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Bis(ethylxanthato)phenylantimony(III)

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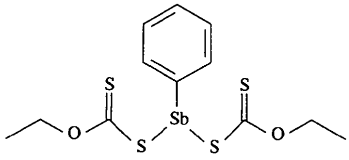
Abstract

The Sb atom in the title compound, bis(*O*-ethyl dithiocarbonato-*S*)phenylantimony(III), $[Sb(C_6H_5)(C_3H_5OS_2)_2]$, is in sixfold coordination to the C atom of the phenyl group [Sb—C 2.163 (3) Å] and five S atoms of three xanthate ligands. Of these, two S atoms form primary bonds [Sb—S 2.5377 (19) and 2.4987 (17) Å] and there are two intramolecular secondary bonds [Sb···S 3.1051 (15) and 2.9981 (16) Å], making the ligands asymmetrically chelating. The final contact is a weak intermolecular secondary bond [Sb···S 3.905 (2) Å]. The geometry thus described can best be considered as distorted pentagonal pyramidal, but if the antimony lone pair of electrons is stereochemically active, the arrangement becomes pseudo-pentagonal bipyramidal.

Comment

If only short primary bonds (Table 1) are considered, the basic structure of the title compound, (1), is trigonal pyramidal as would be expected for an AB_2E molecule. The two Sb—S separations [2.538 (2) and 2.499 (2) Å to the S1 and S3 atoms, respectively] (Fig. 1) are, however, slightly different and the S1—Sb—S3 angle [77.52 (6)°)] is unusually small. Angles subtended at antimony between sulfurs and the bonding carbon of the phenyl group are more normal with values of 95.89 (8) and 95.22 (8)°.



(1)

As with other dithio ligands of this type (Tiekink & Winter, 1992; Haiduc, Sowerby & Lu, 1995; Haiduc & Sowerby, 1995), there is the possibility of further ligand interaction as the formally non-bonded S atoms may also enter into coordination. If this occurs, ligands can become either bridging or chelating, with each mode leading to symmetric and asymmetric variants. A result of this added bonding will be an increase in the antimony coordination number and distortion of the pyramidal geometry.

Such interactions occur in compound (1), resulting in secondary Sb···S intramolecular separations of 3.1051 (15) and 2.9981 (16) Å to the S2 and S4 atoms, respectively, these being the S atoms which are formally doubly bonded to C atoms. It is also clear that there is the expected partial delocalization of the C=S double bond as the 'short' C—S separations (*ca* 1.65 Å) are slightly longer than double bonds (*ca* 1.62 Å), while the 'long' C—S bonds (*ca* 1.73 Å) are shorter than a conventional single bond (*ca* 1.81 Å). There is also the expected inverse correlation between Sb—S and C—S distances at a given S atom. If these interac-

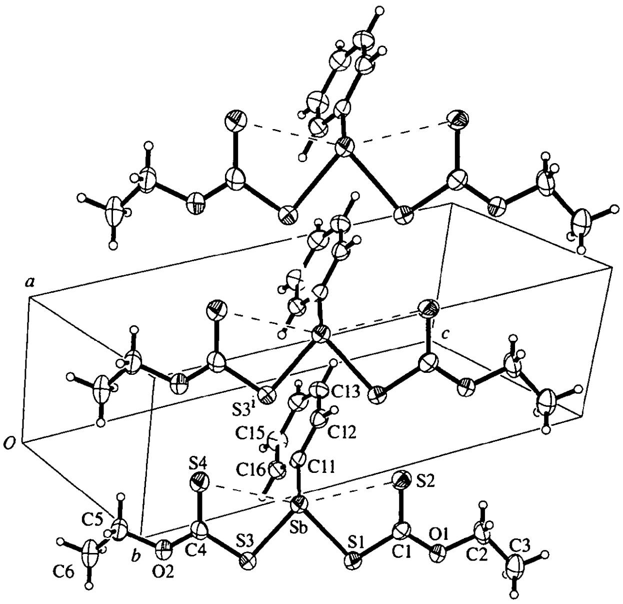


Fig. 1. A view of the structure of (1) with the atom-numbering scheme. Displacement ellipsoids enclose 70% probability surfaces and H atoms are shown as spheres of arbitrary radii. Dashed and dotted lines represent intra- and intermolecular Sb···S interactions, respectively. The latter link molecules into chains running parallel to the crystallographic *a* axis [symmetry code: (i) 1 + *x*, *y*, *z*].

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tions are taken into account, coordination about antimony is raised to five and the polyhedron can be described as distorted square pyramidal. The four S atoms are in fact coplanar to within 0.03 Å, with the Sb atom 0.174 (2) Å below this plane. The extent of distortion from square-pyramidal geometry is substantial; although angles between the apical C and basal S atoms range between 83.30 (8) and 95.89 (8)°, those between S atoms themselves vary from 62.67 (5) to 153.58 (3)°. Two of the smallest angles are between the S atoms of each short bite ligand. The angle between the two primary bonded S atoms is also small [77.52 (6)°], while that between the secondary bonded atoms is very wide [153.58 (3)°]. These angles are better understood if the weak intermolecular secondary interaction of 3.905 (3) Å between antimony and a symmetry-related $S3^i$ atom [symmetry code: (i) $1+x$, y, z] is taken into consideration. This atom lies in the plane of the four S atoms making angles of 63.92 (4) and 91.99 (5)° with the S4 and S2 atoms, respectively, so that the polyhedron is better described as pentagonal pyramidal. Finally, there is the problem of the antimony lone pair of electrons. If these electrons are stereochemically active, and the fact that the Sb atom lies below the plane of the basal S atoms goes some way to supporting this, the geometry could be considered to be pseudo-pentagonal bipyramidal.

Comparisons can be made with the following structures: $Sb(S_2COEt)_3$ (Gottardi, 1961; Hoskins, Tiekink & Winter, 1985), containing asymmetrically chelating ligands [Sb—S 2.511 (2) and 3.002 (3) Å] related by a threefold axis, but no short intermolecular contacts; $SbMe(S_2COEt)_2$ (Wieber, Wirth & Burschka, 1983), again containing asymmetrically chelating ligands [Sb—S 2.581 (2)/2.834 (2) and 2.617 (2)/2.904 (2) Å] and, as in (1), an intermolecular Sb···S contact [3.353 (2) Å], which raises the antimony coordination number to six and links the molecules into infinite chains; the dithiocarbamate $SbMe(S_2CNEt_2)_2$ (Wieber, Wirth, Metter & Burschka, 1985), which has a similar structure [Sb—S 2.554 (2)/2.960 (2) and 2.538 (2)/2.904 (2) Å], but the intermolecular contacts [Sb···S 3.847 (2) Å] are much weaker, giving loose dimers in the solid; and $SbPh[S_2P(O^iPr)_2]$ (Gupta, Rai, Mehrotra, Jain, Hopkins & Tiekink, 1985), which contains independent molecules and again asymmetrically chelating ligands [Sb—S 2.516 (3)/3.056 (2) and 2.529 (3)/3.067 (3) Å].

Experimental

Compound (1) was prepared by a variant of the method of Gupta, Jain, Rai & Mehrotra (1983) by refluxing a mixture of one equivalent of phenylantimony dichloride and two equivalents of potassium ethylxanthate in dichloromethane overnight. After filtering off the potassium chloride and evaporating the filtrate to dryness, the remaining solid was crystallized twice from a 4:1 mixture of petrol and chloroform (yield 95%, m.p. 365 K). Crystals suitable for X-ray investigation were obtained by slow diffusion of pentane into a saturated solution of the compound in chloroform in a closed system.

Crystal data

$[Sb(C_6H_5)(C_3H_5OS_2)_2]$
$M_r = 441.23$
Triclinic
$P\bar{1}$
$a = 5.795 (4)$ Å
$b = 9.059 (4)$ Å
$c = 16.081 (7)$ Å
$\alpha = 84.24 (4)°$
$\beta = 84.20 (4)°$
$\gamma = 77.85 (5)°$
$V = 818.3 (9)$ Å^3
$Z = 2$
$D_x = 1.791$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31 reflections
$\theta = 12–13°$
$\mu = 2.190$ mm^{-1}
$T = 150.0 (2)$ K
Plate
0.50 × 0.30 × 0.04 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.415$, $T_{max} = 0.636$
2879 measured reflections
2879 independent reflections

2679 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.07°$
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity variation: ±2.0%

Refinement

Refinement on F^2
$R(F) = 0.0190$
$wR(F^2) = 0.0417$
$S = 1.144$
2879 reflections
173 parameters
H atoms: riding model
$w = 1/[\sigma^2(F_o^2) + (0.013)^2 + 0.81P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL96*
Extinction coefficient: 0.0012 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sb—S1	2.5377 (19)	O1—C2	1.460 (3)
Sb—S2	3.1051 (15)	C2—C3	1.502 (4)
Sb—S3	2.4987 (17)	S3—C4	1.738 (3)
Sb—S4	2.9981 (16)	C4—O2	1.328 (3)
Sb—C11	2.163 (3)	C4—S4	1.648 (3)
S1—C1	1.731 (3)	O2—C5	1.462 (3)
C1—O1	1.330 (3)	C5—C6	1.496 (4)
C1—S2	1.648 (3)		
S1—Sb—S2	62.67 (5)	Sb—S4—C4	78.48 (10)
S1—Sb—S3	77.52 (6)	Sb—C11—C12	117.90 (18)
S1—Sb—S4	142.35 (4)	Sb—C11—C16	122.99 (19)
S2—Sb—S3	139.68 (3)	O1—C1—S2	125.5 (2)
S2—Sb—S4	153.58 (3)	O1—C1—S1	111.11 (19)
S3—Sb—S4	64.96 (5)	S2—C1—S1	123.37 (16)
S1—Sb—C11	95.89 (8)	C1—O1—C2	119.4 (2)
S2—Sb—C11	83.30 (8)	O1—C2—C3	106.2 (2)
S3—Sb—C11	95.22 (8)	O2—C4—S4	126.2 (2)
S4—Sb—C11	84.95 (8)	O2—C4—S3	110.4 (2)
Sb—S1—C1	95.52 (11)	S4—C4—S3	123.41 (16)
Sb—S2—C1	78.29 (10)	C4—O2—C5	119.6 (2)
Sb—S3—C4	93.08 (11)	O2—C5—C6	106.5 (2)

Data collection: *STADI4* (Stoe & Cie, 1995*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL96*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: MU1305). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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