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Neutral and anionic aryloxy halides of bismuth(III)

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The preparation and crystal structures of the aryloxy bismuth halide compounds $[Bi_2Cl_4(thf)_2(\mu-OC_6H_3Me_2-2,6)_2]$, $[Bi_2Cl_4(thf)_2(\mu-OC_6H_2Me_3-2,4,6)_2]$, $[NMe_4]_2[Bi_2(OC_6H_3Me_2-2,6)_6(\mu-Cl)_2]$ and $[PPh_4]_2[BiBr_3(OC_6H_2Me_3-2,4,6)_2]$ are described. The former two compounds, which are isostructural, are neutral and comprise loosely bound polymers of more strongly bound dimers. Within the dimeric unit, the two bismuth centres are bridged by two aryloxide groups with each bismuth additionally carrying two chlorine atoms and one thf ligand. Asymmetric chlorine bridges between dimers result in the polymeric structure. The latter two structures contain aryloxy bismuth halide anions. In the structure of $[Bi_2(OC_6H_3Me_2-2,6)_6(\mu-Cl)_2]^{2-}$ two chlorine atoms form bridges between $Bi(OC_6H_3Me_2-2,6)_3$ units whereas in $[BiBr_3(OC_6H_2Me_3-2,4,6)_2]^{2-}$ a monomeric species is present. Also reported are the preparations of the compounds $[PPh_4]_2[Bi_2Br_2(OC_6H_2Me_3-2,4,6)_4(\mu-Br)_2]$, $[PPh_4]_2[BiBr_2(OC_6H_3Me_2-2,6)_3]$ and $SbCl_2(OC_6H_2Bu^t_3-2,4,6)$.

A number of technologically useful and important materials contain bismuth. With particular regard to oxo-species, these include (an example is given in parentheses) bismuth-containing copper oxide based superconductors ($Bi_2Sr_2CaCu_2O_8$),[1] bismuthate superconductors ($BaPb_{1-x}Bi_xO_3$),[2] ferroelectric materials ($SrBi_2Ta_2O_9$),[3] oxide ion conductors (Bi_2WO_6)[4] and hydrocarbon oxidation and ammination catalysts (MoO_3–Bi_2O_3).[5] In the last case, a number of bismuth–oxide–chloride systems have also been investigated with regard to the oxidative coupling of methane and dehydrogenation of ethane.[6] Potential precursors to all of the above materials are bismuth alkoxides, alkoxy anions or oxo–alkoxides but detailed reports of such compounds are still relatively scarce. Examples which have been structurally characterised include $Bi(OC_6H_3Me_2-2,6)_3$,[7] $Bi(OBu^t)_3$,[8] $[Bi_2\{OCH(CF_3)_2\}_4\{\mu-OCH(CF_3)_2\}_2(thf)_2]$ (thf = tetrahydrofuran),[9] $[Bi_2(OC_6F_5)_4(\mu-OC_6F_5)_2(thf)_4]$,[9] $[Bi_2(OC_6F_5)_4(\mu-OC_6F_5)_2(tol)_2]$ (tol = toluene),[9] $[Bi(OSiPh_3)_3(thf)_3]$,[10] $[Bi_2(\mu_2,\eta^1-OC_2H_4OMe)_4(\eta^1-OC_2H_4OMe)_2]_\infty$,[10–12] $K[Bi(OBu^t)_4]$,[13] $Na[Bi(OC_6F_5)_4(thf)]$,[14] $Na_4[Bi_2(\mu_6-O)(OC_6F_5)_8(thf)_4]$,[14] $[Bi_6(\mu_3-O)_7(\mu_3-OC_6F_5)\{Bi(OC_6F_5)_4\}_3(thf)_2]$,[15] $[Bi_6(\mu_3-O)_7(\mu_3-OC_6F_5)\{Bi(OC_6F_5)_4\}_3]\cdot 2tol$,[15] $Na[Bi_3(\mu_4-O)(OC_6F_5)_8(thf)_x]$ ($x = 1$ or 3),[16] $Na[Bi_4(\mu_3-O)_2(OC_6F_5)_9(thf)_2]$,[16] $Na_2[Bi_4(\mu_3-O)_2(OC_6F_5)_{10}(thf)_2]$,[16] $[Bi_6(\mu_3-O)_2(\mu_4-O)(OC_6F_5)_{12}(thf)_2]$,[16] $[Bi_6(\mu_3-O)_2(\mu_4-O)(OC_6F_5)_{12}(tol)]$,[16] $[Bi_4(\mu_3-O)_2(\mu_2-OBu^t)_2(OBu^t)_6]$[17] and $[Bi_6(\mu_3-O)_3(\mu_2-OR)_7(OR)_5]$ ($R = 2,6-Cl_2C_6H_3$).[18] Many of these compounds and their relationship to bismuth oxide-based materials and catalysts have been described in more detail in a recent review, with numerous key references cited, by Whitmire whose group has been one of the most active in this field.[19]

Only the first two of the above compounds are monomeric in the solid state with the expected trigonal pyramidal coordination geometry around the bismuth centre. In the other examples, coordination numbers of four to six are observed resulting from the Lewis acidity anticipated for bismuth(III) when bonded to electronegative groups.[20]

All of the above compounds contain bismuth(III) although some pentavalent species containing alkoxide groups, *viz.* $Ph_3Bi(OR)_2$, $Ph_3BiBr(OR)$ and $Ph_4Bi(OR)$ ($R = C_6F_5$, C_6Cl_5) have recently been described by Hoppe and Whitmire.[21]

As part of our interest in the chemistry of bismuth, we undertook to prepare and characterise a range of alkoxy halides of bismuth(III) the results of which are described herein. This study was motivated in part because we were not aware of any previously structurally characterised examples, although the structures of a number of antimony complexes relevant to this study have been reported, namely $SbCl(OEt)_2$,[22] $SbCl_2(OEt)$,[22] $SbCl(OBu^t)_2$,[23] $Sb_4Cl(O)(OBu^t)_3$[23] and $[Sb_2Cl_4(NHMe_2)_2(\mu-OEt)_2]$[24] together with the mixed bismuth–vanadium alkoxy chloride complex $[\{BiCl_3OV(OC_2H_4OCH_3)_3\}_2]$,[25] and also because of the recent interest, noted above, in bismuth–oxide–chloride based catalyst systems.

Results and discussion

The reaction between $BiCl_3$ and one equivalent of either $Na[OC_6H_3Me_2-2,6]$ or $Na[OC_6H_2Me_3-2,4,6]$ in thf solution afforded, after work-up and crystallisation, orange crystals of complexes which were shown by X-ray crystallography to be $[Bi_2Cl_4(thf)_2(\mu-OC_6H_3Me_2-2,6)_2]$ **1** and $[Bi_2Cl_4(thf)_2(\mu-OC_6H_2Me_3-2,4,6)_2]$ **2** respectively. Crystallographic data for these and subsequent structures are presented in Table 1. The two structures are very similar and consist primarily of dimeric units as indicated in the formulas and shown in Figs. 1 and 2; in each case the dimer resides on a crystallographic C_2 axis which runs perpendicular to the Bi_2O_2 mean plane. Within the dimer, each bismuth centre is five-coordinate with the expected square-based pyramidal geometry[20,†] in which the apical site is occupied by a chlorine atom, Cl(1) [**1**, Bi(1)–Cl(1) 2.456(2); **2**, Bi(1)–Cl(1) 2.4563(13) Å] (the C_2 axis requires that the two apical chlorine atoms adopt a *syn* rather than an *anti* arrangement with respect to the Bi_2O_2 plane). The second chlorine, Cl(2), lies in the basal plane *trans* to the aryloxide oxygen O(1), the Bi–Cl distance being somewhat longer as a result of the *trans* influence of the oxygen [**1**, Bi(1)–Cl(2) 2.585(2); **2**, Bi(1)–Cl(2) 2.5695(13) Å]. The two Bi–O(1) distances [**1**, Bi(1)–O(1) 2.211(5), Bi(1)–O(1A) 2.463(5); **2**, Bi(1)–O(1) 2.187(3), Bi(1)–O(1A) 2.497(3) Å] are significantly different such that the aryloxide groups bridge the bismuth centres asymmetrically, the longer Bi–O bond being

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† As discussed in ref. 20 and refs. therein, three-coordinate bismuth(III) is trigonal pyramidal (as expected by VSEPR) and, with suitably electronegative groups (X), moderately Lewis acidic. In terms of the bonding model whereby this Lewis acidity is associated with the Bi–X σ*-orbitals, coordination of one, two or three ligands occurs *trans* to one of the Bi–X bonds resulting in disphenoidal, square-based pyramidal and octahedral structures respectively. There is no specific geometrical requirement for the Bi(III) lone pair in this model although in the four- and five-coordinate geometries, the lone pair would generally be described as stereochemically active.

Table 1 Selected crystallographic details for the complexes **1**, **2**, **3** and **5**[a]

	1	**2**	**3**	**5**
Empirical formula	$C_{12}H_{17}BiCl_2O_2$	$C_{13}H_{19}BiCl_2O_2$	$C_{28}H_{39}BiClNO_3$	$C_{66}H_{62}BiBr_3O_2P_2$
M	473.14	487.16	682.03	1397.81
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	14.266(3)	15.769(3)	12.418(3)	11.5964(5)
b/Å	14.629(3)	13.743(3)	13.841(3)	13.1136(6)
c/Å	14.468(3)	14.405(3)	16.892(3)	38.747(2)
β/°	99.90(3)	95.58(3)	91.77(3)	95.77(1)
U/Å^3	2974.4(10)	3107.0(11)	2902.1(10)	5862.5(4)
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$
Z	8	8	4	4
μ/mm^{-1}	12.203	11.685	6.194	5.150
Extinction coefficient	0.00015(3)	0.00018(2)	0.00018(6)	0.00084(8)
Reflections measured	9327	9560	17745	36656
Independent reflections	3396	3549	6572	13388
R_{int}	0.0650	0.0283	0.0358	0.1043
Final R indices, $[I > 2\sigma(I)]$	0.0395	0.0241	0.0282	0.0659

[a] Data collected at 173(2) K.

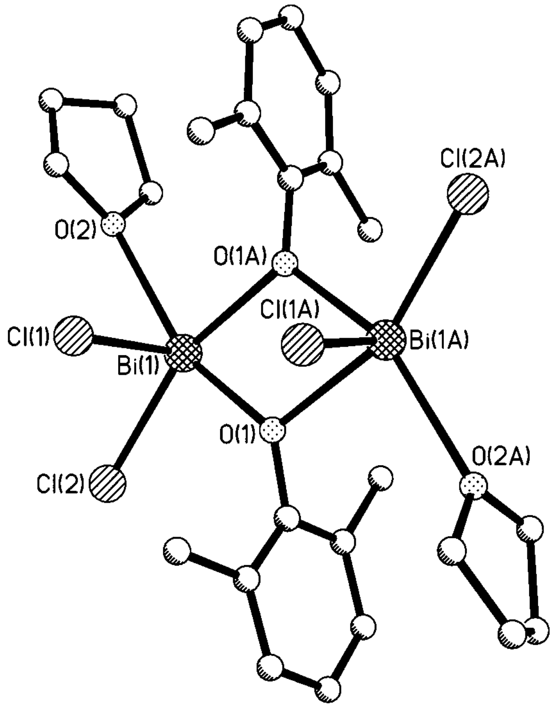


Fig. 1 A view of the dimeric unit in **1** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Selected bond lengths: Bi(1)–Cl(1) 2.456(2), Bi(1)–Cl(2) 2.585(2), Bi(1)–Cl(2B) 3.297(2), Bi(1)–O(1) 2.211(5), Bi(1)–O(1A) 2.463(5), Bi(1)–O(2) 2.648(6) Å.

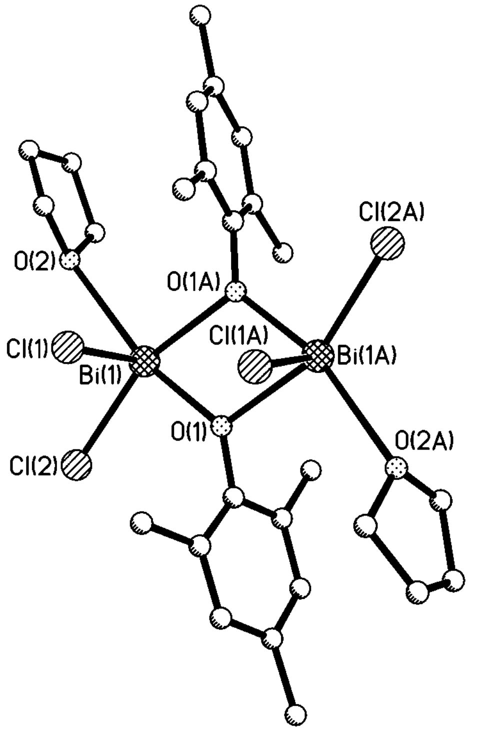


Fig. 2 A view of the dimeric unit in **2** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Selected bond lengths: Bi(1)–Cl(1) 2.4563(13), Bi(1)–Cl(2) 2.5695(13), Bi(1)–Cl(2B) 3.3317(14), Bi(1)–O(1) 2.187(3), Bi(1)–O(1A) 2.497(3), Bi(1)–O(2) 2.680(3) Å.

trans to the chlorine Cl(2). *trans* to the shorter Bi–O bond is the thf ligand for which the Bi–O distance [**1**, Bi(1)–O(2) 2.648(6); **2**, Bi(1)–O(2) 2.680(3) Å] is significantly longer than both the Bi(1)–O(1) distances as expected for a dative bond involving a relatively weakly bound ligand. All of these Bi–O distances are comparable to previously established values. For alkoxide groups bound to bismuth, a wide range is observed between about 2.1 and 2.9 Å as noted by Whitmire[19] (see also refs. 7–18), the shorter distances generally being found for terminal OR groups or in situations where the coordination numbers and/or steric congestion is low. Bi–O bond lengths to coordinated thf ligands are usually longer as stated above, typical values ranging from 2.6 to 2.8 Å.[26]

It is interesting to note that it is the aryloxide groups which form the stronger bridging interactions rather than the chlorine atoms [chlorine bridges are well established in oligomeric chlorobismuth(III) structures; for some examples see refs. 20, 26(*b*), (*c*), (*e*)], but weak interactions involving Cl(2) are present as shown for **1** in Fig. 3. Thus an interaction exists between the chlorine atom Cl(2) of one dimer and the adjacent bismuth atom of a neighbouring dimer unit (the dimer units as shown in Fig. 3 are related by the crystallographic *c* glide), this longer interaction [**1**, Bi(1)···Cl(2B) 3.297(2); **2**, Bi(1)···Cl(2B) 3.3317(14) Å] being approximately *trans* to Cl(1). The overall structure may therefore be described as a loosely bound polymer of more strongly bound dimers, somewhat similar to the situation found in the structure of [BiI_3(hmpa)] [hmpa = $OP(NMe_2)_3$] although the dimer units in that case have C_i rather than C_2 symmetry.[27] This results in bismuth coordination environments in **1** and **2** which are close to octahedral if the longer Bi···Cl interactions are included.

There are no examples of which we are aware of neutral bismuth alkoxy halides with which to compare **1** and **2**, but the structure of the antimony compound [$Sb_2Cl_4(NHMe_2)_2$-

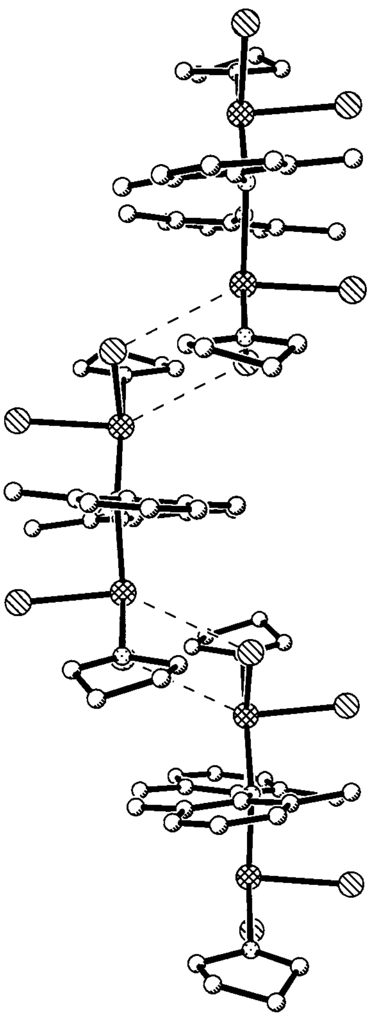


Fig. 3 A view of the polymeric structure of **1**.

(μ-OEt)$_2$] has been reported by Wright and co-workers.[24] The structure of [$Sb_2Cl_4(NHMe_2)_2(\mu\text{-}OEt)_2$] is dimeric with OEt groups which bridge slightly more asymmetrically than do the bridging aryloxy groups in **1** and **2** [Sb–O 2.005(4) and 2.478(4) Å]. The coordination sphere of each antimony is completed by two chlorine atoms and one $NHMe_2$ ligand such that the overall geometry is square-based pyramidal. Unlike in **1** and **2**, however, the two square-based pyramids share an edge between the apex of the pyramid and a basal vertex resulting in a dimer with C_i symmetry (in **1** and **2** the square pyramids share a basal edge). Some degree of intermolecular interaction involving bridging chlorine atoms is present but the distances are long and structurally not as well defined as in **1** and **2**. The structure of the unligated compound $SbCl_2(OEt)$ is also known.[22] This compound also contains a dimeric diantimony unit with slightly asymmetric bridging OEt groups [the four Sb–O distances are 1.961(9), 1.998(9), 2.359(6) and 2.507(6) Å] and chlorine atoms which may be described as terminal [Sb–Cl 2.463(2), 2.416(3), 2.400(2) and 2.411(3) Å]. As in the structures of **1** and **2**, the monomer units share a basal edge but in such a way that the apices are *anti* rather than *syn* (*i.e.* the dimer units have C_i rather than C_2 symmetry). Two of the chlorine atoms, one for each antimony, bridge very asymmetrically between dimer units [Sb $\cdots$ Cl 3.439(4) and 3.394(4) Å] consistent with a description of the structure similar to **1** and **2** as a loosely bound polymer of dimers. The other two chlorine atoms form weak links between these dimer chains [Sb $\cdots$ Cl 3.311(3) and 3.215(3) Å] resulting in a more two-dimensional structure.

We were also able to prepare an antimony complex containing two chlorine atoms and one alkoxy group, namely $SbCl_2(OC_6H_2Bu^t{}_3\text{-}2,4,6)$, the synthesis of which is described in the Experimental section. Attempted crystal structure analysis revealed that the crystals obtained contain a monomeric species hydrogen bonded to a molecule of the free alcohol $HOC_6H_2Bu^t{}_3\text{-}2,4,6$ as shown below, *i.e.* [$SbCl_2(OC_6H_2Bu^t{}_3\text{-}2,4,6)(HOC_6H_2Bu^t{}_3\text{-}2,4,6)$]. However, the structure was of poor quality and is not suitable for publication or much further discussion, although the data and subsequent refinement were sufficient to unambiguosly locate the heavy atom positions; unit cell data is provided in the Experimental section.

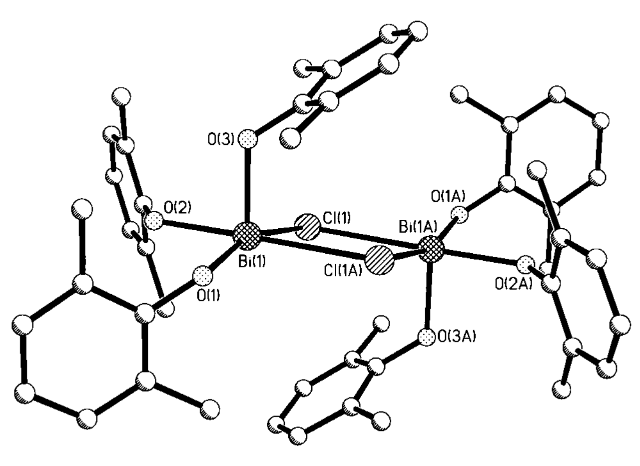
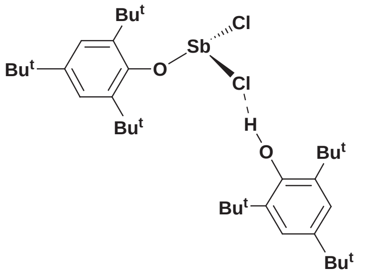
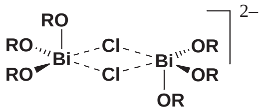


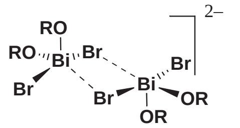
Fig. 4 A view of the dimeric dianion in **3** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Selected bond lengths: Bi(1)–Cl(1) 3.0020(12), Bi(1)–Cl(1A) 2.9325(13), Bi(1)–O(1) 2.154(3), Bi(1)–O(2) 2.152(3), Bi(1)–O(3) 2.113(3) Å.



In addition to the preparation and characterisation of neutral alkoxy bismuth halides, we were also interested in looking at anionic species. The Lewis acidity of bismuth(III) when coordinated to electronegative substituents means that the addition of, for example, a halide anion source provides a ready mechanism of preparing anionic bismuthate compounds.[26a,b] Thus addition of [NMe_4]Cl to the neutral, tris(aryloxide) $Bi(OC_6H_3Me_2\text{-}2,6)_3$[7] in CH_2Cl_2 solution afforded, after work-up, crystals of the ionic compound [NMe_4]$_2$[$Bi_2(OC_6H_3Me_2\text{-}2,6)_6(\mu\text{-}Cl)_2$] **3**, the structure of which was established by X-ray crystallography (Fig. 4). Compound **3** exists as discrete ions in the solid state with no short interionic contacts. The bismuth part comprises crystallographically centrosymmetric, dianionic units (Fig. 4) of formula [$Bi_2(OC_6H_3Me_2\text{-}2,6)_6(\mu\text{-}Cl)_2$]$^{2-}$ in which each bismuth centre resides in a square-based pyramidal coordination environment being bonded to three terminal aryloxide groups and two bridging chlorine atoms. The two chlorines are both in basal sites and bridge almost symmetrically although with quite long Bi–Cl bonds (see below) [Bi(1)–Cl(1) 3.0020(12), Bi(1)–Cl(1A) 2.9325(13) Å]. The two remaining basal sites are occupied by aryloxide groups for which the Bi–O distances are identical [Bi(1)–O(1) 2.154(3), Bi(1)–O(2) 2.152(3) Å] as expected in view of the similarity of the *trans* Bi–Cl bond lengths. The remaining aryloxide resides in the apical site and has the shortest Bi–O bond [Bi(1)–O(3) 2.113(3) Å] consistent with the absence of any *trans* ligand or group; this latter distance is close to the short end of the range of Bi–O distances mentioned above[19] and to the Bi–O lengths in the neutral compound $Bi(OC_6H_3Me_2\text{-}2,6)_3$.[7] The angles around the bismuth centre are unexceptional and do not deviate significantly from idealised values. It is interesting to note that it is the chlorine atoms which bridge in the structure of **3** unlike in **1** and **2**, where it is the aryloxide groups which are bridging, but the nature of the bridging interaction is somewhat unusual. In most bridging halide bismuth compounds, the bridges are either symmetric with Bi–X bonds only slightly longer than terminally bonded halides, or are asymmetric with one short and one long bond [see refs. 20, 26(*a*), (*b*), (*c*), (*e*) and 27 for examples]. In the case of **3** however, as mentioned above, all Bi–Cl bonds are close to 3 Å and therefore quite long (a terminal Bi–Cl bond distance is typically about 2.6 Å[20]). An overall description of **3** as comprising two neutral $Bi(OC_6H_3Me_2\text{-}2,6)_3$ units loosely associated with two chloride anions might therefore be appropriate as illustrated below.



A compound similar to **3** was also isolated from the reaction between the tris(aryloxide) $Bi(OC_6H_2Me_3\text{-}2,4,6)_3$[28] and the bromide source $[PPh_4]Br$. The structure was established by X-ray crystallography to be $[PPh_4]_2[Bi_2Br_2(OC_6H_2Me_3\text{-}2,4,6)_4(\mu\text{-}Br)_2]$ **4** containing a centrosymmetric dianionic dimeric unit analogous to that found in **3** except that it contained one terminal bromine and two terminal aryloxide groups rather than three terminal aryloxides. The bridging bromines (note that as with **3**, it is the halides which bridge rather than the aryloxide groups) were notably asymmetric but problems with poor data prevented a satisfactory refinement and no further details will be described here. The basic structure is represented, however, in the diagram below and unit cell data are given in the Experimental section.



Another crystalline compound isolated from the reaction system which afforded **4** was shown by X-ray crystallography to be the species $[PPh_4]_2[BiBr_3(OC_6H_2Me_3\text{-}2,4,6)_2]$ **5** which contains the monomeric bismuth dianion $[BiBr_3(OC_6H_2Me_3\text{-}2,4,6)_2]^{2-}$ (Fig. 5); there are no short interionic contacts. The coordination geometry about the bismuth centre is square-based pyramidal with all three bromines in the basal plane and one of the aryloxide groups in the apical site. The Bi–O distances differ from each other in much the same way as is found in the structure of **3** in that the apical Bi–O length [Bi(1)–O(2) 2.119(7) Å] is significantly shorter than the basal Bi–O distance [Bi(1)–O(1) 2.193(7) Å] which lies *trans* to a bromine. Of the three Bi–Br bond lengths, those of the two bromines which lie *trans* to each other are similar [Bi(1)–Br(1) 2.8218(13), Bi(1)–Br(2) 2.793(2) Å] but significantly shorter than the unique bromine *trans* to the basal aryloxide group [Bi(1)–Br(3) 3.1107(12) Å].

A compound related to **5** was obtained from the reaction between $[PPh_4]Br$ and $Bi(OC_6H_3Me_2\text{-}2,6)_3$[7] and shown by X-ray crystallography to have the formula $[PPh_4]_2[BiBr_2(OC_6H_3Me_2\text{-}2,6)_3]$ **6**. A monomeric bismuth dianion is present as in **5** although in this case there are two bromines and three aryloxide groups. Problems with the crystal structure refinement, however, preclude a more detailed description and discussion of the structure; unit cell data are given in the Experimental section. An interesting structure for comparison with **5** and **6** is $[Na_2(thf)_4][Bi(SC_6F_5)_5]$[29] which contains a monomeric bismuth pentathiolate dianion.

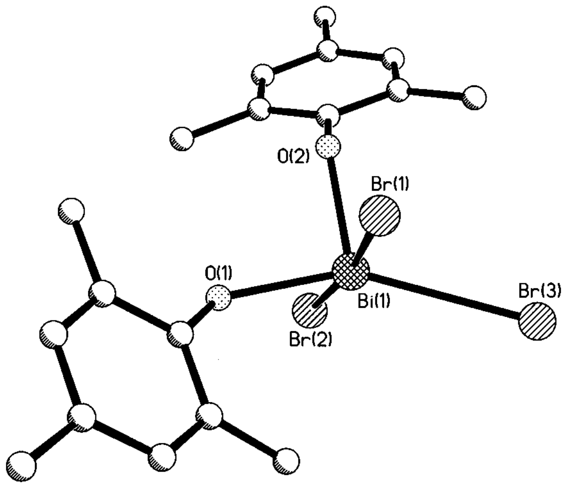


Fig. 5 A view of the monomeric bismuth dianion in **5** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Selected bond lengths: Bi(1)–O(1) 2.193(7), Bi(1)–O(2) 2.119(7), Bi(1)–Br(1) 2.8218(13), Bi(1)–Br(2) 2.793(2), Bi(1)–Br(3) 3.1107(12) Å.

The structures presented and described herein show that a range of neutral and anionic mixed aryloxy–halide bismuth(III) complexes can be readily prepared and there is every reason to expect a rich structural chemistry for this class of compound. This structural variety is further enhanced by the ability of both the halide and aryloxide groups to engage in bridging interactions which, in the case of the halides, may range from symmetric to very asymmetric; such variety is a common feature of systems where secondary bonding interactions are important aspects of the solid state structure.[20] The extent to which the species reported here retain any integrity in solution is unclear and halide and aryloxide exchange is likely, especially in coordinating solvents as we have observed many times before in related aryl bismuth halide chemistry.[26*a*,*b*,30] This state of affairs often leads to compounds being isolated which are not consistent with the reaction stoichiometry and it is therefore sometimes difficult to design rational syntheses to specific compounds. However, this is to be expected in systems which rapidly exchange in solution; the products which crystallise are often the least soluble and not necessarily the major species present in solution.

Experimental

General procedures

All reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk or dry-box techniques using oven-dried or flame-dried glassware. All solvents used were distilled under nitrogen and dried over appropriate drying agents (CaH_2 for CH_2Cl_2, Na for hexanes and sodium–benzophenone for thf and Et_2O). $BiCl_3$ (99.99%) and all other starting materials were procured from Aldrich and generally used without further purification although in the case of the phenols, it was sometimes necessary for these to be dried.

Preparations

$[Bi_2Cl_4(thf)_2(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2]$ 1. A solution of $BiCl_3$ (1.000 g, 1.59 mmol) in thf (20 cm^3) was added to a stirred solution of $Na[OC_6H_3Me_2\text{-}2,6]$, prepared from dried $HOC_6H_3Me_2\text{-}2,6$ (0.387 g, 3.17 mmol) and sodium metal (0.073 g, 3.17 mmol), in thf (10 cm^3) at room temperature resulting in an immediate colour change to bright orange and the formation of a white precipitate. After stirring for a further 20 min, this solution was cooled to −20°C and the solid allowed to settle out. The remaining orange solution was then transferred to another Schlenk tube *via* cannula and the solvent volume was reduced to about 2 cm^3 under vacuum. Addition of an overlayer of n-hexane (8 cm^3) and subsequent solvent diffusion at room temperature over a period of 1 h afforded orange, needle-like crystals of **1** (20% isolated yield). Completely satisfactory elemental analytical data were difficult to obtain due to the lability of the coordinated thf ligands which result in low carbon and high chlorine values. $C_{12}H_{17}BiCl_2O_2$ requires C, 30.45; H, 3.60; Cl, 15.00. Found: C, 28.60; H, 3.60; Cl, 15.75%.

[$Bi_2Cl_4(thf)_2(\mu\text{-}OC_6H_2Me_3\text{-}2,4,6)_2$] 2. A solution of $BiCl_3$ (0.500 g, 1.59 mmol) in thf (20 cm^3) was added to a stirred solution of Na[$OC_6H_2Me_3$-2,4,6], prepared from dried $HOC_6H_2Me_3$-2,4,6 (0.220 g, 1.62 mmol) and sodium metal (0.037 g, 1.61 mmol), in thf (10 cm^3) at room temperature resulting in an immediate colour change to bright orange-yellow and formation of a white precipitate. After stirring for a further 20 min, the solution was cooled to −20°C and the solid allowed to settle out. The remaining yellow-orange solution was transferred to another Schlenk tube *via* cannula and the solvent volume was reduced to about 2 cm^3 by vacuum. Addition of an overlayer of n-hexane (8 cm^3) and subsequent solvent diffusion at room temperature over a period of 1 h afforded yellow-orange, needle-like crystals of **2** (19 % isolated yield). Completely satisfactory elemental analytical data were difficult to obtain due to the lability of the coordinated thf ligands which result in low carbon and high chlorine values. $C_{13}H_{19}BiCl_2O_2$ requires C, 32.05; H, 3.95; Cl, 14.55. Found: C, 27.55; H, 3.40; Cl, 16.35%.

$SbCl_2(OC_6H_2Bu^t_3\text{-}2,4,6)$. A solution of $SbCl_3$ (0.500 g, 2.19 mmol) in thf (20 cm^3) was added to a stirred solution of Li[$OC_6H_2Bu^t_3$-2,4,6], prepared from dried $HOC_6H_3Bu^t_3$-2,4,6 (0.576 g, 2.19 mmol) and $LiBu^n$ (1.4 cm^3 of a 1.6 M solution in hexanes), in thf (10 cm^3), giving a pale yellow coloured solution which overnight became greenish-yellow. After this time, the solvent volume was reduced to about 2 cm^3 by vacuum and n-hexane (8 cm^3) was added as an overlayer resulting in colourless block-like crystals after several weeks at room temperature. $C_{36}H_{59}Cl_2O_2Sb$ requires C, 60.35; H, 8.30; Cl, 9.90. Found: C, 60.70; H, 8.90; Cl, 9.10%.

[NMe_4]$_2$[$Bi_2(OC_6H_3Me_2\text{-}2,6)_6(\mu\text{-}Cl)_2$] 3. A solution of Bi($OC_6H_3Me_2$-2,6)$_3$ (0.100 g, 0.175 mmol), prepared according to ref. 7, in CH_2Cl_2 (2 cm^3) was added to a stirred solution of dried [NMe_4]Cl (0.019 g, 0.175 mmol) in CH_2Cl_2 (1.5 cm^3), resulting in a cloudy yellow solution. After stirring for 30 min, the solvent volume was reduced slightly by vacuum and n-hexane (5 cm^3) was added as an overlayer resulting in yellow, needle-like crystals of **3** after standing overnight at room temperature although unreacted [NMe_4]Cl also crystallises as well. Satisfactory analytical data could not be obtained in this case due to co-crystallisation of **3** with unreacted [NMe_4]Cl and the difficulty encountered in separating the two materials. ^1H NMR ($CDCl_3$): δ 6.99, (m, 9H, 2,6-$Me_2C_6H_3$), 3.50, (s, 12H, NMe_4), 2.27 (s, 18H, 2,6-$Me_2C_6H_3$).

[PPh_4]$_2$[$Bi_2Br_2(OC_6H_2Me_3\text{-}2,4,6)_4(\mu\text{-}Br)_2$] 4 and [$PPh_4$]$_2$[$BiBr_3(OC_6H_2Me_3\text{-}2,4,6)_2$] 5. A solution of Bi($OC_6H_2Me_3$-2,4,6)$_3$ (0.050 g, 0.0814 mmol), prepared from reaction of $BiCl_3$ with Na[$OC_6H_2Me_3$-2,4,6] as described for **2** in the appropriate ratios, in CH_2Cl_2 (3 cm^3) was added to dried [PPh_4]Br (0.034 g, 0.0811 mmol) and stirred for 30 min affording a clear yellow solution. After this time, the solvent volume was reduced by vacuum to about 2 cm^3 and n-hexane (5 cm^3) was added as an overlayer. Subsequent solvent diffusion at room temperature over a period of several days afforded a crop of yellow block-like crystals comprising both compounds **4** and **5**. Only variable analytical data could be obtained due to the isolated solid comprising a mixture of two compounds and the difficulty encountered in separating the two materials. ^1H NMR data, however, showed the presence of only one species in solution. ^1H NMR ($CDCl_3$): δ 7.7 (m, PPh_4), 7.21 (m, 2H, 2,4,6-$Me_3C_6H_2$), 2.16 (s, 6H, 2,4,6-$Me_3C_6H_2$), 2.12 (s, 3H, 2,6-$Me_3C_6H_2$).

[PPh_4]$_2$[$BiBr_2(OC_6H_3Me_2\text{-}2,6)_3$] 6. A solution of Bi($OC_6H_3Me_2$-2,6)$_3$ (0.100 g, 0.175 mmol), prepared according to ref. 7, in CH_2Cl_2 (2 cm^3) was added to a stirred solution of dried [PPh_4]Br (0.073 g, 0.174 mmol) in CH_2Cl_2 (1.5 cm^3), affording a clear golden yellow solution. After 30 min the solvent volume was reduced by vacuum and n-hexane (5 cm^3) was added as an overlayer. Subsequent solvent diffusion overnight at room temperature afforded golden yellow, needle-like crystals of **6**. $C_{72}H_{67}BiBr_2O_3P_2$ requires C, 61.30; H, 4.80; Br, 11.35; P, 4.40. Found: C, 60.25; H, 4.90; Br, 10.33; P, 3.54%. ^1H NMR ($CDCl_3$): δ 7.7 (m, 40H, PPh_4), 6.90 (m, 9H, 2,6-$Me_2C_6H_3$), 2.32 (s, 18H, 2,6-$Me_2C_6H_3$).

X-Ray crystallography

All crystals were mounted under argon on glass fibres using grease. Data collections were performed on a Siemens (Bruker) SMART area detector diffractometer using graphite monochromated Mo-Kα radiation, at −100°C. In each case a full hemisphere of reciprocal space was scanned by 0.3° ω steps.

Structures were solved and refined by standard methods. Absorption corrections were applied using SADABS[31] and extinction coefficients were refined.

Unit cell data for [$SbCl_2(OC_6H_2Bu^t_3\text{-}2,4,6)(HOC_6H_2Bu^t_3\text{-}2,4,6)$]: triclinic, $P\bar{1}$, $a = 9.375(5)$, $b = 9.880(4)$, $c = 22.975(8)$ Å, $\alpha = 92.75(3)$, $\beta = 95.83(2)$, $\gamma = 117.38(4)°$.

Unit cell data for **4**: triclinic, $P\bar{1}$, $a = 12.501(3)$, $b = 13.698(3)$, $c = 14.287(3)$ Å, $\alpha = 101.34(3)$, $\beta = 106.84(3)$, $\gamma = 105.16(3)°$.

Unit cell data for **6**: triclinic, $P\bar{1}$, $a = 13.040(3)$, $b = 13.548(3)$, $c = 20.361(4)$ Å, $\alpha = 70.77(3)$, $\beta = 74.01(3)$, $\gamma = 65.60(3)°$.

CCDC reference number 186/1192.

See http://www.rsc.org/suppdata/dt/1998/4049/ for crystallographic files in .cif format.

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