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Structure of Tris(2-pyridinethiolato)antimony(III) (TPTA), [Sb(C_5H_4NS)$_3$]

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Abstract. $M_r = 452{\cdot}2$, rhombohedral, $R\bar{3}c$, $a = 12{\cdot}568$ (1), $c = 37{\cdot}909$ (8) Å, $V = 5185{\cdot}6$ Å^3, $Z = 12$, $D_x = 1{\cdot}74$, $D_m = 1{\cdot}73$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}12$ mm^{-1}, $F(000) = 2664$, room temperature. Final $R = 0{\cdot}029$ for 710 unique non-zero reflections. Each molecule consists of three planar 2-pyridinethiol ligands surrounding an Sb atom in C_3 symmetry. A gap in the Sb coordination can be attributed to a stereochemically active lone pair of electrons and the proximity of the rotation-equivalent molecule. Since the distance Sb—Sb′ = 3·657 (1) Å between the two molecules is less than the sum of the van der Waals radii, a weak intermolecular interaction is very likely.

Introduction. The monothio complexation behaviour of Sb^{III} has so far received comparatively little attention. Furthermore the investigation of the coordination behaviour of 2-pyridinethiol compounds is interesting due to the important role of the thione–thiol equilibrium in biological systems. Hence the interest in the crystal and molecular structure of the title compound (TPTA hereafter).

Experimental. Compound and its crystals prepared by one of us (PK), D_m measured by flotation in tetrachloroethylene/1,3-dibromobutane, m.p. 466 K, measured crystal with almost parallelepiped form, dimensions 0·20 × 0·12 × 0·15 mm, Philips PW 1100 computer-controlled four-circle single-crystal diffractometer, lattice parameters from θ values of 35 strong reflections, $R\bar{3}c$ from systematic absences, graphite-monochromated Mo $K\alpha$, θ–2θ mode, three standard reflections without significant intensity variation, 5990 reflections measured, $2\theta_{\max} = 50°$, index range h: 0→14, k: −7→0, l: −40→40, 1006 unique reflections, $R_{\rm int} = 0{\cdot}064$, 710 observed with $I > 2\sigma(I)$, no absorption correction, direct methods with *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977), six non-H atoms located on E map, remainder from Fourier synthesis, full-matrix least-squares refinement on F, H atoms located on a ΔF map, atomic coordinates for all atoms, $U_{\rm iso}$ for H and U_{ij} for non-H atoms refined, $R = 0{\cdot}029$, $R_w = 0{\cdot}023$, $S = 1{\cdot}446$, $W = (F_o/A)^2$ for $F_o < A$, else $W = (A/F_o)^2$, $A = 200$, $(\Delta/\sigma)_{\max}$ 0·63, $(\Delta/\sigma)_{\rm average}$ 0·17, max. and min. height in final difference Fourier synthesis 0·70 and −0·55 e Å^{-3}, atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), computer programs used: *DATRED* (Main, 1970), *MULTAN*77 (Main *et al.*, 1977) and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. The final positional parameters and isotropic temperature coefficients are given in Table 1.* Interatomic distances and angles are in Table 2. A clinographic projection of the TPTA molecule is shown in Fig. 1. The metal atom is surrounded by three S and three N atoms; there is a large gap in its coordination sphere due to the existence of a stereochemically active lone pair. As in the case of tris(1-pyrrolidinecarbodithioato)Sb^{III} (Kavounis, Kokkou, Rentzeperis & Karagiannidis, 1980) the molecule is closely approached by its rotation equivalent (*cf.* Fig. 2) and the two Sb atoms have their lone pairs facing each other. The two molecules form again a sort of a double molecule, which may be considered as the repeating unit in the crystal. The distance Sb—Sb′ = 3·657 (1) Å is less than the sum, 4·00 Å, of the corresponding van der Waals radii (Bondi, 1964), so that a weak intermolecular interaction takes place. Since the Sb atom lies on a threefold axis, with its lone pair oriented along it and the three equivalent planar 2-pyridinethiol ligands arranged around it, the TPTA molecules have C_3 symmetry.

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* Lists of structure factors, anisotropic thermal parameters of the non-H atoms, C—H bond lengths and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39240 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and isotropic temperature factors* (Å^2)

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

	x	y	z	B_{eq}/B_{iso}*
Sb	0·00000	0·00000	0·20176 (1)	3·4
S	0·1739 (1)	0·0314 (1)	0·16410 (4)	4·4
N	0·1390 (5)	−0·1140 (5)	0·2185 (1)	3·8
C(1)	0·2179 (5)	−0·0512 (4)	0·1923 (1)	3·3
C(2)	0·1738 (8)	−0·1732 (7)	0·2412 (1)	4·4
C(3)	0·2794 (7)	−0·1779 (6)	0·2380 (2)	6·2
C(4)	0·3575 (6)	−0·1149 (7)	0·2103 (2)	6·3
C(5)	0·3258 (6)	−0·0515 (6)	0·1871 (2)	4·6
H(C2)	0·117 (4)	−0·215 (4)	0·259 (1)	1·8 (1·2)
H(C3)	0·298 (5)	−0·219 (5)	0·253 (1)	2·9 (1·5)
H(C4)	0·434 (7)	−0·111 (6)	0·208 (2)	6·2 (1·9)
H(C5)	0·384 (5)	0·002 (5)	0·170 (1)	3·1 (1·4)

* $B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{\mathbf{U}}$ for non-H atoms.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Sb–S	2·472 (2)	Sb–S–C(1)	93·9 (2)
S–C(1)	1·760 (7)	S–C(1)–N	115·9 (5)
		S–C(1)–C(5)	121·1 (4)
C(1)–N	1·34 (1)	N–C(1)–C(5)	122·9 (6)
N–C(2)	1·35 (1)	C(1)–N–C(2)	116·7 (7)
C(2)–C(3)	1·36 (1)	N–C(2)–C(3)	124·0 (6)
C(3)–C(4)	1·38 (1)	C(2)–C(3)–C(4)	118·0 (8)
C(4)–C(5)	1·37 (1)	C(3)–C(4)–C(5)	119·3 (8)
C(5)–C(1)	1·37 (1)	C(4)–C(5)–C(1)	118·9 (6)
Sb···N	2·830 (7)	Sb···N–C(1)	89·9 (4)
		Sb···N–C(2)	151·2 (5)
		N···Sb–S	59·3 (1)

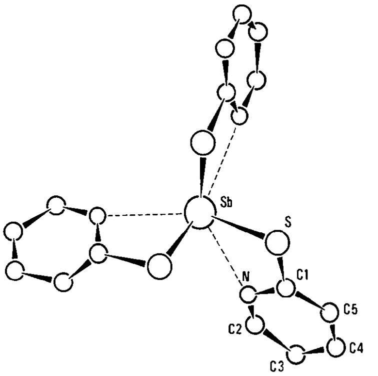

Fig. 1. Clinographic projection of the TPTA molecule.

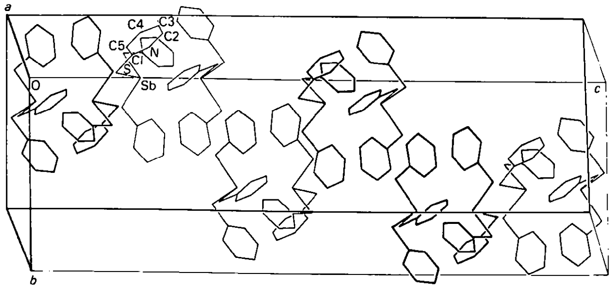

Fig. 2. Clinographic projection of the molecular packing in the unit cell.

The three Sb–S bonds, at 90·0 (1)° to one another, are 2·472 (2) Å in length, somewhat shorter than 2·52 Å, the corresponding Sb–S distance in antimony(III) xanthate (AX hereafter) (Gottardi, 1961), and 2·55 Å, the average Sb–S distance in antimony(III) tris(diphenyldithiophosphinate) (ATPP hereafter) (Begley, Sowerby & Haiduc, 1980). It compares well, however, with the mean Sb–S distance of 2·469 Å in antimony(III) tris(thioacetate) (AA hereafter) (Hall & Sowerby, 1980).

The three equivalent Sb–N intramolecular distances, 2·830 (7) Å, are longer than the length of a normal Sb–N single bond, *e.g.* 2·53–2·64 Å in the 1:1 adduct $SbCl_3.(C_6H_5)_2NH$ (Lipka, 1980), but are considerably shorter than the sum, 3·58 Å, of the corresponding van der Waals radii (Bondi, 1964). Careful examination of the difference Fourier map did not show the presence of H in the neighbourhood of the N atom. This is confirmed by the IR spectrum which, compared with that of the free mercaptopyridine, shows the absence of $\bar{\nu}$(NH) at 3160 cm^{-1} and the presence of two new bands, namely $\bar{\nu}$(SbN) at 630 cm^{-1} and $\bar{\nu}$(SbS) at 390 cm^{-1}. The mass spectrum shows main peaks at masses 451 $Sb(SC_5H_4N)_3$, 231 $Sb(SC_5H_4N)$, 199 $Sb(C_5H_4N)$ and 153 (SbS). All these observations lead to the conclusion that there are no N–H···Sb bridging bonds in TPTA, but rather partial single Sb–N bonds. This type of bonding, often referred to as secondary bonding, occurs also in the compounds AX, ATPP and AA mentioned above and it has been shown to be important in the structures of some other Sb complexes (Hall & Sowerby, 1980, and literature cited therein).

The Sb atom, between planes of S and N atoms, occupies the common apex of two trigonal pyramids whose bases, formed by the S and the N atoms respectively, are rotated with respect to each other. The distance of Sb from the plane of the N atoms is 0·633 (1) Å.

The S–C bond distances, 1·760 (7) Å, are longer than those in AX, but compare well with those in AA. The Sb–S–C bond angles, 93·9 (2)°, are a little greater than the corresponding ones in both the above compounds.

The mean C–C and C–N distances in the pyridine ring are 1·37 (1) and 1·35 (1) Å. These values and the corresponding bond angles are in good agreement with the values found in most pyridine compounds (Kokkou, Fortier, Rentzeperis & Karagiannidis, 1983, and literature cited therein).

A projection of the structure showing the molecular packing of TPTA in the unit cell is shown in Fig. 2.

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The Low-Temperature X-ray Diffraction Study of Bis[diisopropyl(phenyl)phosphine]-hexahydridoosmium, $[Os(C_{12}H_{19}P)_2H_6]$

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Abstract. $M_r = 584{\cdot}8$, monoclinic, $P2_1/n$, $a = 17{\cdot}196\,(5)$, $b = 13{\cdot}799\,(5)$, $c = 10{\cdot}969\,(4)$ Å, $\beta = 98{\cdot}31\,(3)°$, $U = 2575\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}48$ g cm^{-3} [$U = 2632\,(1)$ Å^3, 292 K], $D_x = 1{\cdot}49$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 50{\cdot}9$ cm^{-1}, $F(000) = 1176$, 200 K, $R(R_w) = 0{\cdot}034$ (0·032) for 5696 reflections. The Os—P bond lengths are 2·340 (1) and 2·347 (1) Å and the P—Os—P bond angle is 156·2 (1)°. Crystallographic evidence was obtained for only three of the six hydride ligands. The positions of the five located atoms bound to osmium are consistent with a triangular dodecahedral coordination geometry. The structure is compared with those of other eight-coordinate polyhydride complexes.

Introduction. Polyhydridophosphine complexes of the elements towards the centre of the second and third transition series have recently been the subject of renewed interest in terms of their synthesis (Chaudret, Commenges & Poilblanc, 1982; Crabtree & Hlatky, 1982; Green, Huffman & Caulton, 1983), structure (Howard, Mead & Spencer, 1983; Chaudret, Devillers & Poilblanc, 1983; Gregson, Howard, Nicholls, Spencer & Turner, 1980) and because they have been shown to be active in the cleavage of carbon–hydrogen bonds (Baudry, Ephritikhine & Felkin, 1980, 1982).

Douglas & Shaw (1970) reported the first osmium hexahydride, $[OsH_6(PMe_2Ph)_2]$, as a pale yellow oil. Recent work on the polyhydrides of tungsten and rhenium (Howard, Gregson, Spencer & Turner, 1981; Gregson, Howard, Nicholls, Spencer & Turner, 1980) suggested that the ligand diisopropyl(phenyl)phosphine afforded polyhydride complexes of improved stability and crystallinity. This proved to be the case with osmium also and $[OsH_6(PPhPr^i_2)_2]$ was synthesized in good yield (Connelly, Howard, Spencer & Woodley, 1984) as colourless crystals. Previous structural work on eight-coordinate polyhydrides has revealed the prevalence of the triangular dodecahedral coordination geometry. However, the structural preferences of $ML_6L'_2$ are not well established (Kepert, 1982). For this reason, $[OsH_6(PPhPr^i_2)_2]$ represents an interesting extension to the series of polyhydride complexes we have previously characterized by X-ray and neutron diffraction. It is also a key starting material in our investigation of osmium hydride chemistry and we therefore undertook the low-temperature X-ray structure determination.

Experimental. $[OsH_6(PPhPr^i_2)_2]$ prepared as described by Connelly, Howard, Spencer & Woodley (1984), crystals suitable for X-ray diffraction grown by slow cooling of a saturated solution in petroleum ether (b.p. 313–333 K), D_m by flotation in aqueous thallous formate. A room-temperature single-crystal X-ray investigation preceded the low-temperature study, but only the results of the latter are presented here. No phase changes were observed between 293 and 200 K, the temperature at which the diffracted intensities were recorded using a Nicolet *P3m* four-circle automated diffractometer. Measurement parameters are given in Table 1. Structure solved by Patterson and Fourier

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