

# Coordination complexes of the bismuth(III) thiolates $\text{Bi}(\text{SC}_6\text{F}_5)_3$ and $\text{Bi}(\text{SC}_6\text{Cl}_5)_3$ with pyridine ligands

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Received 21st May 2003, Accepted 25th June 2003

First published as an Advance Article on the web 14th July 2003

The chloro-aryl bismuth thiolate  $\text{Bi}(\text{SC}_6\text{Cl}_5)_3$  has been prepared from the reaction between  $\text{BiPh}_3$  and the thiol  $\text{HSC}_6\text{Cl}_5$  by analogy with the previously described synthesis of the fluoro-aryl species  $\text{Bi}(\text{SC}_6\text{F}_5)_3$ . The compound  $\text{Bi}(\text{SC}_6\text{Cl}_5)_3$  is only sparingly soluble but can be isolated as a dmf adduct  $[\text{Bi}(\text{SC}_6\text{Cl}_5)_3(\text{dmf})_2]$  (dmf = *N,N*-dimethylformamide) which adopts a five-coordinate square-based pyramidal geometry in which the two dmf ligands lie in the basal plane with a mutually *cis* configuration. Treatment of either  $\text{Bi}(\text{SC}_6\text{F}_5)_3$  or  $\text{Bi}(\text{SC}_6\text{Cl}_5)_3$  with pyridine or 2,2'-bipyridyl ligands affords the coordination complexes *fac*- $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{py})_3]$  (two crystalline polymorphs), *fac*- $[\text{Bi}(\text{SC}_6\text{Cl}_5)_3(\text{py})_3]$ , *fac*- $[\text{Bi}(\text{SC}_6\text{F}_5)_3(4\text{-pic})_3]$  (4-pic = 4-picoline),  $[\text{Bi}(\text{SC}_6\text{Cl}_5)_3(4\text{-pic})_2]$ ,  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{bipy})]$  (bipy = 2,2'-bipyridyl),  $[\text{Bi}(\text{SC}_6\text{Cl}_5)_3(\text{bipy})]$ ,  $[\text{Bi}_2(\text{SC}_6\text{Cl}_5)_6(2\text{-pic})_3]$  (2-pic = 2-picoline) and  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(4\text{-pic})]$ . Five- and four-coordinate complexes adopt square-based pyramidal and equatorially vacant, trigonal bipyramidal (disphenoidal) geometries respectively, the former having the two ligands *cis* to each other in the basal plane. The compound  $[\text{Bi}_2(\text{SC}_6\text{Cl}_5)_6(2\text{-pic})_3]$  contains both five- and four-coordinate mononuclear units. A salt with the formula  $[4\text{-picH}][\text{Bi}_3(\text{SC}_6\text{F}_5)_{11}]$  was also isolated in which the anion contains a central bismuth bonded to five thiolate ligands with a square-based pyramidal geometry. Two *cis*-basal thiolates act as bridging groups to two outer bismuth centres each of which is four-coordinate with the expected disphenoidal geometry in which the bridging thiolate is in an axial position. The structure of the dinuclear arylbismuth thiolate compound  $[\text{Bi}_2\text{Ph}_2(\text{SC}_6\text{F}_5)_4(4\text{-pic})_2]$  is also described. Intramolecular conformations and intermolecular associations in all structures are dominated by  $\pi$ - $\pi$ -interactions.

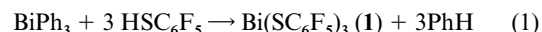
Neutral thiolates of bismuth(III) are known from a number of studies but relatively few compounds are well characterised and structural data remain scarce. Compounds of the general formula  $\text{Bi}(\text{SR})_3$  are known for R = Ph,<sup>1</sup>  $\text{C}_6\text{F}_5$  (**1**),<sup>2,3</sup> 4-Me $\text{C}_6\text{H}_4$ ,<sup>3b</sup> 2,6-Me $_2\text{C}_6\text{H}_3$ ,<sup>3b</sup> 3,5-Me $_2\text{C}_6\text{H}_3$ ,<sup>3b</sup> 2-CO $_2\text{MeC}_6\text{H}_4$ ,<sup>1b</sup> 4-FC $_6\text{H}_4$ ,<sup>4</sup> 2,4,6-Bu $_3\text{C}_6\text{H}_2$ ,<sup>5</sup> Et,<sup>6</sup> benzyl,<sup>6,7</sup>  $\text{CH}_2\text{CH}_2\text{OH}$ <sup>6</sup> and Bu<sup>t</sup><sup>8</sup> although only **1**<sup>3a</sup> and  $\text{Bi}(\text{S}-2,4,6\text{-Bu}_3\text{C}_6\text{H}_2)_3$ <sup>5</sup> have been characterised by X-ray crystallography. Other examples of bismuth(III) thiolate compounds include the ionic species  $[\text{AsPh}_4][\text{Bi}(\text{SC}_6\text{F}_5)_4]^{2a}$  and  $[\text{Na}_2(\text{thf})_4][\text{Bi}(\text{SC}_6\text{F}_5)_3]^{3a}$  (thf = tetrahydrofuran), the latter having been characterised crystallographically,<sup>3a</sup> and a range of Lewis base adducts of **1** comprising  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{SPPPh}_3)]$ ,  $[\text{K}(18\text{-crown-6})][\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{NCS})]$ ,  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{OPPh}_3)_2]$ ,  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{hmpa})_2]$  (hmpa = hexamethylphosphoramide),  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{dmpu})_2]$  (dmpu = *N,N'*-dimethylpropylene urea) and  $[\text{Bi}(\text{SC}_6\text{F}_5)_3\{\text{S}=\text{C}(\text{NHMe})_2\}_3]$  all of which were structurally characterised.<sup>9</sup> More recently, a range of dithiolate derivatives has been prepared including the structurally characterised compounds  $\text{Bi}_2(\text{SCH}_2\text{CH}_2\text{S})_3$  and  $\text{Bi}_2(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S})_3$  which exhibit both intra- and inter-molecular  $\text{Bi} \cdots \text{S}$  interactions,<sup>10</sup> as well as a range of tris-thiolate compounds exhibiting intramolecular *O*- or *N*-coordination. Structurally characterised examples of the latter types include  $\text{Bi}(\text{SC}_6\text{H}_4\text{-2-CO}_2\text{Me})_3$ ,  $\text{Bi}(\text{SCH}_2\text{CH}_2\text{NH}_2)_3$  and  $\text{Bi}(\text{SCH}_2\text{CO}_2\text{Me})_3$ .<sup>11</sup> Recent studies have also highlighted important applications of bismuth thiolates, for example in the chemical vapour deposition of  $\text{Bi}_2\text{S}_3$ <sup>7</sup> and in medicine.<sup>12</sup>

Herein we describe the preparation and structures of a range of pyridine adducts of **1** and of  $\text{Bi}(\text{SC}_6\text{Cl}_5)_3$  (**2**). These studies were prompted by our previous work both on the coordination chemistry of **1**<sup>9</sup> and on the coordination of pyridine ligands to bismuth halides and arylbismuth halides.<sup>13</sup> Thus, in the former case, adducts of the form  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{L})_2]$  and  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{L})_3]$  were found to have *cis* and *fac* ligand geometries respectively whereas a preference for *mer* and *trans* pyridine ligand geom-

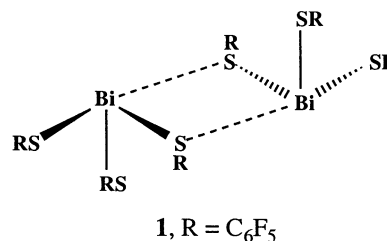
etries was observed for the species  $[\text{BiX}_3(\text{L})_3]$  and  $[\text{BiArX}_2(\text{L})_2]$  (X = halide, Ar = aryl) respectively.<sup>†</sup>

## Results

Compound **1** was prepared, with typical isolated yields of 70%, from  $\text{BiPh}_3$  and three equivalents of the thiol  $\text{HSC}_6\text{F}_5$  according to eqn. (1)

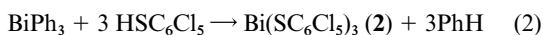


as described in ref. 3b. The structure of orange crystalline **1** was reported in ref. 3a, and comprises loosely bound centrosymmetric dimers with a long  $\text{Bi} \cdots \text{S}$  contact *trans* to one of the primary Bi-S bonds, but on a number of occasions during the present study, both dark and light orange crystalline forms of **1** were observed. Mass spectra and microanalytical data for both apparent modifications were consistent with the formula of **1**, *i.e.*  $\text{Bi}(\text{SC}_6\text{F}_5)_3$ , and the possibility that the two forms might represent different polymorphs was discounted by unit cell measurements performed on bulk powders and single crystals of each; the unit cell reported for **1** in ref. 3a was found in all cases.

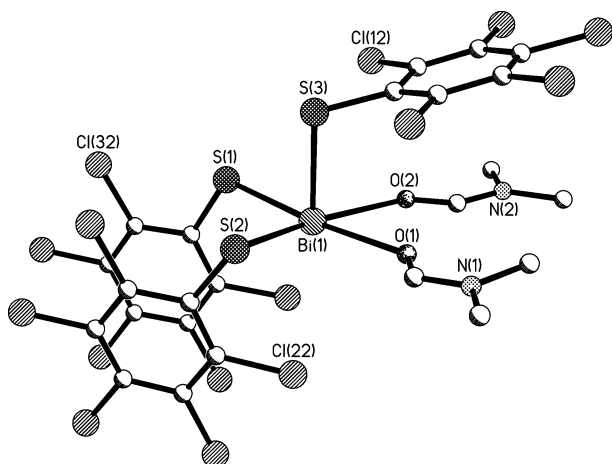
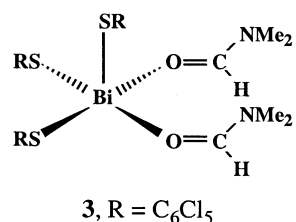


<sup>†</sup> Five- and six-coordinate compounds adopt square-based pyramidal and octahedral geometries respectively as described in refs. 9 and 13 and refs. therein. In the former case the ligands lie in the basal plane.

The perchloro-aryl derivative  $\text{Bi}(\text{SC}_6\text{Cl}_5)_3$  (**2**) was prepared in an analogous fashion according to eqn. (2)

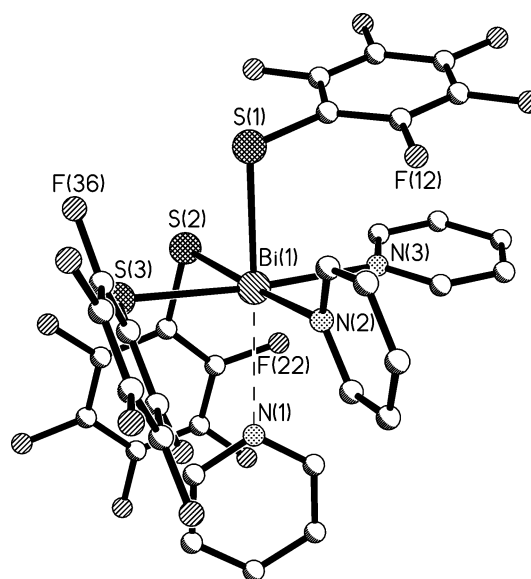


and was obtained as an orange powder in similar isolated yields (91%). Compound **2**, however, is much less soluble than **1** and dissolves only in strongly coordinating solvents. Pyridine adducts are described below but a useful solvent in which to conduct reactions of **2** is dmf (*N,N*-dimethylformamide). From a dmf solution of **2**, crystals of the adduct  $[\text{Bi}(\text{SC}_6\text{Cl}_5)_3(\text{dmf})_2]$  (**3**) were obtained. A view of the molecular structure of **3** is shown in Fig. 1 and reveals a five-coordinate square-based pyramidal geometry in which the two dmf ligands lie in the basal plane with a mutually *cis* configuration. Compound **3** is thus similar to bis-ligand derivatives of **1** such as  $[\text{Bi}(\text{SC}_6\text{F}_5)_2(\text{OPPh}_3)_2]$ ,  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{hmpa})_2]$  and  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{dmpu})_2]$ .<sup>9</sup> The apical thiolate has the shortest Bi–S bond as expected from previous studies.<sup>9</sup> Intra- and inter-molecular solid-state interactions for this and all other structures are described and discussed below.

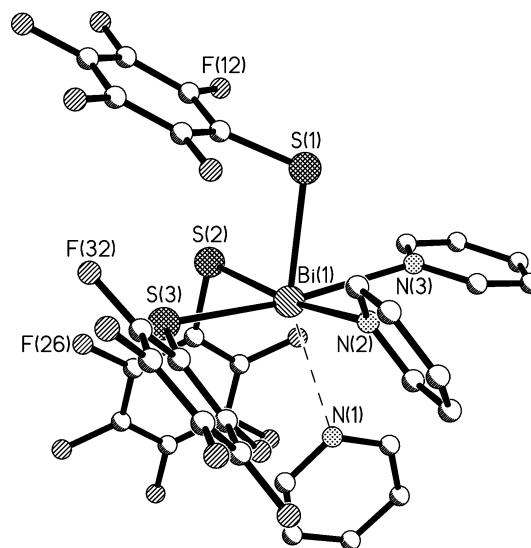


**Fig. 1** A view of the molecular structure of **3**. Selected bond distances (Å) include Bi(1)–S(1) 2.661(2), Bi(1)–S(2) 2.634(2), Bi(1)–S(3) 2.581(2), Bi(1)–O(1) 2.577(5), Bi(1)–O(2) 2.664(6).

Treatment of **1** with an excess of pyridine (py) afforded a yellow crystalline tris-pyridine adduct  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{py})_3]$  (**4**) which was obtained as two polymorphs. One polymorph (**4a**) was obtained from a reaction between **1** and pyridine in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{BiPh}_3$  with the aim of preparing a pyridine adduct of an arylbismuth thiolate (see later). The second polymorph (**4b**) was prepared similarly but in the absence of  $\text{BiPh}_3$ . A small quantity of orange crystals was also obtained in the latter reaction although these could not be obtained in a pure form and have not been identified (see later). The molecular structure of **4** in **4a** is shown in Fig. 2 and reveals an octahedral geometry with a *fac*-configuration [*cf.* *fac*- $[\text{Bi}(\text{SC}_6\text{F}_5)_3\{\text{S}=\text{C}(\text{NHMe})_2\}_3]$ ].<sup>9</sup> One of the pyridine ligands is significantly further from the bismuth centre than the other two [Bi(1)–N(1) 2.837(4) vs. Bi(1)–N(2) 2.778(4) and Bi(1)–N(3) 2.753(4) Å] although all *trans* N–Bi–S angles are close to 180° [S(1)–Bi(1)–N(1) 177.9(1), S(2)–Bi(1)–N(2) 172.20(9), S(3)–Bi(1)–N(3) 171.47(10)]. The longer Bi–N(1) distance is reflected in the *trans* thiolate having the shorter Bi–S distance



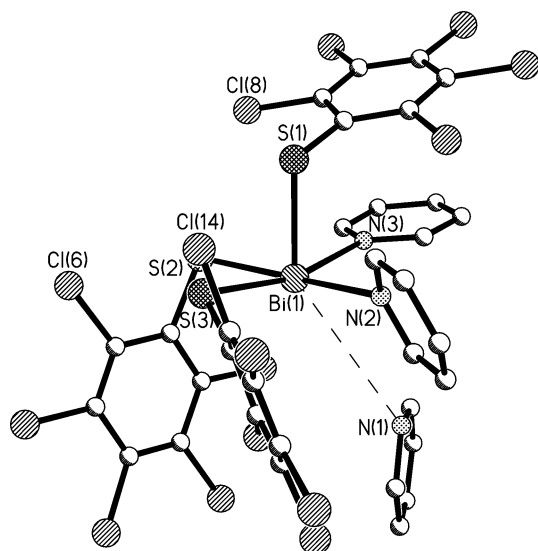
**Fig. 2** A view of the molecular structure of **4a**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.6244(13), Bi(1)–S(2) 2.6388(13), Bi(1)–S(3) 2.6398(14), Bi(1)–N(1) 2.837(4), Bi(1)–N(2) 2.778(4), Bi(1)–N(3) 2.753(4); S(1)–Bi(1)–N(1) 177.9(1), S(2)–Bi(1)–N(2) 172.20(9), S(3)–Bi(1)–N(3) 171.47(10).



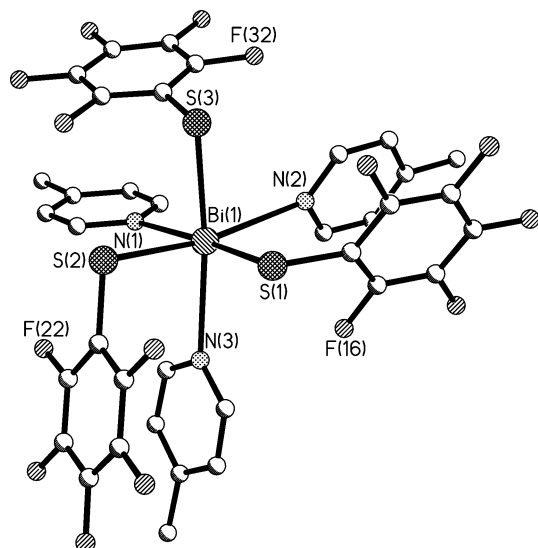
**Fig. 3** A view of the molecular structure of **4b**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.5916(9), Bi(1)–S(2) 2.6447(10), Bi(1)–S(3) 2.6424(8), Bi(1)–N(1) 3.055(3), Bi(1)–N(2) 2.710(3), Bi(1)–N(3) 2.748(3); S(1)–Bi(1)–N(1) 154.4(7), S(2)–Bi(1)–N(2) 168.18(6), S(3)–Bi(1)–N(3) 172.17(7).

(see caption to Fig. 2). The structure of **4b** is shown in Fig. 3 and reveals a broadly similar *fac*-octahedral structure also with one pyridine more loosely bound than the other two, the most notable difference being that the S–Bi–N angle involving the more loosely bound pyridine is distinctly non-linear [154.4(7)]. Other bond distances and angles are given in the caption to Fig. 3 and differences in the conformations of the pyridine ligands and thiolate groups are discussed below.

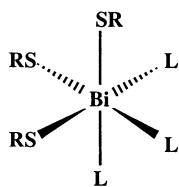
A tris-pyridine adduct *fac*- $[\text{Bi}(\text{SC}_6\text{Cl}_5)_3(\text{py})_3]$  (**5**) was isolated from the reaction between **2** and an excess of pyridine, the structure of which is shown in Fig. 4. The structure is similar to that of **4b** in having one pyridine much more loosely bound [3.982(9) vs. 2.795(8) and 2.728(9) Å] with a non-linear S–Bi–N arrangement [144.8(2) vs. 165.8(2) and 166.28(19)]. In contrast, the reaction between **1** and 4-picoline (4-pic) afforded the adduct *fac*- $[\text{Bi}(\text{SC}_6\text{F}_5)_3(4\text{-pic})_3]$  (**6**) (Fig. 5) in which the three picoline ligands are all bonded to the bismuth centre with similar Bi–N distances and near linear S–Bi–N angles.



**Fig. 4** A view of the molecular structure of **5**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.577(3), Bi(1)–S(2) 2.639(3), Bi(1)–S(3) 2.659(3), Bi(1)–N(1) 3.982(9), Bi(1)–N(2) 2.795(8), Bi(1)–N(3) 2.728(9); S(1)–Bi(1)–N(1) 144.8(2), S(2)–Bi(1)–N(2) 165.8(2), S(3)–Bi(1)–N(3) 166.28(19).



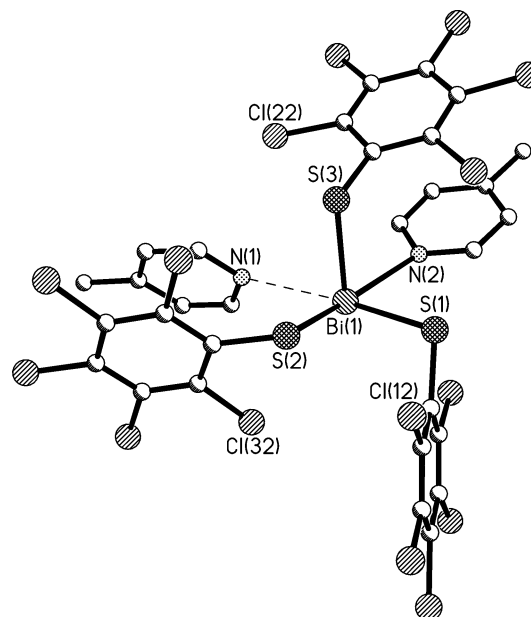
**Fig. 5** A view of the molecular structure of **6**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.639(1), Bi(1)–S(2) 2.6395(9), Bi(1)–S(3) 2.6599(9), Bi(1)–N(1) 2.757(3), Bi(1)–N(2) 2.788(3), Bi(1)–N(3) 2.773(3); S(1)–Bi(1)–N(1) 176.01(7), S(2)–Bi(1)–N(2) 168.96(6), S(3)–Bi(1)–N(3) 174.00(6).



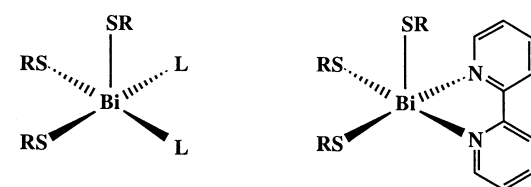
**4a,b**, R = C<sub>6</sub>F<sub>5</sub>, L = py; **5**, R = C<sub>6</sub>Cl<sub>5</sub>, L = py  
**6**, R = C<sub>6</sub>F<sub>5</sub>, L = 4-pic

Crystals of a bis-ligand adduct of **2**, namely [Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>-(4-pic)<sub>2</sub>] (**7**) were obtained from a solution of **2** in dmf and 4-picoline. The structure is shown in Fig. 6 and reveals a square-based pyramidal geometry with *cis*-basal ligands leading to a structure analogous to **3** and bis-ligand adducts of **1**,<sup>9</sup> although the Bi–N distances are markedly different [2.660(8) vs. 2.827(8) Å].

Both **1** and **2** form adducts with 2,2'-bipyridyl (bipy) namely [Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(bipy)] (**8**) and [Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>(bipy)] (**9**). Although not

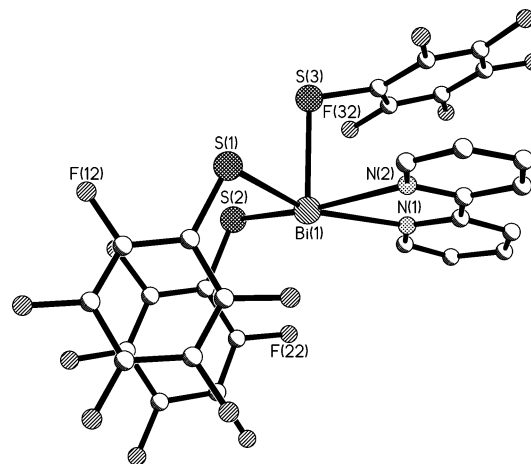


**Fig. 6** A view of the molecular structure of **7**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.619(2), Bi(1)–S(2) 2.654(3), Bi(1)–S(3) 2.580(3), Bi(1)–N(1) 2.827(8), Bi(1)–N(2) 2.660(8); S(1)–Bi(1)–N(1) 167.9(2), S(2)–Bi(1)–N(2) 162.03(18).



**7**, R = C<sub>6</sub>Cl<sub>5</sub>, L = 4-pic

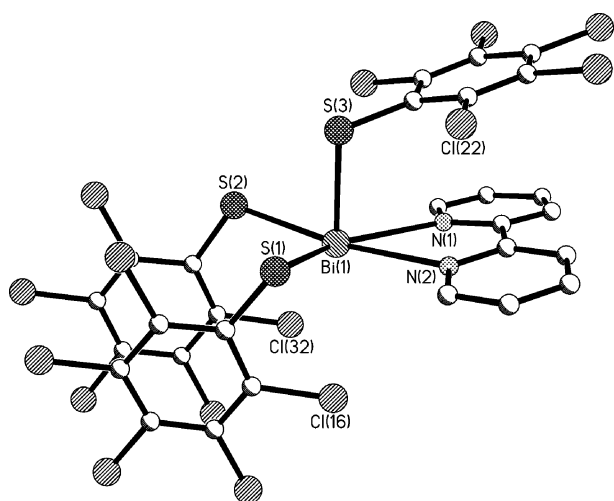
**8**, R = C<sub>6</sub>F<sub>5</sub>; **9**, R = C<sub>6</sub>Cl<sub>5</sub>



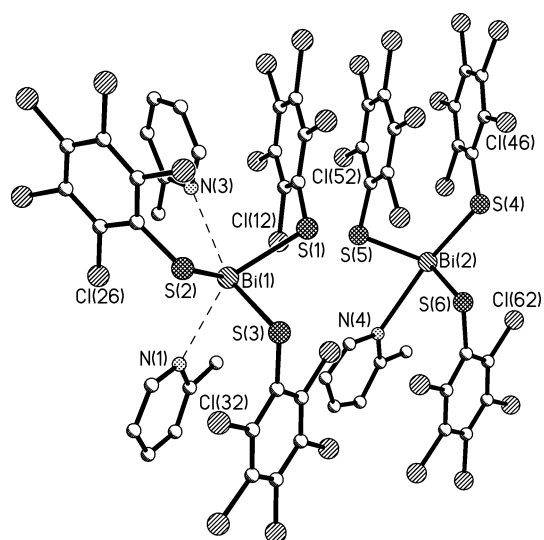
**Fig. 7** A view of the molecular structure of **8**. Selected bond distances (Å) include Bi(1)–S(1) 2.670(2), Bi(1)–S(2) 2.678(2), Bi(1)–S(3) 2.559(2), Bi(1)–N(1) 2.607(6), Bi(1)–N(2) 2.572(7).

isomorphous, the molecular structures are similar (Figs. 7 and 8 respectively) having the bipy ligand in the basal plane of the square-based pyramidal geometry as expected for this stoichiometry.

Crystals of the compound [Bi<sub>2</sub>(SC<sub>6</sub>Cl<sub>5</sub>)<sub>6</sub>(2-pic)<sub>3</sub>] (**10**) (2-pic = 2-picoline) were isolated from the reaction between **2** and 2-picoline. The structure is shown in Fig. 9 and reveals two distinct molecular units present in the asymmetric unit. One of these comprises the species [Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>(2-pic)] in which a single 2-pic ligand is bonded *trans* to one thiolate group [Bi(2)–N(4) 2.789(11) Å] giving an overall disphenoidal coordination around the bismuth. In the other species, two 2-picoline ligands are weakly associated with the bismuth centre [Bi(1)–N(1),



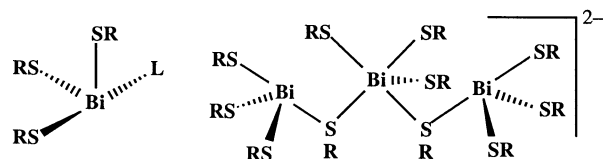
**Fig. 8** A view of the molecular structure of **9**. Selected bond distances (Å) include Bi(1)–S(1) 2.618(4), Bi(1)–S(2) 2.698(4), Bi(1)–S(3) 2.572(4), Bi(1)–N(1) 2.730(8), Bi(1)–N(2) 2.697(8).



**Fig. 9** A view of the molecular structure of **10**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.625(3), Bi(1)–S(2) 2.592(3), Bi(1)–S(3) 2.621(4), Bi(2)–S(4) 2.618(3), Bi(2)–S(5) 2.570(3), Bi(2)–S(6) 2.579(3), Bi(1)–N(1) 2.932(11), Bi(1)–N(3) 2.828(11), Bi(2)–N(4) 2.789(11); S(1)–Bi(1)–N(1) 150.3(3), S(3)–Bi(1)–N(3) 147.1(3), S(4)–Bi(2)–N(4) 159.0(3).

2.932(11); Bi(1)–N(3) 2.828(11) Å] each approximately *trans* to a thiolate.

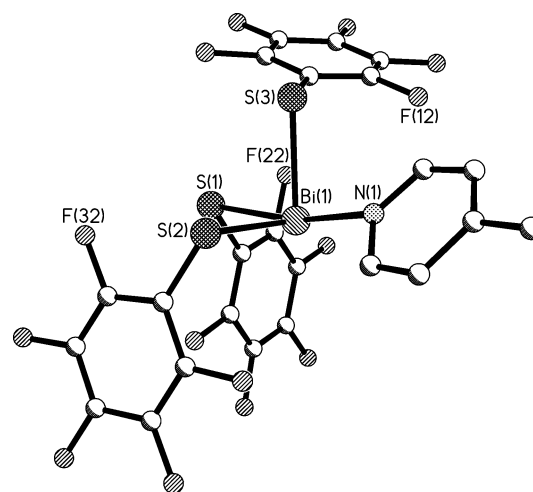
A mono-ligand complex [Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(4-pic)] (**11**), similar to one of the species in **10**, was isolated from a reaction between **1** and less than three equivalents of 4-picoline (with an excess of 4-pic, compound **6** was obtained, see above). The structure is shown in Fig. 10 which reveals a disphenoidal geometry with one 4-picoline ligand bound *trans* to one thiolate [Bi(1)–N(1) 2.706(8) Å]; this thiolate has the longest Bi–S bond [Bi(1)–S(1) 2.627(3) Å]. There are no short intermolecular contacts to the bismuth centre.



**11**, R = C<sub>6</sub>F<sub>5</sub>, L = 4-pic

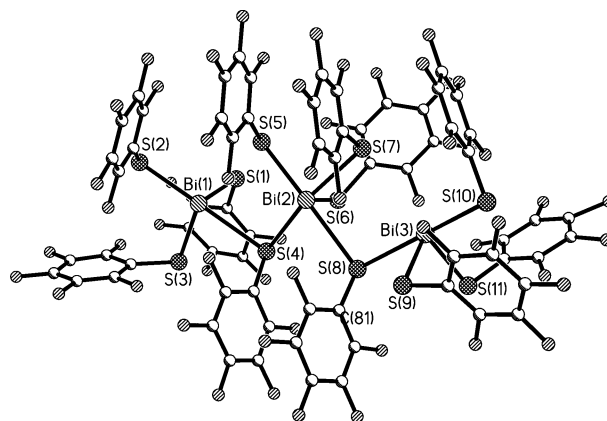
**12**, R = C<sub>6</sub>F<sub>5</sub>

As mentioned above for **4**, in some cases small quantities of orange crystals were sometimes formed in addition to yellow



**Fig. 10** A view of the molecular structure of **11**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.627(3), Bi(1)–S(2) 2.553(4), Bi(1)–S(3) 2.562(4), Bi(1)–N(1) 2.706(8); S(1)–Bi(1)–N(1) 165.2(2).

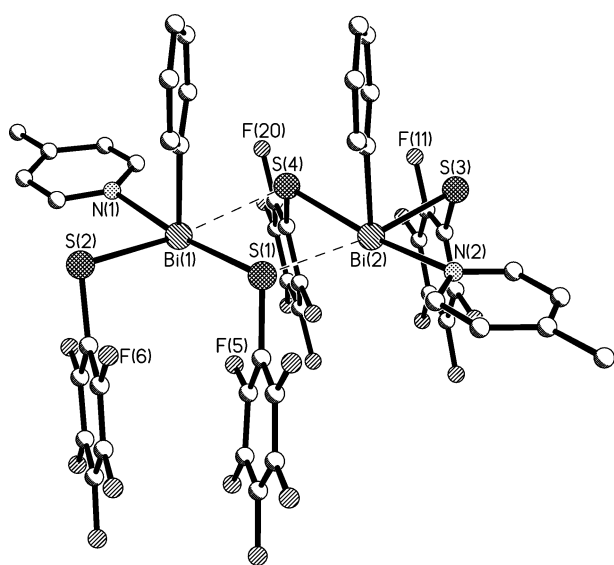
crystalline **4** although these were not formed in sufficient quantity or with satisfactory crystallinity to be identified. In the formation of yellow crystalline **11**, an orange crystalline product was also formed which in this case was identified by X-ray crystallography. The product, **12**, is a salt with the formula [4-picH][[(4-pic)<sub>2</sub>H][Bi<sub>3</sub>(SC<sub>6</sub>F<sub>5</sub>)<sub>11</sub>]]<sup>2-</sup>. A view of the trinuclear anion [Bi<sub>3</sub>(SC<sub>6</sub>F<sub>5</sub>)<sub>11</sub>]<sup>2-</sup> is shown in Fig. 11. A central bismuth is bonded to five thiolate ligands with a square-based pyramidal geometry similar to that found in the species [Na<sub>2</sub>(thf)<sub>4</sub>][Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>5</sub>].<sup>3a</sup> Two *cis*-basal thiolates act as bridging groups to two outer bismuth centres each of which is four-coordinate with the expected equatorially vacant, trigonal bipyramidal geometry in which the bridging thiolate is in an axial position. The Bi–S distances show the expected trends; terminal are shortest and bridging are longest. The cations comprise an isolated protonated 4-picoline, [4-picH]<sup>+</sup>, and a hydrogen bonded picoline–picolinium ion [(4-pic)<sub>2</sub>H]<sup>+</sup>. It is likely that **12** and the orange material formed in preparations of **4** are due to hydrolysis from adventitious water since more strictly anhydrous conditions afford less or no orange material.



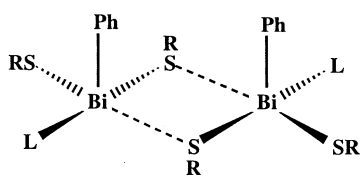
**Fig. 11** A view of the molecular structure of the anion [Bi<sub>3</sub>(SC<sub>6</sub>F<sub>5</sub>)<sub>11</sub>]<sup>2-</sup> in **12**. Selected bond distances (Å) include Bi(1)–S(1) 2.576(3), Bi(1)–S(2) 2.640(4), Bi(1)–S(3) 2.575(3), Bi(1)–S(4) 2.973(3), Bi(2)–S(4) 2.896(3), Bi(2)–S(5) 2.733(3), Bi(2)–S(6) 2.542(3), Bi(2)–S(7) 2.728(3), Bi(2)–S(8) 2.980(3), Bi(3)–S(8) 2.996(3), Bi(3)–S(9) 2.578(3), Bi(3)–S(10) 2.642(3), Bi(3)–S(11) 2.553(4).

As a final point relating to synthesis, we were also interested in making pyridine adducts of arylbismuth thiolates for comparison with the pyridine adducts of arylbismuth halides described in ref. 13 in which *trans* pyridine configurations were observed (the only previous report of an arylbismuth thiolate

of which we are aware describes the compound  $\text{BiPh}_2(\text{SPh})^{14}$ . However, we were not able to isolate arylbismuth thiolates of the form  $\text{BiAr}(\text{SC}_6\text{F}_5)_2$  or  $\text{BiAr}_2(\text{SC}_6\text{F}_5)$  from reactions between **1** and  $\text{BiPh}_3$ . Moreover, reactions between **1** and  $\text{BiPh}_3$  in the presence of pyridine ligands afforded ligand adducts of **1** as was the case in the synthesis of **4a**. On one occasion, however, a reaction between **1** and 4-picoline afforded a small quantity of crystals identified by X-ray crystallography as  $[\text{Bi}_2\text{Ph}_2(\text{SC}_6\text{F}_5)_4(4\text{-pic})_2]$  (**13**) indicating that some aryl containing compound was present as an impurity in that particular sample of **1**. Although we have not been able to reproduce the preparation of **13**, the structure is included here. Compound **13** (Fig. 12) is dimeric with an edge-shared, bis-square-based pyramidal structure in which the phenyl groups are in apical sites and *syn* with respect to the two basal planes. Two thiolates bridge asymmetrically, the longer Bi–S bonds *trans* to terminal thiolates (one on each bismuth centre) and the shorter bonds *trans* to the two 4-picoline ligands.



**Fig. 12** A view of the molecular structure of **13**. Selected bond distances (Å) and angles (°) include Bi(1)–S(1) 2.827(3), Bi(1)–S(2) 2.627(3), Bi(1)–S(4) 3.148(3), Bi(2)–S(1) 3.139(3), Bi(2)–S(3) 2.627(3), Bi(2)–S(4) 2.817(3), Bi(1)–N(1) 2.568(10), Bi(2)–N(2) 2.582(9), Bi(1)–C(1) 2.238(10), Bi(2)–C(25) 2.240(11); S(2)–Bi(1)–S(4) 171.6(3), S(1)–Bi(2)–S(3) 170.7(3).

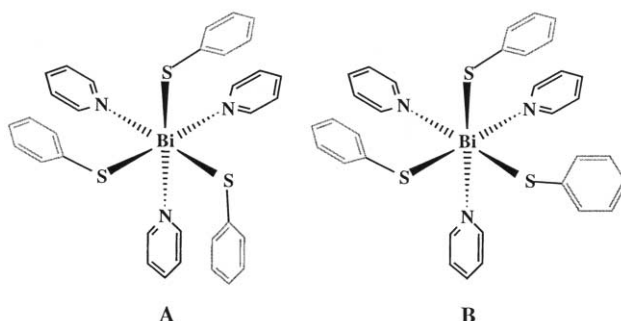


**13**, R =  $\text{C}_6\text{F}_5$ , L = 4-pic

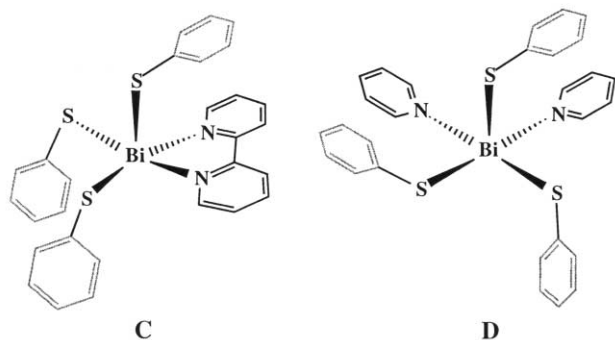
## Discussion

Looking first at the structures described above which contain two or three pyridine ligands bonded to a bismuth centre, it is evident that in no cases do pyridine ligands occupy *trans* sites. Thus octahedral complexes have *fac* configurations and in five-coordinate structures the pyridine ligands are *cis* rather than *trans* to each other in the square-basal plane. This observation is in line with the previously characterised complexes of **1**<sup>9</sup> although in contrast to the situation found for pyridine complexes of arylbismuth halides where *trans* pyridines are the norm.<sup>13</sup> There is little to add to the discussion on this matter given in ref. 13 except to reiterate that general predictions of the preferences for *fac* vs. *mer* or *cis* vs. *trans* configurations cannot yet be made with any confidence.

It is also informative to look at the inter-ligand interactions both in terms of intramolecular conformations and intermolecular associations. In both cases, these interactions are dominated by  $\pi$ -stacking between aryl and/or pyridine rings. If we look first at intramolecular interactions, then for the tris-ligand complexes **4–6**, it is clear that for complexes **4a** and **6** (Figs. 2 and 5) the aryl ring of each thiolate lies parallel to a *cis* pyridine ring as shown schematically in **A**. This results in a propeller arrangement of both thiolate and pyridine groups and approximate molecular  $\text{C}_3$  symmetry. In contrast, only two such parallel intramolecular thiolate–pyridine interactions are present in **4b** and **5** (Figs. 3 and 4). For these two species, one arylthiolate is rotated away as shown in **B** although the three pyridine ligands retain the propeller orientation seen in **A**. Inter-ring separations between thiolate ( $\text{C}_6\text{F}_5$ ) and pyridine rings (ring centroid to ring centroid) range from 3.493 to 3.775 Å for **4a** and from 3.596 to 3.641 Å in **6**.



The bis-ligand complexes **3**, **8** and **9** (Figs. 1, 7 and 8) all have very similar conformations. Thus, the two thiolates *trans* to the two ligands have parallel aryl rings whilst the third, apical thiolate ring lies over the dmf or bipy ligands. This is shown schematically for **8/9** in **C**. Thiolate ring to thiolate ring separations here range from 3.699 Å in **9** to 3.938 Å in **8** although we note that the distance between the  $\text{C}_6\text{F}_5$  groups in **8** is significantly greater than that between the corresponding  $\text{C}_6\text{Cl}_5$  groups in **9**. In complex **7** the arrangement is different in that the thiolates adopt the propeller conformation seen in **4a** and **6** with each of the two 4-picoline ligands parallel to one thiolate aryl ring as shown in **D**. Arrangement **D** can be derived from **A** simply by removing one pyridine ligand. Intramolecular  $\pi$ – $\pi$ -interactions between adjacent thiolate aryl rings and between pyridine and thiolate aryl rings are also present in the structures of **10** and **12** as is evident from Figs. 9 and 11. In the former case (Fig. 9) pyridine to thiolate distances range from 3.492 to 3.671 Å, an intramolecular thiolate to thiolate separation is present (between  $\text{C}_6\text{Cl}_5$  groups) at 3.793 Å and an additional intermolecular  $\pi$ – $\pi$ -interaction is evident between the thiolates S(1) and S(5) [3.946 Å].



Intermolecular associations involving  $\pi$ – $\pi$ -interactions between  $\text{C}_6\text{F}_5$  or  $\text{C}_6\text{Cl}_5$  rings is also a dominant feature in all of the structures reported here and two representative examples

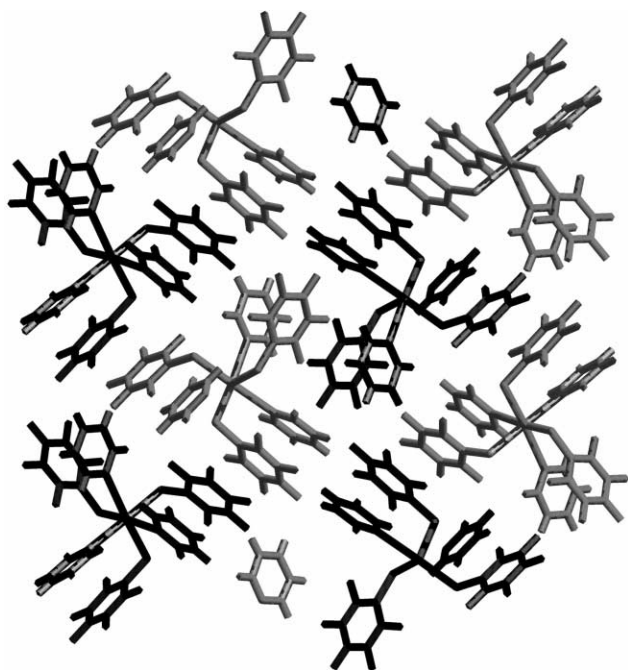


Fig. 13 A view of the packing of molecules of **4a** in the crystal.

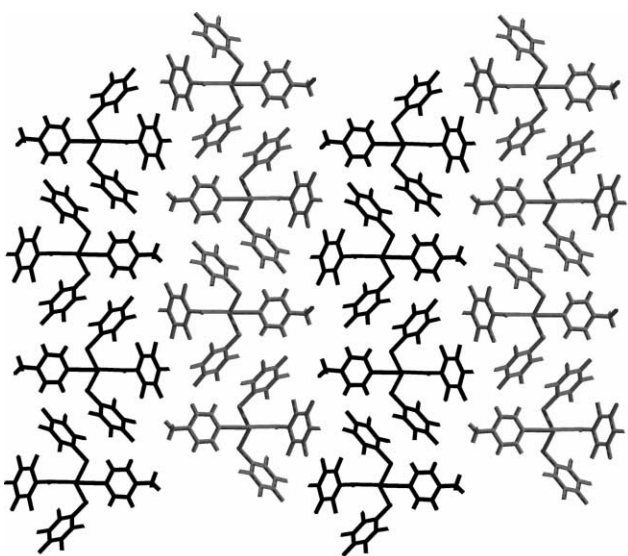


Fig. 14 A view of the packing of molecules of **11** in the crystal.

are shown in Figs. 13 and 14 which illustrate the molecular packing in the crystals of **4a** and **11**. Intermolecular thiolate to thiolate ring separations are 3.878 and 4.567 Å respectively.  $\pi$ -Stacking of the type seen here has been observed in many situations and we note the recent work of Marder described in refs. 15 and refs. therein.

## 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. Dry solvents were obtained from an Anhydrous Engineering Solvent System or were dried over molecular sieves, and were degassed prior to use. Compound **1** was prepared by the literature method.<sup>3</sup> BiPh<sub>3</sub>, pyridine and substituted pyridines were procured commercially and were dried over molecular sieves. 2,2'-Bipyridyl was dried prior to use by the Dean–Stark method. Yields are isolated yields of crystalline material.

### Preparations

**Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub> (2).** HSC<sub>6</sub>Cl<sub>5</sub> (1.92 g, 6.800 mmol) was added to a solution of BiPh<sub>3</sub> (1.00 g, 2.270 mmol) in toluene (40 cm<sup>3</sup>) and the resulting reaction mixture was then refluxed for 96 h during which time it turned from colourless to orange. After this time, the solvent was removed by vacuum at room temperature and the residue was washed with hexane and dried by vacuum affording **2** as an orange powder (2.66 g, 91%). C<sub>18</sub>BiCl<sub>15</sub>S<sub>3</sub> requires C, 20.55. Found C, 22.10%.

**[Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>(dmf)<sub>2</sub>] (3).** Compound **2** (0.105 g, 0.100 mmol) was dissolved in dmf (4 cm<sup>3</sup>) affording an orange solution. Slow solvent evaporation over a period of days afforded yellow block-like crystals of **3** (0.084 g, 80%). C<sub>24</sub>H<sub>14</sub>BiCl<sub>15</sub>O<sub>2</sub>N<sub>2</sub>S<sub>3</sub> requires C, 24.05; H, 1.20; N, 2.35; S, 8.00. Found C, 24.05; H, 0.60; N, 2.50; S, 6.24%.

**[Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(py)<sub>3</sub>] (4a).** Compound **1** (0.190 g, 0.240 mmol) and BiPh<sub>3</sub> (0.064 g, 0.14 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (6 cm<sup>3</sup>) and pyridine (0.30 cm<sup>3</sup>) added resulting in a darkening of the orange colour. Hexane (5 cm<sup>3</sup>) was added as an overlayer and solvent diffusion over a period of days at –30 °C afforded yellow crystals of **4a** (0.124 g, 65%). C<sub>33</sub>H<sub>15</sub>BiF<sub>15</sub>N<sub>3</sub>S<sub>3</sub> requires C, 38.00; H, 1.50; N, 4.05. Found C, 37.30; H, 1.15; N, 3.60%.

**[Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(py)<sub>3</sub>] (4b).** Compound **1** (0.130 g, 0.161 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) and pyridine (0.20 cm<sup>3</sup>) added resulting in a darkening of the orange colour. Hexane (4 cm<sup>3</sup>) was added as an overlayer and solvent diffusion over a period of days at –30 °C afforded yellow crystals of **4b** (0.08 g, 25%). C<sub>33</sub>H<sub>15</sub>BiF<sub>15</sub>N<sub>3</sub>S<sub>3</sub> requires C, 38.00; H, 1.50; N, 4.05. Found C, 38.25; H, 1.20; N, 3.40%. A small quantity of orange crystals were also obtained although these could not be isolated in a pure form and have not been identified.

**[Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>(py)<sub>3</sub>] (5).** Compound **2** (0.028 g, 0.027 mmol) was dissolved in dmf (2 cm<sup>3</sup>) to which pyridine (0.02 cm<sup>3</sup>) was then added after which Et<sub>2</sub>O (4 cm<sup>3</sup>) was added as an overlayer. Solvent diffusion over a period of days at room temperature afforded orange crystals of **5** (0.017 g, 50%). C<sub>33</sub>H<sub>15</sub>BiCl<sub>15</sub>N<sub>3</sub>S<sub>3</sub> requires C, 30.70; H, 1.20; N, 3.25. Found C, 30.45; H, 1.00; N, 3.05%.

**[Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(4-pic)<sub>3</sub>] (6).** Compound **1** (0.407 g, 0.500 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) and 4-picoline (0.141 cm<sup>3</sup>, 1.5 mmol) added resulting in a darkening of the orange colour. Hexane (4 cm<sup>3</sup>) was added as an overlayer and solvent diffusion over a period of days at –30 °C afforded yellow crystals of **6** (0.091 g, 47%). C<sub>36</sub>H<sub>21</sub>BiF<sub>15</sub>N<sub>3</sub>S<sub>3</sub> requires C, 39.85; H, 1.95; N, 3.85; S, 8.85. Found C, 39.50; H, 1.70; N, 3.75; S, 8.60%.

**[Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>(4-pic)<sub>2</sub>] (7).** Compound **2** (0.052 g, 0.050 mmol) was dissolved in dmf (2 cm<sup>3</sup>) to which 4-picoline (0.01 cm<sup>3</sup>) was added after which Et<sub>2</sub>O (5 cm<sup>3</sup>) was added as an overlayer. Solvent diffusion over a period of days at –30 °C afforded a mixture of yellow **7** (0.05 g, 75%) and a small crop of orange crystals. C<sub>30</sub>H<sub>14</sub>BiCl<sub>15</sub>N<sub>2</sub>S<sub>3</sub> requires C, 29.05; H, 1.15; N, 2.25; S, 7.75; Cl, 42.90. Found C, 30.40; H, 0.60; N, 2.35; S, 8.00; Cl, 42.80%.

**[Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(bipy)] (8).** Compound **1** (0.180 g, 0.223 mmol) and 2,2'-bipyridyl (0.140 g, 0.890 mmol) were dissolved in thf (3 cm<sup>3</sup>) and hexane (3 cm<sup>3</sup>) was added as an overlayer. Solvent diffusion over a period of days at –30 °C afforded orange crystals of **8** (0.044 g, 14%). C<sub>28</sub>H<sub>8</sub>BiF<sub>15</sub>N<sub>2</sub>S<sub>3</sub> requires C, 34.95; H, 0.85; N, 2.90. Found C, 34.95; H, 0.70; N, 2.85%.

**[Bi(SC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>(bipy)] (9).** Compound **2** (0.170 g, 0.160 mmol) and 2,2'-bipyridyl (0.025 g, 0.160 mmol) were dissolved in dmf

Table 1 Crystallographic data for compounds 3-13

	[Bi(SC <sub>6</sub> Cl <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (dmf) <sub>2</sub> ] (3)	[Bi(SC <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (py) <sub>3</sub> ] (4a)	[Bi(SC <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (py) <sub>3</sub> ] (4b)	[Bi(SC <sub>6</sub> Cl <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (py) <sub>3</sub> ] (5)	[Bi(SC <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (4-pic) <sub>3</sub> ] (6)	[Bi(SC <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (4-pic) <sub>2</sub> ] (7)	[Bi(SC <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (bipy)] (8)	[Bi(SC <sub>6</sub> Cl <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (bipy)] (9)	[Bi <sub>2</sub> (SC <sub>6</sub> Cl <sub>5</sub> ) <sub>6</sub> ] <sup>-</sup> (2-pic) <sub>3</sub> ] (10)	[Bi(SC <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> (4-pic)] (11)	[(4-picH)- {(4-pic) <sub>2</sub> H}] [Bi <sub>3</sub> (SC <sub>6</sub> F <sub>5</sub> ) <sub>11</sub> ] (12)	[Bi <sub>2</sub> Ph <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (4-pic) <sub>2</sub> ] (13)
Formula	C <sub>24</sub> H <sub>14</sub> BiCl <sub>15</sub> <sup>-</sup> N <sub>2</sub> O <sub>2</sub> S <sub>3</sub>	C <sub>66</sub> H <sub>30</sub> Bi <sub>2</sub> F <sub>30</sub> <sup>-</sup> N <sub>6</sub> S <sub>6</sub>	C <sub>33</sub> H <sub>15</sub> BiF <sub>15</sub> <sup>-</sup> N <sub>3</sub> S <sub>3</sub>	C <sub>33</sub> H <sub>15</sub> BiCl <sub>15</sub> <sup>-</sup> N <sub>3</sub> S <sub>3</sub>	C <sub>36</sub> H <sub>21</sub> BiF <sub>15</sub> <sup>-</sup> N <sub>3</sub> S <sub>3</sub>	C <sub>30</sub> H <sub>14</sub> BiCl <sub>15</sub> <sup>-</sup> N <sub>2</sub> S <sub>3</sub>	C <sub>28</sub> H <sub>8</sub> BiF <sub>15</sub> <sup>-</sup> N <sub>2</sub> S <sub>3</sub>	C <sub>28</sub> H <sub>8</sub> BiCl <sub>15</sub> <sup>-</sup> N <sub>2</sub> S <sub>3</sub>	C <sub>54</sub> H <sub>21</sub> Bi <sub>2</sub> Cl <sub>30</sub> <sup>-</sup> N <sub>3</sub> S <sub>6</sub>	C <sub>24</sub> H <sub>7</sub> BiF <sub>15</sub> <sup>-</sup> NS <sub>3</sub>	C <sub>84</sub> H <sub>23</sub> Bi <sub>3</sub> F <sub>55</sub> <sup>-</sup> N <sub>3</sub> S <sub>11</sub>	C <sub>53</sub> H <sub>34</sub> Bi <sub>2</sub> F <sub>20</sub> <sup>-</sup> N <sub>2</sub> S <sub>4</sub>
<i>M</i>	1199.28	2087.28	1043.64	1290.39	1085.72	1239.34	962.52	1209.27	1192.78	899.47	3097.90	16.25.06
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.5990(13)	8.7632(8)	10.0822(6)	17.820(3)	9.3018(12)	8.7882(7)	9.6388(15)	9.437(3)	8.699(3)	5.4276(5)	15.128(8)	13.7168(18)
<i>b</i> /Å	14.627(2)	13.6101(16)	20.558(2)	14.940(3)	17.925(2)	10.3833(8)	12.2386(15)	14.708(4)	20.999(7)	19.4615(17)	28.483(15)	13.9845(19)
<i>c</i> /Å	26.667(4)	30.018(5)	17.130(2)	17.057(3)	23.774(3)	44.413(4)	13.241(2)	26.464(7)	21.750(7)	25.877(2)	22.941(9)	16.666(2)
<i>α</i> /°									73.156(6)			69.780(2)
<i>β</i> /°	97.1799(3)	95.040(15)	97.476(10)	110.423	98.982(2)	94.538(2)	111.083(13)	97.530(6)	79.295(6)		99.93(4)	81.689(2)
<i>γ</i> /°									83.486(6)			65.438(2)
<i>U</i> /Å <sup>3</sup>	3715.0(9)	3566.3(8)	3520.3(6)	4255.8(15)	3915.3(8)	4040.0(5)	1457.4(4)	3641.7(17)	3729(2)	2733.4(4)	9737(8)	2728.4(6)
<i>Z</i>	4	4	4	4	4	4	2	4	4	4	4	2
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	2.144	1.994	1.969	2.014	1.842	2.038	2.193	2.206	2.125	2.186	2.113	1.978
<i>μ</i> (Mo-K <sub>α</sub> )/mm <sup>-1</sup>	6.025	5.228	5.297	5.265	4.766	5.540	6.386	6.143	5.998	6.800	5.798	6.702
Data collected	23718	22813	22387	35722	25092	40850	9460	31075	32476	14692	51982	8065
Unique data	8509	8195	8045	7495	8904	9280	5281	6413	13093	4834	17128	8065
( <i>R</i> <sub>int</sub> )	(0.0844)	(0.0646)	(0.0352)	(0.1845)	(0.0388)	(0.1237)	(0.0434)	(0.1425)	(0.1006)	(0.0802)	(0.1158)	(0.0000)
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0466,	0.0374,	0.0225,	0.0536,	0.0280,	0.0733,	0.0354,	0.0654,	0.0524,	0.0406,	0.0560,	0.0456,
[ <i>I</i> > 2σ( <i>I</i> )]	0.0889	0.0544	0.0508	0.0848	0.0476	0.1339	0.0577	0.1529	0.0847	0.0640	0.0875	0.0891
(all data)	(0.1051,	(0.0853,	(0.0393,	(0.1443,	(0.0498,	(0.1237,	(0.0540,	(0.1276,	(0.1247,	(0.0742,	(0.1311,	(0.0848,
	0.1044)	0.0627)	0.0527)	0.1098)	0.0518)	0.1462)	0.0604)	0.1820)	0.1052)	0.0732)	0.1076)	0.1003)

(5 cm<sup>3</sup>) and Et<sub>2</sub>O (5 cm<sup>3</sup>) was added as an overlayer. Solvent diffusion over a period of days at room temperature afforded orange crystals of **9** (0.091 g, 47%). C<sub>28</sub>H<sub>8</sub>BiCl<sub>15</sub>N<sub>2</sub>S<sub>3</sub> requires C, 27.81; H, 0.65; N, 2.30; S, 7.95; Cl, 43.95. Found C, 27.35; H, 0.50; N, 2.50; S, 8.60; Cl, 39.40%.

**[Bi<sub>2</sub>(SC<sub>6</sub>Cl<sub>3</sub>)<sub>6</sub>(2-pic)<sub>3</sub>] (10)**. Compound **2** (0.22 g, 0.2 mmol) was dissolved in dmf (2 cm<sup>3</sup>) to which 2-picoline (0.02 cm<sup>3</sup>) was added after which Et<sub>2</sub>O (5 cm<sup>3</sup>) was added as an overlayer. Solvent diffusion over a period of days at room temperature afforded orange crystals of **10** (0.081 g, 34%). C<sub>54</sub>H<sub>21</sub>Bi<sub>2</sub>Cl<sub>30</sub>N<sub>3</sub>S<sub>6</sub> requires C, 27.20; H, 0.90; N, 1.75; S, 8.05; Cl, 44.60. Found C, 26.20; H, 0.60; N, 1.55; S, 8.50; Cl, 44.20%.

**[Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>6</sub>(4-pic)] (11)**. Compound **1** (0.150 g, 0.186 mmol) and 4-picoline (0.2 cm<sup>3</sup>) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) and hexane (3 cm<sup>3</sup>) was added as an overlayer. Solvent diffusion over a period of days at -30 °C afforded yellow crystals of **11** (0.05 g, 15%) and a small crop of orange crystals of **12**. C<sub>24</sub>H<sub>7</sub>BiF<sub>15</sub>NS<sub>3</sub> (**11**) requires C, 32.05; H, 0.80; N, 1.55; S, 10.70. Found C, 32.10; H, 0.50; N, 1.25; S, 11.50%.

### X-Ray crystallography

All crystals were mounted under argon on glass fibres using paraffin oil. Data were collected on a Bruker AXS (formally Siemens) SMART<sup>16,17</sup> area detector diffractometer using graphite monochromated Mo-K<sub>α</sub> radiation, at -100 °C. Intensities were integrated from several series of exposures covering 0.3° in ω.

Structures were solved and refined by standard methods using SHELXTL software.<sup>18</sup> In each case hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the *U*<sub>iso</sub> of the attached carbon.

Absorption corrections were applied using SADABS<sup>19</sup> and extinction coefficients were refined where appropriate. Non-hydrogen atoms were assigned anisotropic parameters and refined without positional constraints for all structures.

Crystallographic data for all structures reported herein are presented in Table 1.

CCDC reference numbers 211633–211644.

See <http://www.rsc.org/suppdata/dt/b3/b305711a/> for crystallographic data in CIF or other electronic format.

### References

- (a) M. E. Peach, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1390 and refs. therein; (b) H. Gilman and H. L. Yale, *J. Am. Chem. Soc.*, 1951, **73**, 2880.
- (a) M. Muller, R. J. H. Clark and R. S. Nyholm, *Transition Met. Chem.*, 1978, **3**, 369; (b) M. E. Peach, *Can. J. Chem.*, 1968, **46**, 2699.
- (a) L. J. Farrugia, F. J. Lawlor and N. C. Norman, *Polyhedron*, 1995, **14**, 311; (b) W. Clegg, M. R. J. Elsegood, L. J. Farrugia, F. J. Lawlor, N. C. Norman and A. J. Scott, *J. Chem. Soc., Dalton Trans.*, 1995, 1219.
- S. C. Hergett and M. E. Peach, *J. Fluorine Chem.*, 1988, **38**, 367.
- D. A. Atwood, A. H. Cowley, R. D. Hernandez, R. A. Jones, L. L. Rand, S. G. Bott and J. L. Atwood, *Inorg. Chem.*, 1993, **32**, 2972.
- M. Wieber and U. Baudis, *Z. Anorg. Allg. Chem.*, 1976, **423**, 47.
- P. Boudjouk, M. P. Remington, D. G. Grier, B. R. Jarabek and G. J. McCarthy, *Inorg. Chem.*, 1998, **37**, 3538.
- A. F. Jansen, O. C. Vaidya and C. J. Willis, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1469.
- L. J. Farrugia, F. J. Lawlor and N. C. Norman, *J. Chem. Soc., Dalton Trans.*, 1995, 1163.
- L. Agocs, N. Burford, T. S. Cameron, J. M. Curtis, J. F. Richardson, K. N. Robertson and G. B. Yhard, *J. Am. Chem. Soc.*, 1996, **118**, 3225; G. G. Briand and N. Burford, *Adv. Inorg. Chem.*, 2000, **50**, 285.
- N. Burford, M. D. Eelman and T. S. Cameron, *Chem. Comm.*, 2002, 1403; G. G. Briand, N. Burford, T. S. Cameron and W. Kwiatkowski, *J. Am. Chem. Soc.*, 1998, **120**, 11374; G. G. Briand, N. Burford and T. S. Cameron, *Chem. Comm.*, 2000, 13; G. G. Briand, N. Burford, M. D. Eelman, T. S. Cameron and K. N. Robertson, *Inorg. Chem.*, 2003, **42**, 3136.
- G. G. Briand and N. Burford, *Chem. Rev.*, 1999, **99**, 2601.
- S. C. James, N. C. Norman and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1999, 2837.
- F. Calderazzo, A. Morvillo, G. Pelizzi, R. Poli and F. Ungari, *Inorg. Chem.*, 1988, **27**, 3730.
- J. C. Collings, K. P. Roscoe, R. L. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard and T. B. Marder, *New J. Chem.*, 2001, **25**, 1410; J. C. Collings, K. P. Roscoe, E. G. Robins, A. S. Batsanov, L. M. Stimson, J. A. K. Howard, S. J. Clark and T. B. Marder, *New J. Chem.*, 2002, **26**, 1740.
- SMART diffractometer control software, Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.
- SAINT integration software, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.
- SHELXTL program system version 5.1, Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.
- G. M. Sheldrick, SADABS: A program for absorption correction with the Siemens SMART system, University of Göttingen, Germany, 1996.