Anionic Phosphine Complexes of Antimony(III) and Bismuth(III) Halogenoanions†

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The reaction between BiI_3, $[PPh_4]I$ and an excess of PMe_2Ph afforded the ionic compound $[PPh_4][BiI_4(PMe_2Ph)_2]$ the structure of which has been determined by X-ray crystallography. The anion $[BiI_4(PMe_2Ph)_2]^-$ comprises an octahedral bismuth centre bonded to four iodines and two *cis* phosphine ligands, although there are some significant distortions from idealised octahedral co-ordination, the origins of which are discussed. From the reaction between $SbBr_3$ and PEt_3, the ionic complex $[PEt_3H][Sb_2Br_7(PEt_3)_2]$ was isolated, probably as a result of adventitious hydrolysis, and also characterised by X-ray crystallography. A discrete dinuclear anion $[Sb_2Br_7(PEt_3)_2]^-$ is present in this complex with a geometry best described as between face-shared bioctahedral and two square-based pyramids sharing a vertex.

In the preceding paper[1] we described the results of structural studies on a range of neutral phosphine complexes of antimony(III) and bismuth(III) halides and discussed these results in relation to other relevant work in both p-block and d-block chemistry. Herein, we concentrate on some examples of anionic complexes in which phosphine ligands are co-ordinated to antimony(III) and bismuth(III) halogenoanions. The only previous such compounds to have been described and structurally characterised are $[PMe_3H]^+{}_n[\{Bi_2Br_7(PMe_3)_2\}_n]^{n-}$ **1**[2] and $[(py)_2H][SbI_4(dmpe)]$ **2**[3] [py = pyridine, dmpe = 1,2-bis(dimethylphosphino)ethane], although the structure of the dimethyl sulfide complex $[SMe_3]_2[Bi_2I_8(SMe_2)_2]$ **3**[4] is also relevant.

Results and Discussion

The reaction between BiI_3, $[PPh_4]I$ and an excess of PMe_2Ph in nitromethane solution afforded, after work-up, orange crystals of the ionic complex $[PPh_4][BiI_4(PMe_2Ph)_2]$ **4** the structure of which was established by X-ray crystallography. A view of the anion $[BiI_4(PMe_2Ph)_2]^-$ is shown in Fig. 1 with selected bond lengths and angles given in Table 1 and atomic positional parameters presented in Table 2. The structure of the anion in **4** comprises a bismuth atom bonded to four iodines and two PMe_2Ph phosphine ligands with a co-ordination geometry around the bismuth centre which is close to octahedral and in which the phosphine ligands are mutually *cis*. The Bi–I distances are all very similar (av. Bi–I 3.048 Å) and within the range generally observed for terminal Bi–I bonds,[5] but the Bi–P distances [Bi–P(1) 3.005(2) and Bi–P(2) 2.981(2) Å] are significantly longer, by approximately 0.2 Å, than those described in ref. 1. A particularly appropriate comparison here is with the complex $[Bi_2Br_6(PMe_2Ph)_2(OPMe_2Ph)_2]$ **5**[6] for which the Bi–P distance, to the same phosphine [2.725(2) Å], is considerably shorter and yet for which the co-ordination number around the bismuth centre is the same, *i.e.* six. Furthermore, there are significant distortions of some of the bond angles in the anion in **4** from idealised octahedral values, those of particular note being the large P–Bi–P angle [112.33(6)°] and the angle between I(3) and I(4) [157.11(2)°].

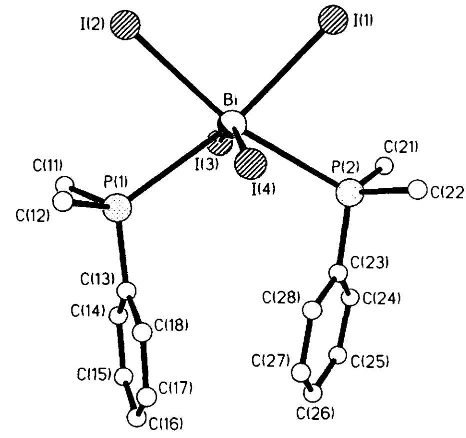

Fig. 1 A view of the anion $[BiI_4(PMe_2Ph)_2]^-$ in **4**

Table 1 Selected bond lengths (Å) and angles (°) for **4**

Bi–P(2)	2.981(2)	Bi–P(1)	3.005(2)
Bi–I(2)	3.029(2)	Bi–I(1)	3.0414(14)
Bi–I(4)	3.0525(10)	Bi–I(3)	3.0724(12)
P(2)–Bi–P(1)	112.33(6)	P(2)–Bi–I(2)	167.01(4)
P(1)–Bi–I(2)	80.08(5)	P(2)–Bi–I(1)	77.92(5)
P(1)–Bi–I(1)	169.50(4)	I(2)–Bi–I(1)	89.86(3)
P(2)–Bi–I(4)	87.75(5)	P(1)–Bi–I(4)	84.39(4)
I(2)–Bi–I(4)	97.61(3)	I(1)–Bi–I(4)	94.05(3)
P(2)–Bi–I(3)	79.62(4)	P(1)–Bi–I(3)	82.90(4)
I(2)–Bi–I(3)	98.86(2)	I(1)–Bi–I(3)	101.77(2)
I(4)–Bi–I(3)	157.11(2)		

Large angular distortions and unusually long bonds were also observed in the structure of the related anionic antimony complex in **2**, *i.e.* $[SbI_4(dmpe)]^-$,[3] and were interpreted in terms of an arrested intermediate along a double nucleophilic substitution reaction coordinate as shown in Scheme 1 where E is Sb or Bi.

Thus, if we consider the substitution of two iodide anions of an $[EI_4]^-$ anion by two two-electron donor ligands (L), an initial encounter geometry may be represented as in **A** in which

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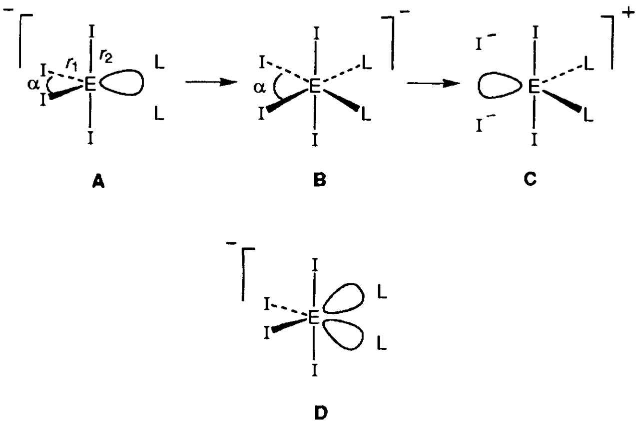
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 2 Atomic coordinates (× 10^4) for **4**

Atom	*x*	*y*	*z*
Bi	7 229.1(2)	7 308.7(2)	2 030.62(10)
I(1)	8 501.8(3)	7 888.4(3)	1 127.7(2)
I(2)	5 442.1(3)	7 924.5(3)	1 185.9(2)
I(3)	7 066.8(3)	5 111.8(3)	1 844.7(2)
I(4)	7 558.6(3)	9 199.2(3)	2 718.1(2)
P(1)	5 691.7(12)	6 956.0(12)	2 788.4(7)
C(11)	4 757(5)	6 114(6)	2 445(3)
C(12)	4 994(5)	8 048(5)	2 876(3)
C(13)	6 005(4)	6 523(5)	3 540(3)
C(14)	5 888(5)	5 561(5)	3 696(3)
C(15)	6 115(5)	5 268(5)	4 282(3)
C(16)	6 447(5)	5 916(5)	4 708(3)
C(17)	6 576(5)	6 878(5)	4 564(3)
C(18)	6 372(5)	7 173(5)	3 994(3)
P(2)	9 193.7(12)	6 687.7(12)	2 615.4(8)
C(21)	9 779(5)	5 791(5)	2 210(3)
C(22)	10 092(5)	7 654(5)	2 727(3)
C(23)	9 217(4)	6 172(5)	3 343(3)
C(24)	9 547(5)	5 247(5)	3 502(3)
C(25)	9 504(6)	4 901(6)	4 066(4)
C(26)	9 130(5)	5 468(6)	4 473(4)
C(27)	8 829(5)	6 387(5)	4 328(3)
C(28)	8 844(5)	6 747(5)	3 764(3)
P(3)	7 867.5(11)	1 816.7(11)	4 840.2(7)
C(31)	9 091(4)	1 445(4)	5 144(3)
C(32)	9 827(4)	1 491(4)	4 804(3)
C(33)	10 749(5)	1 202(4)	5 044(3)
C(34)	10 948(5)	862(5)	5 616(3)
C(35)	10 214(5)	823(4)	5 952(3)
C(36)	9 291(5)	1 123(4)	5 731(3)
C(41)	7 488(4)	2 716(4)	5 321(3)
C(42)	8 176(5)	3 347(5)	5 633(3)
C(43)	7 864(5)	4 069(5)	5 983(3)
C(44)	6 877(5)	4 157(5)	6 015(3)
C(45)	6 218(5)	3 528(5)	5 708(3)
C(46)	6 515(5)	2 816(5)	5 361(3)
C(51)	7 845(4)	2 298(5)	4 113(3)
C(52)	7 644(5)	3 255(5)	3 996(3)
C(53)	7 566(5)	3 594(5)	3 418(3)
C(54)	7 676(5)	2 986(5)	2 973(3)
C(55)	7 870(5)	2 011(5)	3 085(3)
C(56)	7 960(4)	1 671(5)	3 656(3)
C(61)	7 035(4)	812(4)	4 772(3)
C(62)	7 102(4)	73(4)	5 196(3)
C(63)	6 451(5)	−675(5)	5 138(3)
C(64)	5 724(5)	−712(5)	4 655(3)
C(65)	5 636(5)	17(5)	4 238(3)
C(66)	6 293(4)	765(5)	4 299(3)



Scheme 1

the L lone pairs (not shown) point towards the E centre. In this situation, the $[EI_4]^-$ anion has the disphenoidal geometry expected from valence shell electron pair repulsion[7] arguments with the equatorial E–I bond lengths (r_1) similar to or slightly shorter than the axial E–I bonds (r_2), and the lone pair stereochemically active and localised in the equatorial plane as indicated. Furthermore, the Lewis acidity of the $[EI_4]^-$ anion is likely to be associated with the equatorial E–I σ* orbitals, represented in **D**, and it is through these orbitals that the ligands L would be likely to interact resulting in an approach to the E centre *trans* to the equatorial E–I bonds and such that the equatorial iodines and the two ligands would be coplanar. Proceeding along the reaction coordinate, a symmetrical intermediate octahedral complex is represented in **B** with a complete double nucleophilic substitution of the two equatorial iodines (as iodide, I^-) by the ligands L affording the disphenoidal cationic complex $[EI_2(L)_2]^+$ shown in **C**.

In the event that the anions in **2** and **4** both had regular octahedral geometries, there would be little to be gained from thinking in these terms and the lone pairs would simply be described as stereochemically inactive, but the observed distortions can be usefully understood in the following way. If we consider first the bond lengths, in **2**, the long equatorial Sb–I bonds commented upon in ref. 3 can be seen as a likely result of the population of the Sb–I σ* orbitals to such an extent that the iodines are well on the way to being substituted, in other words, the anion in **2** lies on the right-hand side of **B**, in Scheme 1, towards **C**. In **4**, however, the fact that the equatorial Bi–I bond distances are similar to the axial Bi–I bond distances coupled with the long Bi–P bonds, indicates that the anion in **4** lies to the left of **B** towards **A**. Moreover, the angular distortions observed are fully consistent with this analysis. In **A**, the E^{III} lone pair is stereochemically active and localised in the equatorial plane as shown, but on moving along the reaction coordinate, this lone pair effectively switches sides and becomes localised as indicated in **C**; at the symmetrical intermediate point **B**, involving regular octahedral co-ordination, the lone pair is stereochemically inactive as mentioned above. Thus, if the anion in **2** lies towards **C**, the lone pair is becoming localised in the region between the outgoing equatorial iodines such that the I–E–I angle would be expected to increase, exactly as observed. If, however, the anion in **4** lies towards **A**, the lone pair should still be localised largely between the ligands L resulting in a L–E–L angle greater than 90°, also as observed. Thus in both **2** and **4** we may consider the lone pair as being partially stereochemically active, becoming localised along or towards an edge of the octahedron, but the above analysis provides us with some insight as to the octahedral edge towards which we might expect localisation to occur.

The use of crystal structure data in delineating the stereochemical consequences of a particular reaction coordinate is not new and has been discussed in general by Bürgi and Dunitz[8,9] and specifically for some four-co-ordinate phosphorus, antimony and bismuth systems by Schmidpeter and co-workers,[10] Sowerby[11] and ourselves[12] respectively. The most relevant study with regard to the present work concerns a double substitution reaction at four-co-ordinate tin(IV),[13] although in this case there is no lone pair, stereochemically active or otherwise.

The angle between I(3) and I(4) in **4** is significantly less than 180° such that these two iodines are tipped towards the phosphine ligands. The simplest explanation for this is steric in nature in that, with the phosphines at some distance from the bismuth centre, there is room for this pair of *trans* iodines to tip away from the *cis* pair of iodines, I(1) and I(2), in order to minimise I ··· I 90° contacts although the bending energies are likely to be small and such distortions may just as well result from crystal packing forces. This, however, raises an important point with regard to the nature of the structural distortions discussed here, in ref. 1 and, for example, in the bismuth selenocyanate complex $K[N(PPh_3)_2]_2[Bi(SeCN)_6]$[14] which contains a C_{3v} distorted octahedral $[Bi(SeCN)_6]^{3-}$ anion with lone pair localisation towards one face of the octahedron. If the energies associated with these distortions are of the same order as crystal packing forces, the question arises as to which factor is most important and whether any of the electronic arguments offered here or in ref. 1 are realistic. This is not easy to answer without some quantitative calculations but what seems clear is that if crystal packing forces were the dominant factor, we might expect to observe a range of irregular distortions varying from one structure to the next in no particular rational manner. The fact that the observed distortions are generally consistent with simple orbital models is therefore an indication that an electronic origin is, at least in part, a reasonable interpretation.

Before leaving a discussion of the structures of **2** and **4**, we draw attention to a related complex of tellurium(IV). Whether or not the ideas discussed above concerning reaction coordinates are valid, the fact remains that in the anions of both **2** and **4** the E^{III} lone pair has appreciable stereochemical activity such that it is localised towards one edge of the co-ordination octahedron. In the complex $[TeCl_4(tmta)_2]$ (tmta = tetramethylthiourea), a fairly regular octahedral co-ordination geometry was observed for orthorhombic crystals,[15] although in this case the thiourea ligands were mutually *trans*. However, it was observed that after the crystals had been standing for a number of years, a phase change had occurred to a monoclinic modification in which the overall co-ordination geometry was unchanged but for which significant distortions from a regular octahedral geometry were now apparent.[16] Specifically, it was found that one of the S–Te–Cl angles had significantly increased [to 105.94(5)°] and that the corresponding Te–S and Te–Cl bond lengths had also increased, both of these factors being consistent with lone-pair localisation towards an octahedral edge (*i.e.* the S ··· Cl edge). In terms of a reaction-coordinate analysis, the transition from the undistorted to the distorted structure may be viewed as the beginnings of a change from the complex $[TeCl_4(tmta)_2]$ to the cationic species $[TeCl_3(tmta)]^+$, free chloride, Cl^-, and unco-ordinated tmta. The fact that $[TeCl_4(tmta)_2]$ adopts a *trans* geometry is a notable feature, but we will return to the factors affecting whether *cis* or *trans* geometries are adopted in octahedral $[EX_4(L)_2]^{n-}$ (E = Sb or Bi, n = 1; E = Te, n = 0) complexes and the generality of these reaction-coordinate analyses in a future publication dealing with bis(ligand) complexes of $TeCl_4$ in more detail.[17]

The reaction between $SbBr_3$ and two equivalents of PEt_3 in tetrahydrofuran (thf) afforded, after work-up, pale yellow crystals of an ionic compound identified as $[PEt_3H][Sb_2Br_7(PEt_3)_2]$ **6** by X-ray crystallography and resulting, presumably, from unintentional hydrolysis, something we also encountered in the synthesis of **1**. A view of the anion $[Sb_2Br_7(PEt_3)_2]^-$ is shown in Fig. 2 with selected bond lengths and angles given in Table 3 and atomic positional parameters presented in Table 4. The basic formula of the anion in **6**, *i.e.* $[E_2X_7(L)_2]^-$, is the same as that found in the anion in **1**,[2] but whereas in **1** a polymeric structure based on edge-shared bioctahedral units sharing apical bromines (shown in **E**) was observed, in the anion in **6**, a discrete dinuclear structure is found.

Each antimony centre in **6** is bonded to a single PEt_3 ligand, for which the Sb–P distances are within usual ranges [Sb(1)–P(1) 2.637(5) and Sb(2)–P(2) 2.637(5) Å],[1,3] and two terminal bromines, the Sb–Br distances of which are typical for such bonds [Sb(1)–Br(1) 2.696(3), Sb(1)–Br(2) 2.653(2), Sb(2)–Br(6) 2.635(2), Sb(2)–Br(7) 2.708(2) Å]. In addition, the Sb centres are joined by a bromine [Br(4)] which bridges fairly symmetrically between the two atoms [Sb(1)–Br(4) 3.012(3), Sb(2)–Br(4) 3.087(3), difference Δ = 0.075 Å], and two other bromines [Br(3) and Br(5)] which bridge much more asymmetrically [Sb(1)–Br(3) 2.884(2), Sb(2)–Br(3) 3.373(2), Δ = 0.489 Å; Sb(2)–Br(5) 2.855(2), Sb(1)–Br(5) 3.564(3), Δ = 0.709 Å].

If we consider all of the Sb–Br bonds, the co-ordination geometry around each antimony centre is octahedral, albeit with angular distortions of about 10° from idealised values in many cases, and the overall structure may be described as face-shared bioctahedral. If we ignore the long Sb(1)–Br(5) and Sb(2)–Br(3) interactions, however, the antimony centres have a five-co-ordinate, square-based pyramidal geometry and the overall structure of the anion in **6** is derived from a linking of the two pyramids through a basal vertex of each; clearly, the structure in **6** is intermediate between these two extremes. In terms of the factors affecting structural distortions mentioned in ref. 1, the strong *trans* influence of the phosphine ligands is again

Table 3 Selected bond lengths (Å) and angles (°) for **6**

Sb(1)–P(1)	2.637(5)	Sb(1)–Br(2)	2.653(2)
Sb(1)–Br(1)	2.696(3)	Sb(1)–Br(3)	2.884(2)
Sb(1)–Br(4)	3.012(3)	Sb(1)–Br(5)	3.564(3)
Br(3)–Sb(2)	3.373(2)	Br(4)–Sb(2)	3.087(3)
Sb(2)–Br(6)	2.635(2)	Sb(2)–P(2)	2.637(5)
Sb(2)–Br(7)	2.708(2)	Sb(2)–Br(5)	2.855(2)
P(1)–Sb(1)–Br(2)	86.86(13)	P(1)–Sb(1)–Br(1)	86.75(13)
Br(2)–Sb(1)–Br(1)	94.69(8)	P(1)–Sb(1)–Br(3)	86.44(13)
Br(2)–Sb(1)–Br(3)	87.03(7)	Br(1)–Sb(1)–Br(3)	172.87(8)
P(1)–Sb(1)–Br(4)	93.10(12)	Br(2)–Sb(1)–Br(4)	171.06(9)
Br(1)–Sb(1)–Br(4)	94.24(7)	Br(3)–Sb(1)–Br(4)	84.05(7)
P(1)–Sb(1)–Br(5)	164.74(12)	Br(2)–Sb(1)–Br(5)	104.53(7)
Br(1)–Sb(1)–Br(5)	102.12(7)	Br(3)–Sb(1)–Br(5)	84.10(6)
Br(4)–Sb(1)–Br(5)	74.06(6)	Sb(1)–Br(3)–Sb(2)	82.10(6)
Sb(1)–Br(4)–Sb(2)	85.12(5)	Br(6)–Sb(2)–Br(7)	94.14(8)
Br(6)–Sb(2)–P(2)	89.43(12)	Br(6)–Sb(2)–Br(5)	89.20(8)
P(2)–Sb(2)–Br(7)	87.51(13)	Br(7)–Sb(2)–Br(5)	170.57(8)
P(2)–Sb(2)–Br(5)	83.69(13)	P(2)–Sb(2)–Br(4)	95.98(12)
Br(6)–Sb(2)–Br(4)	170.90(9)	Br(5)–Sb(2)–Br(4)	84.15(7)
Br(7)–Sb(2)–Br(4)	93.41(8)	P(2)–Sb(2)–Br(3)	168.61(13)
Br(6)–Sb(2)–Br(3)	98.43(7)	Br(5)–Sb(2)–Br(3)	88.16(7)
Br(7)–Sb(2)–Br(3)	100.06(7)	Sb(2)–Br(5)–Sb(1)	79.15(6)
Br(4)–Sb(2)–Br(3)	75.22(6)		

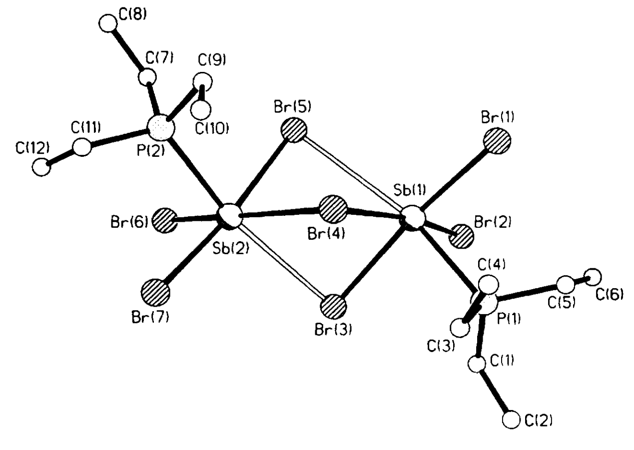
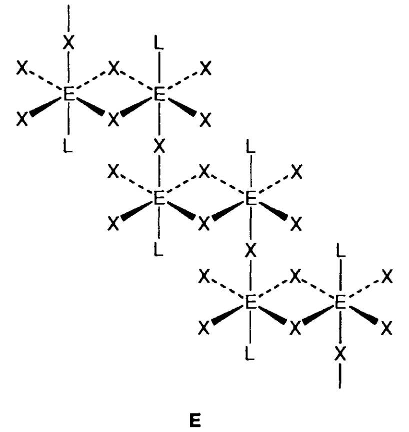


Fig. 2 A view of the anion $[Sb_2Br_7(PEt_3)_2]^-$ in **6**



E

evident, resulting in the highly asymmetric bridging of Br(3) and Br(5), and we may view the structure as one in which each of the Sb^{III} lone pairs is partially stereochemically active becoming localised along the long Sb–Br bonds *trans* to the phosphines.

Table 4 Atomic coordinates (× 10^4) for **6**

Atom	*x*	*y*	*z*
Sb(1)	8 007.6(10)	4 466.0(8)	4 349.0(6)
Br(1)	7 155(2)	3 526(2)	5 444.5(12)
Br(2)	8 502(2)	6 000.3(13)	5 109.9(12)
Br(3)	9 127(2)	5 312.2(14)	3 199.6(11)
Br(4)	7 613(2)	2 877.4(11)	3 297(2)
P(1)	9 712(4)	3 704(4)	4 767(3)
C(1)	10 735(15)	4 527(13)	4 598(12)
C(2)	11 754(14)	4 152(16)	4 748(13)
C(3)	9 973(16)	2 630(14)	4 243(13)
C(4)	9 412(17)	1 734(15)	4 542(13)
C(5)	9 785(16)	3 374(12)	5 689(10)
C(6)	9 813(17)	4 226(15)	6 216(13)
Sb(2)	7 162.6(10)	4 521.5(8)	2 243.2(6)
Br(5)	5 889(2)	5 213.4(14)	3 345.9(11)
Br(6)	6 803(2)	6 107.0(13)	1 519.0(12)
Br(7)	8 133(2)	3 648(2)	1 159.1(11)
P(2)	5 499(4)	3 771(3)	1 739(3)
C(7)	4 465(14)	4 616(14)	1 767(12)
C(8)	3 497(15)	4 215(16)	1 488(13)
C(9)	5 129(16)	2 759(14)	2 289(12)
C(10)	5 702(17)	1 828(13)	2 143(14)
C(11)	5 569(15)	3 323(14)	823(10)
C(12)	5 598(18)	4 136(16)	297(11)
P(3)	7 523(4)	2 762(3)	8 266(4)
C(13)	8 250(18)	3 510(14)	7 666(11)
C(14)	8 040(18)	4 560(17)	7 778(13)
C(15)	6 221(15)	2 949(14)	8 115(13)
C(16)	5 889(17)	2 830(16)	7 350(14)
C(17)	7 854(16)	2 950(13)	9 162(10)
C(18)	8 967(18)	2 777(15)	9 312(14)

Table 5 Crystallographic and structure solution data for compounds **4** and **6**

Compound	**4**	**6**
Formula	$C_{40}H_{42}BiI_4P_3$	$C_{18}H_{46}Br_7P_3Sb_2$
M	1332.23	1158.33
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
Crystal size/mm	0.50 × 0.44 × 0.44	0.27 × 0.13 × 0.10
T/K	160(1)	160(1)
a/Å	13.936(5)	13.393(3)
b/Å	13.834(5)	13.895(4)
c/Å	22.978(10)	18.836(5)
β/°	99.04(5)	
U/Å^3	4375(3)	3505(2)
Z	4	4
D/g cm^{-3}	2.023	2.195
F(000)	2488	2184
μ(Mo-Kα)/mm^{-1}	6.99	9.67
2θ range/°	5–45	5–45
hkl range	−15 to 15, −10 to 14, −20 to 24	−4 to 14, −14 to 14, −20 to 20
No of reflections measured	6215	3466
No. of unique reflections	5717	3309
No. with $F^2 > 2\sigma(F^2)$	4672	2809
R_{int} (on F^2)	0.0362	0.0731
Weighting parameters *a*, *b*	0.0281, 4.5484	0.0833, 30.7313
$R[F^2 > 2\sigma(F^2)]$	0.0223	0.0472
R′ (all data)	0.0677	0.1613
No. of parameters	434	281
Goodness of fit on F^2	1.128	1.078
Extinction coefficient	0.000 37(3)	—
Maximum, minimum in difference map/e Å^{-3}	0.769, −0.656	0.770, −1.129

In ref. 1 we made a number of comparisons between the antimony(III) and bismuth(III) complexes and related transition metal(III) dimers, one aspect of which was that halide bridge asymmetry was generally much less in the transition metal complexes. With this in mind, it is interesting to compare the structure of the anion in **6** with that of the anionic zirconium(III) complex $[Zr_2I_7(PEt_3)_2]^-$ [18] which is quite similar to **6** except that, as with the neutral complexes,[1] the halide bridges in the zirconium complex are much more symmetric which means that a description of this complex as face-shared bioctahedral is entirely appropriate.

In refs. 1 and 19 we commented upon the basic structural types encountered for neutral and cationic antimony(III) and bismuth(III) halide complexes. The results of this study show that for complexes of the general formula $[EX_4(L)_2]^-$ a *cis* geometry seems to be preferred whereas two distinct geometries have been observed for species of the general formula $[E_2X_7(L)_2]^-$, *i.e.* **1** and **6**. We have not isolated any phosphine complexes of the general formula $[E_2X_8(L)_2]^{2-}$ but the SMe_2 complex **3** mentioned in the introduction is an example of this class in which the ligands adopt an *anti* configuration in axial sites in an edge-shared bioctahedral structure.[4]

Experimental

General Procedures.—All experiments were performed under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use. Microanalytical data were obtained at the University of Newcastle.

Antimony and bismuth trihalides (>99%), PEt_3 and PMe_2Ph were procured commercially and used without further purification.

Preparations.—$[PPh_4][BiI_4(PMe_2Ph)_2]$ **4**. Samples of BiI_3 (0.108 g, 0.183 mmol) and $[PPh_4]I$ (0.085 g, 0.183 mmol) were placed in a Schlenk flask and dissolved in nitromethane (10 cm^3) which gave an orange solution. To this, 10 equivalents of PMe_2Ph (0.26 cm^3, 1.831 mmol) were added dropwise with constant stirring which caused an immediate colour change to a very deep yellow. The reaction solution was allowed to stir for 4 h after which time it was filtered through Celite to remove a small amount of black solid which had formed. The volume of the filtrate was then reduced by vacuum to about 8 cm^3 and Et_2O (20 cm^3) was added as an overlayer. Solvent diffusion over a period of several weeks afforded orange coloured crystals of **4** (0.127 g, 53%), one of which was used for X-ray diffraction (Found: C, 36.20; H, 3.15. $C_{40}H_{42}BiI_4P_3$ requires C, 36.05; H, 3.20%).

$[PEt_3H][Sb_2Br_7(PEt_3)_2]$ **6**. A sample of PEt_3 (0.18 cm^3, 1.222 mmol) was added dropwise to a stirred solution of $SbBr_3$ (0.221 g, 0.611 mmol) in thf (10 cm^3) which led to an immediate change from colourless to pale yellow. After stirring for 1 h, the solvent volume was reduced by vacuum to about 5 cm^3 and hexane (15 cm^3) was added as an overlayer. Solvent diffusion over a period of several weeks afforded a yellow solid which was isolated and then redissolved in CH_2Cl_2 (10 cm^3). Hexane (20 cm^3) was added as an overlayer and recrystallisation by solvent diffusion over a period of several weeks afforded pale yellow crystals of **6** one of which was used for X-ray diffraction (0.174 g, 49%) (Found: C, 18.50; H, 3.80. $C_{18}H_{46}Br_7P_3Sb_2$ requires C, 18.65; H, 4.00%).

X-Ray Crystallography.—Crystal data for both structures are given in Table 5 together with other information on data collection and structure determination.

Data collection and reduction. Experimental details are identical to those described in ref. 1 except as detailed below.

Unit cell parameters were refined from 32 (for **4**) and 29 (for **6**) reflections with 2θ values (22–25°) measured on both sides of the beam to minimise systematic errors. Intensities were measured with ω/θ scans and on-line profile fitting[20] for **6** and with a conventional background–peak–background method for **4**. The intensities of 5 standard reflections varied by up to 3% and were remeasured every 60 min.

Structure solution and refinement. Both structures were solved by direct methods.[21] An extinction coefficient was refined for both structures but found to be negligible in the case of **6** and was omitted in the final cycles of refinement. The crystals of **6** were found to be racemically twinned. The enantiopole parameter[22] was refined to a value of 0.49(2) in the final least-squares cycle. Hydrogen atoms were included in geometrical positions using a riding model. For **6** the hydrogen atoms of the methyl groups were allowed to rotate as a rigid group to obtain a best fit to the local electron density. Hydrogen isotropic displacement parameters were set to be 150% of those of the carrier atoms for methyl hydrogens and 120% for all others.

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