Co-ordination Complexes of the Bismuth(III) Thiolate $Bi(SC_6F_5)_3$†

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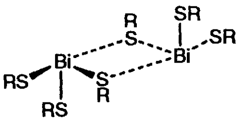
The reaction between $Bi(SC_6F_5)_3$ **1** and $SPPh_3$ afforded crystals of $[Bi(SC_6F_5)_3(SPPh_3)]$ **5** which was characterised by X-ray crystallography. Complex **5** contains a bismuth centre bonded to three SC_6F_5 groups and the sulfur atom of a $SPPh_3$ ligand such that the co-ordination geometry is disphenoidal with the $SPPh_3$ ligand *trans* to one thiolate group. An additional intermolecular interaction is also present due to a weakly bridging thiolate sulfur which results in a centrosymmetric dimer with each bismuth centre having square-based pyramidal five-co-ordination. A similar structure was observed for the anion in the ionic complex $[K(18\text{-crown-}6)][Bi(SC_6F_5)_3(NCS)]$ **6** (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) derived from the reaction between **1** and [K(18-crown-6)]SCN. The anion $[Bi(SC_6F_5)_3(NCS)]^-$ has a disphenoidal geometry with an axial thiolate and *N*-bonded thiocyanate ligand which also bridges between two centrosymmetrically related bismuth centres giving a structure similar to **5**. The reaction between **1** and either $OPPh_3$, hmpa (hexamethylphosphoramide) or dmpu (*N,N'*-dimethylpropyleneurea) afforded the bis(ligand) complexes $[Bi(SC_6F_5)_3(OPPh_3)_2]\cdot CH_2Cl_2$ **8**, $[Bi(SC_6F_5)_3(hmpa)_2]$ **9** and $[Bi(SC_6F_5)_3(dmpu)_2]$ **10** respectively all of which were characterised by X-ray crystallography. The structures of **8–10** are all similar in being monomeric and having a five-co-ordinate, square-based pyramidal geometry around the bismuth centre with one thiolate in the apical site and the two ligands in a *cis* configuration in the basal plane each *trans* to a basal thiolate. The reaction between **1** and *N,N'*-dimethylthiourea, $S{=}C(NHMe)_2$, afforded the tris(ligand) complex $[Bi(SC_6F_5)_3\{S{=}C(NHMe)_2\}_3]$ **11**. An X-ray crystallographic study revealed a six-co-ordinate complex with a geometry close to that of a regular octahedron with the three thiolates and three thiourea ligands both having *fac* configurations. The structures are discussed in terms of the SC_6F_5 group having properties analogous to chloride, and hence being a pseudohalide, and also in terms of ligand co-ordination occuring through the thiolate Bi–S σ* orbitals.

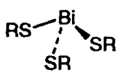
In a recent paper[1] we reported a synthesis and the crystal structure of the bismuth(III) thiolate $Bi(SC_6F_5)_3$ **1**. Compound **1** exists in the solid state as weakly bound dimers in which each bismuth centre has a four-co-ordinate, disphenoidal geometry with one Bi–S bond being significantly longer than the other three (see below, the three shortest bonds define a trigonal pyramid); the only other structurally characterised bismuth(III) thiolate is $Bi(SC_6H_2Bu^t{}_3\text{-}2,4,6)_3$ **2**[2] which is monomeric in the solid state with no short intermolecular Bi · · · S contacts.

The reasons for the difference between these two structures, *i.e.* why **1** is dimeric whereas **2** is monomeric, can be attributed both to the greater steric bulk of the $SC_6H_2Bu^t{}_3$-2,4,6 group in **2** and also to the more electron-withdrawing character of the SC_6F_5 group in **1**. This latter feature should render the bismuth centre in compound **1** more Lewis acidic and hence more prone to associative intermolecular interactions, further evidence for which was provided by the observation that in the reaction between $BiCl_3$ and $Na(SC_6F_5)$, it was the ionic complex $[Na_2(thf)_4][Bi(SC_6F_5)_5]$ **3** (thf = tetrahydrofuran) which was formed (**1** was prepared from the reaction between $BiPh_3$ and 3 equivalents of HSC_6F_5 in refluxing toluene). Compound **3** contains a five-co-ordinate thiolate anion $[Bi(SC_6F_5)_5]^{2-}$,[1] *i.e.* a complex of **1** and two SC_6F_5 anions.

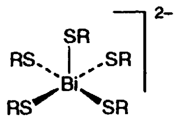
Prior to our own work in this area, there had been two previous reports concerning the synthesis of compound **1**;[3,4] in ref. 4, the ionic compound $[AsPh_4][Bi(SC_6F_5)_4]$ **4** was also described. Furthermore, the point was made[4] that the SC_6F_5 group [in **1** and in a range of other $E(SC_6F_5)_x$ element complexes] had much in common with chloride and should therefore be considered as a pseudohalide. Since bismuth(III) halides form a range of co-ordination complexes with Lewis-base ligands,[5] we reasoned that **1** should have an analogous chemistry and herein we describe our results which show that this prediction was well founded.



1, R = C_6F_5



2, R = $C_6H_2Bu^t{}_3$-2,4,6



3, R = C_6F_5

Results and Discussion

By comparison with ligand complexes of bismuth(III) halides,[5] we should expect for **1**, complexes of the general formula $[Bi(SC_6F_5)_3(L)_n]$ where n = 1, 2 or 3. Perhaps the simplest way to envisage the structures of and bonding in such complexes is to assume that the acceptor orbitals associated with the bismuth

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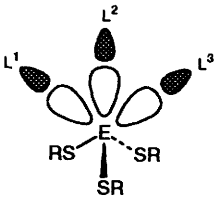
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

centre, which are responsible for its Lewis acidity, are the Bi–S σ* orbitals. This idea has been discussed recently for a range of bismuth(III) compounds,[6] and a representation of the three Bi–S σ* orbitals, together with a σ-donor orbital from each of three ligands, L^1, L^2 and L^3, is shown in A. In terms of the co-ordination geometry of the resulting complexes $[Bi(SC_6F_5)_3(L)_n]$, this bonding model leads directly to disphenoidal, square-based pyramidal and octahedral geometries for four-, five- and six-co-ordination with one, two and three ligands respectively. Examples of all of these types are discussed below.

The reaction between compound **1** and 3–4 equivalents of $SPPh_3$ afforded orange crystals of the 1 : 1 complex $[Bi(SC_6F_5)_3(SPPh_3)]$ **5** the structure of which was established by X-ray crystallography; selected bond lengths and angles are given in Table 1 and atomic positional parameters are presented in Table 2. The structure of **5** is such that the bismuth centre is bonded to three SC_6F_5 groups with Bi–S distances Bi(1)–S(1) 2.58(1), Bi(1)–S(2) 2.62(2) and Bi(1)–S(3) 2.57(1) Å. In addition, a single $SPPh_3$ ligand is bonded to the bismuth through sulfur [Bi(1)–S(4) 3.01(1) Å] approximately *trans* to S(2) [S(2)–Bi(1)–S(4) 168.8(5)°]; the co-ordination of S(4) *trans* to S(2) is undoubtedly responsible for the fact that Bi(1)–S(2) is longer than the other two $Bi–SC_6F_5$ bonds [note that the Bi–S(4) distance to the $SPPh_3$ ligand is the longest of all Bi–S bonds]. A view of complex **5** is shown in Fig. 1 from which it is evident that a longer Bi • • • S intermolecular interaction is also present resulting in a centrosymmetric (crystallographic) dimeric structure, the longer interaction [Bi(1)–S(2′) 3.15(1) Å] being *trans* to the Bi(1)–S(3) bond [S(3)–Bi(1)–S(2′) 164.0(5)°]. There is no apparent lengthening of the Bi(1)–S(3) bond as a



A

Table 1 Selected bond lengths (Å) and angles (°) for complex **5**

Bi(1)–S(1)	2.58(1)	Bi(1)–S(2)	2.62(2)
Bi(1)–S(3)	2.57(1)	Bi(1)–S(4)	3.01(1)
Bi(1)–S(2′)	3.15(1)		
S(1)–Bi(1)–S(2)	85.8(5)	S(1)–Bi(1)–S(3)	95.6(5)
S(1)–Bi(1)–S(4)	83.6(4)	S(2)–Bi(1)–S(3)	89.0(5)
S(2)–Bi(1)–S(4)	168.8(5)	S(3)–Bi(1)–S(4)	96.0(4)
S(1)–Bi(1)–S(2′)	81.1(4)	S(2)–Bi(1)–S(2′)	75.2(5)
S(3)–Bi(1)–S(2′)	164.0(5)	S(4)–Bi(1)–S(2′)	99.2(5)
Bi(1)–S(2′)–Bi(1′)	104.8(6)		

Primed atoms are related to unprimed atoms by inversion through the inversion centre at (0,0,0).

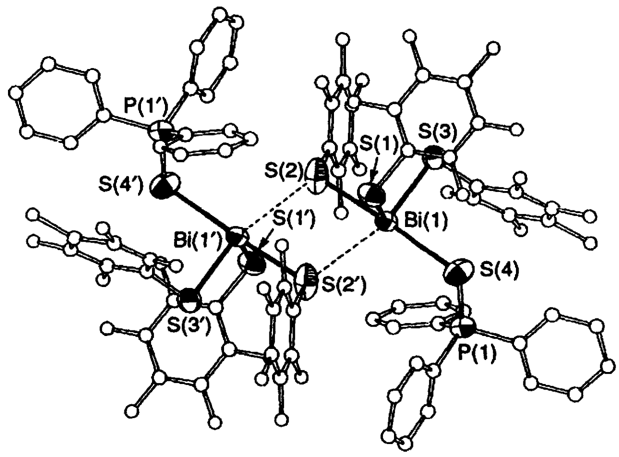


Fig. 1 A view of the crystallographically centrosymmetric dimer of $[Bi(SC_6F_5)_3(SPPh_3)]$ **5** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level

Table 2 Atomic positional parameters for complex **5**

Atom	*x*	*y*	*z*
Bi(1)	1536(1)	391(2)	350(1)
S(1)	934(8)	2473(11)	215(6)
S(2)	536(9)	−26(13)	−643(7)
S(3)	2995(8)	676(13)	−176(5)
S(4)	2434(10)	1271(11)	1497(5)
P(1)	2389(8)	−20(10)	2037(5)
F(112)	1248(20)	2757(28)	−1045(9)
F(113)	2660(28)	3846(35)	−1421(13)
F(114)	4085(22)	4910(30)	−674(16)
F(115)	3925(27)	4837(34)	452(16)
F(116)	2585(20)	3691(26)	859(10)
F(212)	1350(33)	−2342(39)	−358(24)
F(213)	2369(30)	−3665(35)	−1000(37)
F(214)	2937(36)	−2812(69)	−1987(32)
F(215)	2337(40)	−668(63)	−2350(19)
F(216)	1225(37)	571(40)	−1755(17)
F(312)	3631(24)	−1797(29)	1(22)
F(313)	5065(30)	−2597(42)	779(23)
F(314)	6039(27)	−1212(53)	1480(18)
F(315)	5668(28)	1077(49)	1439(15)
F(316)	4310(31)	1940(31)	701(20)
C(111)	1899(17)	3186(24)	−67(11)
C(112)	1932(18)	3241(26)	−656(10)
C(113)	2667(22)	3817(29)	−870(9)
C(114)	3370(20)	4337(30)	−495(14)
C(115)	3338(19)	4282(30)	95(13)
C(116)	2602(21)	3706(27)	309(9)
C(211)	1255(18)	−886(23)	−1060(11)
C(212)	1526(25)	−1985(25)	−875(13)
C(213)	2109(29)	−2635(24)	−1182(18)
C(214)	2421(26)	−2186(35)	−1675(17)
C(215)	2149(28)	−1087(37)	−1860(13)
C(216)	1566(25)	−437(25)	−1552(13)
C(311)	3748(12)	264(18)	357(8)
C(312)	3873(22)	−918(18)	319(14)
C(313)	4626(27)	−1449(21)	650(18)
C(314)	5254(21)	−798(36)	1018(15)
C(315)	5128(21)	383(35)	1057(15)
C(316)	4375(21)	914(20)	726(14)
C(411)	3475(18)	−91(27)	2540(12)
C(412)	4207(22)	652(25)	2452(12)
C(413)	5053(19)	609(28)	2815(15)
C(414)	5168(19)	−176(32)	3265(14)
C(415)	4436(25)	−918(29)	3353(13)
C(416)	3590(21)	−876(26)	2990(14)
C(421)	1397(23)	82(32)	2439(15)
C(422)	865(28)	1086(27)	2406(16)
C(423)	103(27)	1186(30)	2719(18)
C(424)	−127(24)	284(38)	3064(17)
C(425)	405(28)	−720(32)	3097(16)
C(426)	1168(26)	−821(26)	2784(17)
C(431)	2239(18)	−1394(20)	1684(11)
C(432)	1337(15)	−1733(24)	1455(12)
C(433)	1215(16)	−2706(26)	1109(13)
C(434)	1994(22)	−3340(22)	993(13)
C(435)	2896(18)	−3001(24)	1223(13)
C(436)	3019(14)	−2028(25)	1568(12)

result of this interaction although the large e.s.d.s mask any small differences that might be present. With the Bi(1)$\cdots$S(2′) interaction included, the overall co-ordination geometry around the bismuth centres is square-based pyramidal with the bridging thiolates and the $SPPh_3$ ligand in the basal plane.

A similar structure was observed for the anion $[Bi(SC_6F_5)_3(NCS)]^-$ in the yellow ionic complex [K(18-crown-6)]$[Bi(SC_6F_5)_3(NCS)]$ **6** (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) obtained from the reaction between compound **1** and [K(18-crown-6)]SCN a view of which is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3 and atomic positional parameters are presented in Table 4. The bismuth centre in **6** is bonded to three SC_6F_5 groups [Bi(1)–S(2) 2.614(2), Bi(1)–S(3) 2.645(2) Bi(1)–S(4) 2.564(2) Å] and one thiocyanate group through the nitrogen atom [Bi(1)–N(1) 2.577(6) Å] such that the co-ordination geometry defined by the one nitrogen and three sulfur atoms is disphenoidal with the nitrogen and one sulfur in axial sites. Of the three Bi–S distances, Bi(1)–S(3) which is *trans* to the NCS ligand is the longest with Bi(1)–S(2) being slightly longer than Bi(1)–S(4). This latter feature is the result of a long interaction between the sulfur atom of a thiocyanate group in an adjacent anion [Bi(1)–S(1′) 3.178(2) Å] which is approximately *trans* to S(2) [S(2)–Bi(1)–S(1′) 165.8(1)°]. This Bi(1)$\cdots$S(1′) interaction results in a centrosymmetric (crystallographic) dimer structure for the anion in **6** (Fig. 3) and an overall square-based pyramidal geometry around each bismuth centre as in **5**. There are no other short Bi$\cdots$S or Bi$\cdots$F contacts in either **5** or **6**.

Table 3 Selected bond lengths (Å) and angles (°) for complex **6**

Bi(1)–N(1)	2.577(6)	Bi(1)–S(2)	2.614(2)
Bi(1)–S(3)	2.645(2)	Bi(1)–S(4)	2.564(2)
Bi(1)–S(1′)	3.178(2)	N(1)–C(1)	1.141(7)
C(1)–S(1)	1.619(6)		
N(1)–Bi(1)–S(2)	87.2(1)	N(1)–Bi(1)–S(3)	168.0(1)
N(1)–Bi(1)–S(4)	88.1(1)	S(2)–Bi(1)–S(3)	88.18(6)
S(2)–Bi(1)–S(4)	95.95(6)	S(3)–Bi(1)–S(4)	81.31(5)
N(1)–Bi(1)–S(1′)	99.9(2)	S(2)–Bi(1)–S(1′)	165.8(1)
S(3)–Bi(1)–S(1′)	87.1(1)	S(4)–Bi(1)–S(1′)	96.5(1)

Primed atoms are related to unprimed atoms by inversion through the inversion centre at (0, $\frac{1}{2}$, 0).

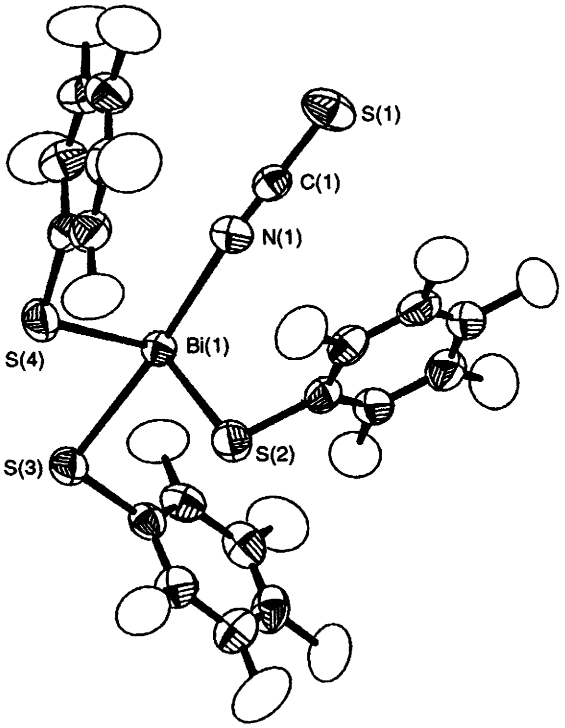


Fig. 2 A view of the anion $[Bi(SC_6F_5)_3(NCS)]^-$ in **6** showing the atom numbering scheme. Ellipsoids are drawn at the 30% level

Table 4 Atomic positional parameters for complex **6**

Atom	*x*	*y*	*z*
Bi(1)	927(1)	4438(1)	1725(1)
K(1)	5790(2)	879(1)	4171(1)
S(1)	−66(2)	3148(2)	−1979(1)
S(2)	1179(2)	2400(1)	1715(1)
S(3)	1569(2)	5057(2)	3568(1)
S(4)	3143(2)	4937(2)	1789(1)
N(1)	756(5)	3723(5)	−78(4)
O(1)	7694(5)	−348(5)	4463(4)
O(4)	6510(6)	667(5)	6007(4)
O(7)	5368(5)	2510(4)	5767(4)
O(10)	4495(5)	2629(4)	4039(4)
O(13)	5217(7)	1237(6)	2483(4)
O(16)	6780(5)	−380(5)	2680(4)
F(212)	−1459(4)	2210(4)	1627(3)
F(213)	−3089(4)	1294(5)	112(4)
F(214)	−2448(5)	375(4)	−1583(3)
F(215)	−106(5)	329(4)	−1760(3)
F(216)	1558(4)	1253(3)	−255(3)
F(312)	1480(3)	3049(4)	4178(4)
F(313)	−413(5)	1998(4)	4497(5)
F(314)	−2590(4)	2738(4)	4282(3)
F(315)	−2875(4)	4572(5)	3749(4)
F(316)	−989(4)	5641(4)	3450(3)
F(412)	4254(5)	3117(4)	523(4)
F(413)	4530(6)	2818(5)	−1262(4)
F(414)	3650(5)	4211(6)	−2157(3)
F(415)	2557(6)	5969(6)	−1254(4)
F(416)	2358(5)	6341(4)	570(4)
C(1)	401(5)	3491(4)	−862(4)
C(2)	7905(12)	−497(11)	5319(9)
C(3)	7658(11)	320(14)	6077(8)
C(5)	6536(13)	1715(10)	6729(7)
C(6)	5625(12)	2293(9)	6603(6)
C(8)	4730(12)	3319(8)	5682(8)
C(9)	4507(8)	3490(6)	4788(7)
C(11)	4253(12)	2789(10)	3201(8)
C(12)	4415(9)	1947(11)	2425(7)
C(14)	5519(10)	433(14)	1746(6)
C(15)	6567(12)	−83(10)	1867(6)
C(17)	7857(11)	−790(9)	2858(9)
C(18)	8040(10)	−1068(10)	3687(9)
C(211)	107(5)	1778(4)	728(4)
C(212)	−1079(6)	1766(5)	800(4)
C(213)	−1931(6)	1282(6)	25(5)
C(214)	−1579(8)	824(6)	−822(5)
C(215)	−425(8)	805(5)	−917(5)
C(216)	408(6)	1277(5)	−147(5)
C(311)	311(5)	4373(5)	3783(3)
C(312)	404(5)	3443(5)	4055(4)
C(313)	−552(7)	2907(6)	4226(5)
C(314)	−1652(6)	3282(6)	4117(5)
C(315)	−1786(5)	4191(7)	3851(4)
C(316)	−818(6)	4733(6)	3696(4)
C(411)	3291(5)	4741(5)	618(4)
C(412)	3824(6)	3843(6)	116(5)
C(413)	3960(8)	3688(7)	−806(6)
C(414)	3529(6)	4393(8)	−1268(5)
C(415)	3003(7)	5269(8)	−784(6)
C(416)	2900(6)	5452(6)	131(5)

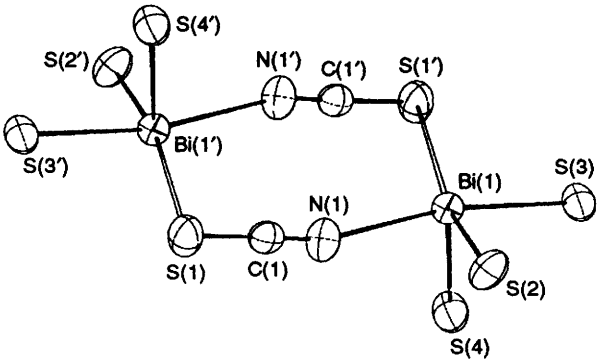


Fig. 3 A view of the crystallographically centrosymmetric anionic dimer of [K(18-crown-6)][Bi(SC_6F_5)$_3$(NCS)] **6** showing the Bi, thiolate S and SCN atoms only. Ellipsoids are drawn at the 50% level

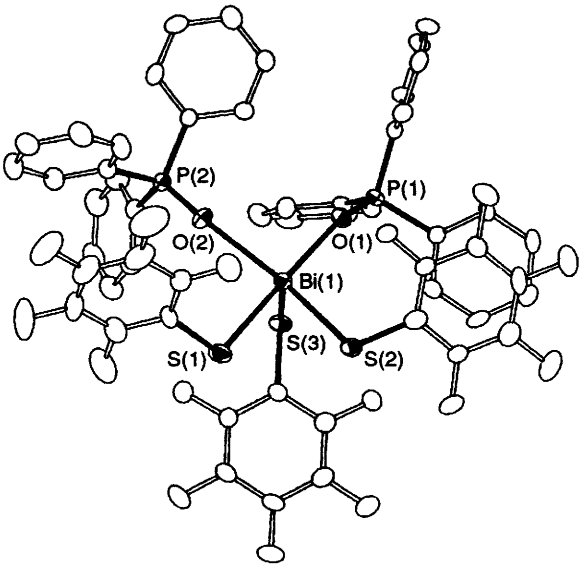


Fig. 4 A view of the structure of [Bi(SC_6F_5)$_3$($OPPh_3$)$_2$]·CH_2Cl_2 **8** showing the atom numbering scheme. Ellipsoids are drawn at the 20% level

With regard to the thiocyanate group in complex **6**, a number of bonding modes have previously been observed in complexes of this group with bismuth,[7] in particular *N*- and *S*-bonded terminal thiocyanates and bridging examples such as in [Bi_2(phen)$_4$(NCS)$_4$(μ-NCS)$_2$] (phen = 1,10-phenanthroline)[8] and [NH_4(18-crown-6)][$BiCl_3$(NCS)] **7**.[9] In both examples where bridging occurs, it is of a centrosymmetric form Bi_2(μ-NCS)$_2$ analogous to **6** with similar Bi–N and Bi–S distances. Complex **7** is, in fact, rather similar to **6** in terms of the formula and differs only in the presence of NH_4^+ rather than K^+ and in having chloride rather than the SC_6F_5 group. The structure of the anionic bismuth part is, however, a little different in that the centrosymmetric Bi_2Cl_6(μ-NCS)$_2$ units are further linked by bridging chloride interactions into polymeric chains wherein each bismuth is six-co-ordinate. The lesser degree of aggregation in **6** *vs* **7** is presumably a consequence of the much larger size of the SC_6F_5 group.

The reaction between complex **1** and an excess of either $OPPh_3$, hmpa (hmpa = hexamethylphosphoramide) or dmpu [dmpu = *N*,*N*′-dimethylpropyleneurea (1,3-dimethyl-1,3-diazinan-2-one] resulted, after work-up, in yellow crystals of the bis(ligand) complexes [Bi(SC_6F_5)$_3$($OPPh_3$)$_2$]·CH_2Cl_2 **8**, [Bi(SC_6F_5)$_3$(hmpa)$_2$] **9** and [Bi(SC_6F_5)$_3$(dmpu)$_2$] **10** respectively. The structures of **8**–**10** were established by X-ray crystallography which revealed that they are all similar in comprising a five-co-ordinate square-based pyramidal bismuth centre bonded to three SC_6F_5 groups, one apical and two basal, and the two oxygen atoms of the *O*-donor ligands, the latter occupying *cis* positions in the basal plane. Views of complexes **8**–**10** are shown in Figs. 4–6 respectively with selected bond lengths and angles given in Tables 5, 7 and 9 and atomic positional parameters presented in Tables 6, 8 and 10. In all three structures, the Bi–S bonds *trans* to the *O*-donor atoms are significantly longer than the unique apical Bi–S bond (average difference for **8** = 0.027, for **9** = 0.090 and for **10** = 0.033 Å). Furthermore, the longer of the basal Bi–S bonds is always *trans* to the shorter Bi–O bond. Thus for **8**, the relevant distances

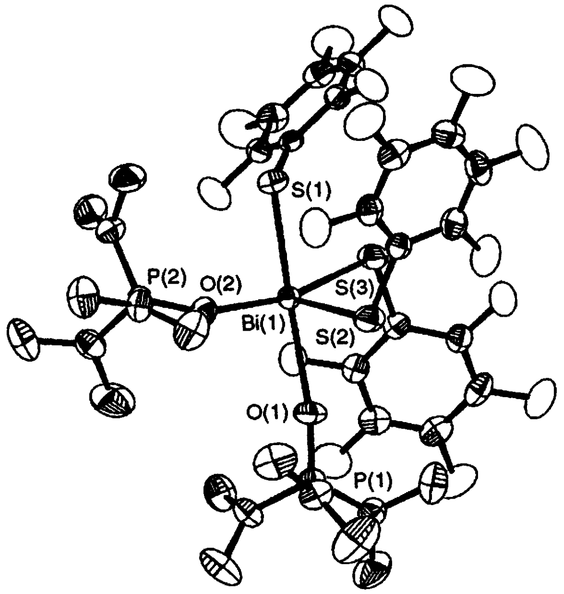


Fig. 5 A view of the structure of [Bi(SC_6F_5)$_3$(hmpa)$_2$] **9** showing the atom numbering scheme. Ellipsoids are drawn at the 30% level

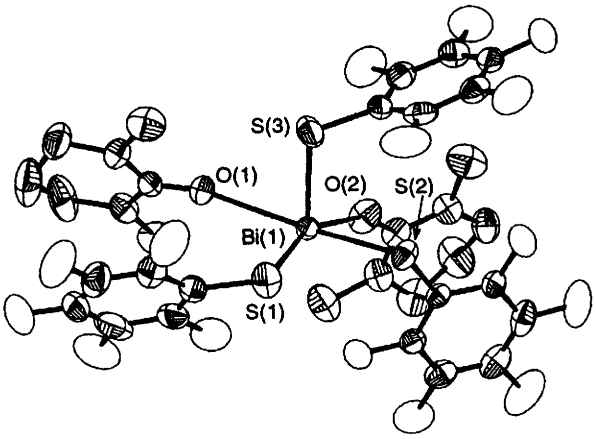


Fig. 6 A view of the structure of [Bi(SC_6F_5)$_3$(dmpu)$_2$] **10** showing the atom numbering scheme. Ellipsoids are drawn at the 30% level

Table 5 Selected bond lengths (Å) and angles (°) for complex **8**

Bi(1)–S(1)	2.613(2)	Bi(1)–S(2)	2.617(2)
Bi(1)–S(3)	2.588(2)	Bi(1)–O(1)	2.627(5)
Bi(1)–O(2)	2.586(6)		
S(1)–Bi(1)–S(2)	77.48(8)	S(1)–Bi(1)–S(3)	91.73(8)
S(1)–Bi(1)–O(1)	167.5(1)	S(1)–Bi(1)–O(2)	91.3(2)
S(2)–Bi(1)–S(3)	96.29(8)	S(2)–Bi(1)–O(1)	105.5(1)
S(2)–Bi(1)–O(2)	163.5(2)	S(3)–Bi(1)–O(1)	75.9(1)
S(3)–Bi(1)–O(2)	96.1(2)	O(1)–Bi(1)–O(2)	88.0(2)

Table 6 Atomic positional parameters for complex **8**

Atom	*x*	*y*	*z*
Bi(1)	3090(1)	1489(1)	1804(1)
S(1)	4444(2)	710(1)	1355(1)
S(2)	3242(2)	487(1)	2513(1)
S(3)	4814(2)	2118(1)	2394(1)
P(1)	1994(2)	2934(1)	2778(1)
P(2)	2783(2)	2776(1)	464(1)
O(1)	2143(5)	2414(3)	2340(2)
O(2)	2826(5)	2222(3)	876(3)
F(312)	5762(7)	983(4)	410(4)
F(313)	5018(10)	892(4)	−764(4)
F(314)	2829(9)	592(4)	−1216(3)
F(315)	1335(8)	409(4)	−477(4)
F(316)	2043(5)	488(4)	693(3)
F(412)	3689(5)	184(3)	3785(2)
F(413)	2336(6)	380(4)	4585(3)
F(414)	294(6)	1002(3)	4261(3)
F(415)	−381(5)	1408(3)	3133(3)
F(416)	919(4)	1154(3)	2320(2)
F(512)	5258(5)	1307(3)	3492(2)
F(513)	6865(5)	383(3)	3787(3)
F(514)	8329(5)	107(3)	3043(3)
F(515)	8204(5)	754(3)	2017(3)
F(516)	6651(5)	1697(3)	1734(2)
C(111)	3025(4)	3572(2)	2792(3)
C(112)	3557(6)	3660(3)	2307(2)
C(113)	4394(5)	4135(3)	2320(3)
C(114)	4698(5)	4522(3)	2819(4)
C(115)	4166(6)	4434(3)	3304(3)
C(116)	3329(5)	3960(3)	3291(2)
C(121)	573(4)	3273(2)	2621(2)
C(122)	−322(5)	2863(2)	2383(2)
C(123)	−1439(4)	3095(3)	2268(2)
C(124)	−1662(4)	3738(3)	2393(3)
C(125)	−768(5)	4148(2)	2631(3)
C(126)	350(4)	3915(2)	2745(2)
C(131)	2190(5)	2633(3)	3520(2)
C(132)	3200(4)	2298(3)	3729(3)
C(133)	3417(5)	2065(3)	4305(3)
C(134)	2624(6)	2165(3)	4673(2)
C(135)	1614(5)	2500(3)	4465(2)
C(136)	1397(4)	2733(3)	3889(3)
C(211)	1616(4)	3321(3)	507(2)
C(212)	1078(5)	3295(3)	996(2)
C(213)	149(5)	3697(3)	1025(2)
C(214)	−241(4)	4126(3)	566(3)
C(215)	298(5)	4152(2)	78(2)
C(216)	1226(5)	3750(3)	48(2)
C(221)	4104(4)	3234(3)	614(3)
C(222)	5097(6)	2887(3)	830(3)
C(223)	6145(5)	3206(5)	954(3)
C(224)	6201(6)	3872(5)	863(3)
C(225)	5208(8)	4218(3)	648(3)
C(226)	4160(6)	3899(3)	524(3)
C(231)	2539(5)	2526(3)	−293(2)
C(232)	3273(4)	2678(3)	−681(3)
C(233)	3014(6)	2476(3)	−1267(3)
C(234)	2021(6)	2122(3)	−1464(2)
C(235)	1287(5)	1970(3)	−1076(3)
C(236)	1546(5)	2172(3)	−491(3)
C(311)	3902(6)	736(3)	585(2)
C(312)	4670(6)	844(3)	204(4)
C(313)	4302(9)	802(4)	−403(3)
C(314)	3166(10)	652(4)	−631(2)
C(315)	2398(7)	543(4)	−251(4)
C(316)	2766(6)	585(3)	357(3)
C(411)	2353(5)	668(3)	3029(2)
C(412)	2714(5)	469(3)	3611(3)
C(413)	2024(6)	579(3)	4029(2)
C(414)	972(6)	888(3)	3866(3)
C(415)	611(4)	1086(3)	3284(3)
C(416)	1302(5)	976(3)	2866(2)
C(511)	5854(3)	1504(2)	2597(2)
C(512)	5930(3)	1165(2)	3125(2)
C(513)	6773(4)	696(2)	3278(2)
C(514)	7541(4)	566(2)	2903(2)
C(515)	7466(3)	905(2)	2374(1)
C(516)	6622(3)	1373(2)	2222(2)
Cl(1)	8847(5)	1114(3)	−47(2)
Cl(2)	9570(4)	1808(2)	968(2)
C(1)	8586(4)	1258(2)	620(1)

are (for Bi–S followed by Bi–O) 2.613(2)/2.627(5) and 2.617(2)/2.586(6), for **9** the distances are 2.626(1)/2.547(3) and 2.670(1)/2.502(3) and for **10** they are 2.574(2)/2.728(5) and 2.587(2)/2.645(4) Å. In all cases, the Bi atom lies close to the mean plane defined by the four basal atoms [**8**, 0.020(1) below; **9**, 0.096(1) below; **10**, 0.118(1) Å above (below and above refering to the apical SC_6F_5 group)]. In addition, for **8** there is a close Bi ··· F contact [Bi(1)–F(416) 3.102(6) Å] *trans* to the apical Bi–S bond which may be viewed as occupying the sixth site of a co-ordination octahedron (albeit rather weakly). A similar situation exists for **9** where the Bi(1) ··· F(316) distance is 3.254(7) Å and for **10** where the Bi(1) ··· F(126) distance is 3.194 Å.

Table 7 Selected bond lengths (Å) and angles (°) for complex **9**

Bi(1)–S(1)	2.626(1)	Bi(1)–S(2)	2.558(1)
Bi(1)–S(3)	2.670(1)	Bi(1)–O(1)	2.547(3)
Bi(1)–O(2)	2.502(3)		
S(1)–Bi(1)–S(2)	94.40(4)	S(1)–Bi(1)–S(3)	86.03(3)
S(1)–Bi(1)–O(1)	167.49(7)	S(1)–Bi(1)–O(2)	82.00(7)
S(2)–Bi(1)–S(3)	95.26(5)	S(2)–Bi(1)–O(1)	74.76(7)
S(2)–Bi(1)–O(2)	88.78(8)	S(3)–Bi(1)–O(1)	100.95(8)
S(3)–Bi(1)–O(2)	167.62(7)	O(1)–Bi(1)–O(2)	91.4(1)

An interesting point with regard to the structures of complexes **5** and **8** concerns the Bi–S–P and Bi–O–P angles which are 105.7(6)° for **5** and 160.5(3) and 164.7(4)° [for O(1) and O(2) respectively] for **8**. The significantly larger angles in phosphine oxide complexes compared with phosphine sulfide complexes are quite general and have been commented upon by Burford.[10] The more acute angle at sulfur may account for why **1** forms a mono(ligand) complex with $SPPh_3$ in contrast to a bis(ligand) complex with $OPPh_3$, since in the former case, the effective steric size of the ligand is probably greater.

The reaction between compound **1** and an excess of *N*,*N′*-dimethylthiourea, $S{=}C(NHMe)_2$, afforded, after work-up, red-purple crystals of the tris(ligand) complex $[Bi(SC_6F_5)_3\{S{=}C(NHMe)_2\}_3]$ **11**. A view of the structure is shown in Fig. 7 with selected bond lengths and angles given in Table 11 and atomic positional parameters presented in Table 12. Molecules of **11** reside on a crystallographic C_3 axis for which the unique $Bi{-}SC_6F_5$ and $Bi{-}S{=}C(NHMe)_2$ distances are 2.721(2) and 2.946(3) Å respectively. The C_3 site symmetry requires that the three SC_6F_5 groups adopt a *fac* configuration as must the three $S{=}C(NHMe)_2$ ligands. The interbond angle between the thiolate sulfurs is 94.61(8)° whereas that between the thiourea sulfurs is slightly smaller at 90.27(11)° which is consistent with the larger size of the SC_6F_5 group and the longer Bi–S bond distance to the thiourea ligands.

The structures of complexes **5**, **6** and **8**–**11** described above reveal that **1** is a Lewis acid which can co-ordinate one, two or three ligands in a manner which is similar to that of many ligand complexes of bismuth trihalides, although in the case of the halides, additional halide bridges are usually present in the mono- and bis-ligand complexes which result in six-co-ordination around the bismuth centre;[5] this is probably the result of the much smaller size of halide *vs*. SC_6F_5 as mentioned

Table 8 Atomic positional parameters for complex **9**

Atom	*x*	*y*	*z*
Bi(1)	−705(1)	1734(1)	2788(1)
P(1)	1600(1)	−1019(1)	1714(1)
P(2)	2002(1)	2557(1)	3091(1)
S(1)	−1732(1)	3846(1)	3143(1)
S(2)	−223(1)	2332(1)	1190(1)
S(3)	−3060(1)	1651(1)	3043(1)
F(112)	−2476(3)	2346(2)	4806(2)
F(113)	−4799(3)	2376(3)	5844(2)
F(114)	−6852(3)	3865(3)	5431(2)
F(115)	−6533(3)	5319(3)	3974(2)
F(116)	−4209(3)	5277(2)	2907(2)
F(212)	−2760(3)	2994(3)	898(2)
F(213)	−4234(3)	5116(4)	614(2)
F(214)	−3490(3)	6975(3)	578(2)
F(215)	−1277(4)	6699(3)	851(2)
F(216)	174(3)	4600(3)	1174(2)
F(312)	−4123(3)	861(3)	1999(2)
F(313)	−3890(3)	−1279(3)	1830(2)
F(314)	−2459(4)	−3090(2)	2619(2)
F(315)	−1239(3)	−2703(2)	3570(2)
F(316)	−1533(2)	−569(2)	3795(2)
N(11)	2618(4)	−515(3)	902(2)
N(12)	1020(4)	−1801(3)	1388(2)
N(13)	2364(3)	−1853(3)	2365(2)
N(21)	2981(3)	3188(3)	2337(2)
N(22)	2689(4)	1439(3)	3653(2)
N(23)	1244(4)	3483(3)	3757(2)
O(1)	574(3)	−107(2)	2146(2)
O(2)	1267(3)	2189(3)	2704(2)
C(11)	3147(8)	−910(7)	99(4)
C(12)	3093(6)	384(5)	981(4)
C(13)	91(6)	−1220(6)	928(4)
C(14)	1441(8)	−3017(5)	1425(4)
C(15)	3685(5)	−2477(6)	2100(5)
C(16)	1700(5)	−2142(5)	3246(3)
C(21)	3877(5)	3631(5)	2491(4)
C(22)	3172(6)	3182(5)	1469(3)
C(23)	3406(5)	1523(6)	4163(4)
C(24)	2864(7)	294(5)	3502(5)
C(25)	838(6)	4705(4)	3465(4)
C(26)	462(5)	3136(5)	4606(3)
C(111)	−3253(3)	3821(3)	3819(2)
C(112)	−3462(4)	3097(3)	4582(3)
C(113)	−4649(5)	3102(4)	5119(3)
C(114)	−5687(4)	3848(4)	4908(3)
C(115)	−5518(4)	4578(4)	4170(3)
C(116)	−4321(4)	4547(3)	3637(3)
C(211)	−1235(4)	3709(4)	1049(2)
C(212)	−2374(5)	3881(4)	907(3)
C(213)	−3138(5)	4980(5)	758(3)
C(214)	−2753(5)	5913(4)	731(3)
C(215)	−1650(5)	5773(4)	876(3)
C(216)	−912(4)	4683(4)	1038(3)
C(311)	−2824(4)	230(3)	2896(3)
C(312)	−3408(4)	−4(4)	2402(3)
C(313)	−3292(5)	−1113(5)	2316(3)
C(314)	−2565(5)	−2026(4)	2709(3)
C(315)	−1971(4)	−1822(4)	3188(3)
C(316)	−2111(4)	−720(4)	3285(3)

Table 9 Selected bond lengths (Å) and angles (°) for complex **10**

Bi(1)–S(1)	2.574(2)	Bi(1)–S(2)	2.587(2)
Bi(1)–S(3)	2.548(2)	Bi(1)–O(1)	2.645(4)
Bi(1)–O(2)	2.728(5)		
S(1)–Bi(1)–S(2)	82.25(6)	S(1)–Bi(1)–S(3)	92.7(1)
S(1)–Bi(1)–O(1)	89.1(1)	S(1)–Bi(1)–O(2)	157.4(1)
S(2)–Bi(1)–S(3)	89.3(1)	S(2)–Bi(1)–O(1)	166.0(1)
S(2)–Bi(1)–O(2)	88.2(1)	S(3)–Bi(1)–O(1)	80.0(1)
S(3)–Bi(1)–O(2)	107.6(2)	O(1)–Bi(1)–O(2)	103.7(2)

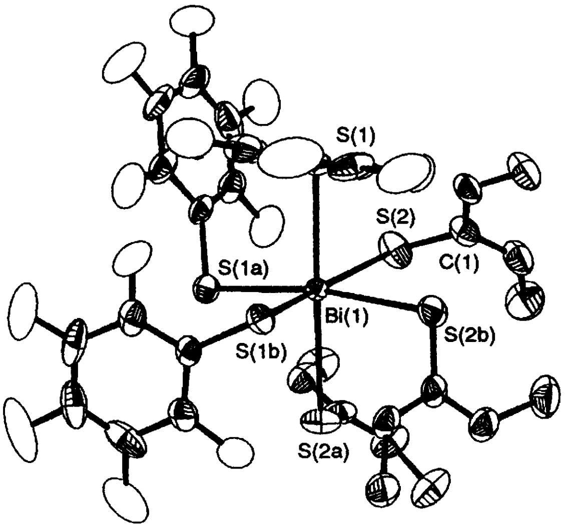


Fig. 7 A view of the structure of $[Bi(SC_6F_5)_3\{S{=}C(NHMe)_2\}_3]$ **11** showing the atom numbering scheme. Ellipsoids are drawn at the 30% level

above in connection with the structures of **6** and **7**. The suggestion that the SC_6F_5 group may be considered as a pseudohalide[4] is therefore reasonable.

In terms of the bonding in the ligand complexes, the use of Bi–S σ* orbitals in **1** to co-ordinate up to three ligands is clearly consistent with the observed structures in terms of the co-ordination geometries adopted. For four- and five-co-ordinate structures, these geometries are in accord with the predictions of VSEPR (valence-shell electron pain repulsion); for the six-co-ordinate structure of **11**, the octahedral geometry and the resulting stereochemical inactivity of the Bi^{III} lone pair follows naturally from the model whereas VSEPR predictions for this co-ordination number and electron count are not unambiguous. As a further point, it is clear from the structures that the thiolate Bi–S bond lengths are significantly lengthened as a result of the *trans* co-ordination of a ligand and also that the two S–Bi–L bond distances are correlated in such a way that as the Bi–L distance gets shorter, the Bi–S distance gets longer. All of these data are consistent with the σ*-orbital model in which ligand electron pair donation populates an antibonding orbital.

As a final point, it is interesting to compare the structures of some of the complexes reported herein with a number of ligand adducts of bismuth(III) alkoxides. In ref. 1, we commented upon the relationship between the structure of **1** and that of the analogous alkoxide complex $Bi(OC_6F_5)_3$ **12**.[11] When **12** is recrystallised from toluene, it crystallises as a dimer and as a toluene adduct. Complex **1** does not incorporate toluene when recrystallised from this solvent and, although a bridging thiolate interaction is present, it is much weaker than the corresponding bridging alkoxide in **12** as judged by the more symmetrical nature of the bridging Bi–O bond distances in the latter. Crystallisation of **12** from thf–hexane yields crystals of $[Bi_2(OC_6F_5)_4(\mu\text{-}OC_6F_5)_2(thf)_4]\cdot C_6H_{14}$ **12a** and $[Bi_2(OC_6F_5)_4(\mu\text{-}OC_6F_5)_2(thf)_4]$ **12b**, which differ in whether hexane of crystallisation is present or not, both of which contain two thf ligands per bismuth centre but which have six-co-ordinate bismuth centres as a result of bridging OC_6F_5 groups in contrast to the lack of bridging SC_6F_5 groups in **8**–**10**. This feature is again evident in the structure of the complex

Table 10 Atomic positional parameters for complex **10**

Atom	*x*	*y*	*z*
Bi(1)	3012(1)	2318(1)	3038(1)
S(1)	4916(2)	1330(2)	3773(2)
S(2)	4398(2)	1167(2)	1569(1)
S(3)	4021(5)	3871(3)	2025(2)
N(12)	715(5)	3900(5)	6008(4)
N(16)	2436(6)	4655(5)	5371(5)
N(22)	81(5)	2382(5)	1244(5)
N(26)	−597(6)	1641(6)	2951(5)
F(112)	6184(6)	2274(6)	4721(6)
F(113)	5568(8)	2546(6)	6670(7)
F(114)	3397(11)	2149(6)	8030(5)
F(115)	1879(9)	1332(7)	7425(5)
F(116)	2564(5)	977(5)	5452(5)
F(212)	2868(5)	−142(4)	3361(3)
F(213)	1393(6)	−1315(5)	3288(5)
F(214)	1075(5)	−1386(5)	1465(6)
F(215)	2243(6)	−247(6)	−268(5)
F(216)	3753(5)	928(4)	−216(3)
F(312)	6258(7)	2907(5)	302(7)
F(313)	6368(5)	3184(5)	−1704(5)
F(314)	4313(6)	4384(5)	−2325(3)
F(315)	2152(6)	5261(5)	−987(5)
F(316)	1974(7)	5038(6)	987(5)
O(1)	2116(5)	3636(4)	4449(3)
O(2)	933(5)	2542(5)	2411(5)
C(11)	1779(6)	4047(5)	5238(4)
C(12)	−62(9)	3293(9)	5870(9)
C(13)	217(10)	4441(11)	6926(7)
C(14)	1192(14)	4753(13)	7144(10)
C(15)	2021(13)	5224(9)	6239(9)
C(16)	3511(9)	4882(9)	4512(8)
C(21)	176(5)	2205(5)	2204(5)
C(22)	896(9)	3015(9)	424(8)
C(23)	−795(8)	2023(8)	953(6)
C(24)	−1816(11)	1747(11)	1836(8)
C(25)	−1446(8)	1188(9)	2728(8)
C(26)	−491(10)	1406(9)	3992(7)
C(111)	4369(7)	1613(5)	5049(5)
C(112)	5098(8)	2019(7)	5400(7)
C(113)	4825(12)	2189(8)	6349(10)
C(114)	3761(16)	1958(8)	7053(8)
C(115)	2934(12)	1551(8)	6787(8)
C(116)	3293(9)	1383(6)	5747(6)
C(211)	3369(5)	426(4)	1575(4)
C(212)	2746(6)	−164(5)	2440(5)
C(213)	1988(7)	−778(6)	2425(7)
C(214)	1813(7)	−803(7)	1525(8)
C(215)	2407(8)	−255(7)	639(7)
C(216)	3166(7)	379(5)	670(5)
C(311)	4101(11)	3947(6)	751(5)
C(312)	5244(9)	3480(6)	3(7)
C(313)	5292(7)	3625(6)	−1017(6)
C(314)	4258(7)	4219(5)	−1327(5)
C(315)	3170(8)	4671(6)	−651(6)
C(316)	3083(8)	4549(6)	343(6)

Table 11 Selected bond lengths (Å) and angles (°) for complex **11**

Bi(1)–S(1)	2.721(2)	Bi(1)–S(2)	2.946(3)
S(1)–Bi(1)–S(1a)	94.61(8)	S(1)–Bi(1)–S(1b)	94.61(8)
S(1)–Bi(1)–S(2)	81.62(9)	S(1)–Bi(1)–S(2a)	170.83(8)
S(1)–Bi(1)–S(2b)	94.03(9)	S(2)–Bi(1)–S(2a)	90.3(1)
S(2)–Bi(1)–S(2b)	90.3(1)		

Symmetry transformations used to generate equivalent atoms: a, $-y, x-y, z$; b, $-x+y, -x, z$.

Table 12 Atomic positional parameters for complex **11**

Atom	*x*	*y*	*z*
Bi(1)	0	0	−2590(1)
S(1)	120(2)	1618(2)	−2156(1)
S(2)	−1351(2)	460(3)	−3101(1)
F(112)	665(8)	1296(7)	−1320(2)
F(113)	2602(11)	2114(11)	−1004(3)
F(114)	4291(8)	3340(10)	−1432(4)
F(115)	4088(7)	3871(8)	−2174(3)
F(116)	2186(6)	3143(6)	−2511(2)
N(1)	−440(9)	1647(8)	−3729(3)
N(2)	156(8)	2408(7)	−3127(3)
C(1)	−485(9)	1577(10)	−3333(4)
C(11)	−1187(14)	830(13)	−4010(4)
C(21)	944(13)	3378(11)	−3296(5)
C(111)	1358(8)	2129(8)	−1934(3)
C(112)	1500(13)	1920(10)	−1542(4)
C(113)	2478(18)	2315(16)	−1363(4)
C(114)	3346(15)	2954(16)	−1589(6)
C(115)	3248(11)	3204(12)	−1955(6)
C(116)	2261(11)	2837(9)	−2134(4)

[$Bi_2\{OCH(CF_3)_2\}_4\{\mu\text{-}OCH(CF_3)_2\}_2(thf)_2$] **13**[11] which, as a mono(ligand) complex, is analogous to **5** the main difference being that the alkoxide bridges are much more developed in **13** than are the bridging thiolate interactions in **5**. The comparisons between **1** and **12** are therefore consistent with the view that the bismuth centre in **14** is the more Lewis acidic as a result of the greater electron-withdrawing character of the OC_6F_5 *vs.* the SC_6F_5 group. An example of a tris(ligand) complex of an alkoxide is [$Bi(OSiPh_3)_3(thf)_3$].[12]

Experimental

General.—All experiments were performed under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use. Microanalytical data were obtained at the University of Newcastle. Bismuth trichloride (99.9%), HSC_6F_5 and other reagents were procured commercially and used without further purification.

Preparations.—In a typical reaction, crystals of complexes **5**, **8** and **11** were obtained by reacting a solution of **1** in thf (typically about 0.1 g, 0.125 mmol of **1** in 10 cm^3 thf) with 3–4 equivalents of the corresponding ligand. After stirring for 1 h, all volatiles were removed by vacuum and the resulting solid was redissolved in CH_2Cl_2 (5 cm^3) to which hexanes (≈30–40 cm^3) were added as an overlayer. Solvent diffusion over a period of days at −30 °C afforded crystals of **5**, **8** and **11**. Compounds **9** and **10** were prepared similarly but by dissolving **1** directly in CH_2Cl_2 (5 cm^3), adding either hmpa or dmpu and overlayering with hexanes. Colours and analytical data for **5** and **8**–**11** are as follows: **5**, orange (Found: C, 39.35; H, 1.20. $C_{36}H_{15}BiF_{15}PS_4$ requires C, 39.30; H, 1.40); **8**, yellow (Found: C, 45.65; H, 2.10. $C_{54}H_{30}BiF_{15}O_2P_2S_3\cdot CH_2Cl_2$ requires C, 45.65; H, 2.25); **9**, yellow (Found: C, 31.85; H, 3.00; N, 7.35. $C_{30}H_{36}BiF_{15}N_6O_2P_2S_3$ requires C, 30.95; H, 3.10; N, 7.20); **10**, yellow (Found: C, 33.80; H, 2.10; N, 5.10. $C_{30}H_{24}BiF_{15}N_4O_2S_3$ requires C, 33.90; H, 2.30; N, 5.25); **11**, red-purple (Found: C, 28.70; H, 1.90; N, 7.30. $C_{27}H_{24}BiF_{15}N_6S_6$ requires C, 29.00; H, 2.15; N, 7.50%).

The urea and diphenyl sulfoxide complexes [$Bi(SC_6F_5)_3\{S{=}C(NH_2)_2\}$] **14** and [$Bi(SC_6F_5)_3(OSPh_2)_2$] **15** were prepared as yellow crystalline materials in a similar manner to **5** although

Table 13 Crystallographic and structure solution data for compounds **5**, **6**, **8**–**11**

	5	**6**	**8**	**9**	**10**	**11**
Formula	$C_{36}H_{15}BiF_{15}PS_4$	$C_{31}H_{24}BiF_{15}KNO_6S_4$	$C_{54}H_{30}F_{15}BiO_2P_2S_3{\cdot}CH_2Cl_2$	$C_{30}H_{36}BiF_{15}N_6O_2P_2S_3$	$C_{30}H_{24}BiF_{15}N_4O_2S_3$	$C_{27}H_{24}BiF_{15}N_6S_6$
M_r	1100.67	1167.83	1447.81	1164.75	1062.69	1118.86
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Trigonal
a/Å	14.275(1)	11.3600(7)	11.866(1)	11.7175(8)	11.5075(8)	14.784(1)
b/Å	11.6308(9)	12.7417(7)	20.599(2)	12.4263(10)	13.0926(7)	
c/Å	23.446(2)	15.0991(9)	22.998(2)	17.077(2)	13.9520(10)	33.144(2)
α/°		107.434(4)		76.224(8)	76.218(5)	
β/°	97.06(3)	97.888(5)	100.386(8)	69.389(8)	69.829(6)	
γ/°		91.402(5)		71.034(6)	71.298(5)	
U/Å^3	3863.3(5)	2060.4(2)	5529.2(9)	2179.5(3)	1849.6(2)	6273.6(7)
θ range for cell/°	17.7–19.2	17.6–19.4	17.5–20.1	17.5–20.8	17.6–20.8	17.5–21.1
Z	4	2	4	2	2	6
D_c/g cm^{-3}	1.892	1.882	1.739	1.775	1.908	1.777
F(000)	2112	1132	2832	1140	1028	3252
μ(Mo-Kα)/cm^{-1}	49.22	46.92	35.49	43.62	50.47	46.1
T/K	292	292	293	292	292	292
Scan mode	θ–2θ	θ–2θ	θ–2θ	θ–2θ	θ–2θ	θ–2θ
θ range/°	2.4–25.0	2.1–25.0	2.3–25.0	2.3–25.0	2.4 < –25.0	2.8–25.0
Crystal size/mm	0.38 × 0.20 × 0.13	0.33 × 0.27 × 0.13	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.3	0.43 × 0.40 × 0.40	0.3 × 0.3 × 0.2
Range of transmission coefficients	0.554–0.352	0.81–1.18	0.83–1.29	0.87–1.12	0.83–1.21	0.85–1.14
No. of data collected	7639	7532	9960	8045	6860	1412
No. of unique data	5426	7230	9709	7640	6508	1407
hkl range	0–16, 0–13, –27 to 27	–13 to 13, –14 to 15, –17 to 0	–14 to 13, –24 to 0, 0–27	–13 to 0, –14 to 13, –20 to 18	–13 to 0, –15 to 14, –16 to 15	0–15, 0–15, –39 to 0
R_{merge}	0.022	0.028	0.055	0.014	0.027	0.011
No. of data in refinement	5426	7230	9709	7640	6508	1407
No. of refined parameters	262	532	604	544	500	168
Final R	0.154	0.033	0.051	0.026	0.036	0.032
Final wR_2	0.433	0.084	0.116	0.056	0.094	0.094
Goodness-of-fit, S	1.133	1.046	0.853	1.023	1.041	1.157
Largest max., min. remaining features in electron density map/e Å^{-3}	+8.72, –2.32	+0.87, –0.83	+0.88, –1.29	+0.74, –0.61	+1.19, –1.33	+0.57, –0.35
Max., mean shift/e.s.d. in last cycle	0.005, 0.001	0.001, 0.0005	0.001, 0.0005	0.022, 0.001	0.1, 0.002	0.005, 0.001

$R_{merge} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)$, R is the conventional $R = \Sigma|(F_o - F_c)|/\Sigma|F_o|$ for those $F_o > 4\sigma(F_o)$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)]^2/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

X-ray quality crystals were not obtained (Found for **14**: C, 25.45; H, 0.25; N, 3.65. $C_{19}H_4BiF_{15}N_2S_4$ requires C, 25.85; H, 0.45; N, 3.15. Found for **15**: C, 41.90; H, 1.40. $C_{42}H_{20}BiF_{15}O_2S_5$ requires C, 41.65; H, 1.65%).

Complex **6** was prepared as yellow crystals by addition of 1 equivalent of [K(18-crown-6)]SCN to **1** in thf with crystallisation as for **5** (Found: C, 32.50; H, 1.85; N, 1.40. $C_{31}H_{24}BiF_{15}KNO_6S_4$ requires C, 31.90; H, 2.10; N, 1.20%).

Typical crystalline yields for all complexes were about 50%.

X-Ray Crystallography.—Crystallographic data and details of the data collection procedures and structure refinement for all structures are presented in Table 13. The following section deals with the structure of complex **6**; details for the other structures where different are given in parentheses. Data were collected on an Enraf-Nonius Turbo-CAD4 diffractometer, running under CAD4-Express software, and with graphite-monochromated X-radiation (λ = 0.710 69 Å). Accurate unit-cell parameters were determined by refinement of setting angles of 25 (23 for **5**) optimal high-angle reflections which were flagged during data collection. Standard reflections were measured every 2 h during data collection, and a 7% (**5**, 8; **8**, 13; **9**, 10; **10**, 4; **11**, 3%) decrease in intensities was noted and an interpolated correction applied. Corrections were applied for Lorentz-polarisation and absorption (DIFABS[13]) (ψ scans for **5**) effects. The structure was solved for the heavy atoms by direct methods (SHELX 86) (for **5**, data were inadvertently collected on a twinned crystal. Although reflections from only one of the distinct twins were indexed, and used to give a unique cell, it was apparent from the structure solution that there were many coincident reflections from the other twin. This results in many of the F_os being more intense than the calculated F_cs, and hence the high residuals. Nevertheless, the overall chemical features of **5** were well enough defined though the accuracy of the metrical parameters is low. Out of the 7639 measured reflections, a total of 1602 had intensities less than or equal to zero, and these reflections were deleted from the data file) (initially for **11**, as the statistics of the *E*-intensities indicated a non-centrosymmetric space group, the structure was solved in *R*3, but it became clear during subsequent refinement that the true space group was $R\bar{3}$). Subsequent difference syntheses gave all other non-H atomic positions. All non-hydrogen atoms were allowed anisotropic thermal motion (for **5**, only the Bi, S and F atoms were allowed anisotropic thermal motion). Hydrogen atoms were included at calculated positions (C–H 0.93 Å) and were assigned isotropic thermal parameters 1.2 times those of their attached carbon atom (phenyl groups for **8** were refined as rigid groups with idealised geometry, C–C 1.395 Å, angles 120°). Refinement was by full matrix least-squares on F^2 using the weighting scheme $w = [\sigma^2(F_o)^2 + (0.0558P)^2]^{-1}$ where $P = [F_o + 2F_c]/3$; $\sigma(F_o)^2$ was estimated from counting statistics [**5**, $(0.157P)^2 + 613.0P$; **8**, $0.0784P$; **9**, $0.0167P$; **10**, $(0.0694P)^2 + 0.96P$; **11**, $0.0617P$] Neutral-atom scattering factors were taken from ref. 14 with corrections for anomalous dispersion. Calculations were carried out using SHELXL 93.[15]

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

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