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Preliminary Communication

A cationic, four-coordinate, ten-electron bismuth(III) complex: synthesis and structure of $[\text{BiPh}_2(\text{HMPA})_2][\text{BF}_4]$ (HMPA = hexamethylphosphoramide)

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Abstract

The synthesis and structure of the cationic, four-coordinate, ten-electron bismuth(III) complex $[\text{BiPh}_2(\text{HMPA})_2]^+$ (HMPA = hexamethylphosphoramide) is reported. The coordination geometry around the bismuth centre is that of a trigonal bipyramid with one equatorial site vacant and with phenyls in the other equatorial positions and the HMPA ligands in axial sites.

An interesting area of the chemistry of the heavier Group 15 elements, in terms of both structure and potential reactivity, is that of cationic compounds with low coordination numbers. Within this field the compounds most studied are the phosphonium ions, $[\text{R}_2\text{P}]^+$, where R is usually a good π -donor group such as dialkylamido [1]. Well characterised examples involving arsenic, antimony and bismuth are much less common, and with these elements there is a marked tendency towards increasing Lewis acidity of the element centre with a concomitant increase in coordination number. This is illustrated by the dimeric nature of the cation $[\text{cyclo-AsS}_2\text{C}_2\text{H}_4]^+$ in the solid state [2], and by the structure of the decamethylarsocenium cation $[\text{As}(\eta\text{-C}_5\text{Me}_5)_2]^+$ [3] in which the C_5Me_5 rings are π rather than σ -bonded to the arsenic centre. Alternatively, coordination by two-electron donor ligands can be observed affording species of the general formula $[\text{EX}_2(\text{L})_n]^+$. Structurally characterised exam-

ples for antimony and bismuth include crown ether complexes of SbCl_2^+ and $\text{BiCl}_2/\text{Br}_2^+$, viz. $[\text{SbCl}_2(18\text{-C-6})]^+$ [4], $[\text{BiCl}_2(18\text{-C-6})]^+$ [5], $[\text{BiBr}_2(18\text{-C-6})]^+$ [6] and $[\text{BiCl}_2(\text{MeCN})(18\text{-C-6})]^+$ [7], together with the related polyethylene glycol complexes $[\text{BiBr}_2(\text{hexaethylene glycol})]^+$ and $[\text{BiI}_2(\text{pentaethylene glycol})]^+$ [6] in which the crown and polyether ligands are hexa- or penta-dentate. The arene complex $[\text{BiCl}_2(\text{C}_6\text{Me}_6)]\text{-}[\text{AlCl}_4]$ has also been described [8], and in all cases the EX_2^+ unit is bent with X–E–X angles in the range 89.1–94.0°; only one example is known where the EX_2^+ fragment is linear, namely the HMPA complex $[\text{BiI}_2(\text{HMPA})_4]^+$ [9]. A further example in this general class is the octahedral catecholate complex $[\text{Sb}(\text{O}_2\text{C}_6\text{H}_4)(1,10\text{-phen})_2]^+$ [10].

Diorganocations of antimony and bismuth, R_2E^+ , have not hitherto been structurally characterised but Ph_2Sb^+ is reportedly formed on electrochemical oxidation of Ph_4Sb_2 in THF solution [11], and infrared, Raman and analytical data have been presented for the arsine oxide complex $[\text{BiPh}_2(\text{OAsPh}_2)_2][\text{ClO}_4]$ (1) [12]. Herein, we describe the synthesis and X-ray crystal structure of a complex of Ph_2Bi^+ , $[\text{BiPh}_2(\text{HMPA})_2]\text{-}[\text{BF}_4]$ (2), which is related to 1.

The reaction between Ph_2BiBr [13], AgBF_4 and two equivalents of HMPA (hexamethylphosphoramide, $\text{OP}(\text{NMe}_2)_3$) in THF solution afforded, after work up, colourless crystals of 2. * Spectroscopic data ** were consistent with the expected formula and the structure

* HMPA (0.058 g, 0.325 mmol) was added dropwise to a stirred solution of Ph_2BiBr (0.072 g, 0.172 mmol) in THF (5 cm³) at room temperature. This was followed by the addition of a solution of AgBF_4 (0.032 g, 0.162 mmol) in THF (5 cm³) which led to the formation of a pale yellow precipitate that turned dark grey after a few minutes. The mixture was filtered through Celite and the colourless filtrate was reduced in volume by vacuum to about 5 cm³. Hexane (20 cm³) was added as an overlayer, and solvent diffusion over a period of days at –20°C afforded colourless crystals of 2 (70%).

** Spectroscopic data for 2. NMR (CD_2Cl_2): ¹H δ 8.24 (d, 4H, *o*-C₆H₅, *J* = 8 Hz), 7.69 (t, 4H, *m*-C₆H₅, *J* = 8 Hz), 7.38 (t, 2H, *p*-C₆H₅, *J* = 8 Hz), 2.46 (d, 36H, $\text{OP}(\text{NMe}_2)_3$, *J*_{PH} = 9.5 Hz); ¹³C(¹H) δ 137.1 (s, *o*-C₆H₅), 132.6 (s, *m*-C₆H₅), 129.4 (s, *p*-C₆H₅), 37.3 (d, $\text{OP}(\text{NMe}_2)_3$, *J*_{PC} = 4.5 Hz); ³¹P(¹H) (H_3PO_4) δ 26 (s, $\text{OP}(\text{NMe}_2)_3$); ¹¹B ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) δ –1; ¹⁹F ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) δ +0.3. Elemental analysis, C₂₄H₄₆BBiF₄N₆O₂P₂ requires C, 35.65; H, 5.75; N, 10.40. Found C, 35.85; H, 5.65; N, 10.25.

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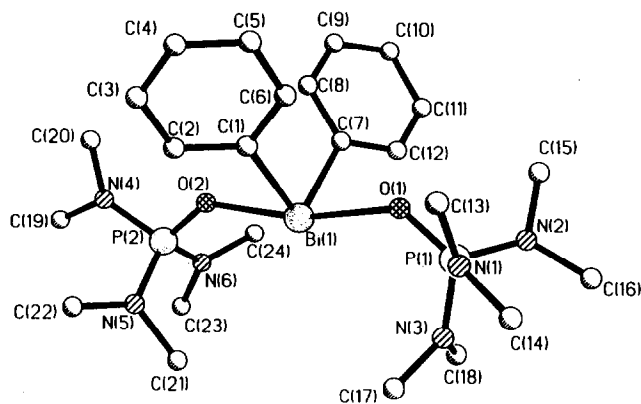


Fig. 1. A view of the structure of the cation $[\text{BiPh}_2(\text{HMPA})_2]^+$ in 2 showing the atom numbering scheme. All methyl and phenyl group hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi(1)–C(1) 2.239(13), Bi(1)–C(7) 2.255(15), Bi(1)–O(1) 2.358(8), Bi(1)–O(2) 2.370(8) Å; O(1)–Bi(1)–O(2) 167.5(3), O(1)–Bi(1)–C(1) 87.5(4), O(2)–Bi(1)–C(1) 84.5(4), O(1)–Bi(1)–C(7) 85.3(4), O(2)–Bi(1)–C(7) 85.5(4), C(1)–Bi(1)–C(7) 93.2(5)°.

was established by X-ray crystallography, * the results of which are shown in Fig. 1. The solid state structure of **2** is ionic and comprises separated $[\text{BiPh}_2(\text{HMPA})_2]^+$ cations (hereafter 2^+) and tetrafluoroborate anions with no close interionic contacts. The structure of 2^+ comprises a central bismuth atom bonded to two phenyl groups and two HMPA ligands with a coordination geometry which can be described as trigonal bipyramidal with one vacant equatorial site or disphenoidal. In terms of this description, the phenyl groups are in equatorial positions (C(1)–Bi(1)–C(7) 93.2(5)°) and the HMPA ligands are *trans* in axial sites (O(1)–Bi(1)–O(2) 167.5(3)°); the Bi–C bond lengths (av. 2.247 Å) and Bi–O distances (av. 2.364 Å) are unexceptional and within normal ranges [9,13,14].

* Crystal data for **2**: $\text{C}_{24}\text{H}_{46}\text{BBiF}_4\text{N}_6\text{O}_2\text{P}_2$, $M = 808.4$, monoclinic, space group $P2_1/c$, $a = 14.641(6)$, $b = 16.005(7)$, $c = 15.179(7)$ Å, $\beta = 104.96(3)^\circ$, $V = 3436(3)$ Å³, $Z = 4$, $D_x = 1.56$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 5.28$ mm⁻¹, $F(000) = 1608$, $T = 295$ K.

Data were collected on a Siemens P3m diffractometer for a unique quadrant of reciprocal space with $3 < 2\theta < 55^\circ$. The structure was solved by heavy atom methods and full-matrix least-squares refinement (361 parameters) converged to final residual indices $R = 0.064$, $wR = 0.066$, $S = 1.37$ using 3892 data for which $I > 2\sigma(I)$. Hydrogen atoms were placed in idealised positions (C–H 0.96 Å).

$R = \sum |\Delta| / \sum |F_o|$; $wR = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$; $S = [\sum w\Delta^2 / (\text{N.O.} - \text{N.V.})]^{1/2}$; $\Delta = F_o - F_c$.

The atomic coordinates, thermal parameters, and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

We have commented previously on the structures of four-coordinate, ten-electron bismuth complexes [15]. The overall structure of 2^+ , *i.e.* disphenoidal, is that expected on the basis of VSEPR arguments for a four-coordinate centre with ten valence electrons and is similar to that found in the anions $[\text{BiBr}_2\text{Ph}_2]^-$ and $[\text{BiI}_2\text{Ph}_2]^-$ [13]; in all cases, the more electronegative atoms or ligands are found, as expected, in the axial sites. Such deviations as are observed from this standard structure are found in macromolecular, solid-state materials or when bulky and/or π -donor ligands are present [15]. The predicted structure for the cation in **1** (*i.e.* 1^+) is similar [12] and both complexes may also be viewed as ligand-stabilised Ph_2Bi^+ cations, which would be expected to be bent, with the *trans* ligands interacting with a vacant Bi 6p orbital.

The structure of **2** is also interesting in comparison with the structure of the indium complex $[\text{In}^{\text{I}}\text{Pr}_2(\text{THF})_2][\text{BF}_4]$ (**3**) [16]. The structure of the cation in **3** (3^+) is shown in the diagram, and has a similar overall disphenoidal coordination geometry but in which the positions of the organo groups and the two-electron donor ligands are reversed. As a ligand complex of $^{\text{I}}\text{Pr}_2\text{In}^+$, the linear geometry of this fragment is unsurprising, but in the absence of a formal lone pair, the *cis* arrangement of the THF ligands (O–In–O 79.6(2)°) is not so readily explained, the most likely explanation being the presence of reasonably short interionic $\text{In} \cdots \text{F}$ contacts (absent in **2** – for which the shortest Bi \cdots F contacts are > 4.2 Å).

Further synthetic and structural studies are in progress: it will be interesting, for example, to explore the reactivity of these species and to make compounds with a chelating bidentate ligand in which an alternative arrangement of ligands is required.



1^+ , L = OAsPh₃, 2^+ , L = HMPA

3^+

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References

- 1 A.H. Cowley and R.A. Kemp, *Chem. Rev.*, **85** (1985) 367.
- 2 N. Burford, B.W. Royan, J.M. Whalen, J.F. Richardson and R.D. Rogers, *J. Chem. Soc., Chem. Commun.*, (1990) 1273. See also C. Payrastré, Y. Madaule and J.G. Wolf, *Tetrahedron Lett.*, **31** (1990)

- 1145 for the synthesis of [As(Et₂N)₂][AlCl₄] and [As(Et₂N)₂]-[CF₃SO₃] which are apparently monomeric in solution.
- 3 P. Jutzi, T. Wippermann, C. Krüger and H.J. Kraus, *Angew. Chem., Int. Ed. Engl.*, 22 (1983) 250.
 - 4 A. Neuhaus, G. Frenzen, J. Pebler and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 618 (1992) 93.
 - 5 N.W. Alcock, M. Ravindran and G.R. Willey, *J. Chem. Soc., Chem. Commun.*, (1989) 1063.
 - 6 R.D. Rogers, A.H. Bond, S. Aguinaga and A. Reyes, *J. Am. Chem. Soc.*, 114 (1992) 2967.
 - 7 M. Schäfer, G. Frenzen, B. Neumüller and K. Dehnicke, *Angew. Chem., Int. Ed. Engl.*, 31 (1992) 334.
 - 8 W. Frank, J. Weber and E. Fuchs, *Angew. Chem., Int. Ed. Engl.*, 26 (1987) 74.
 - 9 W. Clegg, L.J. Farrugia, A. McCamley, N.C. Norman, A.G. Orpen, N.L. Pickett and S.E. Stratford, *J. Chem. Soc., Dalton Trans.*, in press.
 - 10 F. Huber, H. Preut, G. Alonzo and N. Bertazzi, *Inorg. Chim. Acta*, 102 (1985) 181.
 - 11 Y. Mourad, Y. Mugnier, H.J. Breunig and M. Ates, *J. Organomet. Chem.*, 388 (1990) C9.
 - 12 T. Allman, R.G. Goel and H.S. Prasad, *J. Organomet. Chem.*, 166 (1979) 365.
 - 13 W. Clegg, R.J. Errington, G.A. Fisher, D.C.R. Hockless, N.C. Norman, A.G. Orpen and S.E. Stratford, *J. Chem. Soc., Dalton Trans.*, (1992) 1967.
 - 14 W. Clegg, R.J. Errington, G.A. Fisher, R.J. Flynn and N.C. Norman, *J. Chem. Soc., Dalton Trans.*, (1993) 637.
 - 15 W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, D.C.R. Hockless, N.C. Norman, A.G. Orpen and S.E. Stratford, *J. Chem. Soc., Dalton Trans.*, (1992) 3515.
 - 16 B. Neumüller and F. Gahlmann, *J. Organomet. Chem.*, 414 (1991) 271.