The Crystal Structure of Bismuth Diethyldithiophosphinate–Benzene (1/1), $Bi(S_2PEt_2)_3{\cdot}C_6H_6$†

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Crystals of $Bi(S_2PEt_2)_3{\cdot}C_6H_6$ are trigonal with a = 12.342(5) and c = 17.412(7) Å, space group $R3$. The structure has been solved by Patterson and Fourier methods for 906 independent reflections and refined by least squares to R 0.042. The bismuth atom, which lies on a three-fold axis, is surrounded by six sulphur atoms from three symmetrically chelating ligands, mean Bi–S 2.79 Å. The twist angle relating to the two sets of independent sulphur atoms is 34.7°, describing a co-ordination polyhedron lying almost midway between the octahedral and trigonal prismatic extremes. The bismuth lone pair of electrons is considered to be sterically inactive.

We have recently described the structures of a number of compounds in which a heavier Group 5 element is co-ordinated by three, substituted dithiophosphorus ligands. These show essentially trigonally distorted octahedral geometry about the central atom, as in $Sb[S_2P(OR)_2]_3$ where R = Me or Pr^{i};[1] the ethyl analogue also has this structure.[2] Antimony tris(diphenyldithiophosphinate), $Sb(S_2PPh_2)_3$, on the other hand, has a structure based on distorted pentagonal-pyramidal co-ordination[3,4] and, although the basic structural unit in the corresponding bismuth compound is very similar, the compound dimerises in the solid state *via* two Bi$\cdots$S intermolecular interactions giving effectively pentagonal-bipyramidal geometry about each bismuth atom.[4] This tendency for substituted dithiophosphorus ligands to stabilise different and sometimes unusual co-ordination polyhedra is well known[5] and, continuing investigations in this area, we have determined the structure of the related bismuth tris(diethyldithiophosphinate), $Bi(S_2PEt_2)_3$. Apart from $Bi(S_2PPh_2)_3$, the only other bismuth compounds with 'short bite' sulphur ligands for which detailed *X*-ray structures are available are $Bi[S_2P(OPr^i)_2]_3$,[6] $Bi(S_2COPr^i)_3$,[7] and $Bi(S_2CNEt_2)_3$;[8,9] a structure is also available for $Bi(SPPh_2NPPh_2S)_3$,[10] containing a different type of sulphur chelate.

Experimental

The compound was prepared as described previously[11] and crystals suitable for *X*-ray diffraction were obtained by slow recrystallisation from benzene.

Crystal Structure of $Bi(S_2PEt_2)_3{\cdot}C_6H_6$.—*Crystal data.* $C_{18}H_{36}BiP_3S_6$, M = 746.4, trigonal, a = 12.342(5), c = 17.412(7) Å, U = 2 297 Å^3, Z = 3, D_c = 1.62 g cm^{-3}, $F(000)$ = 1 104, space group $R3$ from systematic absences and subsequent refinement, Mo-K_α radiation, λ = 0.7107 Å, μ = 60.2 cm^{-1}, crystal size 0.15 × 0.15 × 0.20 mm.

Structure determination. Intensity data were collected on a Hilger and Watts four-circle diffractometer using a crystal sealed in a thin-walled Lindemann tube. Intensities for 906 independent reflections for which $I > 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Data reduction and subsequent calculations used the CRYSTALS programs;[12] scattering factors were for neutral atoms.[13] The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. As the asymmetric unit consists of one third of the formula unit, the bismuth atom must lie on a special position (0,0,0) with an occupation factor of $\frac{1}{3}$. The refinement converged at R 0.072 with isotropic and R 0.042 with anisotropic thermal parameters. The hydrogen atoms were included at their calculated positions, d(C–H) = 1.0 Å, but not refined, in the final cycles of refinement. A final difference Fourier synthesis showed, except close to the heavy atoms, no peak with a height > 0.4 e Å^{-3}. Table 1 contains the final refined atomic co-ordinates.

Table 1. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Bi(1)	0	0	0
S(1)	−0.065 1(6)	−0.213 8(5)	−0.087 6(3)
P(1)	−0.001 0(6)	−0.272 8(5)	−0.001 3(3)
S(2)	0.065 4(6)	−0.147 8(5)	0.086 9(3)
C(1)	−0.124(4)	−0.420(3)	0.033(2)
C(2)	−0.234(4)	−0.426(4)	0.051(3)
C(3)	0.124(3)	−0.297(3)	−0.037(2)
C(4)	0.239(5)	−0.189(6)	−0.065(3)
C(5)	0.219(4)	0.669(4)	0.161(2)
C(6)	0.227(4)	0.562(4)	0.160(2)

Discussion

Important bond distances and angles are collected in Table 2, and Figure 1 shows a diagram of the molecule and the atom numbering scheme. The structure consists of isolated molecules (there are no intermolecular Bi$\cdots$S interactions within 4.3 Å), and packing of the $Bi(S_2PEt_2)_3$ and benzene molecules in the unit cell is shown in Figure 2. Because of the space-group symmetry, the three chelate groups are related by the three-fold axis passing through the bismuth atom.

One of the surprising features of the structure is the almost symmetrical chelating behaviour of the dithiophosphinate groups giving near equality (2.794 and 2.782 Å) to the two

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

independent Bi–S distances. Ligands of this type are generally chelating but they are more usually asymmetrically bonded giving bismuth–sulphur distances which differ by *ca.* 0.2 Å. In the corresponding antimony compounds, Sb–S bond distances can differ by *ca.* 0.5 Å. Asymmetrical co-ordination necessarily leads to an inverse relationship between the Sb–S and related P–S bond lengths but in the present compound the close similarity of the two P–S distances confirms a more symmetrical chelation. The two independent P–C and C–C bonds are unexpectedly different but, at the level of the quoted standard deviations, differences in the former are probably not significant.

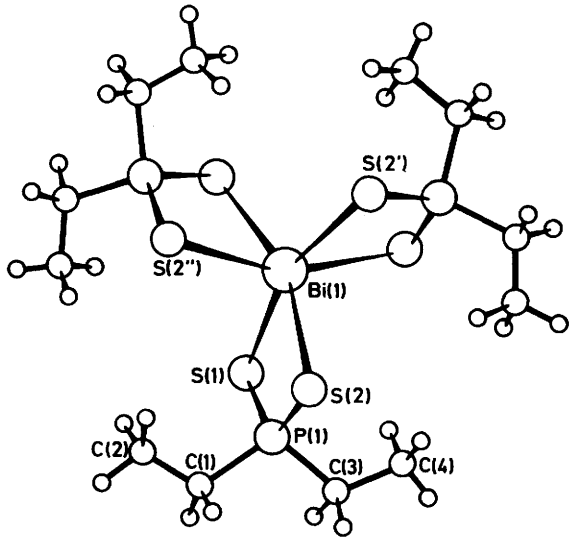

Figure 1. Molecular structure of $Bi(S_2PEt_2)_3$ showing the atom numbering scheme

The BiS_2P chelate ring is planar with angles at bismuth and phosphorus of 73.7 and 112.0° respectively, close to those in related structures. The angles at the two sulphur atoms, 87.0 and 87.4°, are effectively equal, in keeping with symmetrical co-ordination. In related compounds with asymmetrical co-ordination, these angles can differ by *ca.* 10°.

Although co-ordination about bismuth might be described as distorted octahedral, this is not very instructive as the five independent S–Bi–S angles range between 73.7°, in the chelate

Table 2. Bond distances (Å) and angles (°), with e.s.d.s in parentheses, for $Bi(S_2PEt_2)_3{\cdot}C_6H_6$*

Bi(1)–S(1)	2.794(5)	P(1)–C(1)	1.79(3)
Bi(1)–S(2)	2.782(5)	P(1)–C(3)	1.82(3)
S(1)–P(1)	1.999(8)	C(1)–C(2)	1.36(6)
S(2)–P(1)	2.036(7)	C(3)–C(4)	1.47(6)
		C(5)–C(6)	1.40(9)
S(1) ··· S(2)	3.344(6)	C(5)–C(6″)	1.39(9)
S(1) ··· S(1′)	4.056(6)		
S(2) ··· S(2′)	4.042(6)		
S(1)–Bi(1)–S(2)	73.7(1)	S(2)–Bi(1)–S(2′)	93.2(2)
S(1)–Bi(1)–S(1′)	93.0(2)	Bi(1)–S(1)–P(1)	87.4(2)
S(1)–Bi(1)–S(2′)	158.8(2)	Bi(1)–S(2)–P(1)	87.0(2)
S(1)–Bi(1)–S(2″)	103.8(2)		
S(1)–P(1)–S(2)	112.0(3)	C(1)–P(1)–C(3)	108(1)
S(1)–P(1)–C(1)	109(1)	P(1)–C(1)–C(2)	117(3)
S(1)–P(1)–C(3)	109(1)	P(1)–C(3)–C(4)	119(3)
S(2)–P(1)–C(1)	109(1)	C(6)–C(5)–C(6″)	112(5)
S(2)–P(1)–C(3)	109(1)	C(5)–C(6)–C(6′)	128(5)

* Atoms carrying a prime and double prime are related to unprimed atoms by the symmetry operations: $-y, x-y, z$; and $y-x, -x, z$ respectively.

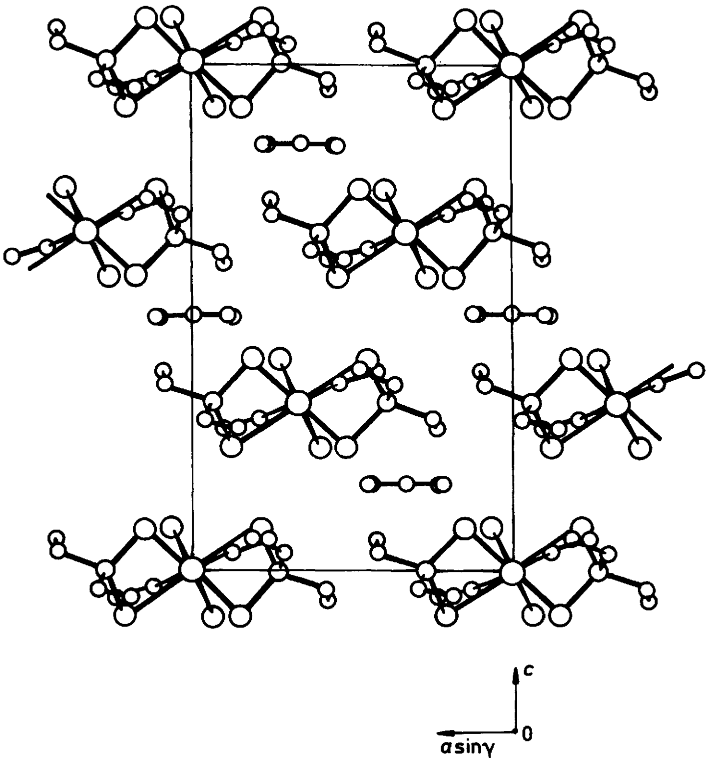

Figure 2. Unit-cell contents

ring, to 158.8°. The triangular faces through the S(1) and S(2) sets of atoms are however parallel and separated by 3.04 Å; the bismuth atom is 1.51 Å from the S(2) set, reflecting the slightly shorter Bi(1)–S(2) distance.

Projection of the six sulphur atoms onto a plane perpendicular to the three-fold axis gives a clearer idea of the overall co-ordination. This shows that the S(1) and S(2) atom sets are related by a twist angle of 34.7°, a value which is almost midway between those for regular octahedral and trigonal-prismatic geometry.

A molecule of benzene [C(5) and C(6) in Table 2], also lying on the three-fold axis, is incorporated into the structure as shown in Figure 2. Closest intermolecular contacts are with S(1) at 3.89 and 4.15 Å and S(2) at 3.81 and 4.09 Å.

The overall structure of $Bi(S_2PEt_2)_3$ represents a further structural variant of those previously determined for Group 5 compounds containing three 'short bite' dithio ligands. It is the only compound which contains both symmetrically chelating ligands and a discrete monomolecular structure, and one can only assume that differences from the $Bi(S_2PPh_2)_3$ structure result from the different electronic and/or steric effects of the organic groups at phosphorus.

The major interest in structures of this type is the possibility of obtaining information on the stereochemical activity of the lone pair of *s* electrons. Certainly it is possible that such electron density could be accommodated above the triangular face of the less strongly bonded sulphur atoms in $Bi[S_2P(OPr^i)_2]_3$ and related antimony compounds. Similarly, the pentagonal-pyramidal structure of $Sb(S_2PPh_3)_3$ could include the lone pair in the vacant position *trans* to the apical atom.

We have, however, argued that the presence of a vacancy in the co-ordination polyhedron does not necessarily prove that the lone pair is active. It is difficult, for example, to argue for activity of the lone pair in $Sb(S_2PPh_2)_3$ when the equivalent position in the bismuth analogue is occupied by a sulphur atom from a neighbouring molecule. Equally it is difficult to be convincing about lone-pair activity in the present compound when the ligands are symmetrically chelating. This unfortunately does not prove that the bismuth lone pair is inactive but the data can be more simply interpreted on that basis.

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Received 12th May 1986; *Paper* 6/896