Pentagonal Pyramidal Co-ordination; *X*-Ray Crystal Structure of Antimony(III) Tris(diphenyldithiophosphinate)

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Summary An *X*-ray crystal structure determination shows that asymmetrical co-ordination of the dithiophosphinate ligands in $Sb(S_2PPh_2)_3$ leads to an $:SbS_6$ system in which the sulphur atoms are co-ordinated to the antimony in distorted pentagonal pyramidal fashion.

COMPOUNDS with pentagonal pyramidal structures are rare among both main group and transition metal derivatives, the reasons being associated with (a) the high energy of this stereochemistry for AB_6 species and (b) the necessity of obtaining for an AB_6E species a pentagonal bipyramidal arrangement in which the lone pair, E, occupies one of the axial positions. One main group compound, the anionic antimony(III) oxalate, $Sb(C_2O_4)_3^{3-}$, has been described as a pentagonal pyramid; this species contains bidentate oxalate groups and belongs to the AB_6E class mentioned above.[1]

In the course of investigating the co-ordination of antimony(III) with other potentially 'short-bite' bidentate ligands, we have determined the crystal structure of the tris(diphenyldithiophosphinate), $Sb(S_2PPh_2)_3$, and the results indicate that this molecule is best described in terms of a distorted pentagonal pyramid. We note here that for species based on seven or more electron pairs, it is often possible to describe the structure, equally validly, as arising by distortion of more than one of the idealized geometries.[2]

Crystal data: triclinic, space group $P\bar{1}$, $a = 11{\cdot}321(3)$, $b = 9{\cdot}413(2)$, $c = 17{\cdot}933(4)$ Å, $\alpha = 100{\cdot}41(2)$, $\beta = 97{\cdot}60(2)$, $\gamma = 95{\cdot}80(2)°$. The structure was solved by

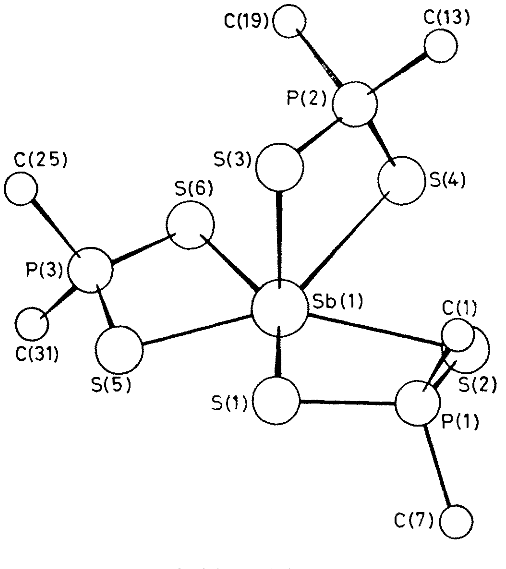

FIGURE. Structure of $Sb(S_2PPh_2)_3$ showing numbering of atoms; the phenyl groups have been omitted for clarity. Bond distances and angles in the $:SbS_6$ unit: Sb(1)–S(1), 2·591(1); Sb(1)–S(2), 2·978(1); Sb(1)–S(3), 2·456(1); Sb(1)–S(4), 3·187(1); Sb(1)–S(5), 2·598(1); Sb(1)–S(6), 2·923(1) Å; S(1)–Sb(1)–S(2), 72·34(3); S(1)–Sb(1)–S(3), 89·90(3); S(1)–Sb(1)–S(4), 138·53(3); S(1)–Sb(1)–S(5), 74·90(3); S(1)–Sb(1)–S(6), 147·57(3); S(2)–Sb(1)–S(3), 93·60(3); S(2)–Sb(1)–Sb(4), 71·81(2); S(2)–Sb(1)–S(5), 145·06(3); S(2)–Sb(1)–S(6), 140·09(3), S(3)–Sb(1)–S(4), 72·32(2); S(3)–Sb(1)–S(5), 98·18(3); S(3)–Sb(1)–S(6), 88·27(3); S(4)–Sb(1)–S(5), 141·13(2); S(4)–Sb(1)–S(6), 70·88(2); S(5)–Sb(1)–S(6), 73·34(3)°.

Patterson and Fourier methods using data for 5837 reflections, and has been refined with anisotropic thermal parameters by least-squares methods to a conventional *R* of 3·3%.† The structure consists of isolated molecules in which primary bonding is with one sulphur atom, S(1), S(3), and S(5), of each ligand (mean Sb–S, 2·55 Å), the angles between these bonds being 89·9, 74·9, and 98·2°. The antimony distances to the second sulphur atoms vary between 2·923 and 3·187 Å, distances well within the sum of the appropriate van der Waals radii (4·05 Å), and clearly representing substantial covalent interaction. The co-ordination number of the central atom is thus increased to seven, if the antimony lone pair is stereochemically active. The structure of the molecule is shown in the Figure.

A pentagonal pyramidal structure for this molecule is suggested for the following reasons. (a) In the primary bonding, the Sb(1)–S(3) distance, *i.e.* that to the apical atom, is substantially shorter than those to S(1) and S(5). (b) The angles at Sb(1) between S(3) and four of the five 'basal' sulphur atoms vary between 88·9 and 98·2° (mean, 92·5; ideal, 90·0°). The angle with the fifth 'basal' atom S(4) is 72·3° and is that between the two sulphur atoms in the same ligand. This is necessarily more acute but is identical with those in the other two ligands. (c) The angles between the atoms forming the base of the pyramid fall into two groups, 70·88—74·90 (mean, 72·7) and 138·53—147·57 (mean, 142·5°), compared with idealised angles of 72 and 144° respectively. (d) Deviations from the best plane through the six basal atoms are Sb(1) 0·05, S(1) −0·34, S(2) 0·40, S(4) −0·35, S(5) 0·06, and S(6) 0·17 Å. This puckering of the plane is expected because of the geometrical constraints imposed by a tris chelate structure and to minimize electrostatic repulsions between adjacent sulphur atoms. (e) There is a large volume of space in the antimony co-ordination sphere *trans* to S(3) which can accommodate the lone pair of electrons.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] M. D. Poore and D. R. Russell, *Chem. Comm.*, 1971, 18.
[2] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.