Bismuth(III) Chloride Complexation with Diphosphine and Diarsine Oxide Ligands: Formation and Crystal Structures of $[BiCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}]_2$ and $[BiCl_3\{As(O)MePh_2\}\{Ph_2As(O)CH_2CH_2As(O)Ph_2\}]_n$†

Gerald R. Willey,*[a] **Martin D. Rudd,**[a] **Christopher J. Samuel**[a] **and Michael G. B. Drew**[b]
[a] *Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*
[b] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, UK*

The reactions of bismuth(III) chloride and $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2AsCH_2CH_2AsPh_2$ (dpae) have been studied. The yellow products isolated initially were characterised by spectroscopic (^1H and ^{31}P NMR, IR) and microanalytical data as the 1:1 addition compounds $BiCl_3{\cdot}dppm$ and $BiCl_3{\cdot}dpae$ respectively. Recrystallisation of these products from boiling acetonitrile/charcoal effected oxidation of the ligands and resulted in the formation of two new molecular adducts whose structures have been determined by X-ray crystallography. Crystals of $[BiCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}]_2$ **1** are triclinic, space group $P\bar{1}$ with $Z = 2$. There are two independent centrosymmetric molecules in the unit cell with similar edge–edge shared bioctahedral structures. Each bismuth centre is six-co-ordinate with approximal octahedral geometry being bonded to two terminal chlorine atoms, two bridging chlorine atoms and two oxygen (ligand) atoms. *In situ* ligand oxidation dppm ⟶ $Ph_2P(O)CH_2P(O)Ph_2$ occurs and the resulting bidentate (*OO'*) chelation gives rise to puckered six-membered $\overline{\text{Bi–O–P–C–P–O}}$ ring formation. Crystals of $[BiCl_3\{As(O)MePh_2\}\{Ph_2As(O)CH_2CH_2As(O)Ph_2\}]_n$ **2** are monoclinic, space group $P2_1/a$ with $Z = 4$. The structure consists of one-dimensional polymeric chains. Here the *in situ* ligand oxidation is more complex and results in the formation of two arsine oxide ligands, *viz.* dpae ⟶ $Ph_2As(O)CH_2CH_2As(O)Ph_2$ + $As(O)MePh_2$ both of which are involved in co-ordination to Bi^{III}. Each bismuth atom is bonded in an approximately *mer*-octahedral arrangement to three terminal chlorine atoms and three oxygen (ligand) atoms. Of the latter, one is provided by a monodentate $As(O)MePh_2$ molecule and the other two by separate $Ph_2As(O)CH_2CH_2As(O)Ph_2$ molecules which, by virtue of their bidentate bridging mode, are linked to adjacent metal centres.

Molecular compounds of bismuth(III) chloride containing X-donor ligands (X = N, P or As) fall under the aegis of the co-ordination chemistry of the Group 15 halides MX_3 (M = As, Sb or Bi; X = halogen).[1] For X = N, many of the earlier adducts have limited spectroscopic characterisation and claims of structural recognition are often exaggerated; for X = P or As there is a general paucity of information. Very recent studies by Norman and co-workers[2-5] have been directed towards this imbroglio and some six or so crystal structures of various phosphine complexes of bismuth(III) halides and halogen anions have now been described. One of the 'problems' associated with σ-donor phosphine and arsine ligands ER_3 (E = P or As; R = alkyl, aryl or halogen) is the fairly facile oxidation $E^{III} \longrightarrow E^V$ that can occur *in situ* and which can lead to the formation of phosphine and arsine oxide $\geqslant$E=O metal derivatives.[6] An elegant example of such specious ligand rearrangement is provided by $[Bi_2Br_6(PMe_2Ph)_2\{P(O)Me_2Ph\}_2]$[3] as obtained from the $BiBr_3$–PMe_2Ph–tetrahydrofuran system following adventitious oxidation of some of the original phosphine ligand to the phosphine oxide. The resulting structure features both $\sigma(P) \longrightarrow$ Bi and $\sigma(O) \longrightarrow$ Bi ligand binding.

In this paper we describe the reactions of bismuth(III) chloride with $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2AsCH_2CH_2AsPh_2$ (dpae) chosen at the outset as potential bidentate chelating ligands. However, the versatility of these ligands in terms of binding modes (in addition to bidentate chelation there is bidentate bridging across two separated metal centres, bidentate bridging across two multiple-bonded metal centres, and bidentate bridging across a linear M–O–M group[7]) added a certain intrigue as to the final outcome. As we shall see, 'normal' bidentate chelation was observed but ligand oxidation resulted in the formation of two unexpected adducts of bismuth(III) chloride whose identities have been revealed by X-ray diffraction studies. Previously we have reported the structural characterisation of two bismuth(III) complexes involving X = S or Se, *viz.* $[BiCl_3{\cdot}Pr^n{}_2P(S)P(S)Pr^n{}_2]_2$ and $[(Me_2N)_3PSeSeP(NMe_2)_3]^{2+}[(BiCl_4)_2]_n{}^{2n-}$ where, again, ligand oxidation *in situ* is a feature.[8]

Experimental

All manipulations of materials were carried out using standard Schlenk techniques in conjunction with a dinitrogen-filled 'dry'-box. Solvents were stored over CaH_2–P_4O_{10} and distilled under a dinitrogen atmosphere immediately prior to use.

Bismuth trichloride and the phosphine (dppm) and arsine (dpae) compounds were obtained commercially and used directly without further purification. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 580B spectrometer with samples as Nujol mulls between CsI plates. The ^1H (400 MHz), ^{13}C (100.6 MHz) and ^{31}P (161.9 MHz) NMR spectra were recorded on a Bruker ACP 400 spectrometer using CD_3CN solutions; the ^{31}P spectra were obtained with gated ^1H decoupling. Chemical shifts to low field of reference compounds ^1H ($SiMe_4$), ^{13}C ($SiMe_4$) and ^{31}P (external 85% H_3PO_4) are reported as positive.

Preparation of Complexes.—(*a*) $BiCl_3{\cdot}dppm$. A solution of dppm (0.122 g, 0.317 mmol) in acetonitrile (25 cm^3) was added

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

dropwise to a stirred and chilled 0 °C solution of $BiCl_3$ (0.10 g, 0.317 mmol) in acetonitrile (30 cm^3). The resulting mixture was stirred at 50 °C for 6 h to give a yellow solution. Following filtration through Celite the solution was concentrated to *ca.* 10 cm^3 by gradual removal of solvent *in vacuo* when a deep yellow semicrystalline solid precipitated from solution. This product was washed with hexane (3 × 20 cm^3) and diethyl ether (2 × 20 cm^3) and pumped to dryness *in vacuo* for several hours at room temperature. Yield: 0.175 g (79%), m.p. 250 °C (with decomp.) (Found: C, 41.20; H, 3.00; Cl, 15.10. $C_{25}H_{22}BiCl_3P_2$ requires C, 42.90; H, 3.15; Cl, 15.20%). IR $\tilde{\nu}/cm^{-1}$(Nujol) 1582s, 1307m, 1272m, 1186m, 1156m, 1092m, 1039m, 1025s, 1000m, 970w, 918m, 850w, 781s, 720vs, 695s, 510m, 500m, 479m, 439w, 420m (ligand), 277vs (br), 252 (sh) ν(BiCl). NMR δ_H 7.28–7.77 (20 H, m, C_6H_5), 4.04 (2 H, t, CH_2).

(*b*) $[BiCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}]_2$ **1**. A sample of $BiCl_3$·dppm (0.15 g, 0.11 mmol) was dissolved in MeCN (25 cm^3) and heated at reflux for 10 min in the presence of activated charcoal. The resulting mixture was filtered rapidly through Celite to give a clear yellow solution which on standing in the refrigerator overnight deposited a crop of bright yellow block crystals. Yield: 0.049 g (31%), m.p. 182–184 °C (Found: C, 40.45; H, 2.75; Cl, 14.40. $C_{50}H_{44}Bi_2Cl_6O_4P_4$ requires C, 41.05; H, 3.05; Cl, 14.55%). IR $\tilde{\nu}/cm^{-1}$(Nujol) 1141s and 1122s ν(P=O), 1189w, 1092m, 1052m, 1025m, 996m, 974m, 781s, 723vs, 686s, 615w, 566w, 539m, 515m, 505m, 496m, 465m, 425m, 413m, 404w (ligand), 258vs (br) ν(BiCl). NMR δ_H 7.68–7.18 (40 H, m, C_6H_5), 3.92 (4 H, t, CH_2).

(*c*) $BiCl_3$·dpae. To a stirred solution of $BiCl_3$ (0.10 g, 0.317 mmol) in acetonitrile (25 cm^3) maintained at 0 °C was added a solution of dpae (0.154 g, 0.318 mmol) in acetonitrile (25 cm^3) over a period of several hours. The resulting mixture was heated to 50 °C and stirred overnight. Filtration through Celite gave a light yellow solution which on concentrating to *ca.* 10 cm^3 deposited a yellow semicrystalline solid. This product was washed with pentane (2 × 20 cm^3) and diethyl ether (2 × 20 cm^3) and pumped *in vacuo* for several hours to complete dryness. Yield: 0.21 g (83%), m.p. 94–97 °C (Found: C, 40.00; H, 3.35; Cl, 13.15. $C_{26}H_{24}As_2BiCl_3$ requires C, 38.95; H, 3.00; Cl, 13.25%). IR $\tilde{\nu}/cm^{-1}$(Nujol) 1302m, 1152m, 1134m, 1081m, 1076m, 1066m, 1056m, 1023m, 999m, 962m, 906w, 851w, 738vs, 707m, 692s, 617w, 578m, 480s, 457s (ligand), 324 (sh), 304vs (br), 282 (sh) ν(BiCl). NMR δ_H 7.30–7.38 (20 H, m, C_6H_5), 2.15 (4 H, s, CH_2); δ_C 133.62, 129.46, 129.21 (C_6H_5), 24.51 (CH_2).

(*d*) $[BiCl_3\{As(O)MePh_2\}\{Ph_2As(O)CH_2CH_2As(O)Ph_2\}]_n$ **2**. A sample of $BiCl_3$·dpae (0.15 g, 0.09 mmol) was dissolved in acetonitrile (30 cm^3) and heated at reflux for 10 min in the presence of activated charcoal. The resulting mixture was filtered rapidly through Celite to give a light yellow solution which on cooling in the refrigerator deposited a crop of small tan needle crystals. Yield: 0.07 g (37%), m.p. 226–227 °C (Found: C, 42.25; H, 3.25; Cl, 9.65. $C_{39}H_{37}As_3BiCl_3O_3$ requires C, 42.80; H, 3.40; Cl, 9.70%). IR $\tilde{\nu}/cm^{-1}$(Nujol) 1183w, 1159m, 1088s, 1038w, 1025w, 996m, 919w, 889m (ligand), 829s ν(As=O), 723vs, 684s, 615w, 601w, 484m, 465s, 454s (ligand), 370 (br, sh), 315 (sh), 278vs (br) ν(BiCl). NMR δ_H 7.39–7.48 (30 H, m, C_6H_5), 2.30 (4 H, s, CH_2), 1.14 (3 H, s, CH_3).

X-Ray Crystallography.—Crystal data are given in Table 1, together with refinement details. Data for both crystals were collected with Mo-Kα radiation using the MARresearch image plate system. The crystals were positioned at 75 mm from the image plate. 95 Frames were measured at 2° intervals with a counting time of 10 min for **1** and 2 min for **2**. Data analysis was carried out with the XDS program.[9] Both structures were

Table 1 Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{50}H_{44}Bi_2Cl_6O_4P_4$	$C_{39}H_{37}As_3BiCl_3O_3$
M	1463.40	1093.78
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/a$
a/Å	10.662(6)	16.291(8)
b/Å	15.334(7)	11.987(10)
c/Å	17.721(8)	19.986(13)
α/°	89.6(1)	
β/°	72.2(1)	102.3(1)
γ/°	70.9(1)	
U/Å^3	2624.7	3812.8
Z	2	4
D_c/mg m^{-3}	1.852	1.905
μ/mm^{-1}	7.166	7.455
$F(000)$	1408	2112
Crystal size/mm	0.02 × 0.01 × 0.02	0.03 × 0.03 × 0.03
θ range for data collection/°	2.66–25.84	1.99–25.05
h,k,l ranges	0–13, −15 to 15, −17 to 18	−17 to 17, 0–14, −23 to 23
Reflections measured	7684	11 227
Independent reflections (R_{int})	4577 (0.072)	6114 (0.042)
Data/parameters	4577/243	6114/411
Goodness-of-fit on F^2	0.843	1.059
Final R indices [$I > 3\sigma(I)$]		
$R1$	0.099	0.071
$wR2$	0.229	0.156
R indices (all data)		
$R1$	0.171	0.167
$wR2$	0.413	0.285
Weighting scheme parameters	$a = 0.14, b = 218.0$	$a = 0.11, b = 93.4$
Largest difference peak and hole/e Å^{-3}	2.278, −1.580	1.587, −1.458

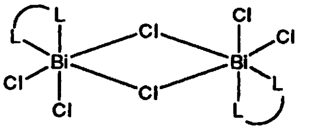
Details in common: $T = 293(2)$ K; λ(Mo-Kα) 0.7107 Å; full-matrix least-square refinement on F^2; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

solved using direct methods with the SHELX 86 program.[10] Empirical absorption corrections were carried out using the DIFABS program.[11] In compound **1** the Bi and P atoms were refined anisotropically and the remaining atoms isotropically. The phenyl rings were refined as rigid groups. The hydrogen atoms were included in calculated positions. In compound **2** all non-hydrogen atoms were refined isotropically, apart from one phenyl ring, atoms of which showed signs of disorder. Hydrogen atoms were included in calculated positions with methyl hydrogens as refineable rigid groups. Both structures were then refined using SHELXL.[12] All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading. The final coordinates for compounds **1** and **2** are given in Tables 2 and 3 and important dimensions in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Direct treatment of an acetonitrile solution of $BiCl_3$ with $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2AsCH_2CH_2AsPh_2$ (dpae) provides the yellow microcrystalline 1:1 molecular adducts $BiCl_3$·dppm or $BiCl_3$·dpae respectively. Of the several structural possibilities a dimeric halogen-bridged structure (see below) is proposed for these compounds as supported by satisfactory spectroscopic data and by virtue of the fact that the bismuth(III) chloride adducts obtained subsequently from the oxidised forms of these ligands adopt this structural type.



In the case of $BiCl_3$·dppm the ^1H NMR spectrum shows a broad multiplet at δ 7.28–7.77 and a triplet at δ 4.04 [*J*(P–H) 10 Hz] confirming the presence of co-ordinated ligand: the triplet nature of the methylene (CH_2) signal reflects splitting by two equivalent phosphine centres following bidentate attachment.[13] The ^{31}P NMR spectrum shows a singlet at δ −19.98 assigned to the co-ordinated PPh_2 groups of the chelating dppm.[14,15] Not surprisingly compound **1**, which adopts this exact structure (see later discussion), shows a similar spectroscopic profile: the ^1H NMR spectrum consists of a broad multiplet δ 7.68–7.18 and a triplet at δ 3.92 [*J*(P–H) 10 Hz] for the phenyl ring and backbone methylene protons of the ligand respectively. However the appearance of the two new bands at 1141 and 1122 cm^{-1} ν(P=O)[16] in the IR spectrum of complex **1** and the emergence of a singlet observed at δ +33.01 in its ^{31}P NMR spectrum confirm the presence of the ligand in its oxidised P^V form. Similar trends are observed for $BiCl_3$·dpae and compound **2**. For the ^1H NMR spectra a broad multiplet at *ca.* δ 7.3–7.5 for the aromatic ring protons and a broadened singlet at *ca.* δ 2.15–2.30 for the backbone CH_2 protons are common to both; the 'extra' singlet at δ 1.14 observed for compound **2** is due to the methyl protons of the arsine ligand $As(O)MePh_2$. The IR spectrum of compound **2** shows an intense band at 829 cm^{-1} ν(As=O)[16] not present in the spectrum of $BiCl_3$·dpae reflecting conversion to arsine(V) oxides.

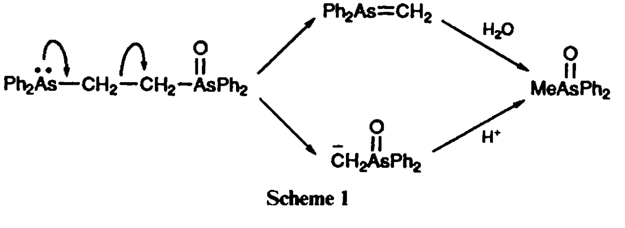
In attempting to grow crystals suitable for diffraction studies, recrystallisation of $BiCl_3$·dppm and $BiCl_3$·dpae using boiling acetonitrile in the presence of activated charcoal afforded pale yellow needle crystals of $[BiCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}]_2$ **1** and $[BiCl_3\{As(O)MePh_2\}\{Ph_2As(O)CH_2CH_2As(O)Ph_2\}]_n$ **2** respectively. The identification of these new molecular adducts featuring *oxide* ligands was only unambiguously established by X-ray diffraction studies.

What we are observing is the *in situ* oxidation of (*a*) dppm $\longrightarrow Ph_2P(O)CH_2P(O)Ph_2$(dppom) and (*b*) dpae $\longrightarrow Ph_2As(O)CH_2CH_2As(O)Ph_2$(dpaoe) + $As(O)MePh_2$. Such reactions in the presence of a metal substrate have been noted previously, *e.g.* the formation of $[CoCl_2\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}]$ from the reaction of $CoCl_2$ and $Ph_2PCH_2CH_2PPh_2$ in acetone solution.[17] One recipe for direct formation involves the heating at reflux of toluene solutions of the parent diphosphine/diarsine for 1 h with H_2O_2 (31.5%) present in excess.[18] In the present reaction systems the adventitious introduction of air/water molecules in conjunction with bismuth(III) chloride provides a feasible pathway for the oxidation of the phosphine and arsine ligands. While not a common reagent bismuth(III) has been used as an oxidising agent in organic chemistry; for example Bi_2O_3 in acetic acid converts α-ketols to α-diketones.[19] Perhaps the more surprising aspect is the cleavage of the C–C bond in the diarsinoethane (dpae). This can be rationalised if it is the 'half-oxidised' As^{III}–As^V compound that undergoes the cleavage. The lone pair of electrons on the more electron-rich As^{III} centre moves towards the more electron-demanding As^V and expels a carbanion stabilised by the adjacent arsenoxide (Scheme 1).

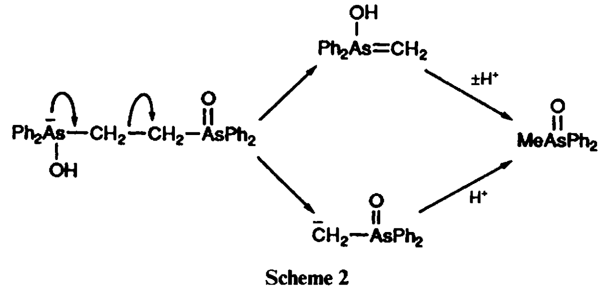
The carbanion $As(O)Ph_2CH_2^-$ has been used as a reagent for organic synthesis, *e.g.* indirect nucleophilic halogenomethylations.[20] Interestingly the isolation of $[UBr_4\{Ph_2As(O)CH_2CH_2AsPh_2\}_2]^{21}$ from the reaction of UBr_4 and $Ph_2AsCH_2CH_2AsPh_2$ in acetone provides an example of such a 'half-oxidised' ligand as mentioned above; the ligand attachment to the metal is unidentate O-donor *via* the $Ph_2As(O)$ moiety with As–O 1.64(1) Å. For comparison the equivalent distance in compound **2** is almost identical.

Alternatively the electron density on the As^{III} may be enhanced by the addition of a nucleophile such as hydroxide as supplied by adventitious water and/or chlorohydroxobismuth(III) species (Scheme 2).

Structure of Compound **1**.—The structure of **1** consists of two independent centrosymmetric structures with similar geometry consisting of edge–edge shared bioctahedra. One molecule is shown in Fig. 1 together with the atomic numbering scheme. Each bismuth atom is linked to two terminal chlorine atoms [2.47(1), 2.50(1); 2.49(1), 2.58(2) Å], two bridging chlorine atoms [Bi–Cl 2.59(1), 3.04(2); 2.68(2), 2.97(2) Å] and to two mutually *cis* oxygen donor atoms from the bidentate ligand $[Ph_2P(O)CH_2P(O)Ph_2]$ attached in the chelating (*OO′*) mode [Bi–O 2.31(3), 2.42(2); 2.21(4), 2.32(5) Å]. The bond lengths show significant variation in the Bi–Cl distances. Thus in each molecule, the two shortest Bi–Cl distances are to terminal chlorine atoms; the next shortest is to the bridging chlorine atom *trans* to oxygen. This chlorine atom also completes the



Scheme 1



Scheme 2

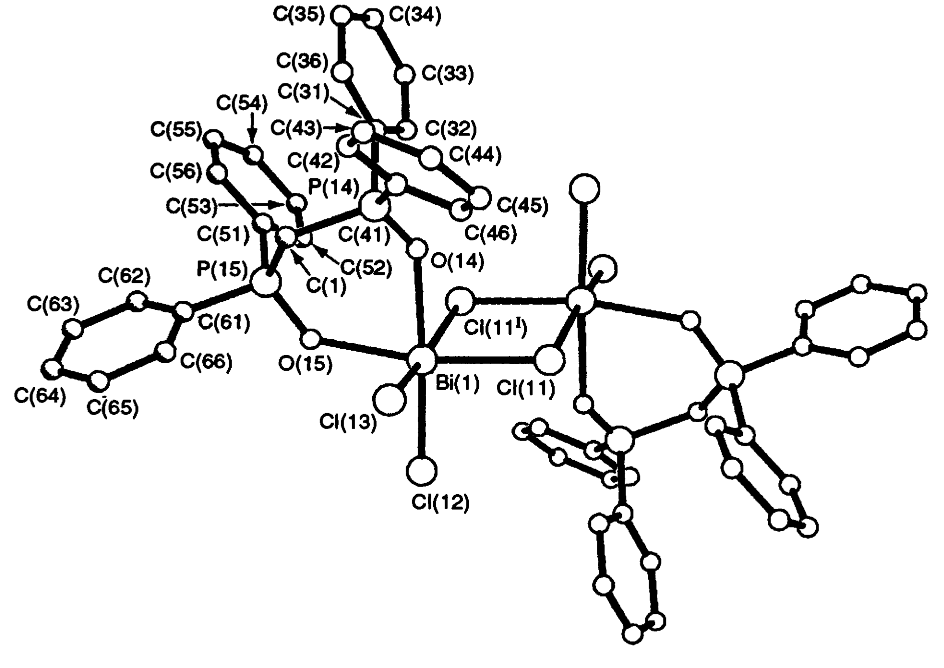


Fig. 1 A view of the centrosymmetric dimeric structure of [BiCl$_3${Ph$_2$P(O)CH$_2$P(O)Ph$_2$}]$_2$ 1. One molecule is shown; the other in the asymmetric unit has similar dimensions. Symmetry relation: I $-x$, $-y$, $-z$

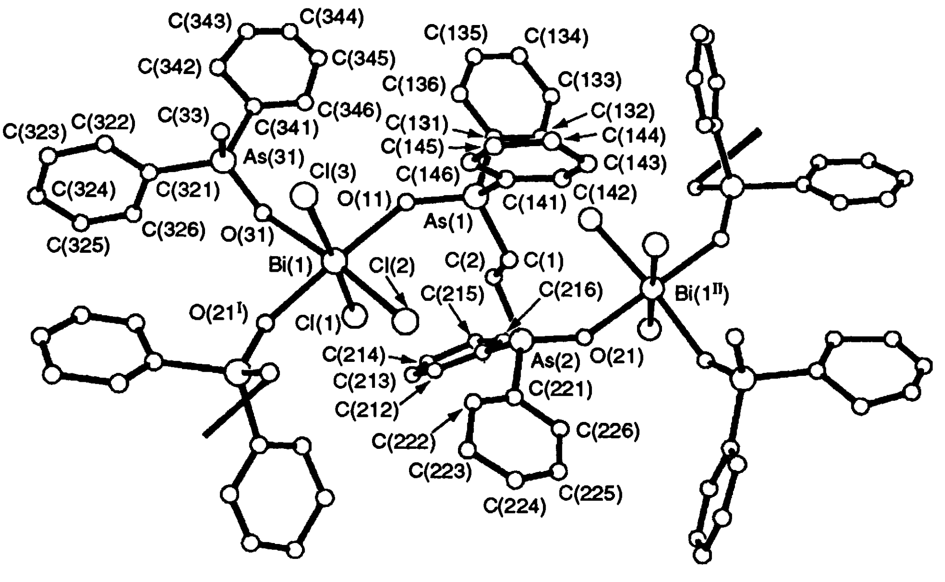


Fig. 2 A view of the polymeric structure of [BiCl$_3${As(O)MePh$_2$}{Ph$_2$As(O)CH$_2$CH$_2$As(O)Ph$_2$}]$_n$ 2. Symmetry relations: I $x - \frac{1}{2}, \frac{1}{2} - y, z$; II $\frac{1}{2} + x, \frac{1}{2} - y, z$

mutually *cis* BiCl$_3$ unit, a moiety often found in bismuth chemistry. The other chlorine bridging atom (*trans* to a terminal chlorine atom) is much more weakly bound at a distance *ca.* 0.4 Å greater than the other bridging distance.

As is apparent from Table 4, the six-co-ordinate environment is quite close to idealised octahedral geometry. Bidentate ligand attachment results in the formation of six-membered Bi–O–P–C–P–O rings with internal angles P–C–P 110(2), 117(2); C–P–O 114(2), 115(2); 110(2), 114(3); Bi–O–P 141(2), 132(2); 129(2), 137(2)° and a ligand 'bite' angle of O–Bi–O 81(1); 84(1)°. For [Bi$_2$Br$_6$(dmpe)$_2$], where dmpe = 1,2-bis(dimethylphosphino)ethane, a similar ligand attachment results in the formation of five-membered Bi–P–C–C–P chelate rings with a ligand bite angle of P–Bi–P 76.3(2)°.[4] Regarding the two bridging chlorine atoms as lying in the equatorial plane, then each pair of terminal chlorine and oxygen atoms is mutually *cis* and occupies one axial and one equatorial position per metal centre. Each oxygen atom lies *trans* to a chlorine atom in accord with a bonding picture of oxygen (σ-lone pair) donation into an empty low-lying Bi–Cl (σ*) acceptor orbital.[22] The present structure is an example of a [Bi$_2$X$_6$(bidentate ligand)$_2$] classification (X = halogen) which is somewhat rare. Indeed the recently reported [Bi$_2$Br$_6$(dmpe)$_2$][4] represents the first example of such a bidentate P-donor chelate complex with Bi$^{\mathrm{III}}$. Similar structures with unidentate ligands include [Bi$_2$Br$_6$(PMe$_3$)$_4$],[3] [Bi$_2$I$_6${P(O)Ph$_3$}$_4$][23] and [Bi$_2$Br$_6$(PMe$_2$Ph)$_2${P(O)Me$_2$Ph}$_2$].[3] General considerations as to why such [Bi$_2$X$_6$L$_4$] compounds adopt this particular centrosymmetric structure in preference to other geometric isomers are discussed in ref. 4.

Structure of Compound 2.—The structure of 2, shown in Fig. 2 together with the atomic numbering scheme, consists of a one-dimensional polymeric structure along the screw axis in the *b* direction. The individual bismuth atoms are bonded in an

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Bi(1)	242(1)	1280(1)	48(1)
Cl(11)	−1866(11)	785(8)	68(6)
Cl(12)	1044(16)	1332(9)	−1429(7)
Cl(13)	−1190(12)	2945(7)	307(6)
O(14)	−451(35)	1262(23)	1479(13)
P(14)	−414(11)	1658(7)	2118(6)
O(15)	1976(24)	1709(16)	301(13)
P(15)	2201(10)	1928(6)	1077(6)
C(1)	597(45)	2435(29)	1917(24)
C(31)	174(33)	860(18)	2727(17)
C(32)	800(32)	−65(20)	2413(14)
C(33)	1366(35)	−734(15)	2864(19)
C(34)	1306(34)	−478(20)	3628(18)
C(35)	680(35)	447(22)	3942(14)
C(36)	114(36)	1116(16)	3491(18)
C(41)	−2092(30)	2398(21)	2722(19)
C(42)	−2227(34)	3004(24)	3344(20)
C(43)	−3538(42)	3626(23)	3773(18)
C(44)	−4713(32)	3642(24)	3579(22)
C(45)	−4578(32)	3035(27)	2957(23)
C(46)	−3267(39)	2414(23)	2528(18)
C(51)	3308(36)	957(21)	1389(22)
C(52)	3762(39)	131(25)	908(19)
C(53)	4790(42)	−642(21)	1023(24)
C(54)	5365(39)	−587(27)	1620(27)
C(55)	4912(46)	239(33)	2102(23)
C(56)	3883(47)	1012(25)	1986(22)
C(61)	2988(27)	2779(16)	923(16)
C(62)	2247(24)	3677(18)	818(18)
C(63)	2919(36)	4327(15)	632(22)
C(64)	4333(37)	4078(21)	551(23)
C(65)	5074(25)	3180(24)	657(21)
C(66)	4402(27)	2531(17)	843(18)
Bi(2)	391(2)	3655(1)	5008(1)
Cl(21)	−971(13)	2575(10)	5297(8)
Cl(22)	−1912(14)	5033(11)	4976(9)
Cl(23)	1534(20)	3141(14)	3503(8)
O(24)	2199(45)	2460(33)	5234(17)
P(24)	−198(13)	3638(8)	7035(7)
O(25)	−185(43)	4097(23)	6290(25)
P(25)	2324(13)	2110(8)	6006(7)
C(2)	727(44)	2453(28)	6804(24)
C(71)	3525(28)	2483(20)	6266(17)
C(72)	3811(33)	2249(21)	6969(15)
C(73)	4854(37)	2480(24)	7148(17)
C(74)	5609(32)	2944(25)	6622(21)
C(75)	5323(31)	3179(22)	5918(19)
C(76)	4280(31)	2948(20)	5740(14)
C(81)	−1901(28)	3689(22)	7614(17)
C(82)	−3016(37)	4379(21)	7482(18)
C(83)	−4382(31)	4492(21)	7944(22)
C(84)	−4633(28)	3916(25)	8538(20)
C(85)	−3519(36)	3226(22)	8671(17)
C(86)	−2152(31)	3113(19)	8209(18)
C(91)	586(32)	4035(20)	7655(14)
C(92)	461(31)	3781(18)	8421(15)
C(93)	972(39)	4177(24)	8911(14)
C(94)	1608(41)	4829(25)	8634(18)
C(95)	1734(36)	5084(21)	7867(19)
C(96)	1223(34)	4687(20)	7377(14)
C(101)	2741(52)	1055(22)	5773(28)
C(102)	2968(49)	769(27)	4986(25)
C(103)	3298(47)	−163(31)	4750(20)
C(104)	3401(49)	−810(22)	5303(27)
C(105)	3174(48)	−524(28)	6090(24)
C(106)	2844(48)	408(32)	6325(20)

Table 3 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Bi(1)	7 630(1)	932(1)	7 603(1)
Cl(1)	8 835(4)	1 082(6)	8 682(3)
Cl(2)	7 574(4)	3 039(5)	7 464(3)
Cl(3)	6 298(4)	678(6)	6 476(3)
O(11)	8 641(9)	852(12)	6 929(7)
O(21)	11 718(9)	3 936(12)	8 295(7)
O(31)	7 568(9)	−1 070(12)	7 815(8)
As(1)	9 246(1)	1 659(2)	6 582(1)
C(1)	9 826(13)	2 709(16)	7 205(9)
C(131)	10 012(13)	737(18)	6 250(9)
C(132)	10 756(15)	1 124(21)	6 195(11)
C(133)	11 299(19)	426(29)	5 943(17)
C(134)	11 062(21)	−568(34)	5 707(13)
C(135)	10 313(24)	−902(24)	5 756(12)
C(136)	9 769(18)	−321(23)	6 004(12)
C(141)	8 602(15)	2 481(19)	5 813(10)
C(142)	8 987(17)	3 241(23)	5 513(12)
C(143)	8 567(22)	3 809(25)	4 961(13)
C(144)	7 744(26)	3 473(43)	4 657(16)
C(145)	7 371(21)	2 725(34)	4 987(12)
C(146)	7 794(17)	2 174(30)	5 551(15)
C(2)	10 393(13)	2 209(18)	7 846(8)
As(2)	10 944(1)	3 247(2)	8 509(1)
C(211)	11 396(13)	2 363(20)	9 279(8)
C(212)	10 880(17)	1 927(20)	9 678(11)
C(213)	11 252(25)	1 255(27)	10 205(12)
C(214)	12 042(21)	937(33)	10 360(15)
C(215)	12 533(21)	1 286(34)	9 910(14)
C(216)	12 186(19)	2 103(31)	9 405(12)
C(221)	10 150(16)	4 307(22)	8 687(11)
C(222)	9 392(18)	4 101(23)	8 707(13)
C(223)	8 810(18)	4 899(27)	8 830(16)
C(224)	9 137(25)	5 954(36)	8 893(21)
C(225)	9 944(29)	6 173(31)	8 857(28)
C(226)	10 438(19)	5 419(24)	8 730(20)
As(3)	7 168(2)	−2 133(2)	7 441(1)
C(321)	6 642(16)	−3 030(18)	7 953(12)
C(322)	5 931(19)	−3 609(31)	7 689(14)
C(323)	5 492(24)	−4 279(27)	8 065(15)
C(324)	5 752(20)	−4 206(31)	8 719(19)
C(325)	6 490(25)	−3 746(33)	9 054(19)
C(326)	6 860(19)	−3 105(24)	8 658(15)
C(33)	6 407(11)	−1 800(17)	6 742(8)
C(341)	7 982(12)	−2 969(15)	7 118(8)
C(342)	7 857(12)	−4 107(15)	7 010(11)
C(343)	8 445(16)	−4 738(14)	6 764(13)
C(344)	9 158(13)	−4 231(24)	6 626(11)
C(345)	9 283(10)	−3 093(25)	6 735(11)
C(346)	8 695(14)	−2 462(16)	6 981(11)

approximately *mer*-octahedral geometry to three terminal chlorine atoms and three oxygen (ligand) atoms. The latter are provided by one As(O)MePh$_2$ molecule and two separate Ph$_2$As(O)CH$_2$CH$_2$As(O)Ph$_2$ (dpaoe) molecules which, by virtue of their bidentate bridging mode, form direct links with two adjacent metal centres. There is some variation within the terminal Bi–Cl distances at 2.540(6), 2.594(6), 2.790(6) Å and the Bi–O distances at 2.241(12), 2.342(14), 2.443(14) Å; there seems no clear reason for this although obviously steric effects in such a crowded environment are likely to be important. As is apparent from Fig. 2, the environment of the bismuth atom is only slightly distorted from ideal octahedral.

What is of interest in this present structure is the clear preference of each dpaoe ligand to adopt a bidentate bridging mode thereby linking two symmetry related BiCl$_3$·As(O)MePh$_2$ units with resultant polymer formation. There is a precedent of such a bridging mode for this particular ligand, *viz.* [(SnPh$_3$Cl)$_2$(dpaoe)][24] where the diarsine oxide ligand spans two tin centres *via* oxygen co-ordination, As–O 1.665(4) Å. (In passing we note that there are several examples of bidentate bridging for the phosphorus(v) counterpart Ph$_2$P(O)CH$_2$CH$_2$P(O)Ph$_2$ (dppoe), *e.g.* [{SnPh$_3$(NO$_3$)}$_2$(dppoe)],[25] [(SnPh$_3$Cl)$_2$(dppoe)][26] and [(SnBu$^n{}_2$Cl$_2$)(dppoe)].[27]) The alternative bonding mode featuring bidentate chelation of dpaoe molecule(s) could, in theory, give rise to

Table 4 Selected dimensions in compounds **1** and **2** (bond lengths in Å and angles in °)

Compound **1**			
Bi(1)–O(15)	2.31(3)	Bi(2)–O(25)	2.21(4)
Bi(1)–O(14)	2.42(2)	Bi(2)–O(24)	2.32(5)
Bi(1)–Cl(13)	2.472(10)	Bi(2)–Cl(21)	2.493(11)
Bi(1)–Cl(12)	2.503(12)	Bi(2)–Cl(23)	2.578(12)
Bi(1)–Cl(11)	2.587(10)	Bi(2)–Cl(22)	2.68(2)
Bi(1)–Cl(11$^{\mathrm{I}}$)	3.045(12)	Bi(2)–Cl(22$^{\mathrm{II}}$)	2.973(13)
O(15)–Bi(1)–O(14)	80.5(9)	O(25)–Bi(2)–O(24)	84.3(12)
O(15)–Bi(1)–Cl(13)	86.6(6)	O(25)–Bi(2)–Cl(21)	91.9(10)
O(14)–Bi(1)–Cl(13)	86.3(9)	O(24)–Bi(2)–Cl(21)	86.3(10)
O(15)–Bi(1)–Cl(12)	96.7(7)	O(25)–Bi(2)–Cl(23)	168.9(11)
O(14)–Bi(1)–Cl(12)	177.2(7)	O(24)–Bi(2)–Cl(23)	88.9(9)
Cl(13)–Bi(1)–Cl(12)	93.1(4)	Cl(21)–Bi(2)–Cl(23)	96.4(5)
O(15)–Bi(1)–Cl(11)	168.6(6)	O(25)–Bi(2)–Cl(22)	88.2(9)
O(14)–Bi(1)–Cl(11)	88.1(7)	O(24)–Bi(2)–Cl(22)	171.4(8)
Cl(13)–Bi(1)–Cl(11)	92.9(4)	Cl(21)–Bi(2)–Cl(22)	89.9(4)
Cl(12)–Bi(1)–Cl(11)	94.7(4)	Cl(23)–Bi(2)–Cl(22)	99.1(6)
O(15)–Bi(1)–Cl(11$^{\mathrm{I}}$)	93.3(6)	O(25)–Bi(2)–Cl(22$^{\mathrm{II}}$)	76.5(10)
O(14)–Bi(1)–Cl(11$^{\mathrm{I}}$)	87.2(9)	O(24)–Bi(2)–Cl(22$^{\mathrm{II}}$)	90.3(10)
Cl(13)–Bi(1)–Cl(11$^{\mathrm{I}}$)	173.5(3)	Cl(21)–Bi(2)–Cl(22$^{\mathrm{II}}$)	168.2(4)
Cl(12)–Bi(1)–Cl(11$^{\mathrm{I}}$)	93.3(4)	Cl(23)–Bi(2)–Cl(22$^{\mathrm{II}}$)	94.8(4)
Cl(11)–Bi(1)–Cl(11$^{\mathrm{I}}$)	85.9(3)	Cl(22)–Bi(2)–Cl(22$^{\mathrm{II}}$)	92.0(4)
Bi(1)–Cl(11)–Bi(1$^{\mathrm{I}}$)	94.1(3)	Bi(2)–Cl(22)–Bi(2$^{\mathrm{II}}$)	88.0(4)
Compound **2**			
Bi(1)–O(21$^{\mathrm{I}}$)	2.241(12)	Bi(1)–Cl(2)	2.540(6)
Bi(1)–O(11)	2.342(14)	Bi(1)–Cl(1)	2.594(6)
Bi(1)–O(31)	2.443(14)	Bi(1)–Cl(3)	2.790(6)
O(21$^{\mathrm{I}}$)–Bi(1)–O(11)	176.6(6)	O(31)–Bi(1)–Cl(1)	88.6(4)
O(21$^{\mathrm{I}}$)–Bi(1)–O(31)	84.6(5)	Cl(2)–Bi(1)–Cl(1)	91.4(2)
O(11)–Bi(1)–O(31)	96.9(5)	O(21$^{\mathrm{I}}$)–Bi(1)–Cl(3)	90.1(4)
O(21$^{\mathrm{I}}$)–Bi(1)–Cl(2)	89.1(4)	O(11)–Bi(1)–Cl(3)	93.0(4)
O(11)–Bi(1)–Cl(2)	89.5(4)	O(31)–Bi(1)–Cl(3)	88.8(4)
O(31)–Bi(1)–Cl(2)	173.6(4)	Cl(2)–Bi(1)–Cl(3)	90.9(2)
O(21$^{\mathrm{I}}$)–Bi(1)–Cl(1)	88.0(4)	Cl(1)–Bi(1)–Cl(3)	177.0(2)
O(11)–Bi(1)–Cl(1)	88.9(4)		

Symmetry transformations used to generate equivalent atoms: for **1**, I $-x, -y, -z$; II $-x, -y + 1, -z + 1$; for **2**, I $x - \frac{1}{2}, -y + \frac{1}{2}, z$; II $\frac{1}{2} + x, \frac{1}{2} - y, z$.

several species either without auxiliary [As(O)MePh$_2$] ligands or with them present, *e.g.* either [BiCl$_3$(dpaoe)]$_2$ with a presumed structure similar to that of **1** or [BiCl$_3$(dpaoe){As(O)MePh$_2$}$_x$] involving some higher-co-ordination Bi$^{\mathrm{III}}$ species. Either way puckered seven-membered ring formation $\overline{\mathrm{Bi{-}O{-}As{-}C{-}C{-}As{-}O}}$ would, of necessity, be involved and perhaps it is this unfavourable conformational arrangement that militates against chelate formation.

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