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Structure of Iodobis(1-pyrrolidinecarbodithioato)antimony(III), [SbI(C₅H₈NS₂)₂]

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Abstract. $M_r = 541.5$, triclinic, $P\bar{1}$, $a = 5.993$ (1), $b = 16.981$ (6), $c = 8.595$ (2) Å, $\alpha = 93.55$ (3), $\beta = 100.16$ (2), $\gamma = 99.44$ (2)°, $V = 845.6$ (4) Å³, $Z = 2$, $D_x = 2.13$, $D_m = 2.14$ (2) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.9$ mm⁻¹, $F(000) = 516$, $T = 295$ K, $R = 0.056$ for 1985 observed reflections. The complex consists of an infinite polymeric chain of Sb[S₂CN(CH₂)₄]₂ units linked by iodine bridges. Antimony and iodine alternate along the a axis. Besides two I atoms at 3.523 (1) and 3.365 (1) Å, the Sb atom is coordinated by four S atoms at 2.502 (3)–2.697 (4) Å forming a distorted polyhedron of an irregular geometrical shape.

Introduction. Complexes of dithiocarbamates (dtc's) with many different central metal ions have been extensively studied. However, only a limited amount of information on the bonding and structural properties is available for non-transition-metal complexes, especially for the $M(\text{dtc})_2X$ type with the central atoms as As, Sb or Bi. Although a significant number of $M(\text{dtc})_2X$

complexes have been prepared recently (Manoussakis, Tsipis & Hadjikostas, 1975; Tsipis & Manoussakis, 1976; Preti, Tosi & Zannini, 1979), to date only a few crystal structures of mixed-ligand halide dithiocarbamate complexes have been investigated. For antimony analogues the structures of |Sb(S₂CNn-Bu₂)₂|Cd₂I₆| (van de Leemput, Cras & Willemse, 1977), [SbI(S₂CNEt₂)₂].CHCl₃ and |SbI(S₂CNEt₂)₂]-(0.5I₂)$_x$, $x \leq 1$ (McKie, Raston, Rowbottom & White, 1981) have been determined. The type of structure in the Et₂dtc analogues is a polymeric chain of the form –Sb(S₂CNEt₂)₂–I–Sb(S₂CNEt₂)₂–; unlike the n-Bu₂dtc analogue, the description of the crystal structure has been made without consideration of the Sb···I contacts. The type of amine group ($-NR_2$) in the complexes mentioned above was ($-NEt_2$) or ($-NBu_2$), whereas a cyclic amine [$-N(CH_2)_4$] has been used in the present work.

Experimental. Air-stable dark-orange needle-like crystals prepared as described previously for bromo

derivatives (Manoussakis *et al.*, 1975) by slow evaporation from $CH_2Cl_2-C_6H_6$ solution. (Found: C, 21·88; H, 2·94; N, 5·15%. Calc.: C, 22·19; H, 2·98; N, 5·17%.) Crystal dimensions 0·3 × 0·15 × 0·1 mm. Density measured by flotation ($CHBr_3-CH_3OH$). The approximate values of the lattice parameters, calculated from rotation and Weissenberg patterns, were refined on a Syntex $P2_1$ four-circle diffractometer on the basis of ten precisely centred reflections using Mo $K\alpha$ radiation. Intensities collected in range $0 < 2\theta < 50°$, $h \pm 7$, $k\,0\rightarrow20$, $l\pm10$, 2993 independent reflections, 1985 with $I \geq 1·96\sigma(I)$ considered as observed and used in structure solution. Two standard reflections, 2·9% intensity variation. All intensities corrected for Lorentz, polarization and absorption effects; empirical absorption corrections (ψ scans) applied (min. transmission factor 0·69, taking max. transmission as unity). Structure solved by heavy-atom method; positions of Sb and I atoms found from three-dimensional Patterson function, positions of other non-H atoms from Fourier maps. Structure refined to $R = 0·056$, $wR = 0·058$ using diagonal-matrix least squares, minimizing function $M = \sum w(|F_o| - |F_c|)^2$ with the Hughes (1941) weighting scheme ($\sqrt{w} = |F_o|/a$ if $|F_o| < a$ or $\sqrt{w} = a/|F_o|$ if $|F_o| \geq a$, where $a = 40$). The choice of the correct weighting scheme in the minimized function was confirmed by nearly symmetrical distribution of the values of the M function through $\sin\theta/\lambda$ and $|F_o|$ intervals. In final cycle shifts of all positional parameters $< 0·1\sigma$, those of thermal parameters $< 0·2\sigma$. Max. height in final difference Fourier synthesis 1·34 e Å^{-3} located near Sb atom. In addition, some other maxima corresponded to the H-atom positions as calculated assuming sp^3 hybridization of the C atoms of the tetramethylene ring and C—H bond distances of 1·09 Å. Positions of H atoms not refined, nor involved in F_c calculations. 1985 reflections in final least-squares cycle, 163 parameters; scattering factors from *International Tables for X-ray Crystallography* (1968). All calculations carried out on a Siemens 4000/150 computer using a system of *NRC* crystallographic programs (Ahmed, Hall, Pippy & Huber, 1966).

Discussion. The final positional and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.*

The structure projection along **b** is in Fig. 1.

The dithiocarbamate ion acts as a bidentate ligand in the same way as observed in many crystal structures of

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Table 1. *Final atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters defined as $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$*

|	x	y	z	$B_{eq}(Å^2)$
Sb(1)	9794 (1)	7556 (1)	8646 (1)	2·97
I(1)	4909 (1)	7162 (1)	10423 (1)	3·91
S(1)	7335 (5)	8492 (2)	7344 (4)	3·32
S(2)	7034 (6)	6388 (2)	6655 (4)	3·98
S(3)	11467 (5)	7317 (2)	6227 (4)	3·17
S(4)	12244 (5)	9052 (2)	8837 (4)	3·30
C(1)	9673 (20)	9261 (8)	7858 (13)	2·97
C(2)	9156 (19)	6564 (8)	5542 (15)	3·02
C(3)	11340 (22)	10709 (8)	7783 (16)	3·40
C(4)	7119 (24)	5461 (9)	3454 (18)	4·55
C(5)	10316 (29)	11319 (10)	6770 (22)	5·84
C(6)	7829 (35)	5161 (13)	1990 (25)	7·27
C(7)	7832 (31)	11079 (10)	6566 (25)	6·25
C(8)	10081 (33)	5564 (11)	1901 (21)	6·87
C(9)	7227 (23)	10186 (8)	6604 (18)	3·91
C(10)	10798 (25)	6280 (9)	3158 (17)	4·19
N(1)	9456 (16)	9986 (6)	7470 (12)	2·92
N(2)	9034 (17)	6135 (6)	4175 (12)	3·13
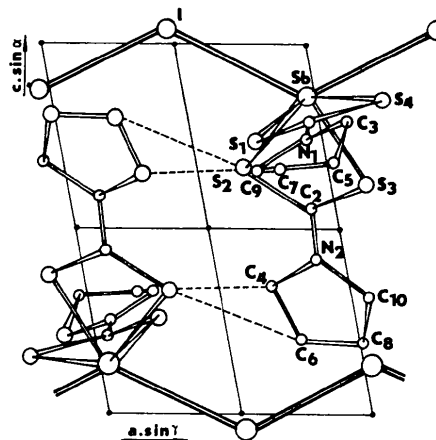
Fig. 1. A projection of the structure onto the (010) plane.

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transition- and non-transition-metal complexes. Sb coordinates four S atoms, where two of the Sb—S distances are slightly longer [Sb—S(2) 2·665 (4), Sb—S(4) 2·697 (4) Å] than the others [Sb—S(1) 2·521 (3) and Sb—S(3) 2·502 (3) Å] (Table 2). Differences in the bond distances within the SbS$_4$ polyhedron are not as remarkable as those observed in the triscomplexes M(dtc)$_3$ where M = As, Sb or Bi (Raston & White, 1975, 1976). Nevertheless, the SbS$_4$ core does not approach well-defined geometry. The localization of any stereochemically active lone pair is not obvious, though the lone pair should exist between the two I atoms. From the projection of the structure in Fig. 1 it is clear that approximately only one half of the Sb environment is occupied by the coordinated dtc ligands, whereas the second part of the Sb environment remains unoccupied. It is obvious that the lone pair could be directed to the opposite side with respect to the dtc ligands where it bisects the I$\cdots$Sb$\cdots$I angle within the

Table 2. *Selected distances* (Å) *and angles* (°) *with e.s.d.'s*

(a) The coordination polyhedron

Sb–I	3·523 (1)	S(1)–Sb–S(4)	69·2 (1)
Sb–I^i	3·365 (1)	S(2)–Sb–S(3)	69·7 (1)
Sb–S(1)	2·521 (3)	Sb–S(1)–C(1)	88·7 (4)
Sb–S(2)	2·665 (4)	Sb–S(4)–C(1)	83·2 (4)
Sb–S(3)	2·502 (3)	Sb–S(2)–C(2)	83·2 (4)
Sb–S(4)	2·697 (4)	Sb–S(3)–C(2)	88·5 (4)
S(1)···S(4)	2·967 (5)		
S(2)···S(3)	2·954 (5)		

Symmetry code: (i) 1+x, y, z.

(b) The dithiocarbamate ligands

S(1)–C(1)	1·72 (1)	S(1)–C(1)–S(4)	118·8 (7)
S(4)–C(1)	1·72 (1)	S(2)–C(2)–S(3)	118·6 (7)
S(2)–C(2)	1·72 (1)	S(1)–C(1)–N(1)	119·3 (9)
S(3)–C(2)	1·71 (1)	S(4)–C(1)–N(1)	121·9 (9)
C(1)–N(1)	1·32 (2)	S(2)–C(2)–N(2)	121·7 (9)
C(2)–N(2)	1·33 (2)	S(3)–C(2)–N(2)	119·7 (9)
N(1)–C(3)	1·50 (2)	C(1)–N(1)–C(3)	125·6 (10)
N(1)–C(9)	1·51 (2)	C(1)–N(1)–C(9)	123·1 (10)
N(2)–C(4)	1·50 (2)	C(2)–N(2)–C(4)	124·9 (10)
N(2)–C(10)	1·49 (2)	C(2)–N(2)–C(10)	123·4 (10)
C(3)–C(5)	1·53 (2)	N(1)–C(3)–C(5)	103 (1)
C(5)–C(7)	1·45 (3)	N(1)–C(9)–C(7)	102 (1)
C(7)–C(9)	1·50 (2)	N(2)–C(4)–C(6)	104 (1)
C(4)–C(6)	1·49 (3)	N(2)–C(10)–C(8)	103 (1)
C(6)–C(8)	1·43 (3)	C(3)–C(5)–C(7)	106 (1)
C(8)–C(10)	1·53 (2)	C(5)–C(7)–C(9)	110 (2)
		C(4)–C(6)–C(8)	110 (2)
		C(6)–C(8)–C(10)	109 (2)

chain. From ^{121}Sb Mössbauer spectroscopic studies of analogues of trigonal-bipyramidal Sb(dtc) complexes (Stevens & Trooster, 1979) it is known that in these complexes the stereochemical lone pair is in an axial or equatorial position. The I atoms, which bridge the Sb[S₂CN(CH₂)₄]₂ units, lie out of the SbS₄ side, as observed in the crystal structure of Sb(Et₂dtc)₂I.CHCl₃ (McKie *et al.*, 1981). The distances Sb–I 3·365 (1), 3·523 (1) Å are shorter than the sum of the van der Waals radii: 2·2 Å for Sb and 2·15 Å for I (Pauling,

1967). The dithiocarbamate-ligand geometry is very similar to that in other dtc complexes whose crystal structures have been solved. The C≐S bond lengths are in the range 1·71 (1) to 1·72 (1) Å and bond lengths of 1·32 (2) and 1·33 (2) Å confirmed double character of the C≐N bond. These parameters are generally a good approximation to the parameters in other dtc complexes. The high degree of π-conjugation in the S₂CNC₂ ligand fragments is reflected in the good planarity of these fragments. The Sb atom lies 0·019 (1) and 0·089 (1) Å out of the S₂CNC₂ ligand planes. The shortest intermolecular distances are between the S(2), C(4) and C(6) atoms and indicate the presence of weak S···C bonds probably through the H atoms of the corresponding C atoms.

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Sodium *trans*-Bis(1,2-ethanediamine)disulfitorhodate(III) Trihydrate, Na[Rh(C₂H₈N₂)₂(SO₃)₂].3H₂O

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Abstract. $M_r = 460·26$, monoclinic, $P2_1/a$, $a = 13·730$ (3), $b = 13·660$ (3), $c = 8·495$ (5) Å, $\beta = 106·74$ (3)°, $V = 1526$ (1) Å³, $Z = 4$, $D_m = 1·98$, $D_x = 2·00$ Mg m⁻³, λ(Ag Kα) = 0·55830 Å, $\mu = 0·746$ mm⁻¹, $F(000) = 936$, $T = 298$ K, $R = 0·067$, $wR = 0·067$ for 3366 independent non-zero reflections.

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