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Crystal Structure of Antimony(III) Monothiobenzoate, $Sb(PhCOS)_3$

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The title compound crystallizes rhombohedrally in the space group R3 *with* a = *20.453(11) and* c = *4.197(1)* Å *(hexagonal setting). The structure was refined by full matrix least squares with 585 independent reflections to* R *equal 0.042 (*R_w = *0.040). Antimony, situated on the threefold axis, is pyramidally coordinated at 2.493(3)* Å *to the sulfur atoms of three ligands. Secondary bonding occurs at 2.802(8)* Å *to the oxygen atoms of the asymmetrically chelating ligands.*

Introduction

This structure was examined as part of a systematic study of the stereochemistry of antimony(III) in SbO_xF_y and SbO_xS_y coordination [1–3]. Previous studies have established that the $5s^2$ lone pair of antimony(III) is stereochemically active and that antimony(III) forms in $M^I(SbF)PO_4 \cdot H_2O$ (M^I = Na, NH_4) five primary (single bonds) and no secondary bond [2], in $K(SbF_2)PO_4$ four primary and one secondary bond [1], and in antimony(III) trismonothiophosphinates $Sb(R_2POS)_3$ (R = cyclo-C_6H_{11}, C_6H_5) three primary bonds and 3 to 4 secondary bonds [3]. For secondary bonds the atom separations are longer than those usually occurring in single bonds but are still considerably smaller than the sum of the appropriate van der Waals' radii.

In the $Sb(R_2POS)_3$ compounds the anisobidentate monothiophosphinate ligands coordinate through short (primary) Sb–O bonds with a mean length of 2.03 Å. The Sb–S distances (secondary bonds) vary between 3.00 and 3.20 Å with one exception. In antimony(III)trismonothioacetate, $Sb(CH_3COS)_3$, primary bonding is to three sulfur atoms of the anisobidentate monothioacetate ligand (mean Sb–S 2.47 Å). Three secondary intramolecular bonds are formed to oxygen (range 2.745 to 2.918 Å) and one intermolecular bond (3.043 Å), leading to polymeric chains in the solid [4]. The monothiobenzoate ligand is electronically and sterically different from the monothioacetate ligand. The present structural study was therefore undertaken to elucidate any differences or similarities between SbL_3 complexes with L = R_2POS^-, CH_3COS^- and $PhCOS^-$. $Sb(PhCOS)_3$ has been already mentioned in the literature, but has not yet been characterized structurally [5, 6]. The thiobenzoate ligand can act as a chelate, also coordinated through sulfur only, even in a bridging manner to soft metal centers like Ag(I), Zn(II) and Re(I) [7–9], or coordinate bidentate bridging through sulfur and oxygen as in $[Ni(PhCOS)_2]_2EtOH$ [10, 11].

Discussion

$Sb(PhCOS)_3$ possesses a crystallographically-imposed threefold symmetry. The thiobenzoate ligand is coordinated through sulfur. The Sb–S distance is 2.493(3) Å. The angles between these primary bonds are 91.1°. Secondary bonding with a Sb–O distance of 2.802(8) Å occurs through the oxygen atoms of the ligands, which act as unsymmetrical chelates. The angles between these bonds are 120.0(2)°. Therefore, the Sb atom and the three oxygen atoms are nearly coplanar (see Fig. 1). Similar distances of primary and secondary bonding has been found in $Sb(CH_3COS)_3$, but here the coordination polyhedron is less symmetrical because one of the ligands, in addition to behaving as a chelate, bridges between the molecules leading to a polymeric chain in the solid. In $Sb(PhCOS)_3$ polymerization occurs along the *c* axis of the unit cell through 3 very weak bonds of 3.463(3) Å length. This distance is slightly shorter than the sum of the van der Waals radii of Sb(III) and sulfur. The phenyl rings are tilted by 63.5° with respect to the COS plane. Conjugation between the COS moiety and the phenyl group seems then not to be possible.

The characteristic vibrational frequencies of $Sb(PhCOS)_3$ – ν_{CO} at 1590 and 1575, $\nu_{phenyl-C}$ at 1210 and ν_{CS} at 920 cm^{-1} – fit nicely in the pattern

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TABLE I. Fractional Coordinates and Anisotropic Thermal Parameters of $Sb(PhCOS)_3$.

Atom	$x\cdot10^4$	$y\cdot10^4$	$z\cdot10^4$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sb	0	0	0	0.87(3)	0.87(1)	1.17(6)	0.44(1)	0	0
S	0017(1)	1014(1)	3361(7)	1.3(2)	1.1(2)	2.1(2)	0.68(7)	0.1(1)	–0.1(1)
O(1)	1229(5)	1477(4)	–0073(20)	2.1(4)	1.8(5)	2.4(5)	0.9(3)	0.5(4)	0.1(4)
C(1)	0916(6)	1683(6)	1856(30)	1.5(5)	1.2(6)	1.6(6)	0.8(3)	0.1(5)	–0.1(5)
C(2)	1237(7)	2446(6)	2927(32)	0.4(6)	1.6(7)	2.5(8)	1.0(4)	–0.7(5)	–0.5(5)
C(3)	0815(8)	2696(8)	4723(37)	1.9(7)	1.8(9)	2.2(8)	–0.6(5)	–1.0(5)	–0.2(5)
C(4)	1194(8)	3493(9)	5618(44)	2.4(4)	2.4(9)	2.7(9)	0.7(5)	0.3(7)	–0.1(6)
C(5)	1915(8)	3972(8)	4782(39)	3.2(8)	0.5(9)	2.9(8)	0.3(5)	–0.6(7)	0.1(6)
C(6)	2342(9)	3746(7)	3038(36)	2.1(6)	0.9(8)	2.9(8)	0.4(4)	–1.1(6)	–0.8(6)
C(7)	2017(9)	2987(9)	2151(41)	2.5(7)	2.7(9)	2.9(9)	1.1(5)	–0.8(7)	0.1(7)

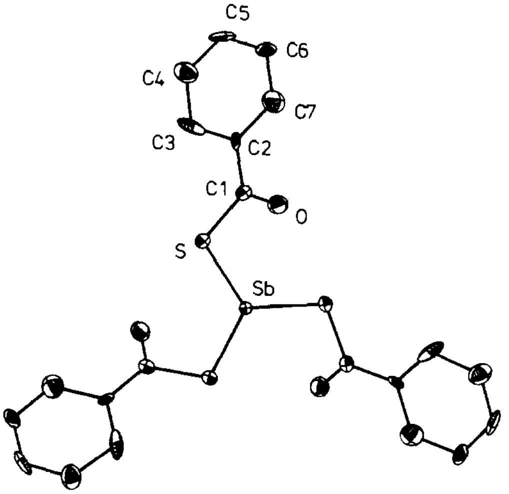

Fig. 1. Molecular structure and atomic numbering scheme for $Sb(PhCOS)_3$, viewing along the hexagonal c axis.

given by Savant, Gopalakrishnan and Patel in their study of several thiobenzoate complexes [7].

Comparison with Sb(III) thiophosphinates where the ligands are primarily coordinated through oxygen atoms shows that in the concept of 'hard' and 'soft' donors and acceptors, Sb(III) is lying on the borderline of 'soft' and 'hard' acceptors. Small differences in the electronic nature and geometrical structure between the ligands R_2POS^- and $RCOS^-$, both with O and S donor atoms, can then switch over the kind of coordination from Sb–S to Sb–O or *vice versa*. The different nature of the R_2POS^- and $RCOS^-$ ligands is also reflected in the structure of their parent acids. In the former, the acid hydrogen atom is bound to oxygen, in the latter to sulfur [12–14].

Experimental

Preparation of $Sb(PhCOS)_3$: A solution of 1.55 g PhCSOH in 40 ml CH_2Cl_2 was treated with 1.45 g $Sb(CH_3COO)_3$ dissolved in 40 ml CH_2Cl_2. The mixture was stirred for 1 h, after which the precipitate was filtered and dried. Recrystallization from CH_2Cl_2 gave 1.2 g (64%) needle-like white crystals. *Analysis*: C found 47.4 (calcd. 47.3%); H 2.8 (2.8); Sb 23.4 (23.6).

Crystal data: rhombohedral (obverse hexagonal setting used) a = 20.453(11), c = 4.197(1) Å, V = 1520.3 Å^3, space group $R3$, $Z = 3, D_c = 1.74$ g·cm^{-3}, μ = 16.8 cm^{-1} (MoK_α radiation). A crystal with dimensions 0.2 × 0.1 × 0.1 mm was used for data collection at room temperature on a Syntex $P2_1$ four-circle diffractometer, equipped with a graphite monochromator. 2164 reflections, up to 2θ = 50°

TABLE II. Bond Lengths (A) and Bond Angles (Deg.) for $Sb(PhCOS)_3$.

Sb–S	2.493(3)
Sb–O	2.802(8)
Sb–S'	3.463(3)
C(1)–S	1.77(2)
C(1)–O	1.23(2)
C(1)–C(2)	1.43(2)
C(2)–C(3)	1.42(3)
C(3)–C(4)	1.46(3)
C(4)–C(5)	1.34(3)
C(5)–C(6)	1.38(3)
C(6)–C(7)	1.40(2)
C(7)–C(2)	1.45(3)
S–Sb–S	91.1(1)
O–Sb–O	120.0(2)
O–Sb–S	58.5(2)
	73.9(2)
	144.9(2)
S'–Sb–S'	61.9(1)
C(1)–O–Sb	91.2(7)
C(1)–S–Sb	91.1(4)
O–C(1)–S	119.1(9)
O–C(1)–C(2)	123(2)
S–C(1)–C(2)	117.6(9)

were measured employing the $\theta/2\theta$ scan technique with variable scan speeds 1.6–29.3° min^{-1}. After averaging of symmetry-related data 585 reflections with $I > 1.96\sigma(I)$ were considered observed. The structure was solved by Patterson and Fourier methods and the positional and anisotropic thermals parameters of all non-hydrogen atoms refined by full matrix least squares to $R = 0.042$ ($R_w = 0.040$). The positions of some hydrogen atoms could be recognized in a final difference synthesis. For all computations the program system E-XTL was used. The final parameters are listed in Table I. Table II contains calculated bond lengths and angles.

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