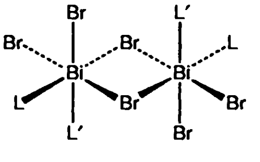
Edge-shared, Bioctahedral, Bismuth Phosphine Complexes

William Clegg,[a] R. John Errington,[a] Richard J. Flynn,[a] Marjorie E. Green,[a] David C. R. Hockless,[a] Nicholas C. Norman,*[a] Vernon C. Gibson*[b] and Kayumars Tavakkoli[b]
[a] *Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, UK*
[b] *Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK*

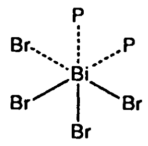
The structures of two edge-shared, bioctahedral, bismuth halide phosphine complexes $[Bi_2Br_6(PMe_3)_4]$ and $[Bi_2Br_6(PMe_2Ph)_2(OPMe_2Ph)_2]$ have been determined and compared with those of related transition-metal complexes.

The co-ordination chemistry of the heavier p-block elements with phosphine ligands is still a rather underdeveloped area and, although a fair number of complexes have been prepared, particularly for In^{III} and Sn^{IV}, very little structural data are available for these or any other elements.[1] Herein we report two structures of general formula $[Bi_2Br_6L_4]$ containing phosphine and phosphine oxide ligands (L) and comment on the differences between these structures and those of some related transition-metal complexes.

The trimethylphosphine complex $[Bi_2Br_6(PMe_3)_4]$ **1** was obtained† by stirring a suspension of $BiBr_3$ in neat PMe_3.[2] The resulting yellow solid was recrystallised from CH_2Cl_2 to give well formed yellow crystals which were characterised by X-ray crystallography.‡ Complex **1** adopts an edge-shared, bioctahedral centrosymmetric structure as shown in Fig. 1 and in the diagram. The two bismuth centres do not deviate markedly from regular octahedral geometry, in common with what is usually found for six-co-ordinate bismuth, and are bridged asymmetrically by two bromine atoms Br(1) and Br(1a).



1 L = L′ = PMe_3
2 L = PMe_2Ph, L′ = $OPMe_2Ph$



A

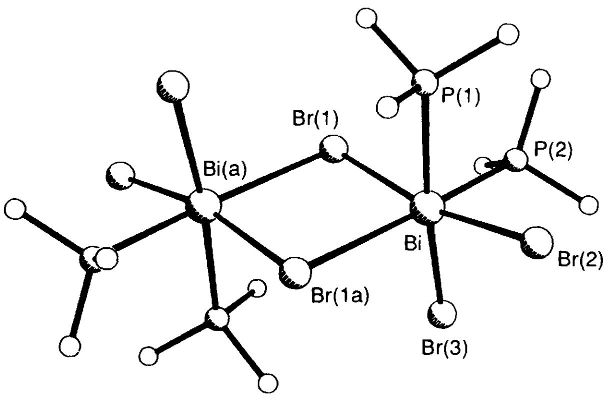


Fig. 1 A view of the molecular structure of complex **1** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Bi–Br(1) 2.875(1), Bi–Br(2) 2.774(1), Bi–Br(3) 2.916(1), Bi–Br(1a) 3.403(1), Bi–P(1) 2.866(3) and Bi–P(2) 2.714(2); Br(1)–Bi–Br(2) 167.3(1), Br(1)–Bi–Br(3) 93.7(1), Br(2)–Bi–Br(3) 97.4(1), Br(1)–Bi–P(1) 86.0(1), Br(2)–Bi–P(1) 82.2(1), Br(3)–Bi–P(1) 172.8(1), Br(1)–Bi–P(2) 86.6(1), Br(2)–Bi–P(2) 89.3(1), Br(3)–Bi–P(2) 80.4(1), P(1)–Bi–P(2) 92.4(1), Br(1)–Bi–Br(1a) 89.8(1), Br(2)–Bi–Br(1a) 94.4(1), Br(3)–Bi–Br(1a) 98.9(1), P(1)–Bi–Br(1a) 88.3(1), P(2)–Bi–Br(1a) 176.2(1) and Bi–Br(1)–Bi(a) 90.2(1)

One way of understanding this structure is in terms of the secondary bonding model advanced by Alcock[3] and discussed more recently in connection with other bismuth halide complexes.[4] As shown in **A** we can view the structure as based on a trigonal-pyramidal $BiBr_3$ centre with three secondary bonds *trans* to the Bi–Br bonds of this unit. If the acceptor orbitals of the $BiBr_3$ molecule are the Bi–Br σ^* orbitals[3,4] this *trans* arrangement is to be expected as is the observed correlation between the *trans* Br–Bi–P bond distances, *i.e.* the shortest Bi–P distance [2.714(2) *vs.* 2.866(3) Å] is *trans* to the longer Bi–Br distance [3.403(1) *vs.* 2.916(1) Å] although care must be exercised here since the bromines are in different environments, *i.e.* one terminal and one bridging. Nevertheless, it is clear that the structure adopted by **1** is the only one that allows the PMe_3 ligands to be *trans* to bromines whilst maintaining an identifiable trigonal-pyramidal $BiBr_3$ unit, and is therefore the one expected on the basis of the secondary bonding model[3] whereby the Lewis bases go *trans* to the most electronegative atoms or groups. Moreover, the observed stereochemical inactivity of the bismuth lone pair is a consequence of this model whereby the co-ordination geometry around the bismuth centre is determined

---

† Trimethylphosphine (20 cm^3) was condensed onto solid $BiBr_3$ (0.905 g, 2.017 mmol) and the resulting mixture stirred for 48 h after which time a yellow solid remained. The PMe_3 was then condensed into a receiving vessel and the resulting yellow material was dissolved in CH_2Cl_2 and cooled (−20 °C) to give pale yellow crystals of complex **1** (0.290 g, 12%). There is no obvious change during the course of the reaction but it would seem that the $BiBr_3$ slowly dissolves to form **1** which then precipitates. NMR (CO_2Cl_2): ^1H, δ 1.90 (d, $^2J_{PH}$ = 7.8 Hz, PMe_3); $^{31}P-\{^1H\}$, δ −33.3 (br, s); the observation of only one PMe_3 environment indicates the likelihood of either a fluxional process or intermolecular exchange (Found: C, 11.95; H, 3.00. Calc. for $C_{12}H_{36}Bi_2Br_6P_4$: C, 12.00; H, 3.00%).

‡ Complex **1**: $C_{12}H_{36}Bi_2Br_6P_2$, 0.18 × 0.32 × 0.36 mm, $M = 1201.7$, monoclinic, space group $P2_1/n$, $a = 7.920(1)$, $b = 12.007(2)$, $c = 16.608(2)$ Å, $\beta = 96.61(2)°$, $U = 1568.9$ Å^3, $Z = 2$, $D_c = 2.543$ g cm^{-3}, $\mu = 18.94$ mm^{-1} (Mo-Kα radiation, $\lambda = 0.710\,73$ Å), $F(000) = 1088$; $R = 0.0294$, $R' = 0.0318$ for 110 parameters, including anisotropic thermal parameters and constrained isotropic H atoms, by refinement on F from 2245 unique observed [$F > 4\sigma_c(F)$] data ($2\theta_{max}$ 50°), $w^{-1} = \sigma_c^2(F) + 16 + 109G + 11G^2 - 58S + 52S^2 - 163GS$ ($G = F_o|F_{max}$, $S = \sin/\sin\sigma_{max}$), measured at 240 K on a Stoe-Siemens diffractometer and corrected semiempirically for absorption.

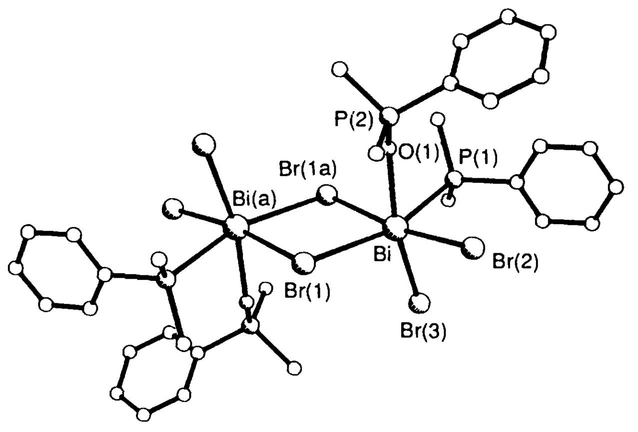
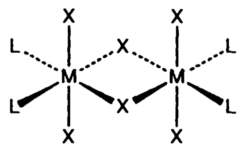


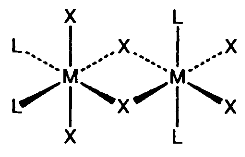
Fig. 2 A view of the molecular structure of complex **2** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Bi–Br(1) 3.362(1), Bi–Br(2) 2.741(1), Bi–Br(3) 2.788(1), Bi–Br(1a) 2.926(1), Bi–P(1) 2.725(2) and Bi–O(1) 2.371(6); Br(1)–Bi–Br(2) 92.7(1), Br(1)–Bi–Br(3) 108.5(1), Br(2)–Bi–Br(3) 92.1(1), Br(1)–Bi–P(1) 165.1(1), Br(2)–Bi–P(1) 92.3(1), Br(3)–Bi–P(1) 85.3(1), Br(1)–Bi–O(1) 86.4(1), Br(2)–Bi–O(1) 88.4(1), Br(3)–Bi–O(1) 165.0(1), P(1)–Bi–O(1) 79.7(1), Br(1)–Bi–Br(1a) 92.3(1), Br(2)–Bi–Br(1a) 171.5(1), Br(3)–Bi–Br(1a) 92.8(1), P(1)–Bi–Br(1a) 81.2(1), O(1)–Bi–Br(1a) 85.0(1) and Bi–Br(1)–Bi(a) 87.7(1)

by the BiBr$_3$ acceptor orbitals rather than by the lone pair itself.

We also carried out a reaction between BiBr$_3$ and PMe$_2$Ph in thf* and isolated crystals of the complex [Bi$_2$Br$_6$(PMe$_2$Ph)$_2$(OPMe$_2$Ph)$_2$] **2**. The structure of this compound, as determined by X-ray crystallography,† is shown in Fig. 2 and is clearly of the same basic type as **1** although in this case some adventitious oxidation has occurred such that the complex contains two phosphine and two phosphine oxide ligands. The Bi–P bond distances in **1** [Bi–P(1) 2.866(3) and Bi–P(2) 2.714(2) Å] and in **2** [Bi–P(1) 2.725(2) Å] are comparable to that found [2.762(3) Å] in the only other example of a bismuth phosphine complex, [{Bi$_2$Br$_7$(PMe$_3$)$_2$}$_n$]$^{n-}$.[5]



B



C

The structures of both **1** and **2** are similar to that of the complex [Bi$_2$I$_6$(OPPh$_3$)$_4$] **3**,[6] but are different from the related metal(III) dimers which have been observed for a number of transition-metal complexes. These latter structures fall into two types **B** and **C**. Structures of type **B** have been reported for [Zr$_2$Cl$_6$L$_4$] (L = PBu$^n_3$,[7] PEt$_3$ or PMe$_2$Ph[8]), whilst those of type **C** have been described for [Ta$_2$Cl$_6$(PMe$_3$)$_4$],[9] [Ru$_2$Cl$_6$(PBu$^n_3$)$_4$][10] and [Rh$_2$Cl$_6$(PBu$^n_3$)$_4$].[11] Cotton *et al.*[8] have stated that the reasons why different structures are adopted for these transition-metal complexes are not well understood and, although we have provided a rationale for the bismuth structures, it is clear that more detailed work is required in order fully to understand the factors which determine the ligand stereochemistry in compounds of general formula [M$_2$X$_6$L$_4$]. One factor which is important for the transition-metal complexes is the possibility of M–M bonding but this is unlikely to be significant for the bismuth examples, the metal–metal distances of which are quite long [**1**, Bi···Bi(a) 4.463; **2**, Bi···Bi(a) 4.365 Å].

Acknowledgements

We thank the SERC for financial support.

References

1 W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1976, **19**, 173.

2 See, for example, V. C. Gibson, C. E. Graimann, P. M. Hare, M. L. H. Green, J. A. Bandy, P. D. Grebnik and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1985, 2025.

3 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

4 W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, N. A. L. Williams, S. E. Stratford, S. J. Nichols, P. S. Jarrett and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1992, 193.

5 W. Clegg, R. J. Errington, G. A. Fisher, M. E. Green, D. C. R. Hockless and N. C. Norman, *Chem. Ber.*, 1991, **124**, 2457.

6 F. Lazarini and S. Milicev, *Acta Crystallogr., Sect. B*, 1976, **32**, 2873.

7 J. H. Wengrovius, R. R. Schrock and C. S. Day, *Inorg. Chem.*, 1981, **20**, 1844.

8 F. A. Cotton, M. P. Diebold and P. A. Kibala, *Inorg. Chem.*, 1988, **27**, 799.

9 A. P. Sattelberger, R. B. Wilson and J. C. Huffman, *J. Am. Chem. Soc.*, 1980, **102**, 7111; *Inorg. Chem.*, 1982, **21**, 2392.

10 F. A. Cotton, M. Matusz and R. C. Torralba, *Inorg. Chem.*, 1989, **28**, 1516.

11 J. A. Muir, M. M. Muir and A. A. Rivera, *Acta Crystallogr., Sect. B*, 1974, **30**, 2062.

Received 11*th February* 1992; *Communication* 2/00705C

---

* Compound **2** was obtained from BiBr$_3$ (0.089 g, 0.198 mmol) and 1 equivalent of PMe$_2$Ph (0.027 g) in tetrahydrofuran (thf) (20 cm^3) as a sparingly soluble yellow powder from which a small number of yellow crystals were obtained after crystallisation (over a period of 2 months) from thf–hexane mixtures at −30 °C (Found: C, 26.25; H, 2.90. Calc. for $C_{32}H_{44}Bi_2Br_6O_2P_4$: C, 25.90; H, 2.95%).

† Complex **2**: $C_{32}H_{44}Bi_2Br_6O_2P_4$, 0.42 × 0.15 × 0.14 mm, M = 1482.0, triclinic, space group $P\bar{1}$, a = 8.007(1), b = 10.367(2), c = 14.761(3) Å, α = 106.95(1), β = 91.39(1), γ = 105.75(1)°, U = 1121.0 Å^3, Z = 1, D_c = 2.195 g cm^{-3}, μ = 13.28 mm^{-1}, $F(000)$ = 688; R = 0.0290, R' = 0.0339 for 208 parameters and 3304 unique observed [$F > 4\sigma_c(F)$] data ($2\theta_{max}$ 50°), $w^{-1} = \sigma_c^2(F) + 1 + 11G + 29G^2 + 3S + 4S^2 - 24GS$, measured at room temperature and corrected for absorption.

Atomic coordinates, thermal parameters and bond lengths and angles for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Instructions to Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.