The Crystal Structures of the Diphenyldithiophosphinates of Antimony(III) and Bismuth(III): $M(S_2PPh_2)_3$ (M = Sb or Bi) †

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Crystal structures have been determined for $M(S_2PPh_2)_3$ (M = Sb or Bi). The antimony compound crystallises in the triclinic space group $P\bar{1}$ with a = 11.321(5), b = 9.413(4), c = 17.933(6) Å, α = 100.41(2), β = 97.60(2), γ = 95.80(2)°, and Z = 2; the structure has been solved by Patterson and Fourier methods and refined to R 0.033 for 5 837 observed reflections. The structure consists of isolated molecules in which the central antimony is surrounded by six sulphur atoms at the corners of a distorted pentagonal pyramid. The distance to the apical atom (2.456 Å) is the shortest; the basal Sb–S distances divide into sets of two short (mean 2.595 Å) and three longer (2.923—3.187 Å) bonds in keeping with anisobidentate co-ordination by the dithiophosphinate groups. The bismuth analogue, $Bi(S_2PPh_2)_3$, is also triclinic ($P\bar{1}$), with a = 11.909(5), b = 24.174(6), c = 15.652(5) Å, α = 107.80(2), β = 92.89(2), γ = 93.11(2)°, and Z = 4; there are two independent molecules in the asymmetric unit. The structure has been solved and refined to R 0.063 for 8 779 observed reflections. Co-ordination about each independent bismuth atom is similar to that in the antimony analogue with short axial distances (2.629 Å) and two short (mean 2.715 Å) and three longer basal Bi–S distances (mean 2.980 Å). However, the molecules dimerise through intermolecular Bi ··· S contacts of 3.173 and 3.301 Å which are *trans* to the apical atoms and complete pentagonal bipyramidal co-ordination about each bismuth atom. In this case, lone-pair activity at bismuth is considered unlikely and, because of the strong structural similarities between the bismuth and antimony compounds, the antimony lone pair is also not considered to be stereochemically active.

Recent structure determinations have shown that the co-ordination polyhedron about antimony(III) in a number of dithiophosphates, $Sb[S_2P(OR)_2]_3$ (R = Me,[1] Et,[2] or Pr^i [1]) is distorted octahedral with three short and three longer Sb–S bonds with the ligand behaving as an anisobidentate group. There is no crystallographically imposed three-fold symmetry but deviations are, in fact, quite small. Structures of this type are interesting in terms of the stereochemical activity of the antimony 5*s* lone pair of electrons and indeed the polyhedra can accommodate the electron pairs above the triangular face formed by the more distant sulphur atoms. In contrast, there are a number of examples of antimony(III) compounds, including $[SbBr_6]^{3-}$ [3] and $[Sb_2X_9]^{3-}$ [4] species, where there is no space in the antimony co-ordination sphere for the electron pair and stereochemical activity is not invoked. We have previously noted [1] that dithiophosphate structures may be rationalised on the basis of the combined effects of the anisobidentate nature of the ligand and the steric requirements of the phosphorus substituents.

A brief report has already appeared [5] on the structure of a related diphenyldithiophosphinate, $Sb(S_2PPh_2)_3$, in which the six sulphur atoms occupy the apices of a distorted pentagonal pyramid. Full details are now presented, together with data for the corresponding bismuth compound.

Experimental

The two compounds $M(S_2PPh_2)_3$ (M = Sb or Bi) were prepared by slightly modified literature methods.[6] Crystals suitable for *X*-ray diffraction were obtained by slow recrystallisation from chloroform and benzene respectively.

Crystallographic data for the compounds are summarised in Table 1.

Structural Determinations.—$Sb(S_2PPh_2)_3$. After preliminary oscillation and Weissenberg photography, single-crystal data were collected in the range $0 < \theta < 25°$ using a Hilger and Watts four-circle diffractometer with Mo-K_α radiation (λ = 0.710 69 Å, graphite monochromator). Observed reflections, for which $I > 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Data reduction and subsequent crystallographic calculations used the CRYSTALS programs;[7] scattering factors were those for neutral atoms.[8] The structure was solved by

Table 1. Crystal data

Formula	$Sb(S_2PPh_2)_3$ $C_{36}H_{30}P_3S_6Sb$	$Bi(S_2PPh_2)_3{\cdot}C_6H_6$ $C_{42}H_{36}BiP_3S_6$
M	868.8	1 034.0
a/Å	11.321(5)	11.909(5)
b/Å	9.413(4)	24.174(6)
c/Å	17.933(6)	15.652(5)
α/°	100.41(2)	107.80(2)
β/°	97.60(2)	92.89(2)
γ/°	95.80(2)	93.11(2)
U/Å^3	1 971	4 272
Z	2	4
D_c/g cm^{-3}	1.46	1.61
F(000)	940	1 880
Space group	$P\bar{1}$	$P\bar{1}$
μ(Mo-K_α)/cm^{-1}	11.3	43.2
Observed reflections	5 837	8 779

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

Table 2. Fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses for $Sb(S_2PPh_2)_3$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	1 541.3(2)	779.4(2)	2 146.7(1)	C(17)	187(4)	3 033(5)	5 302(2)
S(1)	−714.9(7)	−150(1)	1 678.2(5)	C(18)	718(3)	2 802(4)	4 651(2)
P(1)	−887.7(7)	−1 038.6(9)	2 625.9(5)	C(19)	3 333(3)	5 042(3)	3 731(2)
S(2)	701.7(7)	−996(1)	3 237.1(5)	C(20)	2 789(3)	6 261(4)	3 630(2)
C(1)	−1 871(3)	−69(4)	3 193(2)	C(21)	3 470(4)	7 552(4)	3 627(3)
C(2)	−1 862(3)	−250(5)	3 944(2)	C(22)	4 698(4)	7 643(5)	3 731(3)
C(3)	−2 643(4)	414(5)	4 388(3)	C(23)	5 245(4)	6 445(6)	3 833(4)
C(4)	−3 435(4)	1 246(5)	4 083(3)	C(24)	4 567(3)	5 135(4)	3 831(3)
C(5)	−3 451(4)	1 425(5)	3 345(3)	S(5)	1 114.8(8)	1 312(1)	771.2(5)
C(6)	−2 659(4)	787(5)	2 896(2)	P(3)	2 741.0(7)	2 568.6(9)	913.0(5)
C(7)	−1 673(3)	−2 876(4)	2 295(2)	S(6)	3 721.7(8)	2 455(1)	1 896.7(5)
C(8)	−2 899(4)	−3 134(4)	2 237(2)	C(25)	2 395(3)	4 384(4)	868(2)
C(9)	−3 480(4)	−4 539(5)	2 001(3)	C(26)	2 578(4)	5 448(4)	1 521(2)
C(10)	−2 854(6)	−5 655(5)	1 822(3)	C(27)	2 190(5)	6 782(5)	1 490(3)
C(11)	−1 624(5)	−5 423(6)	1 865(4)	C(28)	1 632(5)	7 060(5)	818(3)
C(12)	−1 018(6)	−4 016(5)	2 106(3)	C(29)	1 470(5)	6 012(5)	162(3)
S(3)	1 001.3(7)	3 048.1(9)	2 853.8(5)	C(30)	1 846(4)	4 663(5)	181(3)
P(2)	2 434.6(7)	3 355.3(8)	3 753.2(5)	C(31)	3 512(3)	2 006(4)	117(2)
S(4)	3 347.0(7)	1 690.0(9)	3 724.2(5)	C(32)	3 337(4)	588(4)	−291(2)
C(13)	1 724(3)	3 716(3)	4 598(2)	C(33)	4 062(4)	166(5)	−838(2)
C(14)	2 186(4)	4 848(4)	5 202(2)	C(34)	4 936(4)	1 136(5)	−982(3)
C(15)	1 646(4)	5 045(5)	5 855(2)	C(35)	5 120(5)	2 546(5)	−574(3)
C(16)	645(4)	4 135(5)	5 900(2)	C(36)	4 420(4)	2 982(4)	−25(3)

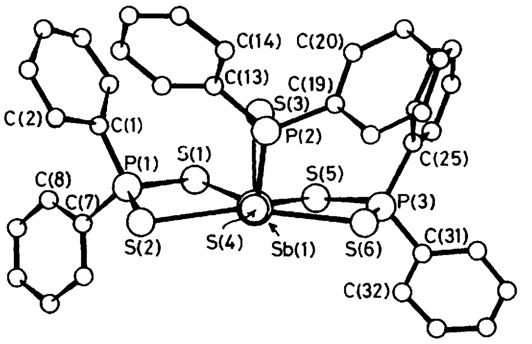

Figure 1. Molecular structure of $Sb(S_2PPh_2)_3$, projected down the S(4)–Sb(1) bond, showing the atom numbering scheme

Patterson and Fourier methods and refined to *R* 0.089 with isotropic thermal parameters by full-matrix least-squares methods. In subsequent cycles of refinement with anisotropic thermal parameters, each ligand molecule was placed in a separate block, giving convergence at *R* 0.039. The refinement was completed after placement of the hydrogen atoms at their calculated positions [*d*(C–H) = 1.0 Å] and the application of a four-coefficient Chebyshev weighting scheme at *R* 0.033. The refined atomic co-ordinates are listed in Table 2.

$Bi(S_2PPh_2)_3$. The approach was similar to that above except that data were collected in the higher layers to 20° only. The asymmetric unit contains two molecules and because of the large number of both variables and reflection data, refinement with isotropic thermal parameters used block-diagonal methods, giving convergence at *R* 0.115. A difference Fourier synthesis at this stage showed the presence of two slightly distorted benzene molecules of solvation, C(150)—C(155) and C(156)—C(161). Subsequent refinement with anisotropic thermal parameters for atoms except those of the solvate molecules was by full-matrix least-squares methods, with each ligand molecule in a separate block. Hydrogen atoms were placed at their calculated positions [*d*(C–H) = 1.0 Å] and refinement converged after applying a Chebyshev weighting scheme at *R* 0.063. Refined atomic co-ordinates are listed in Table 3.

Discussion

$Sb(S_2PPh_2)_3$.—Important bond lengths and angles for $Sb(S_2PPh_2)_3$ are collected in Tables 4 and 5 and the molecular structure and atom numbering scheme are illustrated in Figure 1. The six sulphur atoms of the ligands all bond to the central atom with the distances forming two groups. The first, at distances between 2.456 and 2.598 Å, involve S(1), S(3), and S(5), while distances to S(2), S(4), and S(6) are substantially greater (2.923—3.187 Å) but still well within the sum of the antimony and sulphur van der Waals radii (4.05 Å). The closest Sb $\cdots$ S intermolecular contact is at 5.56 Å.

As a consequence of the anisobidentate character of the ligands there is the usual inverse relationship between the Sb–S(*n*) and the S(*n*)–P bond lengths; the short Sb–S bonds are associated with the longer S–P bonds (mean 2.060 Å) and the long Sb–S bonds with the shorter S–P bonds (mean 1.971 Å).

It is important, at this stage, to note that (*a*) the Sb(1)–S(3) distance (2.456 Å) is substantially shorter than those to S(1) and S(5), and (*b*) the angles between the short Sb–S bonds are 89.90, 74.90, and 98.18°. These are at variance with the usual observations that the three distances from the most strongly bonded atoms to an antimony(III) centre are approximately equal, and the angles between these bonds are *ca.* 90°. Further, when the longer Sb–S interactions are considered, it is clear that the sulphur atoms do not occupy the corners of a trigonally distorted octahedron as is observed for the corresponding dithiophosphate complexes,[1,2] and the most realistic description is in terms of a pentagonal pyramid. This is suggested for the following reasons.

(*a*) The bond distance to the apical atom S(3) is substantially shorter than those to the other two primary bonded sulphur atoms, as expected for pentagonal pyramidal geometry.

(*b*) The angles at Sb(1) between the apical sulphur atom and four of the five basal atoms vary between 88.27 and 98.18° (mean 92.5, ideal 90.0°). The angle with the fifth basal atom, S(4), is 72.32° and is that between the two sulphur atoms in the same ligand. This is necessarily acute but is identical with the corresponding angles in the other two ligands.

(*c*) The angles forming the basal plane of the pyramid fall into two groups, *i.e.* 70.88—74.90 (mean 72.7) and 138.53—147.57, (mean 142.5°) compared with ideal angles of 72 and 144°.

Table 3. Atomic co-ordinates (× 10^3) with estimated standard deviations in parentheses for $Bi(S_2PPh_2)_3$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Bi(1)	282.14(4)	250.45(2)	162.08(3)	C(103)	161(2)	123(1)	698(2)
S(1)	356.6(3)	347.0(2)	116.0(3)	C(104)	98(2)	74(1)	700(1)
S(2)	97.4(4)	325.0(2)	173.1(3)	C(105)	94(3)	26(1)	629(2)
P(1)	195.4(3)	368.1(2)	110.7(2)	C(106)	149(2)	24(1)	550(1)
C(1)	192(1)	446.4(6)	158.0(9)	C(107)	284(1)	8.3(6)	383(1)
C(2)	131(2)	470.0(8)	232(1)	C(108)	224(1)	−22.6(7)	304(1)
C(3)	132(2)	530(1)	270(2)	C(109)	244(2)	−79.9(8)	261(1)
C(4)	188(3)	564.7(9)	232(1)	C(110)	326(2)	−106.3(8)	295(2)
C(5)	250(2)	543.6(9)	160(2)	C(111)	390(3)	−74(1)	372(2)
C(6)	252(2)	482.2(7)	123(1)	C(112)	365(2)	−17.4(9)	415(2)
C(7)	146(1)	353.0(7)	−5(1)	S(103)	241.0(3)	266.4(2)	555.3(2)
C(8)	204(1)	324.7(7)	−75(1)	S(104)	89.4(3)	254.6(2)	363.1(2)
C(9)	162(2)	313.7(8)	−164(1)	P(102)	105.1(3)	291.8(2)	495.3(2)
C(10)	63(3)	330(1)	−182(2)	C(113)	−17(1)	273.5(7)	546.2(8)
C(11)	−8(2)	357(1)	−112(2)	C(114)	−26(1)	220.9(9)	564(1)
C(12)	37(2)	368(1)	−24(1)	C(115)	−123(2)	203(1)	597(1)
S(3)	221.3(3)	198.9(2)	−8.0(2)	C(116)	−212(2)	238(1)	612(1)
S(4)	70.8(3)	172.4(2)	150.9(2)	C(117)	−203(1)	290(1)	596(1)
P(2)	74.4(3)	162.3(2)	21.4(2)	C(118)	−108(1)	308.2(8)	562(1)
C(13)	63(1)	86.1(6)	−47.4(8)	C(119)	121(1)	370.5(6)	524(1)
C(14)	−43(1)	56.4(7)	−67(1)	C(120)	113(2)	397.4(7)	461(1)
C(15)	−52(2)	−3.1(7)	−119(1)	C(121)	123(2)	459.3(8)	485(1)
C(16)	42(2)	−29.5(7)	−152(1)	C(122)	149(2)	491.0(8)	572(1)
C(17)	144(2)	−2.1(7)	−132(1)	C(123)	160(2)	463.8(8)	635(1)
C(18)	157(1)	57.8(7)	−79(1)	C(124)	147(2)	402.6(7)	616(1)
C(19)	−40(1)	194.4(6)	−20(1)	S(105)	531.8(3)	255.6(2)	459.1(3)
C(20)	−133(2)	211(1)	31(2)	S(106)	355.2(3)	324.9(1)	364.1(2)
C(21)	−223(2)	232(1)	−9(2)	P(103)	510.5(3)	327.9(1)	422.9(2)
C(22)	−219(2)	238(1)	−93(2)	C(125)	620(1)	338.7(5)	352.8(9)
C(23)	−130(2)	224.7(9)	−137(1)	C(126)	727(1)	315.9(7)	359(1)
C(24)	−39(1)	202.6(8)	−103(1)	C(127)	810(1)	326.5(8)	308(1)
S(5)	508.2(3)	236.6(2)	135.4(3)	C(128)	792(2)	359.7(8)	251(1)
S(6)	348.2(3)	137.2(1)	187.1(2)	C(129)	691(2)	383.3(8)	247(1)
P(3)	500.4(3)	157.1(1)	150.6(2)	C(130)	603(1)	372.0(7)	297(1)
C(25)	530(1)	105.3(6)	44.5(9)	C(131)	527(1)	391.9(6)	520.7(9)
C(26)	472(2)	106.9(7)	−34(1)	C(132)	598(2)	439.2(8)	527(1)
C(27)	494(2)	66.5(9)	−116(1)	C(133)	604(2)	488.1(8)	605(2)
C(28)	574(2)	27.8(8)	−121(1)	C(134)	540(2)	489.6(8)	672(1)
C(29)	630(2)	25.7(7)	−45(1)	C(135)	470(2)	445(1)	666(1)
C(30)	608(1)	64.7(6)	40(1)	C(136)	462(2)	395.7(9)	590(1)
C(31)	611(1)	150.2(6)	229.9(9)	C(150)	789(3)	527(1)	114(2)
C(32)	718(1)	176.4(8)	229(1)	C(151)	681(3)	538(1)	124(2)
C(33)	804(2)	168.1(9)	284(2)	C(152)	597(2)	496(2)	91(2)
C(34)	784(2)	137(1)	341(1)	C(153)	622(3)	437(2)	57(2)
C(35)	682(2)	109(1)	342(1)	C(154)	737(4)	425(1)	55(2)
C(36)	592(1)	118.1(7)	286(1)	C(155)	818(2)	471(2)	85(2)
Bi(2)	314.02(4)	210.68(2)	398.56(3)	C(156)	519(2)	753(1)	295(1)
S(101)	403.5(3)	132.2(2)	473.7(2)	C(157)	489(2)	697(1)	248(2)
S(102)	146.7(3)	113.5(2)	373.4(3)	C(158)	483(2)	680.1(9)	156(2)
P(101)	256.0(3)	81.9(2)	442.7(2)	C(159)	509(3)	720(2)	113(1)
C(101)	199(1)	77.1(7)	545(1)	C(160)	551(3)	774(2)	161(3)
C(102)	207(2)	124.1(9)	621(1)	C(161)	545(3)	791.8(9)	251(3)

Table 4. Bond distances (Å) with estimated standard deviations in parentheses for $Sb(S_2PPh_2)_3$

Sb(1)–S(1)	2.591(1)	P(1)–S(1)	2.048(1)
Sb(1)–S(2)	2.978(1)	P(1)–S(2)	1.972(1)
Sb(1)–S(3)	2.456(1)	P(1)–C(1)	1.810(3)
Sb(1)–S(4)	3.187(1)	P(1)–C(7)	1.820(3)
Sb(1)–S(5)	2.598(1)		
Sb(1)–S(6)	2.923(1)		
P(2)–S(3)	2.089(1)	P(3)–S(5)	2.044(1)
P(2)–S(4)	1.959(1)	P(3)–S(6)	1.981(1)
P(2)–C(13)	1.803(3)	P(3)–C(25)	1.805(3)
P(2)–C(19)	1.807(3)	P(3)–C(31)	1.798(3)

(*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 from the minimisation of electrostatic repulsions between adjacent sulphur atoms and, for S(4) in particular, the geometrical constraints imposed by the chelate structure. Minor changes in the deviations, *i.e.* S(1) +0.32, S(2) −0.41, S(4) + 0.34, S(5) −0.07, S(6) −0.18, and Sb(1) −0.07 Å, are found if the antimony atom is omitted from the best plane; omission of both Sb(1) and S(4) from the best plane leads to the following deviations: S(1) 0.20, S(2) −0.11, S(5) −0.20, S(6) 0.11. Sb(1) and S(4) are respectively 0.09 and 0.93 Å from this plane.

Although there is no crystallographically imposed symmetry, there is an approximate mirror plane passing through Sb(1),

Table 5. Bond angles (°) with estimated standard deviations in parentheses for Sb(S_2PPh_2)$_3$

S(1)–Sb(1)–S(2)	72.34(3)	S(3)–Sb(1)–S(5)	98.18(3)	S(2)–P(1)–C(1)	111.1(1)	C(13)–P(2)–C(19)	105.8(2)
S(1)–Sb(1)–S(3)	89.90(3)	S(3)–Sb(1)–S(6)	88.27(3)	S(2)–P(1)–C(7)	112.7(1)	Sb(1)–S(5)–P(3)	91.70(4)
S(1)–Sb(1)–S(4)	138.53(3)	S(4)–Sb(1)–S(5)	141.13(2)	C(1)–P(1)–C(7)	105.1(2)	Sb(1)–S(6)–P(3)	83.94(4)
S(1)–Sb(1)–S(5)	74.90(3)	S(4)–Sb(1)–S(6)	70.88(2)	Sb(1)–S(3)–P(2)	95.68(4)	S(5)–P(3)–S(6)	110.49(5)
S(1)–Sb(1)–S(6)	147.57(3)	S(5)–Sb(1)–S(6)	73.34(3)	Sb(1)–S(4)–P(2)	78.05(4)	S(5)–P(3)–C(25)	105.4(1)
S(2)–Sb(1)–S(3)	93.60(3)	Sb(1)–S(1)–P(1)	92.85(4)	S(3)–P(2)–S(4)	113.27(5)	S(5)–P(3)–C(31)	110.0(1)
S(2)–Sb(1)–S(4)	71.81(2)	Sb(1)–S(2)–P(1)	83.52(4)	S(3)–P(2)–C(13)	103.4(1)	S(6)–P(3)–C(25)	113.1(1)
S(2)–Sb(1)–S(5)	145.06(3)	S(1)–P(1)–S(2)	110.4(5)	S(3)–P(2)–C(19)	106.7(1)	S(6)–P(3)–C(31)	111.0(1)
S(2)–Sb(1)–S(6)	140.09(3)	S(1)–P(1)–C(1)	109.8(1)	S(4)–P(2)–C(13)	113.1(1)	C(25)–P(3)–C(31)	106.7(2)
S(3)–Sb(1)–S(4)	72.32(2)	S(1)–P(1)–C(7)	107.6(1)	S(4)–P(2)–C(19)	113.7(1)		

Table 6. Selected torsion angles (°) for Sb(S_2PPh_2)$_3$

S(3)–Sb(1)–S(1)–P(1)	−87.9	Sb(1)–S(1)–P(1)–C(1)	113.7	S(1)–P(1)–C(1)–C(6)	19.0
S(5)–Sb(1)–S(1)–P(1)	173.6	Sb(1)–S(1)–P(1)–C(7)	−132.5	S(1)–P(1)–C(7)–C(8)	−92.7
S(1)–Sb(1)–S(3)–P(2)	146.9	Sb(1)–S(3)–P(2)–C(13)	−131.3	S(3)–P(2)–C(13)–C(18)	48.6
S(5)–Sb(1)–S(3)–P(2)	−138.3	Sb(1)–S(3)–P(2)–C(19)	117.4	S(3)–P(2)–C(19)–C(20)	44.5
S(1)–Sb(1)–S(5)–P(3)	168.8	Sb(1)–S(5)–P(3)–C(25)	−115.6	S(5)–P(3)–C(25)–C(26)	107.2
S(3)–Sb(1)–S(5)–P(3)	81.2	Sb(1)–S(5)–P(3)–C(31)	129.8	S(5)–P(3)–C(31)–C(32)	−29.0

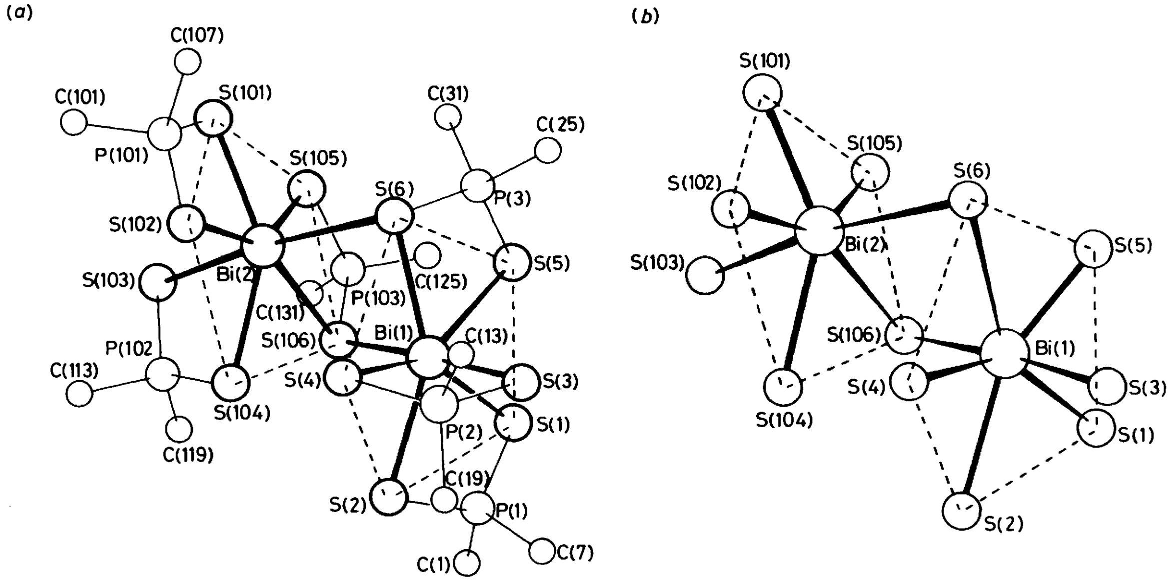

Figure 2. (*a*) Molecular structure of Bi(S_2PPh_2)$_3$ (dimer) showing the atom numbering scheme. The phenyl groups have been omitted for clarity. (*b*) The (BiS_6)$_2$ skeleton showing pentagonal bipyramidal co-ordination

S(3), S(4), and P(2); the deviations from this plane for related atoms are: S(1) −1.52 and S(5) 1.62, S(2) −2.75 and S(6) 2.77, and P(1) −3.22 and P(3) 3.27 Å. The two phenyl groups attached to P(3) are not related by this pseudo-mirror plane, however (see Table 6).

Angles at the sulphur atoms in the three chelate rings fall into two groups, those at S(1), S(3), and S(5) being larger (mean 93.4°) than those at S(2), S(4), and S(6). The Sb(1)–S(4)–P(2) angle is particularly acute, a consequence of this ligand occupying the axial and a basal position in the pentagonal pyramid about antimony.

Each of the SbS_2P rings is closely planar with deviations from the appropriate best plane ranging between 0.04 and 0.09 (mean 0.06 Å). The orientations of the SbS_2P rings are given by the first six torsion angles in Table 6; the final six give the relative orientations of the phenyl groups.

Bi(S_2PPh_2)$_3$.—Bond distances and angles for the two independent molecules in the asymmetric unit are collected in Tables 7 and 8 respectively and a diagram showing the molecular structure and atom numbering scheme is in Figure 2. The molecules are in fact very similar and show the same basic pentagonal pyramidal geometry discussed above for the antimony analogue.

The ligands are anisobidentate forming sets of short and long Bi–S bonds (mean 2.715 and 2.980 Å respectively) and consequently long and short P–S bond lengths (mean 2.031 and 1.989 Å respectively). The Bi–S distances to the atoms defining the apex of the pyramid, *i.e.* S(3) and S(103), are again by far the shortest (2.629 Å).

Deviations from the best plane through the BiS_5 set of atoms defining the pyramid base are: Bi(1) −0.13 (−0.14), S(1) 0.21 (0.20), S(2) −0.32 (−0.31), S(4) 0.40 (0.39), S(5) 0.10 (0.09), and S(6) −0.26 (−0.24) Å [values in parentheses are the corresponding deviations from the plane containing Bi(2) and its associated sulphur atoms]. With the exception of a small positive deviation (0.10 Å) for both S(5) and S(105) compared with a small negative deviation (−0.06 Å) for S(5) in the antimony compound, puckering of the basal planes in the two compounds is very similar. If the bismuth atoms are omitted from the best planes, the deviations are: S(1) 0.18 (0.17), S(2) −0.34 (−0.33), S(4) 0.37 (0.36), S(5) 0.07 (0.07), S(6) −0.28 (−0.27), and Bi(1) 0.07 (0.07) Å.

Pseudo-mirror symmetry about the Bi(1),S(3),S(4),P(2) and Bi(2),S(103),S(104),P(102) planes is present; deviations from these planes for related atoms are: S(1) 1.65 (1.54) and S(5) −1.71 (−1.81), S(2) 2.83 (2.75) and S(6) −2.80 (−2.84), and P(1) 3.20 (3.20) and P(3) −3.33 (−3.41) Å. As for the antimony compound, the phenyl groups attached to P(3) and P(103) are not, however, related by the pseudo-mirror plane (see Table 9).

There is, however, a substantial difference between the $Sb(S_2PPh_2)_3$ and $Bi(S_2PPh_2)_3$ structures in that, in the latter, short intermolecular interactions (see Table 10) lead to dimerisation. The most important of these are between Bi(1) and S(106) (3.173 Å) and Bi(2) and S(6) (3.301 Å), which are effectively *trans* to the apical S(3) and S(103) atoms (174.1 and 167.8° respectively), and thus complete slightly distorted pentagonal bipyramidal geometry about the two bismuth atoms. There is also a weaker interaction between Bi(1) and S(104); S(104) also forms a contact to S(4) which is within the van der Waals radii. The related Bi(2) ··· S(4) contact is >4.3 Å.

A consequence of this intermolecular interaction is the behaviour of one of the diphenyldithiophosphinate ligands as a tridentate, mixed chelating–bridging ligand. This method of co-ordination is not common but it has been observed for a dithiophosphate group in $Sn[S_2P(OPh)_2]_2$ [9] and for one of the ligands in both $Sb[OC(O)Me]_3$ and $Sb[SC(O)Me]_3$.[10]

Torsion angles describing the orientations of the BiS_2P rings and the phenyl groups are collected in Table 9; for more ready comparison with the antimony torsion angles, the co-ordinates of the atoms in the Bi(1) molecule have been reflected in the pseudo-mirror plane and those of the Bi(2) molecule inverted. The $Bi(S_2P)_3$ skeletons of the two independent molecules are almost identical and there are no important differences from the torsion angles describing the heavy-atom skeleton in $Sb(S_2PPh_2)_3$. Changes are, however, to be expected in the torsion angles describing the phenyl group orientations as a consequence of dimerisation in the bismuth compound. As shown in Table 9, these are most marked for the groups at P(3) and P(103). There is a smaller effect for the P(1) and P(101) groups and, as expected, changes for the phenyl groups at P(2) and P(102), *i.e.* those farthest from the dimerisation sites, are changed by the smallest amounts.

Table 7. Bond lengths (Å) for $Bi(S_2PPh_2)_3$ with estimated standard deviations in parentheses

Bi(1)–S(1)	2.754(4)	Bi(1)–S(2)	2.913(4)
Bi(1)–S(3)	2.629(3)	Bi(1)–S(4)	3.027(4)
Bi(1)–S(5)	2.767(4)	Bi(1)–S(6)	3.020(4)
S(1)–P(1)	2.017(5)	S(2)–P(1)	1.986(6)
P(1)–C(1)	1.81(1)	P(1)–C(7)	1.80(1)
S(3)–P(2)	2.061(5)	S(4)–P(2)	1.969(5)
P(2)–C(13)	1.82(1)	P(2)–C(19)	1.79(1)
S(5)–P(3)	2.007(5)	S(6)–P(3)	2.004(5)
P(3)–C(25)	1.81(1)	P(3)–C(31)	1.81(2)
Bi(2)–S(101)	2.752(4)	Bi(2)–S(102)	2.914(4)
Bi(2)–S(103)	2.629(4)	Bi(2)–S(104)	3.018(4)
Bi(2)–S(105)	2.760(4)	Bi(2)–S(106)	2.991(4)
S(101)–P(101)	2.030(5)	S(102)–P(101)	1.982(5)
P(101)–C(101)	1.80(2)	P(101)–C(107)	1.80(1)
S(103)–P(102)	2.046(5)	S(104)–P(102)	1.983(5)
P(102)–C(113)	1.79(1)	P(102)–C(119)	1.81(2)
S(105)–P(103)	2.022(5)	S(106)–P(103)	2.010(5)
P(103)–C(125)	1.81(1)	P(103)–C(131)	1.81(3)

Table 8. Bond angles (°) for $Bi(S_2PPh_2)_3$ with estimated standard deviations in parentheses

S(1)–Bi(1)–S(2)	71.3(1)	S(1)–Bi(1)–S(3)	88.2(1)	Bi(1)–S(3)–P(2)	91.9(2)	Bi(1)–S(4)–P(2)	82.7(2)
S(1)–Bi(1)–S(4)	140.9(1)	S(1)–Bi(1)–S(5)	75.4(1)	S(3)–P(2)–C(13)	106.5(5)	S(3)–P(2)–S(4)	112.3(2)
S(1)–Bi(1)–S(6)	144.8(1)	S(2)–Bi(1)–S(3)	89.6(1)	S(4)–P(2)–C(13)	112.9(5)	S(3)–P(2)–C(19)	107.1(5)
S(2)–Bi(1)–S(4)	75.0(1)	S(2)–Bi(1)–S(5)	146.6(1)	C(13)–P(2)–C(19)	105.4(7)	S(4)–P(2)–C(19)	112.2(5)
S(2)–Bi(1)–S(6)	143.8(1)	S(3)–Bi(1)–S(4)	72.2(1)	P(2)–C(13)–C(18)	121(1)	P(2)–C(13)–C(14)	119(1)
S(3)–Bi(1)–S(5)	92.6(1)	S(3)–Bi(1)–S(6)	91.7(1)	P(2)–C(19)–C(24)	120(1)	P(2)–C(19)–C(20)	121(1)
S(4)–Bi(1)–S(5)	137.0(1)	S(4)–Bi(1)–S(6)	71.1(1)				
S(5)–Bi(1)–S(6)	69.4(1)						
Bi(1)–S(1)–P(1)	88.9(2)	Bi(1)–S(2)–P(1)	85.0(2)	Bi(1)–S(5)–P(3)	93.3(2)	Bi(1)–S(6)–P(3)	86.1(2)
S(1)–P(1)–S(2)	111.4(2)	S(1)–P(1)–C(1)	108.9(6)	S(5)–P(3)–C(25)	107.8(5)	S(5)–P(3)–S(6)	110.8(2)
S(1)–P(1)–C(7)	109.3(6)	S(2)–P(1)–C(1)	111.6(6)	S(6)–P(3)–C(25)	110.8(5)	S(5)–P(3)–C(31)	112.0(5)
S(2)–P(1)–C(7)	111.4(6)	C(1)–P(1)–C(7)	104.1(7)	C(25)–P(3)–C(31)	104.5(6)	S(6)–P(3)–C(31)	110.7(5)
P(1)–C(1)–C(2)	121(1)	P(1)–C(1)–C(6)	120(1)	P(3)–C(25)–C(30)	122(1)	P(3)–C(25)–C(26)	119(1)
P(1)–C(7)–C(8)	124(1)	P(1)–C(7)–C(12)	118(1)	P(3)–C(31)–C(36)	121(1)	P(3)–C(31)–C(32)	118(1)
S(101)–Bi(2)–S(102)	71.4(1)	S(101)–Bi(2)–S(103)	89.2(1)	Bi(2)–S(103)–P(102)	91.7(1)	Bi(2)–S(104)–P(102)	82.3(2)
S(101)–Bi(2)–S(104)	140.1(1)	S(101)–Bi(2)–S(105)	74.9(1)	S(103)–P(102)–C(113)	106.8(5)	S(103)–P(102)–S(104)	112.8(2)
S(101)–Bi(2)–S(106)	145.3(1)	S(102)–Bi(2)–S(103)	91.6(1)	S(104)–P(102)–C(113)	110.9(5)	S(103)–P(102)–C(119)	107.4(5)
S(102)–Bi(2)–S(104)	73.8(1)	S(102)–Bi(2)–S(105)	146.2(1)	C(113)–P(102)–C(119)	107.6(7)	S(104)–P(102)–C(119)	111.2(5)
S(102)–Bi(2)–S(106)	143.3(1)	S(103)–Bi(2)–S(104)	72.6(1)	P(102)–C(113)–C(118)	122(1)	P(102)–C(113)–C(114)	120(1)
S(103)–Bi(2)–S(105)	90.7(1)	S(103)–Bi(2)–S(106)	89.1(1)	P(102)–C(119)–C(124)	117(1)	P(102)–C(119)–C(120)	122(1)
S(104)–Bi(2)–S(105)	138.4(1)	S(104)–Bi(2)–S(106)	71.4(1)				
S(105)–Bi(2)–S(106)	70.4(1)						
Bi(2)–S(101)–P(101)	90.4(2)	Bi(2)–S(102)–P(101)	86.8(2)	Bi(2)–S(105)–P(103)	92.5(1)	Bi(2)–S(106)–P(103)	86.2(2)
S(101)–P(101)–S(102)	111.2(2)	S(101)–P(101)–C(101)	109.2(6)	S(105)–P(103)–C(125)	110.5(5)	S(105)–P(103)–S(106)	110.9(2)
S(101)–P(101)–C(107)	109.2(5)	S(102)–P(101)–C(101)	110.8(6)	S(106)–P(103)–C(125)	112.5(4)	S(105)–P(103)–C(131)	110.8(5)
S(102)–P(101)–C(107)	111.8(5)	C(101)–P(101)–C(107)	104.4(8)	C(125)–P(103)–C(131)	104.6(6)	S(106)–P(103)–C(131)	107.8(5)
P(101)–C(101)–C(102)	121(1)	P(101)–C(101)–C(106)	121(1)	P(103)–C(125)–C(130)	119(1)	P(103)–C(125)–C(126)	121(1)
P(101)–C(107)–C(108)	122(1)	P(101)–C(107)–C(112)	120(2)	P(103)–C(131)–C(136)	120(1)	P(103)–C(131)–C(132)	123(1)

Table 9. Selected torsion angles (°) for $Bi(S_2PPh_2)_3$; values in parentheses are for the Bi(2) molecule

S(3)-Bi(1)-S(1)-P(1)	−87.0	(−89.2)	Bi(1)-S(1)-P(1)-C(1)	115.7	(118.5)	S(1)-P(1)-C(1)-C(6)	−49.8	(−38.4)
S(5)-Bi(1)-S(1)-P(1)	−174.5	(179.9)	Bi(1)-S(1)-P(1)-C(7)	−129.9	(−128.0)	S(1)-P(1)-C(7)-C(8)	−39.2	(−49.1)
S(1)-Bi(1)-S(3)-P(2)	145.1	(148.9)	Bi(1)-S(3)-P(2)-C(13)	−133.8	(−129.9)	S(3)-P(2)-C(13)-C(18)	24.1	(41.1)
S(5)-Bi(1)-S(3)-P(2)	−139.5	(−136.2)	Bi(1)-S(3)-P(2)-C(19)	113.8	(114.9)	S(3)-P(2)-C(19)-C(20)	42.8	(48.5)
S(1)-Bi(1)-S(5)-P(3)	172.0	(176.7)	Bi(1)-S(5)-P(3)-C(25)	−106.2	(−117.7)	S(5)-P(3)-C(25)-C(26)	8.4	(56.4)
S(3)-Bi(1)-S(5)-P(3)	78.8	(87.6)	Bi(1)-S(5)-P(3)-C(31)	140.6	(127.1)	S(5)-P(3)-C(31)-C(32)	57.6	(25.7)

Table 10. Intermolecular distances (Å) and angles (°) for $Bi(S_2PPh_2)_3$

Bi(1)-S(106)	3.173(3)	S(101)-Bi(2)-S(6)	96.8(1)
Bi(2)-S(6)	3.301(3)	S(102)-Bi(2)-S(6)	80.4(1)
Bi(1)-S(104)	3.967(3)	S(103)-Bi(2)-S(6)	167.8(1)
S(4)-S(104)	3.297(5)	S(104)-Bi(2)-S(6)	96.2(1)
		S(105)-Bi(2)-S(6)	101.1(1)
S(1)-Bi(1)-S(106)	86.3(1)	S(106)-Bi(2)-S(6)	92.0(1)
S(2)-Bi(1)-S(106)	86.7(1)	Bi(1)-S(106)-Bi(2)	83.43(8)
S(3)-Bi(1)-S(106)	174.1(1)	Bi(1)-S(6)-Bi(2)	80.83(8)
S(4)-Bi(1)-S(106)	111.2(1)	Bi(1)-S(4)-S(104)	77.6(1)
S(5)-Bi(1)-S(106)	88.0(1)	Bi(2)-S(104)-S(4)	92.0(1)
S(6)-Bi(1)-S(106)	94.0(1)		

There are no close contacts with the benzene molecules of solvation which are incorporated into the lattice for efficiency of packing.

One of the main points of interest in these structures is the possibility of obtaining evidence for the stereochemical activity or otherwise of the lone pair of electrons associated with Sb^{III} and Bi^{III}. For the former, it is tempting to assume that the empty axial site is occupied by the lone pair. In such a case, the heavy atom should lie below the five sulphur atoms forming the base of the pentagonal pyramid.

From the data in (*d*) above, three of the five sulphur atoms show substantial deviations from the best plane through all five atoms, two of the atoms lying above the plane and one below. The other two atoms are displaced below the mean plane, as is the antimony atom. It is difficult to know whether this is adequate evidence for stereochemical activity by the lone pair or whether it is merely a function of the poor planarity of the basal atoms. If S(4) is removed from the atoms used to define the best plane, the relative deviations of the remaining four atoms are reduced but the antimony atom now lies above the plane. It is thus extremely difficult to deduce whether there is any stereochemical effect of the lone pair which may occupy the vacant axial position. The bismuth situation is similarly ambiguous but here, even with the increased size of the central atom, it is difficult to imagine how the lone pair could be active, as the seventh co-ordination site is occupied by a sulphur atom from a neighbouring molecule. In view of the general similarities in structure of the two $M(S_2PPh_2)_3$ units, the evidence is against there being lone-pair activity in the antimony case also.

Pentagonal pyramidal co-ordination about antimony is rare, but has been described previously in $[Sb(ox)_3]^{3-}$ (ox = oxalate)[11] and in the diethyldithiocarbamate, $Sb(S_2CNEt_2)_3$;[12] in the latter compound there is, however, an intermolecular contact at 3.38 Å to a neighbouring sulphur atom raising the effective co-ordination number to seven. In a second determination of the dithiocarbamate structure,[13] the co-ordination polyhedron about the central atom was described as distorted dodecahedral with the lone pair occupying one of the positions. Tris(diethyldithiocarbamato)bismuth(III) and the antimony compound above are isostructural but differ in the increased strength of the intermolecular interaction (3.20 Å) in the bismuth compound.[12,13]

In both $SbMe(S_2COEt)_2$[14] and $BiMe(S_2CNEt_2)_2$[15] the ligands are chelating but the co-ordination number of the Group 5 atom in each case is raised to six by intermolecular interactions to give pentagonal pyramidal geometry about the central atom. Two bridging sulphur atoms raise the bismuth co-ordination number to six in the complex dithiolene anion, $[Bi\{S_2C_2(CN)_2\}_2]^-$, which can be described as highly distorted octahedral if the lone pair is inactive or pentagonal bipyramidal if the lone pair, rather unusually, occupies an electrostatically unfavourable equatorial position.[16]

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