Kurzmitteilung / Short Communication

A Phosphine Complex of Bismuth(III): X-ray Crystal Structure of $[PMe_3H][Bi_2Br_7(PMe_3)_2]$

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The reaction between $BiBr_3$ and one equivalent of PMe_3 in THF affords, after recrystallisation from $MeCN/Et_2O$, yellow crystals of $[PMe_3H][Bi_2Br_7(PMe_3)_2] \cdot 2\ (MeCN)$ (**1**), which has been characterised by X-ray crystallography. Compound **1** is the first reported bismuth-phosphine complex and comprises a polymeric anion, the monomeric unit of which contains a planar Bi_2Br_6 core, each bismuth being further bonded to a PMe_3 ligand and an additional bromide such that the bismuth resides in an octahedral coordination environment. The latter bromides form linear bridges between monomeric units; the phosphines are *trans* with respect to the Bi_2 unit, with a Bi – P distance of 2.762(3) Å. The reaction between BiI_3 and PEt_3 in THF affords, after recrystallisation from $MeCN/Et_2O$, orange crystals of $[PEt_4]_4[Bi_6I_{22}]$ (**3**) which has also been characterised by X-ray crystallography.

Phosphines are commonly used as ligands in the chemistry of the transition metals[1a], but far less is known concerning their interactions with the heavier p-block elements[1b]. Our current interest in the chemistry of bismuth[2] and the realisation that complexes of this element often exhibit appreciable Lewis acidity[3], prompted us to explore the interaction of bismuth(III) halides with trialkylphosphines. Herein we describe some preliminary results, including a structural characterisation of the first bismuth-phosphine complex.

Treatment of a THF solution of $BiBr_3$ with one equivalent of PMe_3 in toluene resulted in the precipitation of a solid which afforded well-formed pale yellow crystals after recrystallisation from $MeCN/Et_2O$ mixtures. The nature of this material, (**1**), was established by X-ray crystallography, the results of which are shown in Figures 1 and 2. Compound **1** is ionic and consists of $[PMe_3H]^+$ cations, MeCN of crystallisation and a polymeric anion, the monomer of which is $[Bi_2Br_7(PMe_3)_2]^-$ (Figure 1). The latter species can be described as based on a central, approximately planar, Bi_2Br_6 unit which resides on a crystallographic $2/m$ site, C_{2h} [Bi – Br(3) (terminal) = 2.747(1) Å, Bi – Br(1) (bridging) = 2.988(1) Å]. The re-

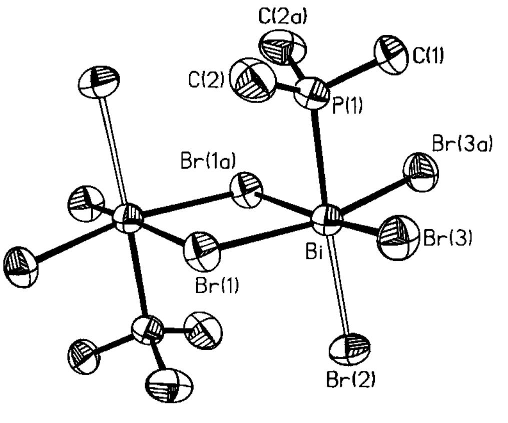

Figure 1. A view of the $[Bi_2Br_7(PMe_3)_2]^-$ anion in **1** showing the atom numbering scheme together with the bridging bromide from an adjacent monomer unit. Ellipsoids are drawn at the 50% level. Selected bond lengths [Å] and angles [deg]: Bi – Br(1) 2.988(1), Bi – Br(2) 3.103(1), Bi – Br(3) 2.747(1), Bi – P(1) 2.762(3); Br(1) – Bi – Br(2) 94.5(1), Br(1) – Bi – Br(3) 89.9(1), Br(2) – Bi – Br(3) 94.0(1), Br(1) – Bi – Br(1a) 82.5(1), Br(1) – Bi – Br(3a) 169.0(1), Br(3) – Bi – Br(3a) 96.5(1), Br(1) – Bi – P(1) 87.6(1), Br(2) – Bi – P(1) 177.3(1), Br(3) – Bi – P(1) 84.2(1), Bi – Br(2) – Bi(b) 180

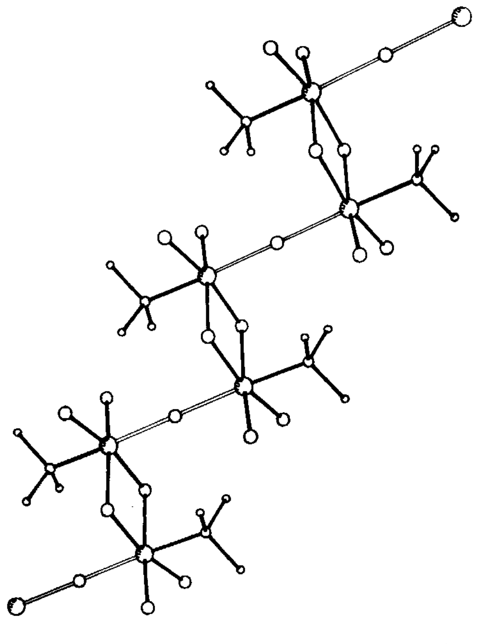

Figure 2. A section of the polymeric $[\{Bi_2Br_7(PMe_3)_2\}_n]^{n-}$ anion

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maining coordination around the bismuth centres, which are octahedral (thus implying a stereochemically inactive lone pair), is completed by *trans* PMe_3 ligands [Bi–P = 2.762(3) Å] and *trans* bromides [Bi–Br(2) = 3.103(1) Å], the latter forming linear (Bi–Br–Bi = 180.0°) bridges between the monomers (Figure 2).

Not only is **1** the first bismuth-phosphine complex, it is also, as far as we are aware, the first structure containing a bismuth–phosphorus bond of any kind. As such, we shall quote the Bi–P bond length [2.762(3) Å] without further comment but we note the interest in the adsorption of bismuth (and antimony) on III–V semiconductor surfaces, such as GaP and InP[4], the surface structural characterisation of which is aided by information on relevant bond distances[5,6].

Some comparison with other bismuth halide species is appropriate. The basic Bi_2X_{10} unit, seen in **1** (Figure 1), is found also in $[Bi_2Br_{10}]^{4-}$ [7,8], and linear halide bridges between these units are observed in the structures of $Cs_3[Bi_2Cl_9]$ (which is also polymeric)[9] and $[C_5H_5NH]_6[Bi_4Cl_{18}]$[10], but we shall leave more detailed comparisons to a future publication.

^1H and ^{31}P solution NMR data for **1** are consistent with the solid state structure although the signals due to the PMe_3 ligand are broad, indicating the likelihood of some kind of exchange phenomenon. The iodide derivative **2** (prepared as for **1** but using BiI_3) is similar although the phosphorus signal due to the PMe_3 ligand was too broad to observe in this case.

$[PMe_3H][Bi_2X_7(PMe_3)_2] \cdot 2(MeCN)$
1: X = Br
2: X = I

$[PEt_4]_4[Bi_6I_{22}]$
3

The analogous chemistry with PEt_3 proceeds quite differently. Treatment of a THF solution of BiI_3 with one equivalent of PEt_3 resulted in the precipitation of an orange powder from which orange crystals were obtained after recrystallisation from MeCN/Et_2O mixtures. These crystals were shown by X-ray crystallography to contain $[PEt_4]_4[Bi_6I_{22}]$ (**3**); a view of the $[Bi_6I_{22}]^{4-}$ anion is shown in Figure 3. Compound **3** contains the largest discrete halo-anion of bismuth so far reported, the previous largest being $[Bi_4Cl_{18}]^{6-}$ [10], but it is structurally similar to $[Bi_4Br_{16}]^{4-}$ [11] and also to BiI_3[12], as a fragment of which it may be considered. Other structurally characterised iodobismuth anions include $[BiI_4]_x^{x-}$ [13], $[BiI_6]^{3-}$ [14], $[Bi_2I_9]^{3-}$ [15], and $[Bi_3I_{12}]^{3-}$ [16].

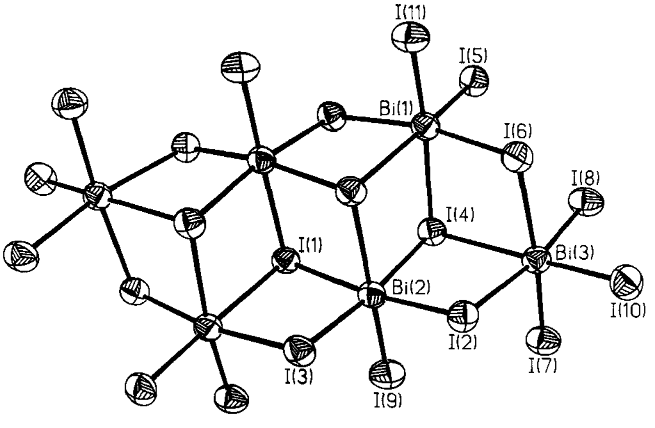

Figure 3. A view of the $[Bi_6I_{22}]^{4-}$ anion in **3** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond lengths [Å] and angles [deg]: Bi(1)–I(4) 3.468, Bi(1)–I(5) 2.896, Bi(1)–I(6) 2.998, Bi(1)–I(11) 2.858, Bi(1)–I(1a) 3.340, Bi(1)–I(3a) 3.256, Bi(2)–I(1), 3.196, Bi(2)–I(2) 3.007, Bi(2)–I(3) 3.047, Bi(2)–I(4) 3.150, Bi(2)–I(9) 2.844, Bi(2)–I(1a) 3.404, Bi(3)–I(2) 3.348, Bi(3)–I(4) 3.351, Bi(3)–I(6) 3.363, Bi(3)–I(7) 2.904, Bi(3)–I(8) 2.916, Bi(3)–I(10) 2.893; *cis* I–Bi–I 81.6–96.4, *trans* I–Bi–I 167.6–179.5, Bi–μ_2-I–Bi 94.8–98.0, Bi–μ_3-I–Bi 89.7–96.6

Clearly, all of the above reactions are complex and we will not speculate further at this stage on mechanistic details. The formation of anionic complexes in conjunction with phosphonium cations, however, is suggestive of hydrolysis due to traces of water and/or hydrogen halide in the reaction mixture although we stress that all of the reported reactions are repeatable even with freshly prepared and purified reagents. Full details of our ongoing studies in this and related areas will be the subject of a future full paper.

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Experimental

NMR: Bruker AMX 500, room temperature. ^1H chemical shifts are referenced to Me_4Si, ^{31}P shifts to 85% H_3PO_4. All ^{31}P spectra were obtained with gated ^1H decoupling.

Synthesis of Compound **1**: A solution of PMe_3 in toluene (0.20 ml of a 0.674 M solution, 0.134 mmol) was added to a solution of $BiBr_3$ (0.060 g, 0.134 mmol) in THF (10 ml). The pale yellow colour due to the $BiBr_3$ darkened to a deep yellow with concomitant production of a yellow precipitate. After stirring for 4 h at room temp. all volatiles were removed by vacuum. Addition of MeCN (5 ml) resulted in a yellow solution and a pale yellow solid residue. The yellow solution was transferred to a clean flask, layered with Et_2O (20 ml), cooled to −25°C and stored for several days after which time yellow crystals of **1** had formed (0.021 g, 26%).

The orange iodide complex **2** was prepared in a similar manner using BiI_3. Satisfactory microanalytical data could not be obtained for **1** or **2** due to the facile loss of solvent of crystallisation.

NMR (CD_3CN): Compound **1**, ^1H: δ = 1.92 (dd, 9H, PMe_3H, $^3J_{HH}$ = 5.6, $^2J_{PH}$ = 15.9 Hz), 2.64 (broad d, 18H, PMe_3, $^2J_{PH}$ = 14.4 Hz), 6.32 (d decets, 1H, PMe_3H, $^3J_{HH}$ = 5.6, $^1J_{PH}$ = 508.6 Hz). – ^{31}P: δ = 2.4 (d decets, PMe_3H, $^2J_{PH}$ = 15.9, $^1J_{PH}$ = 508.6 Hz), 21.0 (broad s, PMe_3, peak width at half height = 333 Hz). – Compound **2**, ^1H: δ = 1.77 (dd, 9H, PMe_3H, $^3J_{HH}$ = 5.4, $^2J_{PH}$ = 15.6 Hz), 1.56 and 2.19 (broad singlets, 18H, PMe_3), 6.32 (d decets, 1H, PMe_3H, $^3J_{HH}$ = 5.4, $^1J_{PH}$ = 509.3 Hz). – ^{31}P: δ = 2.2 (d decets, PMe_3H, $^2J_{PH}$ = 15.6, $^1J_{PH}$ = 509.3 Hz).

Synthesis of Compound **3**: PEt_3 (30 µl, 0.203 mmol) was added to a solution of BiI_3 (0.120 g, 0.203 mmol) in THF (10 ml). The dark orange colour due to the BiI_3 became lighter with concomitant precipitation of an orange solid. After stirring for 4 h at room temp., all volatiles were removed by vacuum. Addition of MeCN (10 ml) resulted in an orange solution and an orange solid residue. The solution was transferred to a clean flask, layered with Et_2O (25 ml), cooled to −25°C and stored for several days after which time orange crystals of **3** had formed (0.046 g, 29%).

Reactions with $BiCl_3$ and $BiBr_3$ were carried out in a similar manner but in no case could satisfactory analytical data be obtained due to facile loss of solvent of crystallisation.

X-ray Crystallographic Studies: Crystallographic data for **1** at 240 K. Crystal dimensions 0.61 × 0.31 × 0.19 mm, M_r = 1288.6; orthorhombic, a = 8.031(3), b = 20.541(9), c = 10.371(3) Å; V = 1710.9 $Å^3$; space group *Pnnm*, Z = 2; D_c = 2.501 g cm^{-3}; μ(Mo-K_α) = 18.5 mm^{-1}. Data measured on a Stoe-Siemens diffractometer using Mo-K_α radiation (λ = 0.71073 Å) (graphite-monochromated), ω/Θ scan mode with $2\Theta_{max}$ = 50°, *hkl* ranges 0–9, 0–24, 0–12, respectively, with equivalents (*hkl* < 0). 5735 reflections measured, of which 1610 were unique, and 1390 with $F > 4\sigma_c(F)$

used for structure determination. Data corrected for Lorentz/polarisation effects and absorption (semi-empirically). Minimum and maximum transmission factors 0.002 and 0.026, respectively. The structure was solved by direct methods[17] with atomic scattering factors taken from ref.[18] Anisotropic thermal motion parameters for all atoms refined to minimise $\Sigma w\Delta^2$, $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 188 + 2808\,G + 4011\,G^2 - 667H + 771H^2 - 6873GH$ ($G = F_o/F_{max}$, $H = \sin\Theta/\sin\Theta_{max}$)[19]. H atoms not located. For 81 refined parameters, $R = 0.067$, $R' = 0.030$, Goodness of fit 1.06. Largest feature in final difference map near Bi[20].

Table 1. Atomic coordinates ($\times\ 10^4$) for compound **1**

Atom	x	y	z	Site Occupancy
Bi	3210(1)	4159(1)	0	0.50
Br(1)	5000	5000	1899(1)	0.50
Br(2)	0	5000	0	0.25
Br(3)	2148(1)	3371(1)	1976(1)	1.00
P(1)	5973(3)	3358(1)	0	0.50
C(1)	5358(15)	2494(6)	0	0.50
C(2)	7293(13)	3479(5)	1396(11)	1.00
P(2)	5670(9)	405(3)	0	0.25[a]
C(3)	5000	0	1438(13)	0.50
C(4)	7820(32)	399(13)	0	0.25[a]
N(1)	2547(47)	1188(19)	0	0.50
C(10)	1494(34)	1514(12)	0	0.50
C(11)	140(42)	1957(10)	0	0.50

[a] Disordered atoms with half the normal site occupancy.

Several atoms lie in special positions (Table 1). The central Bi_2Br_2 ring of the anion lies on an inversion centre, with a two-fold axis passing through the bridging Br atoms and a mirror plane through the Bi and P atoms. Br(2), linking the anions together into a polymer, lies on an inversion centre. The cation is disordered over an inversion centre, such that P(2) and one methyl group, C(4), have alternative sites of half-occupancy, while the other two methyl groups [C(3) and its symmetry equivalent by inversion] coincide in the two alternatives; the crystallographic symmetry of the disordered cation is C_{2h} ($2/m$), with P(2) and C(4) on the mirror plane and C(3) on the two-fold axis. The acetonitrile solvent molecules are ordered on mirror planes. The space group was determined from systematic absences, and chosen in preference to the non-centrosymmetric *Pnn*2 on the basis of intensity statistics and successful refinement of the simple disorder model. Orthorhombic Laue symmetry was confirmed by the measurement of several equivalent sets of data ($R_{int} = 0.048$).

Preliminary data for **3** at 240 K. Crystal dimensions $0.15 \times 0.33 \times 0.35$ mm, monoclinic; $a = 35.876(9)$, $b = 14.730(5)$, $c = 23.063(5)$ Å, $\beta = 111.05(2)°$, $V = 11374$ Å^3; space group $C2/c$, $Z = 8$. ω/Θ scan mode with $2\Theta_{max} = 50°$. *hkl* ranges −42 to 42, 0 to 17, 0 to 27, respectively, with equivalents ($k < 0$). Structure solution from direct methods and Fourier difference synthesis accomplished using 5347 unique observed reflections [$F > 4\sigma_c(F)$], current R value 0.097. The $[PEt_4]^+$ cations and $[Bi_6I_{22}]^{4-}$ anion have refined satisfactorily; various models to deal with disordered solvent of crystallisation are currently being tried.

CAS Registry Numbers

1: 136016-56-3 / **1** · 2 MeCN: 136086-42-5 / **2**: 136016-58-5 / **3**: 136016-60-9

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