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FULL PAPER

Pyridine adducts of arylbismuth(III) halides

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A range of bismuth trihalide and arylbismuth(III) halide complexes with pyridine ligands has been prepared and structurally characterised. The complex $[BiI_3(py)_3]$ (py = pyridine) is octahedral with the iodide and pyridine ligands arranged in a *mer* configuration. A seven-co-ordinate complex $[BiCl_3(py)_4]$ is also described. The compounds $[BiCl_2Ph(4\text{-Mepy})_2]$ (4-Mepy = 4-methylpyridine), $[BiBr_2Ph(4\text{-Mepy})_2]$, $[BiBr_2Ph(4\text{-Bu}^t\text{py})_2]$ (4-Bu^{t}py = 4-*tert*-butylpyridine) and $[BiI_2Ph(4\text{-Bu}^t\text{py})_2]$ all have a five-co-ordinate, square-based pyramidal bismuth centre in which the phenyl group occupies the apical position with two *trans* halides and two *trans* pyridine ligands residing in the basal plane. In the solid state these moieties are dimerised through a pair of weak asymmetric halide bridging interactions. The complexes $[BiBr_2Ph(py)_2]$ and $[BiI_2Ph(4\text{-Mepy})_2]$ have similar monomeric units but in the former case these are weakly associated into polymeric chains rather than dimers whereas, for the latter, dimers are formed through a single bridging iodide. In the structure of the ionic compound [4-Bu^{t}pyH][$BiCl_3Ph$(4-Bu^{t}py)] the $[BiCl_3Ph(4\text{-Bu}^t\text{py})]^-$ anion is monomeric with a square-based pyramidal structure in which the phenyl group is in an apical site whilst the three chlorides and 4-Bu^{t}py ligand occupy the basal positions. An example of a diphenylbismuth halide complex is seen in the structure of $[BiIPh_2(4\text{-Mepy})]$, the monomeric unit of which contains a four-co-ordinate bismuth centre with a geometry based on an equatorially vacant trigonal bipyramid in which the two phenyl groups are equatorial and the iodide and 4-methylpyridine ligand are axial. A weak association into polymeric chains occurs through long Bi · · · I interactions approximately *trans* to one phenyl group. All compounds are discussed in terms of their structure and bonding and compared with related materials previously characterised.

The Lewis acidity of bismuth(III) halides and their co-ordination chemistry with two-electron donor ligands is now well established although there are as yet no comprehensive reviews of this field. Reviews dealing with some aspects of this topic are given in ref. 1 whereas those listed in ref. 2 deal with more theoretical features such as the concept of secondary bonding interactions arising from the Lewis acidity, co-ordination geometry, lone pair stereochemical activity and the nature of acceptor orbitals. In this paper we describe a range of co-ordination compounds where the ligands are pyridine (or derivatives thereof), many of which exhibit structures of types not previously seen. In order to place the present work in context, therefore, the main structural types characterised in earlier studies are briefly described below.

The range of adducts formed by the bismuth trihalides BiX_3 (X = Cl, Br or I) has been discussed in some detail in ref. 3 and will not be reproduced here. In the present context, however, we note that six-co-ordinate complexes of the general form $[BiX_3(L)_3]$, where L is a two-electron donor ligand, adopt octahedral geometries and are known with both *fac* and *mer* configurations: *e.g.* *fac*-$[BiCl_3(tu)_3]$ (tu = thiourea),[4] *fac*-$[BiCl_3(dmso)_3]$ (dmso = dimethyl sulfoxide),[5] *fac*-$[BiCl_3(thf)_3]$ (thf = tetrahydrofuran),[6] *fac*-$[BiBr_3(thf)_3]$,[3c] *mer*-[trichlorotris{1-phenyl-3-(2-pyridyl)thiourea-*S*}bismuth][7] and *mer*-[trichlorotris(imidazolidine-2-thione-*S*)bismuth].[8] In none of these examples is there much evidence for any stereochemical activity associated with the bismuth(III) lone pair.

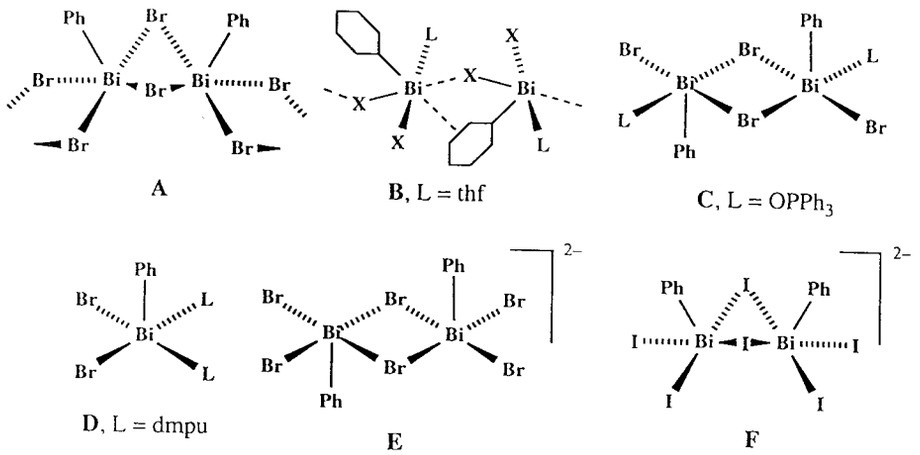
The monoaryl dihalides, BiX_2Ar, and the mono- and bis-ligand complexes derived from them, $[BiX_2Ar(L)]$ and $[BiX_2Ar(L)_2]$,† tend to adopt structures in which the bismuth centre has a five-co-ordinate, square-based pyramidal geometry with the aryl group in the apical position. Examples include polymeric $BiBr_2Ph$, a small unit of which is shown in **A**,[9] ‡ $[BiX_2Ph(thf)]$ (X = Cl, Br or I) for which a one-dimensional structure is found (two monomers are shown in **B**),[12] $[BiBr_2Ph(OPPh_3)]$ which is dimeric (**C**)[13] and $[BiBr_2Ph(dmpu)_2]$ (dmpu = *N*,*N*′-dimethylpropyleneurea) where a monomeric structure **D** is observed.[13] In situations where the ligand L in the mono adducts $[BiX_2Ar(L)]$ is a halide anion, dimeric species of the general formula $[Bi_2X_6Ph_2]^{2-}$ are observed for which the structures $[NBu^n_4]_2[Bi_2Br_6Ph_2]$ **E**[12b] and $[NEt_4]_2[Bi_2I_6Ph_2]$ **F**[12a] are typical.

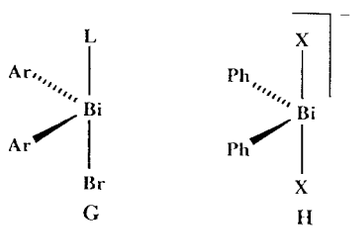
The diaryl monohalides, $BiXAr_2$, and the monoligand complexes derived from them, $[BiXAr_2(L)]$,† generally adopt structures in which the bismuth centre is four-co-ordinate (disphenoidal). Thus in $[BiBr(2,4,6\text{-}Me_3C_6H_2)_2]$[14] a polymeric one-dimensional arrangement with single bromide bridges between bismuth centres is found, although the structure of $[BiCl\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2]$[15] with bulky aryl groups is monomeric, whilst the ligand complex $[BiBr(2,4,6\text{-}Me_3C_6H_2)_2(hmpa)]$ (hmpa = hexamethylphosphoramide)[13] **G** and the anions $[BiX_2Ph_2]^-$ **H**[12] are monomeric.

The structure and bonding in the compounds mentioned above has been discussed in more detail in refs. 2(*b*),(*c*), aspects of which will be further explored below. In most cases, related antimony compounds are also known, references to which are given in ref. 13.

† In general, the number of ligands (L) which bind to the bismuth centre is equal to the number of electronegative X groups as described in the discussion section.[2b,3c]

‡ Two exceptions to this structure type are found in $BiBr_2(2,4,6\text{-}Me_3C_6H_2)$[10] and $BiCl_2(2,4,6\text{-}Ph_3C_6H_2)$;[11] in the former, adjacent pairs of bismuth atoms are bridged by one bromine and one aryl–bismuth π interaction whilst in the latter a weakly bound dimeric structure is observed presumably due to the bulkiness of the aryl group in this case.





Results

Solutions of BiI_3 and an excess of pyridine afforded crystals of the complex *mer*-$[BiI_3(py)_3]$ **1** (py = pyridine) as a pyridine solvate (Fig. 1). Crystallographic data for this and all other structures are given in Table 1. All angles around the bismuth centre in **1** are close to 90 or 180° such that there is little evidence for any stereochemical activity associated with the bismuth(III) lone pair consistent with previous examples of octahedral $[BiX_3(L)_3]$ structures (*mer* or *fac*, see above). The Bi–N bond lengths range from 2.533(4) to 2.625(4) Å but the bond to N(3) *trans* to I(2) is longer than the other two Bi–N bonds. Similarly, the Bi–I bond *trans* to the pyridine is shorter than the two mutually *trans* Bi–I bonds (all lengths are given in the caption to Fig. 1) indicating that iodine has a higher *trans* influence than pyridine. There are few examples of similar bismuth–pyridine complexes to compare with **1** but we note four in particular. The anion in the compound $[BiI_2(py)_3(dppom)][BiI_4(py)_2]$[16] (dppom = bis(diphenylphosphino)methane dioxide) is octahedral with the pyridines in a *cis* configuration, *i.e. cis*-$[BiI_4(py)_2]^-$, with Bi–N distances 2.70(2) and 2.75(3) Å. In the complex $[Mg(py)_2(H_2O)_4][BiBr_4(py)_2]_2$[17] an analogous bromo anion is present although in this case the geometry is *trans*, *i.e. trans*-$[BiBr_4(py)_2]^-$. Also relevant is the structure of the octahedral anion $[BiCl_5(py)]^{2-}$ present in the complexes $[Hpy]_2[BiCl_5(py)]$ (Bi–N 2.535(7) Å)[17] and $[C_5H_5NCSNEt_2]$-$[BiCl_5(py)]$ (Bi–N 2.615(8) Å).[18]

Crystals of a complex of $BiCl_3$ and pyridine were obtained by similar procedures, a partial structure determination for which revealed the presence of four co-ordinated pyridines, *i.e.* $[BiCl_3(py)_4]$ **2**. The structure determination was not of sufficient quality to be fully reported here due to pyridine disorder problems (unit cell dimensions are given in the Experimental section) but was sufficient to establish the molecular structure, a representation of which is shown in the diagram which illustrates a seven-co-ordinate bismuth centre having a pentagonal bipyramidal geometry in which the pyridine ligands are all in the equatorial plane. This structure is not unlike that observed for the $[BiI_2(py)_3(dppom)]^+$ cation described in ref. 16.

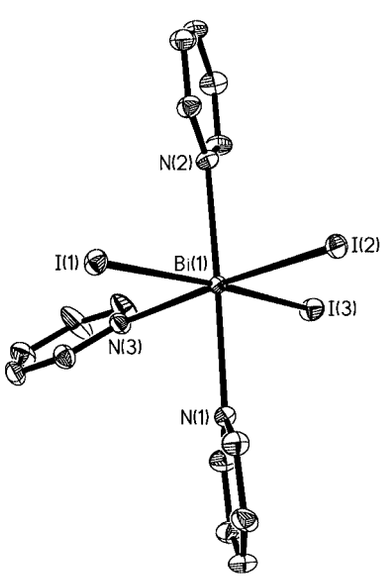
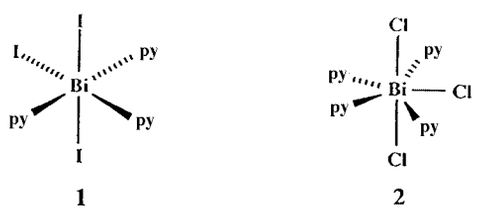


Fig. 1 A view of the molecular structure of complex **1**. Atoms are drawn as ellipsoids of 30% probability. Hydrogen atoms are omitted. Bond lengths include Bi(1)–N(1) 2.533(4), Bi(1)–N(2) 2.563(4), Bi(1)–N(3) 2.625(4), Bi(1)–I(1) 3.0367(7), Bi(1)–I(2) 2.9609(7) and Bi(1)–I(3) 3.0309(7) Å.



Treatment of solutions of BiX_2Ph (X = Cl, Br or I) with pyridine, or derivatives thereof, afforded complexes with the basic formula $[BiX_2Ph(L)_2]$ in reasonable isolated yields (in many cases the same compounds were isolated when the diphenyl compounds $BiXPh_2$ were used although this is not unexpected in view of the facile group exchange reactions previously encountered for these types of compound[9,12,13]). The compounds $[BiCl_2Ph(4\text{-}Mepy)_2]$ **3** (4-Mepy = 4-methylpyridine) (Fig. 2), $[BiBr_2Ph(4\text{-}Mepy)_2]$ **4** (Fig. 3), $[BiBr_2Ph(4\text{-}Bu^tpy)_2]$ **5** (4-Bu^tpy = 4-*tert*-butylpyridine) (Fig. 4) and $[BiI_2Ph(4\text{-}Bu^tpy)_2]$ **6** are all similar and have as their basic structural unit a five-co-ordinate, square-based pyramidal bismuth centre in which the phenyl group occupies the apical position with two *trans* halides and two *trans* pyridine ligands residing in the basal plane. All interbond angles are close to 90 or 180° although the N–Bi–N angles are somewhat less than the X–Bi–X angles possibly for steric reasons (see Figure captions). As is clear

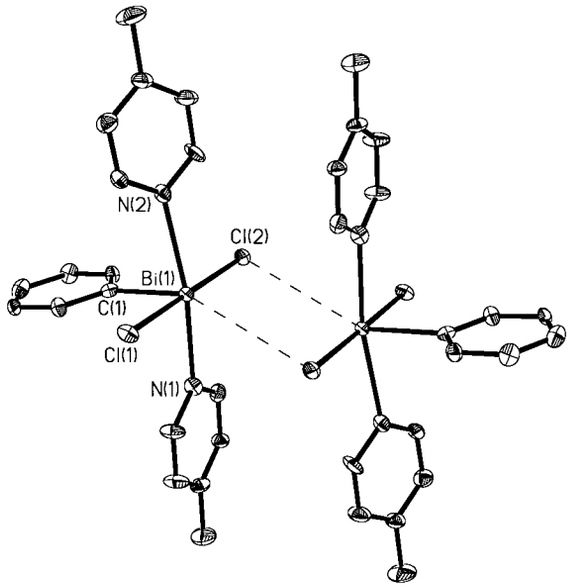


Fig. 2 A view of the molecular structure of complex **3** showing the weakly bonded dimers. Details as in Fig. 1. Bond lengths and angles include Bi(1)–C(1) 2.275(9), Bi(1)–N(1) 2.504(8), Bi(1)–N(2) 2.547(8), Bi(1)–Cl(1) 2.678(2), Bi(1)–Cl(2) 2.701(2) and Bi(1)–Cl(2a) 3.657(3) Å; C(1)–Bi(1)–Cl(2a) 151.2(2), Bi(1)–Cl(2)–Bi(1a) 90.02(7), N(1)–Bi(1)–N(2) 167.8(2) and Cl(1)–Bi(1)–Cl(2) 178.01(7)°.

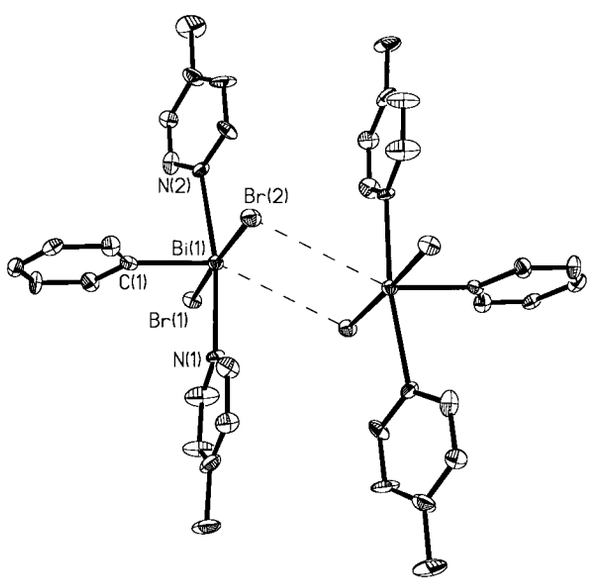


Fig. 3 A view of the molecular structure of complex **4** showing the weakly bonded dimers. Details as in Fig. 1. Bond lengths and angles include Bi(1)–C(1) 2.263(12), Bi(1)–N(1) 2.519(9), Bi(1)–N(2) 2.564(9), Bi(1)–Br(1) 2.840(2), Bi(1)–Br(2) 2.845(2) and Bi(1)–Br(2a) 3.772(2) Å; C(1)–Bi(1)–Br(2a) 151.7(3), Bi(1)–Br(2)–Bi(1a) 91.03(4), N(1)–Bi(1)–N(2) 169.9(3) and Br(1)–Bi(1)–Br(2) 175.29(4)°.

from the diagram and Figs. 2–4, pairs of these monomeric units form weakly bonded dimers through very asymmetric halide bridging interactions, the longer secondary Bi···X bond being approximately *trans* to the phenyl group. For **3**, **4** and **5** the primary and secondary Bi–X distances are, respectively Bi–Cl 2.701(2), 3.657(3); Bi–Br 2.845(2), 3.772(2); Bi–Br 2.805(1), 3.691(2) Å and the *trans* C–Bi···X angles are 151.2(2), 151.7(3) and 158.36(12)°. Crystallographic details for **3**–**5** are given in Table 1 and further bond length and angle data are presented in the Figure captions. The quality of the data set for **6** was poor and its analysis is therefore not reported here although unit cell dimensions are given in the Experimental section.

As observed for the structures of complexes **3**–**6**, the structure of $[BiBr_2Ph(py)_2]$ **7** (Fig. 5) has a monomeric unit with

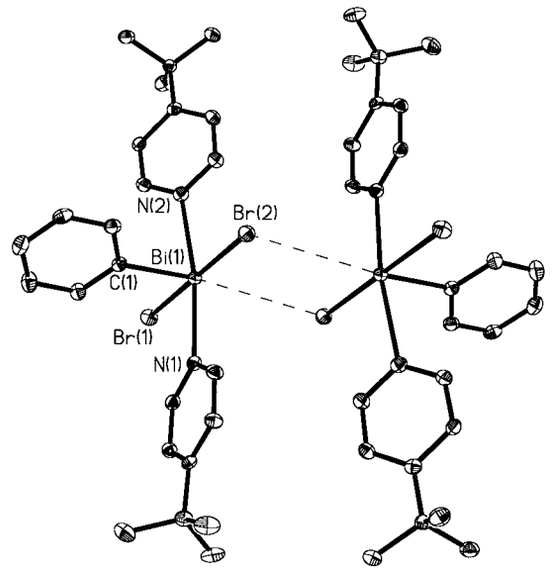


Fig. 4 A view of the molecular structure of complex **5** showing the weakly bonded dimers. Details as in Fig. 1. Bond lengths and angles include Bi(1)–C(1) 2.265(5), Bi(1)–N(1) 2.542(4), Bi(1)–N(2) 2.527(4), Bi(1)–Br(1) 2.885(1), Bi(1)–Br(2) 2.805(1) and Bi(1)–Br(2a) 3.691(2) Å; C(1)–Bi(1)–Br(2a) 158.36(12), Bi(1)–Br(2)–Bi(1a) 105.80(4), N(1)–Bi(1)–N(2) 169.46(14) and Br(1)–Bi(1)–Br(2) 177.40(2)°.

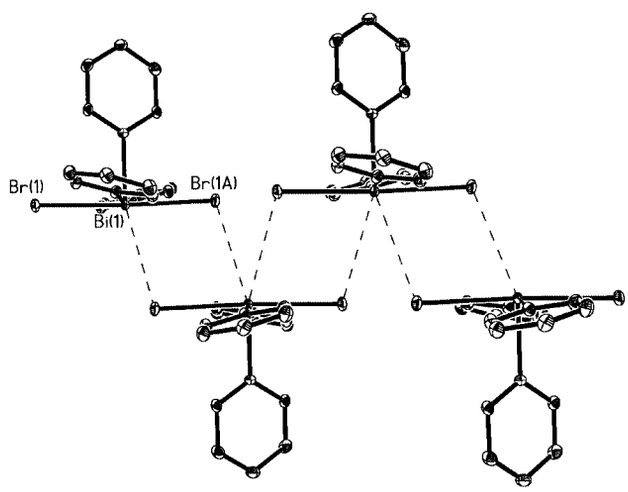
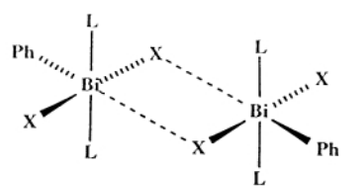
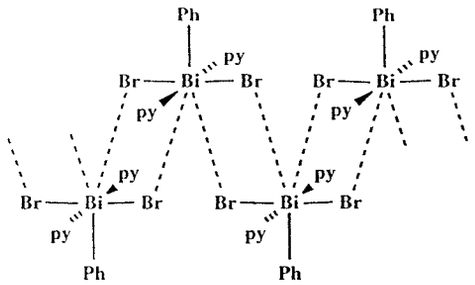


Fig. 5 A view of the molecular structure of complex **7** showing four monomers as part of the polymeric chain. Each monomer resides on a crystallographic C_2 axis and the polymeric chain lies along the crystallographic *c* axis. Other details as in Fig. 1. Bond lengths and angles include Bi(1)–C(1) 2.282(8), Bi(1)–N(1) 2.547(5), Bi(1)–Br(1) 2.8445(6) and Bi(1)–Br(1a) 3.9861(7) Å; C(1)–Bi(1)–Br(1b) 145.30(1), Bi(1)–Br(1)–Bi(1a) 90.51(12), N(1)–Bi(1)–N(1a) 167.6(2) and Br(1)–Bi(1)–Br(1a) 177.32(3)°.

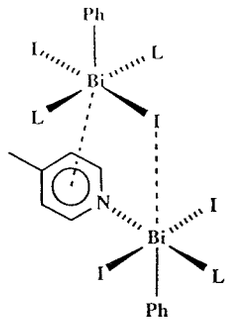


3, X = Cl, L = 4-Mepy; **4**, X = Br, L = 4-Mepy;
5, X = Br, L = 4-Bu^{t}py; **6**, X = I, L = 4-Bu^{t}py

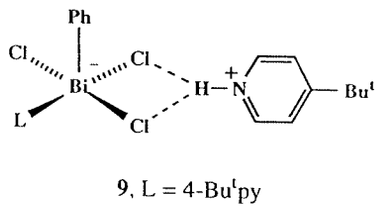
mutually *trans* halides and *trans* pyridines in the square-basal plane. However, unlike **3**–**6**, the monomers in **7** are weakly associated into polymeric chains, as shown for four such units in Fig. 5, rather than dimers. In the case of **7** the intermolecular interactions also comprise asymmetric halide bridges although



7



8, L = 4-Mepy



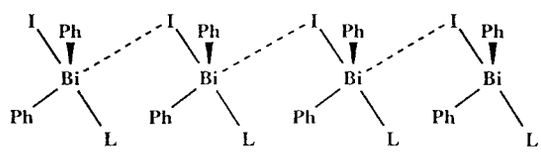
9, L = 4-Bu^{t}py

now there are two such interactions per bismuth rather than one. As a result the bridges are even more asymmetric; Bi–Br 2.8445(6), 3.9861(7) Å. Since both halides are involved in bridging, two long Bi · · · Br contacts occur approximately *trans* to the phenyl group; C–Bi · · · Br 145.30(1)°. Each monomer resides on a crystallographic C_2 axis and is related to other monomers in the polymer chain by the crystallographic *c* glide.

In the structure of $[BiI_2Ph(4\text{-Mepy})_2]$ **8**, monomeric units structurally similar to those found in complexes **3**–**7** are also present although these are linked into dimers through a single bridging iodine and a weak 4-methylpyridine to bismuth π interaction as shown in the diagram. Owing to the poor quality of the data set obtained for **8**, however, the structure will not be discussed further. Unit cell data are given in the Experimental section.

As a final structure in this sub-section on monoaryl compounds an ionic species, possibly formed by hydrolysis of a precursor complex $[BiCl_2Ph(4\text{-Bu}^t\text{py})_2]$, was identified as [4-Bu^{t}pyH][$BiCl_3$Ph(4-Bu^{t}py)] **9** (Fig. 6) by X-ray crystallography. The $[BiCl_3Ph(4\text{-Bu}^t\text{py})]^-$ anion is monomeric with a square-based pyramidal structure in which the phenyl group is in the apical site whilst the three chlorines and 4-Bu^{t}py ligand occupy the basal positions. All interbond angles are close to either 90 or 180° and the distances are unexceptional. In the crystal structure the cation $[4\text{-Bu}^t\text{pyH}]^+$ is hydrogen bonded to the anion, as shown in the diagram and Fig. 6, in a manner where two chlorines act as a chelate to the N–H hydrogen bond donor. Hydrogen bonding interactions of this type where a metal dichloride chelates to a N–H or O–H group have recently been discussed.[19]

As an example of a diphenylbismuth halide complex the structure of $[BiIPh_2(4\text{-Mepy})]$ **10** is shown in Fig. 7. The monomeric unit of **10** contains a four-co-ordinate bismuth centre, the geometry of which is equatorially vacant trigonal bipyramidal (disphenoidal) with two phenyl groups equatorial and the iodine and 4-methylpyridine ligand axial. As is clear from Fig. 7 however, a weak association into polymeric chains occurs through long Bi · · · I interactions approximately *trans* to one phenyl group [C(1)–Bi · · · I 161.1(2)°] although the bridging Bi · · · I distance [4.3099(9) Å] is considerably longer than the primary Bi–I distance [Bi–I 3.0229(8) Å].



10, L = 4-Mepy

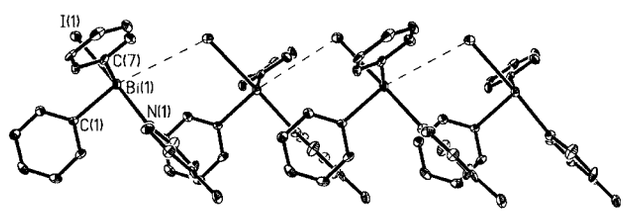


Fig. 7 A view of the molecular structure of complex **10** showing four monomers as part of the polymeric chain. Details as in Fig. 1. Bond lengths and angles include Bi(1)–C(1) 2.267(8), Bi(1)–C(7) 2.246(8), Bi(1)–N(1) 2.604(7), Bi(1)–I(1) 3.0229(8) and Bi(1)–I(1a) 4.3099(9) Å; N(1)–Bi(1)–I(1) 174.2(2), C(1)–Bi(1)–C(7) 96.2(3) and C(1)–Bi(1)–I(1a) 161.1(2)°.

The structure of a complex with the empirical formula $[BiIPh_2(dmap)]$ **11** (dmap = 4-dimethylaminopyridine) was also determined. Whilst the data were not of a sufficient quality to discuss in detail, an unusual structure was clearly present involving linked pairs of $[BiPh_2(dmap)_2]^+$ cations and $[BiI_2Ph_2]^-$ anions as shown in the diagram. Similar cationic and anionic units have been previously observed as described in refs. 12 and 16. Unit cell data are given in the Experimental section.

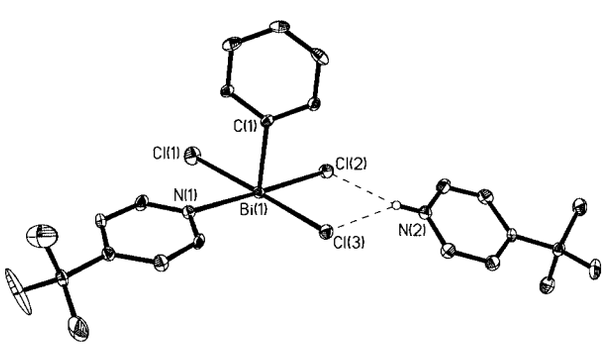
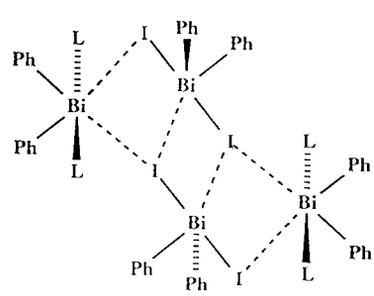


Fig. 6 A view of the molecular structure of the anion in complex **9**. Atoms are drawn as ellipsoids of 30% probability. Hydrogen atoms are omitted except for the one bonded to N(2). Bond lengths include Bi(1)–C(1) 2.241(6), Bi(1)–N(1) 2.676(5), Bi(1)–Cl(1) 2.630(2), Bi(1)–Cl(2) 2.604(2), Bi(1)–Cl(3) 2.788(2), Cl(2) · · · H(2A) 3.144(6) and Cl(3) · · · H(2A) 2.357(6) Å.



11, L = dmap

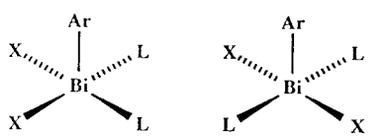
Discussion

Many of the structures described in the previous section are of new types but a number of structural trends are never-

theless apparent. In general, the Lewis acidity of arylbismuth halides results in the formation of complexes of general formula $[BiX_nAr_{3-n}(L)_n]$ with a co-ordination number around the bismuth centre equal to $(3 + n)$ (some of these ideas have been discussed previously in refs. 2(*b*), 3(*c*), 13 and 20). Thus, as detailed in the Introduction, for the trihalides with three monomeric ligands L, this rule results in six-co-ordinate compounds of the general formula $[BiX_3(L)_3]$, as seen in **1**, although as is evident from the structure of **2**, higher co-ordination numbers are possible albeit rare. In all cases including **1**, the co-ordination geometry of the $[BiX_3(L)_3]$ species is close to regular octahedral with little evidence of a stereochemically active bismuth(III) lone pair (in terms of bond length or angular distortions).[2c] Both *fac* and *mer* configurations are known although we note that complexes with oxygen donors are *fac* whereas those with sulfur donors tend to be *mer*. In the case of nitrogen donor ligands, with only one example, *i.e.* **1**, it is not very sensible to make any general comments although the *mer* structure of **1** is certainly consistent with what is found for some of the other complexes examined in this study as will become apparent.

In cases where one of the ligands L is formally X^-, complexes with the general formulae $[BiX_4(L)_2]^-$ (*cis* and *trans*), $[BiX_5(L)]^{2-}$ and $[BiX_6]^{3-}$ result, examples of all of which have been characterised; the former two types are discussed above and examples of $[BiX_6]^{3-}$ anions are described in ref. 21. With reference to the discussion which follows, it is also worth noting the structures of bis-ligand complexes of the form $[BiX_3(L)_2]$ which are either dimeric or polymeric due to the presence of bridging halides (here a bridging halide X acts like the third ligand L in $[BiX_3(L)_3]$). Their structures have been described in refs. 3(*b*) and 3(*c*) and will not be discussed in detail here except to note that in almost all cases the two ligands on each bismuth centre (usually O and P donors) are *cis*[3b,c] the only exception being in the polymeric complex $[BiCl_3(dmso)_2]$ where the dmso ligands are *trans*.[3d]

For the monoarylbismuth dihalides the basic unit relevant to this study is the five-co-ordinate bis-ligand species $[BiX_2Ar(L)_2]$. In this case the co-ordination geometry is square-based pyramidal with the aryl group in the apical site and the halide atoms and ligands in the basal plane. Two isomers are possible depending on whether the halide atoms and ligands are mutually *cis* (**I**) or *trans* (**J**).



I **J**

For the complexes **3**–**8** the observed geometry is *trans* (**J**) but for the complex $[BiBr_2Ph(dmpu)_2]$[13] a *cis* structure (**I**) is found. These results, together with the observations made concerning *fac* and *mer* preferences for the $[BiX_3(L)_3]$ complexes (and the *cis* and *trans* preferences for the $[BiX_3(L)_2]$ complexes), indicate that oxygen donor ligands tend to prefer mutually *cis* co-ordination whereas pyridine donors, albeit with only one example, prefer to be mutually *trans*. There is no obvious explanation for this feature and it is possible that the two isomers have similar stabilities in any case so we must beware of overinterpretation. Nevertheless, the point has been made[2b,3c,13] that *fac*-$[BiX_3(L)_3]$ and geometries such as **I** (and **G**) can be understood if the acceptor orbitals through which the ligands bind are the Bi–X σ* orbitals. This leads directly to structures in which the ligands L are *trans* to X. Clearly this is not the case in complexes such as **1** and **3**–**8**. Some insight can be had from the fact that bonding of this sort in L→Bi–X moieties is no more than an asymmetric three-centre, four-electron interaction and that in the structure **J** the X–Bi–X and N→Bi←N units are also of the three-centre, four-electron type albeit symmetrical and not amenable to a donor–acceptor definition. The distinction between the bonding in **I** and **J** and between *mer*- and *fac*-$[BiX_3(L)_3]$ (and *cis*- and *trans*-$[BiX_3(L)_2]$) is, therefore, more one of degree than of kind and the stabilities of both are likely to be similar making rationalisation of any particular isomer rather difficult. A further insight into these systems, though again with little predictive power, is that whereas *fac*-$[BiX_3(L)_3]$ and **I** can be viewed as ligand complexes of the pyramidal BiX_3 or BiX_2Ar species (the expected ground state structure), *mer*-$[BiX_3(L)_3]$ and **J** can be thought of as ligand complexes of T-shaped BiX_3 or BiX_2Ar moieties. Although the T-shaped form is never the ground state structure, its energy is not prohibitively high compared with that of the pyramidal form. T-Shaped geometries in trivalent Group 15 compounds have been discussed extensively by Arduengo and co-workers.[22]

As a final point regarding the structures **3**–**8** we note that in all cases weak intermolecular interactions lead to dimers or polymers and that, specifically, these interactions involve a close contact between a halide and the bismuth centre approximately *trans* to the apical phenyl group. Although these interactions are weak, as evidenced by the long Bi···X distances, they are much more commonly encountered in these pyridine complexes than in other systems previously studied, *i.e.* neutral O- and S-donor complexes and halogeno anions; similar interactions are, however, seen in $[NEt_4][BiI_2Ph_2]$,[12b] $[BiBr(2,4,6\text{-}Me_3C_6H_2)_2(Ph_2SO)]$[13] and in cationic complexes of the form $[BiAr_2(L)_2]^+$[16] (see also ref. 23). No obvious explanation presents itself but a similar interaction is also found in **10** resulting in the polymeric structure obseved. In the complex $[BiBr(2,4,6\text{-}Me_3C_6H_2)_2(Ph_2SO)]$[13] the weak interactions are such that a dimer is present in the solid state.

Further work is in progress more fully to understand the bonding in halogenobismuth(III) complexes (and secondary bonding in general[2a]) and also to utilise the directional nature of this type of bonding to design and prepare solid state network structures.

Experimental

General considerations

All reactions were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk or dry-box techniques and oven-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). The compound $BiCl_3$ (99.99%) was procured from Aldrich and generally used without further purification (filtration to remove insoluble BiOX was occasionally necessary). Substituted pyridines were also from Aldrich and dried over molecular sieves. Pyridine, from BDH, was handled in a similar manner. Arylbismuth halides were prepared according to literature routes.[9,12,13]

Most of the arylbismuth halide complexes described here were produced by micro-scale procedures designed to afford crystals suitable for structural studies. The small quantities produced make any numerical values for yields rather uncertain but in all cases they were good and the purity of the materials was established by elemental analysis in most cases. For the monoaryl complexes **3**–**9** the starting materials used were of the form BiX_2Ph although as mentioned in the text these complexes were also obtained in many cases when the starting compound was the diaryl species $BiXPh_2$.

Preparations

$[BiI_3(py)_3]\cdot py$ 1. A solution of BiI_3 (0.05 g, 0.08 mmol) in pyridine (1 cm^3) was cooled at −20 °C over three months during

Table 1 Selected crystallographic details for the complexes **1**, **3**–**5**, **7**, **9** and **10**[a]

	1	**3**	**4**	**5**	**7**	**9**	**10**
Empirical formula	$C_{20}H_{20}BiI_3N_4$	$C_{18}H_{19}BiCl_2N_2$	$C_{18}H_{19}BiBr_2N_2$	$C_{24}H_{31}BiBr_2N_2$	$C_{16}H_{15}BiBr_2N_2$	$C_{24}H_{32}BiCl_3N_2$	$C_{18}H_{17}BiIN$
Formula weight, M	453.04	543.23	632.15	716.31	604.10	663.85	583.21
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$Pca2_1$
a/Å	9.129(2)	9.6039(7)	9.812(3)	9.828(2)	13.520(3)	16.891(3)	10.786(2)
b/Å	11.301(2)	13.2094(9)	13.392(5)	11.673(2)	14.687(2)	8.996(2)	9.463(2)
c/Å	13.191(2)	15.6045(11)	15.845(6)	12.475(3)	8.699(2)	17.280(5)	17.611(4)
α/°	81.626(14)			101.65(3)			
β/°	99.90(3)	99.777(1)	102.15(3)	101.75(3)	99.60(1)	98.59(2)	
γ/°	68.692(13)			108.01(3)			
V/Å^3	1253.0(4)	1950.9(2)	2035.4(12)	1277.5(4)	1703.15(8)	2596.3(11)	1797.5(6)
Z	2	4	4	2	4	4	4
μ/mm^{-1}	10.744	9.312	12.589	10.041	15.039	7.113	11.520
Extinction coefficient	N/A	0.00040(7)	0.00042(7)	N/A	0.00038(9)	0.00086(6)	0.00053(4)
Reflections measured	9327	10152	12854	13086	8717	15965	10964
Independent reflections	5681	3433	4636	5769	1949	5926	3981
R_{int}	0.0305	0.0790	0.0999	0.0331	0.0582	0.0726	0.0596
Final R [$I > 2\sigma(I)$]	0.0258	0.0418	0.0646	0.0371	0.0340	0.0419	0.0303

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

which time small red crystals of complex **1** were formed. $C_{20}H_{20}BiI_3N_4$ (*i.e.* **1**·py as found in the structure) requires C, 26.50; H, 2.20; N, 6.20. $C_{15}H_{15}BiI_3N_3$ (*i.e.* **1**) requires C, 21.80; H, 1.85; N, 5.10. Found: C, 19.40; H, 1.65; N, 4.50% indicating some further loss of pyridine from the crystals.

[$BiCl_3(py)_4$] 2. A solution of $BiCl_3$ in pyridine was layered with hexane and cooled at −20 °C over several days yielding colourless crystals of complex **2**. Satisfactory elemental analysis was not obtained due to facile loss of pyridine.

[$BiCl_2Ph$(4-Mepy)$_2$] 3. Several drops of 4-Mepy were added to a small spatula of $BiCl_2Ph$ in a thin-walled glass tube. This was layered with hexane and clear block-like crystals of complex **3** were obtained over two days at −20 °C. $C_{18}H_{19}BiCl_2N_2$ requires C, 39.80; H, 3.55; Cl, 13.05; N, 5.15. Found: C, 39.65; H, 3.15; Cl, 13.50; N, 5.10%.

[$BiBr_2Ph$(4-Mepy)$_2$] 4. This compound was prepared in a similar manner to **3** using $BiBr_2Ph$. $C_{18}H_{19}BiBr_2N_2$ requires C, 34.20; H, 3.05; Br, 25.30; N, 4.45. Found: C, 32.10; H, 2.90; Br, 25.90; N, 4.30%.

[$BiBr_2Ph$(4-Bu^{t}py)$_2$] 5. This compound was prepared in a similar manner to **3** using $BiBr_2Ph$ and a few drops of 4-Bu^{t}py. $C_{24}H_{31}BiBr_2N_2$ requires C, 40.25; H, 4.35; N, 3.90. Found: C, 41.20; H, 4.40; N, 3.85%.

[BiI_2Ph(4-Bu^{t}py)$_2$] 6. This compound was prepared in a similar manner to **3** using BiI_2Ph and a few drops of 4-Bu^{t}py. $C_{24}H_{31}BiI_2N_2$ requires C, 35.60; H, 3.85; I, 31.30; N, 3.45. Found: C, 35.55; H, 3.40; I, 31.00; N, 3.40%.

[$BiBr_2Ph$(py)$_2$] 7. This compound was prepared in a similar manner to **3** using $BiBr_2Ph$ and a few drops of py. Satisfactory elemental analyses could not be obtained due to ready loss of pyridine.

[BiI_2Ph(4-Mepy)$_2$] 8. This compound was prepared in a similar manner to **3** using BiI_2Ph and a few drops of 4-Mepy. $C_{18}H_{19}BiI_2N_2$ requires C, 29.75; H, 2.65; I, 34.95; N, 3.85. Found: C, 29.30; H, 2.00; I, 34.50; N, 3.70%.

[4-Bu^{t}pyH][$BiCl_3Ph$(4-Bu^{t}py)] 9. This compound was prepared in a similar manner to **3** using $BiCl_2Ph$ and a few drops of 4-Bu^{t}py. Elemental analyses indicated a mixture of products.

[$BiIPh_2$(4-Mepy)] 10. Crystals of complex **10** were obtained as a minor product in the crystallisation of **8** and were also yellow block-like crystals.

X-Ray crystallography

All crystals were mounted in air onto glass fibres. Crystals for low temperature data collection were mounted using grease, whilst samples for room temperature analysis were fixed to the glass fibre using glue. Data collections were performed on a Siemens (Bruker) SMART area detector diffractometer using graphite monochromated Mo-Kα radiation, at −100 °C, except for complexes **6** and **8** for which data were collected on a Siemens (Bruker) P4 four circle diffractometer at room temperature.

For the structures of complexes **1**, **5** and **7** a full sphere of reciprocal space was scanned by 0.3° ω steps. For other compounds studied using the area detector diffractometer a full hemisphere of reciprocal space was scanned by 0.3° ω steps. Structures were solved and refined by standard methods. The crystal of **4** was a non-merohedral twin with twin law (1 0 0, 0 −1 0, 0 0 1/3).[24]

As noted in the text, the structure determinations for complexes **2**, **6**, **8** and **11** were of poor quality and various problems were encountered during refinement. Specifically, these were associated with pyridine disorder (**2**), high thermal motion in some of the ligand carbon atoms (**6** and **8**), weak data (**6** and **8**), the possibility of the presence of a satellite crystal (**8**) and high residual electron density and absorption problems (**2**, **6** and **11**) leading to poor R indices. Although little doubt remains concerning the gross molecular structures (which are discussed in the text), full crystallographic details are not reported. Unit cell data, however, are as follows: **2**, orthorhombic, space group $Pnma$, $a = 16.007(3)$, $b = 15.322(3)$, $c = 9.083(2)$ Å; **6**, triclinic, space group $P\bar{1}$, $a = 10.104(2)$, $b = 11.893(3)$, $c = 13.120(2)$ Å, $\alpha = 102.33(5)$, $\beta = 102.42(3)$, $\gamma = 110.02(2)$°; **8**, monoclinic, space group $P2_1/c$, $a = 17.646(4)$, $b = 10.453(2)$, $c = 23.588(9)$ Å, $\beta = 103.50(3)$°; **11**, triclinic, space group $P\bar{1}$, $a = 10.564(2)$, $b = 13.657(3)$, $c = 13.718(3)$ Å, $\alpha = 96.22(3)$, $\beta = 91.54(3)$, $\gamma = 103.65(3)$°.

Crystallographic data for the compounds [(2,6-Me_2py)$_2$H]$_2$-[$Bi_2Br_6Ph_2$] **12** and [(4-Bu^{t}py)$_2$H][4-Bu^{t}pyH][$SbBr_4Ph$] **13**, which were also characterised as part of this study, have also been deposited. The dianion in the former is closely similar to that found in [NBu$^n_4$]$_2$[$Bi_2Br_6Ph_2$][12b] although in the example seen here a weak π to bismuth interaction is present between one of the pyridine rings in each of the [(2,6-Me_2py)$_2$H]$^+$ cations;

aryl π to Bi interactions have been noted in complexes such as $[BiX_2Ph(thf)]$ (X = Cl, Br or I) (**B**) and arene π to Bi interactions are described in ref. 25. The anion in $[(4\text{-}Bu^tpy)_2H][4\text{-}Bu^tpyH][SbBr_4Ph]$ is analogous to that in $[C_5H_5NH]_2[SbCl_4Ph]$ and contains a hydrogen bonding interaction similar to that found in **9**.[26]

CCDC reference number 186/1497.

See http://www.rsc.org/suppdata/dt/1999/2837/ for crystallographic files in .cif format.

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