	112.5
N(1)—C(5)—C(6)	112.2 (1.5)		
C(5)—C(6)—C(7)	109.9 (2.0)		

Discussion. Fig. 1 shows a clinographic projection of the TDCA molecule. As expected its structure is similar to that of tris(diethyldithiocarbamato)antimony(III) (Raston & White, 1976) and tris(1-pyrrolidinedithiocarbamato)antimony(III) (TPCA) (Kavounis *et al.*, 1980) from which it differs in that it contains propyl groups instead of ethyl or pyrrolidine groups.

As in the crystals mentioned above and in tris(diethyldithiocarbamato)bismuth(III) (Raston & White, 1976) and tris(diethyldithiocarbamato)arsenic(III) (Colapietro, Domenicano, Scaramuzza & Vacigo, 1968; Raston & White, 1975), the characteristic feature of the TDCA molecule is a large gap in the coordination sphere of the metal atom, which is linked to three asymmetrically bidentate ligands. The gap is due to the existence of a stereochemically active

lone pair. The angular distortion of the SbS_6 core is again very pronounced, due to the close proximity of a second symmetry-equivalent molecule (*cf.* Fig. 2). As a result the usual D_3 symmetry of the MS_6 core in metal dithiocarbamates is reduced not to an approximate C_3 symmetry, as in most of the dithiocarbamates mentioned above, but to a very close approximation of C_s symmetry, as in TPCA. The centrosymmetrically related S'(2) of the neighboring molecule approaches the Sb atom quite closely. The distance $Sb-S'(2) = 3.471(4)$ Å is less than the sum, 3.80 Å, of the corresponding van der Waals radii (Bondi, 1964), so that a weak intermolecular interaction takes place. The two groups $Sb-S(1)-S(2)$ and $Sb-S(3)-S(4)$ are almost coplanar and perpendicular to the third group $Sb-S(5)-S(6)$ which constitutes the mirror plane of the core.

As expected from other dithiocarbamate structures with the same metal coordination, three of the $Sb-S$ bonds, nearly at right angles to one another, are practically covalent and the corresponding distances are shorter than the rest (*cf.* Table 2). In particular, the distance $Sb-S(5)$ is much shorter than all the others. This may be attributed to the lone pair which is expected to be in the plane of the group $Sb-S(5)-S(6)-C(15)$ and approximately opposite to S(5).

All three S_2CN ligand fragments are planar to a very good approximation and the Sb atom does not deviate from these planes by more than 0.515 Å*. The angles between the three planes are 87.4 (1), 84.9 (1) and 15.77 (4)°; that is one plane is almost perpendicular to the other two, which are almost coplanar. The general features of these fragments are similar to those found in other dithiocarbamates: the three $S-C$ bonds not adjacent to the covalent $Sb-S$ bonds have double-bond character and are shorter than the other three (*cf.* Table

* See deposition footnote.

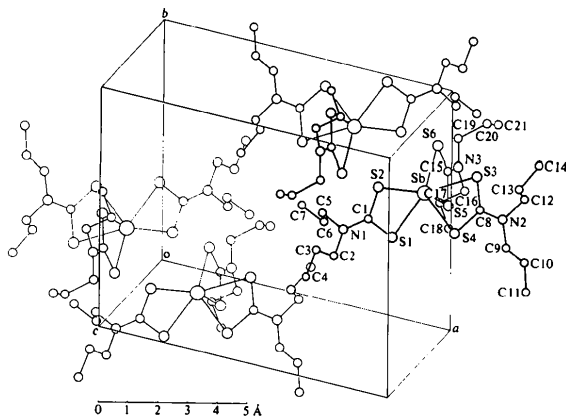


Fig. 2. Clinographic projection of the molecular packing in the unit cell.

2). The C—N bonds also have double-bond character. The mean values 1.69 and 1.74 Å for the S—C bonds and 1.35 Å for the C—N bonds compare well with the values found in the other dithiocarbamates mentioned above.

The terminal propyl groups of each ligand adopt their more usual conformation, lying on alternate sides of the ligand plane.*

Thanks are due to the University of Thessaloniki for the use of computing facilities.

* See deposition footnote.

References

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
COLAPIETRO, M., DOMENICANO, A., SCARAMUZZA, L. & VACIAGO, A. (1968). *Chem. Commun.* pp. 302–303.

- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press.
KAVOUNIS, C. A., KOKKOU, S. C., RENTZEPERIS, P. J. & KARAGIANNIDIS, P. (1980). *Acta Cryst.* **B36**, 2954–2958.
MAIN, P. (1970). Private communication. Univ. of York, England.
MAIN, P., WOOLFSON, M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain-la-Neuve, Belgium.
RASTON, C. L. & WHITE, A. H. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2425–2429.
RASTON, C. L. & WHITE, A. H. (1976). *J. Chem. Soc. Dalton Trans.* pp. 791–794.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1976). The XRAY system. Tech. Rep. TR-446. Computer Science Center, University of Maryland, College Park, Maryland.

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1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3- μ -hydrido-2,3- μ -(α - β - η : α - σ -styryl)-triangulo-triosmium

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Abstract. $C_{18}H_8O_{10}Os_3$, $M_r = 954.84$, monoclinic, $C2/c$, $a = 18.717(6)$, $b = 7.636(2)$, $c = 30.211(10)$ Å, $\beta = 91.88(3)^\circ$, $U = 4315.5$ Å³, $Z = 8$, $D_c = 2.94$ Mg m⁻³, $\mu(Mo K\alpha) = 17.7$ mm⁻¹. The structure was refined to an R of 0.064 for 2502 unique observed diffractometer data. The three Os atoms lie at the vertices of a triangle; two of these atoms are each coordinated to three terminal carbonyls and the other is coordinated to four. The styryl ligand σ -coordinates to one Os atom and π -coordinates to another, asymmetrically bridging the shortest Os—Os bond. The distribution of the carbonyl ligands indicates that the hydride bridges the same short edge.

Introduction. The complex $Os_3(CO)_{10}(NCCH_3)_2$ has been shown to be an important, reactive starting material in many reactions of small organic molecules with trinuclear Os clusters (Tachikawa & Shapley, 1977; Johnson, Lewis & Pippard, 1981). The aceto-

nitrile ligands are easily displaced by other groups. A recent publication has reported the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with amides and aldehydes (Johnson, Lewis, Odiaka & Raithby, 1981). In a continuation of this series of reactions of $Os_3(CO)_{10}(NCCH_3)_2$, the complex has been treated with styrene. Here we report the structure of a product from this reaction.

The title compound was prepared by reacting excess styrene with $Os_3(CO)_{10}(NCCH_3)_2$ in refluxing cyclohexane for 30 min (Goudsmit, 1981). The product was purified by thin-layer chromatography. The molecular geometry could not be unambiguously determined by spectroscopic techniques and a single-crystal X-ray analysis was undertaken. Recrystallization from cyclohexane yielded orange, rectangular blocks. 4471 intensities were recorded ($7 < 2\theta < 50^\circ$) on a Stoe four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, using ω scans, and a