Neutral Thiolates of Antimony(III) and Bismuth(III)†

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A range of bismuth(III) and antimony(III) thiolates, $Bi(SR)_3$ ($R = C_6F_5$, $4\text{-}MeC_6H_4$, $2,6\text{-}Me_2C_6H_3$ or $3,5\text{-}Me_2C_6H_3$) and $Sb(SR)_3$ ($R = 4\text{-}MeC_6H_4$ or $3,5\text{-}Me_2C_6H_3$) has been synthesised and the structures of the two antimony complexes have been determined. Both structures reveal a trigonal-pyramidal antimony centre bonded to three thiolate groups with, for the $4\text{-}MeC_6H_4$ complex, additional intermolecular $Sb\cdots S$ interactions and, for the $3,5\text{-}Me_2C_6H_3$ complex, intermolecular arene to antimony interactions. The syntheses and structures of the organotransition-metal complexes $[Bi(SC_6F_5)\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Mo or W) are also reported in which the bismuth centre is bonded to one SC_6F_5 group and two $M(CO)_3(\eta\text{-}C_5H_5)$ fragments with no short intermolecular interactions.

Neutral thiolates of antimony(III) and bismuth(III) are known from a number of studies but relatively few compounds are well characterised and structural data are scarce. For bismuth, compounds which have been described include $Bi(SPh)_3$ **1**,[1] $Bi(SC_6F_5)_3$ **2**,[2,3] $Bi(o\text{-}SC_6H_4CO_2Me)_3$,[1b] $Bi(SEt)_3$,[4] $Bi(SCH_2Ph)_3$,[4] $Bi(SCH_2CH_2OH)_3$,[4] $Bi(SBu^t)_3$,[5] $Bi(SC_6H_4F\text{-}4)_3$[6] and $Bi(SC_6H_2Bu^t{}_3\text{-}2,4,6)_3$ **3**,[7] and more recently we have reported preliminary data for the arenethiolate complexes $Bi(SR)_3$ ($R = 4\text{-}MeC_6H_4$ **4**, $2,6\text{-}Me_2C_6H_3$ **5** or $3,5\text{-}Me_2C_6H_3$ **6**);[3] only **2**[3] and **3**[7] have been characterised by X-ray crystallography. Other examples of bismuth(III) thiolate compounds include the ionic species $[AsPh_4][Bi(SC_6F_5)_4]$[2a] and $[Na_2(thf)_4][Bi(SC_6F_5)_5]$ **7** (thf = tetrahydrofuran),[3] the latter having been characterised crystallographically,[3] and we have prepared a range of Lewis-base adducts of **2** comprising $[Bi(SC_6F_5)_3(SPPh_3)]$ **8**, $[K(18\text{-crown-}6)][Bi(SC_6F_5)_3(NCS)]$ **9** (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane), $[Bi(SC_6F_5)_3(OPPh_3)_2]$ **10**, $[Bi(SC_6F_5)_3\{OP(NMe_2)_3\}_2]$ **11**, $[Bi(SC_6F_5)_3\{O\overline{CNMe(CH_2)_3N}Me\}_2]$ **12** and $[Bi(SC_6F_5)_3\{S{=}C(NHMe)_2\}_3]$ **13** all of which were structurally characterised.[8] The compound $BiPh_2(SPh)$ has also been described.[9]

Reports of antimony(III) thiolates include descriptions of the neutral tris(thiolato) compounds $Sb(SPh)_3$,[1a,10] $Sb(SXC_6H_4X\text{-}4)_3$ (X = Br, NH_2, NO_2, Me **14** or Bu^t),[11] $Sb(SC_6F_5)_3$,[2a,12] $Sb(SBu^t)_3$,[5] $Sb(SPr^i)_3$[10] and $Sb(SC_6Cl_5)_3$[13] together with a variety of salts containing the $[Sb(SC_6F_5)_4]^-$ anion,[2a] none of which has been structurally characterised. Compounds for which structural data are available, however, include $Sb(SMe)(1,2\text{-}S_2C_6H_4)$[14] and $[Sb_2(1,2\text{-}S_2C_2H_4)_2(\mu\text{-}1,2\text{-}S_2C_2H_4)]$[15] as well as the co-ordination complexes $[W(CO)_5\{S(Bu^t)Sb(SBu^t)_2\}]$[16] and $[Mn(CO)_2(\eta\text{-}C_5H_4Me)\{Sb(SPh)_3\}]$.[17] In the tungsten complex the $Sb(SBu^t)_3$ group bonds through one of the sulfur atoms whereas in the manganese complex it is the antimony centre through which the $Sb(SPh)_3$ ligand bonds.

Herein we describe full details of the preparation of the bismuth complexes **2** and **4**–**6**[3] together with synthetic and structural data for two antimony tris(thiolates) and the first examples of organotransition-metal bismuth thiolates.

Results and Discussion

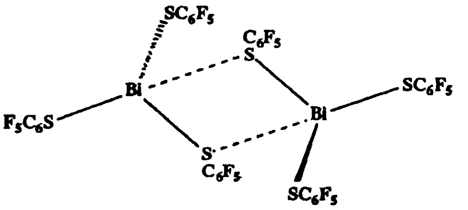
The bismuth compound **2** has been described previously[2] but a particularly convenient and high-yield preparation is available from the reaction between $BiPh_3$ and 3 equivalents of the thiol HSC_6F_5 in refluxing toluene according to equation (1) as

$$BiPh_3 + 3HSC_6F_5 \longrightarrow Bi(SC_6F_5)_3 + 3PhH \qquad (1)$$

described in ref. 3 and, in more detail, in the Experimental section.

The structure of compound **2** was established by X-ray crystallography and reveals that **2** exists in the solid-state as a centrosymmetric, asymmetrically thiolate-bridged dimer; a view of the molecular structure and details of the crystallographic study are available in ref. 3 and will not be repeated here. The structure of **3**, in contrast, is monomeric with no short intermolecular contacts, presumably due to the larger steric requirements of the $2,4,6\text{-}Bu^t{}_3C_6H_2$ groups.[7]

The reaction between $BiCl_3$ and 3 equivalents of $Na[SC_6F_5]$ afforded the ionic compound **7** rather than neutral **2**,[3] but reactions between $BiCl_3$ and 3 equivalents of the thiolato compounds $Na[SR]$ ($R = 4\text{-}MeC_6H_4$, $2,6\text{-}Me_2C_6H_3$ or $3,5\text{-}Me_2C_6H_3$) in thf solution afforded, after work-up, the fluffy orange crystalline complexes $Bi(SR)_3$ **4**–**6**. No X-ray-quality crystals were obtained but analytical and spectroscopic data were consistent with their formulation. Compound **1** can also be made in reasonable yields by this route although this has been described previously in the literature.[1] Whilst **1** does afford well formed orange crystals, a satisfactory structure could not be obtained due to the effects of twinning[3] and subsequent efforts to resolve this matter were not successful. Compound **1** is also available from the reaction between $BiPh_3$ and HSPh in refluxing toluene, but analogous reactions between $BiPh_3$ and RSH ($R = 2,6\text{-}Me_2C_6H_3$ or $3,5\text{-}Me_2C_6H_3$) did not afford the complexes **5** and **6** presumably due to the



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

lower acidity of the SH function in association with alkylated arene groups relative to the C_6F_5 group, and also steric factors.

The antimony compounds $Sb(SR)_3$ ($R = 4\text{-}MeC_6H_4$ **14** or $3,5\text{-}Me_2C_6H_3$ **15**) were prepared in a similar manner to the bismuth complexes **4** and **6** as described in the Experimental section; compound **14** has been described previously, having been obtained from the reaction between $SbCl_3$ and 3 equivalents of $HSC_6H_4Me\text{-}4$ in the presence of a base.[11] Both **14** and **15** were isolated as yellow crystals which were suitable for X-ray crystallography.

The structure of compound **14** is shown in Figs. 1 and 2 with selected bond lengths and angles given in Table 1 and atomic positional parameters in Table 2. The essential structure (Fig. 1) comprises an antimony atom bonded to three $SC_6H_4Me\text{-}4$ groups (average Sb–S 2.434 Å) with the expected trigonal-pyramidal co-ordination geometry (average S–Sb–S 93.52°, sum of angles 280.55°). The three arenethiolate groups are arranged in a propeller-like fashion such that the molecule has approximate C_3 symmetry and is therefore chiral, this chirality being the same for all molecules of **14** in the crystal since the space group, $P2_1$, is also chiral. In addition to the three primary Sb–S bonds, there is also a longer secondary, intermolecular interaction [Sb $\cdots$ S(1a) 3.7732(8) Å] approximately *trans* to the Sb–S(1) bond [S(1)–Sb–S(1a) 149.76(2)°]. This interaction is significantly less than the sum of the van der Waals radii for Sb and S (4.05 Å) and the resultant one-dimensional arrangement of molecules along the crystallographic 2_1 axes is illustrated in Fig. 2. The co-ordination of S(1a) approximately *trans* to S(1) leads to a slight, although only marginally significant, lengthening of the Sb–S(1) bond [2.4393(7) Å] compared to those of Sb–S(2) [2.4284(8) Å] and Sb–S(3) [2.4333(8) Å], in common with intermolecular secondary bonding interactions in general, but the large difference between the primary and secondary Sb–S bond lengths (1.334 Å) in the present example characterise this system as having only very weak secondary bonding.[18]

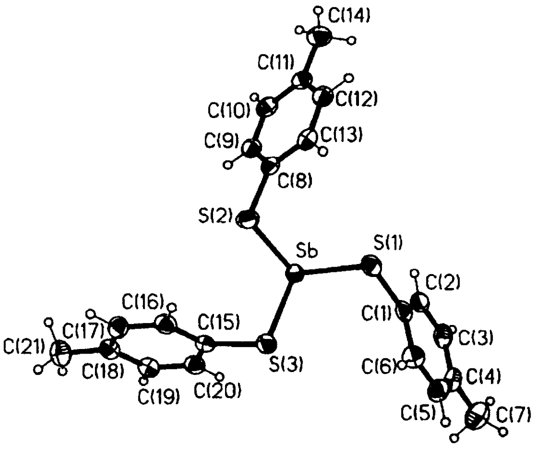

Fig. 1 Molecular structure of compound **14** showing the atom numbering scheme. Atoms are drawn as 50% probability ellipsoids

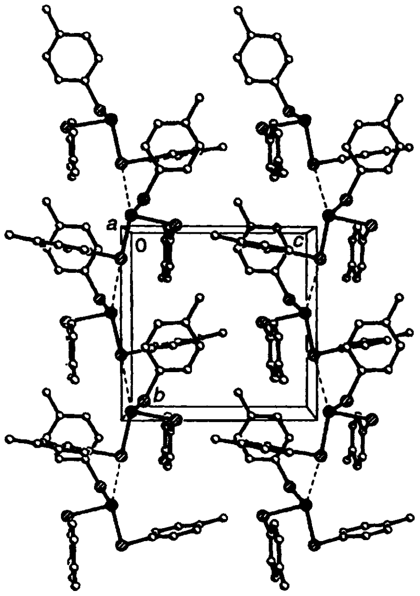

Fig. 2 Several molecular units of compound **14** in the crystal viewed down the *a* axis. The secondary Sb $\cdots$ S interactions are indicated as dashed lines and the resultant one-dimensional chains lie parallel to the crystallographic 2_1 axes

In the structures of the bismuth tris(thiolate) compounds **2** and **3** secondary bonding is significant and absent respectively.[3,7] Structurally characterised antimony thiolate compounds do not include any simple tris(thiolato) derivatives analogous to **14** for comparison, but two examples of $Sb(SR)_3$ compounds acting as ligands to organotransition-metal centres are known, as mentioned in the Introduction. The compounds are $[W(CO)_5\{S(Bu^t)Sb(SBu^t)_2\}]$[16] and $[Mn(CO)_2(\eta\text{-}C_5H_4Me)\{Sb(SPh)_3\}]$[17] for which the relevant average Sb–S bond lengths and S–Sb–S bond angles are 2.428 Å, 94.71° and 2.434 Å, 98.4° respectively, comparable to the corresponding values in **14** and **15** (see below). Other relevant examples of antimony–sulfur compounds include $SbPh_2(SC_6H_3Me_2\text{-}2,6)$ (Sb–S 2.439 Å),[19] $SbPh(SCH_2CH_2S)$ containing a chelating ethane-1,2-dithiolate group which has two primary Sb–S bonds (2.43 and 2.46 Å) with a longer secondary intermolecular interaction (3.34 Å) *trans* to one of the primary Sb–S bonds,[20]

Table 1 Selected bond lengths (Å) and angles (°) for compound **14**

Sb–S(1)	2.4393(7)	Sb–S(2)	2.4284(8)
Sb–S(3)	2.4333(8)	Sb $\cdots$ S(1a)	3.7732(8)
S(1)–Sb–S(2)	94.83(3)	S(1)–Sb–S(3)	93.82(3)
S(2)–Sb–S(3)	91.90(3)	S(1)–Sb–S(1a)	149.76(2)
S(2)–Sb–S(1a)	97.57(3)	S(3)–Sb–S(1a)	113.15(2)
Sb–S(1)–C(1)	97.05(9)	Sb–S(2)–C(8)	99.35(9)
Sb–S(3)–C(15)	98.94(8)		

Symmetry operator: a $-x, y - \frac{1}{2}, -z$.

Table 2 Atomic positional parameters ($\times 10^4$) for compound **14**

Atom	*x*	*y*	*z*
Sb	812.99(13)	−526.2(2)	554.95(14)
S(1)	1513.4(7)	1684.1(7)	84.9(7)
C(1)	2207(3)	1357(3)	−1480(3)
C(2)	1407(3)	1184(3)	−2592(3)
C(3)	1975(3)	936(3)	−3795(3)
C(4)	3332(3)	873(3)	−3910(3)
C(5)	4106(3)	1069(3)	−2788(3)
C(6)	3567(3)	1300(3)	−1587(3)
C(7)	3964(4)	591(4)	−5202(3)
S(2)	175.0(7)	−56.7(8)	2785.1(7)
C(8)	−1378(3)	688(3)	2447(3)
C(9)	−2518(3)	−28(3)	2292(3)
C(10)	−3719(3)	582(3)	2116(3)
C(11)	−3818(3)	1931(3)	2106(3)
C(12)	−2657(3)	2650(3)	2267(3)
C(13)	−1465(3)	2048(3)	2429(3)
C(14)	−5111(3)	2617(4)	1913(3)
S(3)	2992.0(7)	−1220.6(7)	1293.2(7)
C(15)	2559(2)	−2715(3)	2059(3)
C(16)	2404(3)	−2755(3)	3415(3)
C(17)	2174(3)	−3925(3)	4032(3)
C(18)	2070(3)	−5085(3)	3330(3)
C(19)	2218(3)	−5027(3)	1968(3)
C(20)	2450(3)	−3867(3)	1333(3)
C(21)	1849(4)	−6349(4)	4013(4)

the dinuclear species $[Sb_2(1,2\text{-}S_2C_2H_4)_2(\mu\text{-}1,2\text{-}S_2C_2H_4)]$, in which one of the ethane-1,2-dithiolate groups bridges between the two antimony centres, with primary Sb–S distances (average 2.437 Å) and longer secondary Sb···S interactions (average 3.49 Å) *trans* to primary Sb–S bonds,[15] $Sb(SMe)(1,2\text{-}S_2C_6H_4)$ containing a 1,2-dithiocatechol group with primary Sb–S distances (average 2.45 Å) and secondary Sb···S distances (average 3.50 Å),[14] and the bis(dithiocatecholate) anion in $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ (average Sb–S 2.530 Å).[21] Interbond angles within the primary SbS_3 co-ordination sphere are generally a little greater than 90° as is the case for **14**.

The structure of compound **15** is shown in Figs. 3 and 4 with selected bond lengths and angles given in Table 3 and atomic positional parameters in Table 4. The molecular structure (Fig. 3) is similar to that of **14** in comprising an antimony centre bonded to three thiolate groups (average Sb–S 2.437 Å) with a trigonal-pyramidal co-ordination geometry, slightly flattened relative to **14** presumably due to the larger steric requirements of the $3,5\text{-}Me_2C_6H_3$ unit [average S–Sb–S 95.39°, sum of angles 286.17°); the conformations of the thiolate groups are such that the molecular symmetry is no higher than C_1. Unlike for **14**, there are no close intermolecular Sb···S interactions, but molecules of **15** are associated in the crystal as a result of arene to antimony interactions. One such interaction between two molecules is shown in Fig. 3 and a packing diagram showing several such interactions is shown in Fig. 4. The antimony-to-ring centroid distance is 3.285 Å and the arene mean plane, C(17)–C(22) bonded to S(3), is inclined by 8.3° relative to the plane defined by the atoms S(1a), S(2a) and S(3a). This tilting of the arene ring results in some of the carbon atoms being significantly closer to the antimony centre than others, the range of Sb···C distances being 3.381(5)–3.742(5) Å. Similar intermolecular interactions between an arene ring and either antimony(III) or bismuth(III) centres are not uncommon and have been observed, for example, in the solid-state structures of the compounds $[BiPhX_2(thf)]$ (X = Cl, Br or I)[22] and $SbPhX_2$ (X = Cl, Br or I)[23] as well as in the bismuth trichloride–arene complexes $[BiCl_3(\eta^6\text{-}C_6H_3Me_3\text{-}2,4,6)]$ and $[Bi_2Cl_6(\eta^6\text{-}C_6Me_6)]$[24a] and benzene complexes of antimony trihalides.[24b]

In ref. 8 we described a number of Lewis-base adducts of compound **2**, namely the complexes **8**–**13**. With regard to the reactivity of **2** we were guided by an original observation by Nyholm and co-workers[2a] that the SC_6F_5 group was anal-

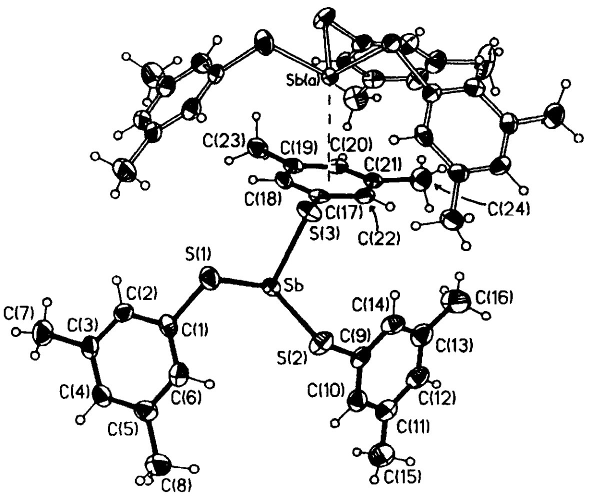

Fig. 3 Structure of compound **15** showing the atom numbering scheme. Two molecular units are shown and the arene to antimony interaction is indicated as a dashed line from antimony to the arene ring centroid. Atoms are drawn as 50% probability ellipsoids

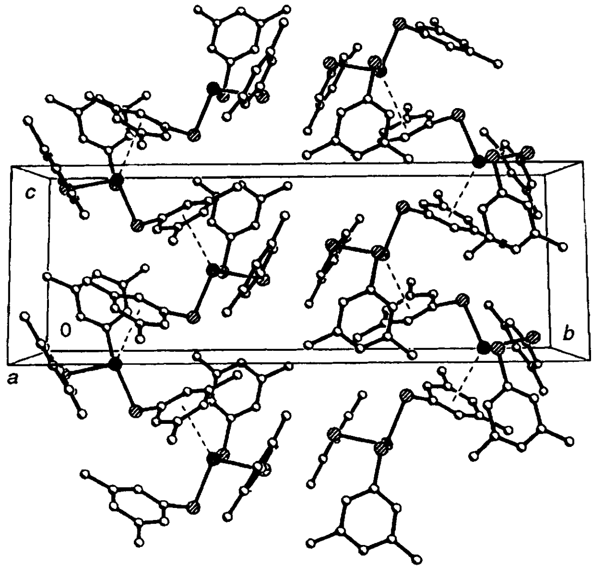

Fig. 4 Several molecular units of compound **15** in the crystal viewed down the *a* axis. The arene to Sb interactions are indicated as dashed lines and the molecules making up resultant one-dimensional chains are related by the crystallographic *c* glide planes

Table 3 Selected bond lengths (Å) and angles (°) for compound **15**

Sb–S(1)	2.437(2)	Sb–S(2)	2.436(2)
Sb–S(3)	2.437(2)	Sb(a)···C(17)	3.470(5)
Sb(a)···C(18)	3.381(5)	Sb(a)···C(19)	3.495(5)
Sb(a)···C(20)	3.667(5)	Sb(a)···C(21)	3.742(5)
Sb(a)···C(22)	3.644(5)		
S(1)–Sb–S(2)	92.71(5)	S(1)–Sb–S(3)	91.97(6)
S(2)–Sb–S(3)	101.49(5)	Sb–S(1)–C(1)	99.5(2)
Sb–S(2)–C(9)	96.8(2)	Sb–S(3)–C(17)	97.2(2)

Symmetry operator: a $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Table 4 Atomic positional parameters (× 10^4) for compound **15**

Atom	*x*	*y*	*z*
Sb	4596.7(3)	3412.05(13)	4606.3(4)
S(1)	2390.5(12)	3553.1(6)	4491(2)
C(1)	2335(5)	3699(2)	6447(6)
C(2)	1828(4)	3317(2)	7306(6)
C(3)	1700(5)	3419(2)	8806(6)
C(4)	2132(5)	3904(2)	9428(6)
C(5)	2643(5)	4290(2)	8593(6)
C(6)	2722(5)	4182(2)	7083(6)
C(7)	1111(6)	3011(2)	9716(7)
C(8)	3095(7)	4815(2)	9308(7)
S(2)	4970.5(13)	4350.8(5)	4096(2)
C(9)	6623(5)	4317(2)	4433(6)
C(10)	7264(5)	4552(2)	5698(6)
C(11)	8554(5)	4531(2)	5961(6)
C(12)	9162(5)	4274(2)	4915(7)
C(13)	8522(5)	4033(2)	3636(7)
C(14)	7242(5)	4055(2)	3414(7)
C(15)	9255(6)	4778(3)	7379(8)
C(16)	9196(6)	3757(3)	2505(9)
S(3)	4327.4(13)	3033.7(6)	2070(2)
C(17)	5475(4)	2522(2)	2430(5)
C(18)	5258(5)	2051(2)	3183(5)
C(19)	6117(5)	1635(2)	3321(5)
C(20)	7185(5)	1699(2)	2687(6)
C(21)	7420(5)	2161(2)	1903(6)
C(22)	6557(5)	2574(2)	1788(5)
C(23)	5871(6)	1113(2)	4083(6)
C(24)	8563(5)	2217(2)	1150(7)

Table 5 Selected bond lengths (Å) and angles (°) for compounds **16** and **17**

16		**17**	
Bi–Mo(1)	2.9525(5)	Bi–W(1)	2.9556(7)
Bi–Mo(2)	2.9583(5)	Bi–W(2)	2.9556(7)
Bi–S	2.662(2)	Bi–S	2.664(3)
Mo(1)–Bi–S	95.23(4)	W(1)–Bi–S	95.06(8)
Mo(2)–Bi–S	107.30(4)	W(2)–Bi–S	106.91(8)
Mo(1)–Bi–Mo(2)	116.80(1)	W(1)–Bi–W(2)	116.78(2)
Bi–S–C(311)	104.7(2)	Bi–S–C(311)	105.5(5)

ogous to chloride in many of its properties (*i.e.* behaved as a pseudohalide) and the reactivity of **2** towards Lewis bases to form 1 : 1, 1 : 2 and 1 : 3 complexes was certainly consistent with this assumption. Thus, **2** has some properties in common with $BiCl_3$. Further support for this assertion was gained from the reaction between **2** and either $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ or $[Bi\{W(CO)_3(\eta\text{-}C_5H_5)\}_3]$[25] which proceeded according to equation (2) and is directly analogous to the reaction shown in equation (3) for $BiCl_3$ and described in ref. 25.

$$2[\mathrm{Bi}\{\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}\}_3] + \mathrm{Bi(SC_6F_5)_3} \longrightarrow 3[\mathrm{Bi(SC_6F_5)}\{\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}\}_2] \quad (2)$$

16 M = Mo, **17** M = W

$$2[\mathrm{Bi}\{\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}\}_3] + \mathrm{BiCl_3} \longrightarrow 3[\mathrm{BiCl}\{\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}\}_2] \quad (3)$$

Compounds **16** and **17** were characterised by normal analytical and spectroscopic methods and also by X-ray crystallography which confirmed the anticipated structures. Both compounds are isomorphous and a view of **16** is shown in Fig. 5. Selected bond lengths and angles for both compounds are given in Table 5 and atomic positional parameters in Tables 6 and 7 for **16** and **17** respectively. Both structures comprise a bismuth atom bonded to one SC_6F_5 group [**16**, Bi–S 2.662(2); **17**, 2.664(3), *cf.* average Bi–S 2.552 Å in **2**[3]] and two $M(CO)_3(\eta\text{-}C_5H_5)$ fragments [**16**, M = Mo, average Bi–Mo 2.955 Å; **17**, M = W, average Bi–W 2.956 Å] with a trigonal-pyramidal co-ordination geometry [**16**, Mo(1)–Bi–S 95.23(4), Mo(2)–Bi–S 107.30(4), Mo(1)–Bi–Mo(2) 116.80(1)°, sum of angles 319.3°; **17**, W(1)–Bi–S 95.06(8), W(2)–Bi–S 106.91(8), W(1)–Bi–W(2) 116.78(2)°, sum of angles 318.7°]. There are no close intermolecular contacts, the shortest such Bi ··· S distance being 4.536(2) Å for **16** and 4.501(4) Å for **17**. The asymmetry in the M–Bi–S angles is probably the result of the canting of the SC_6F_5 group towards the metal fragment with the larger angle, but otherwise the overall structures of **16** and **17** are similar to the primary structure observed in a range of bismuth complexes of general formula $[BiX\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$.[26]

Experimental

General Considerations.—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. Infrared spectra were obtained on a Nicolet 20 SXB FTIR spectrophotometer, ^1H and ^{13}C NMR spectra on Bruker WP 200 and WM 500 spectrometers referenced to $SiMe_4$ and ^{19}F NMR spectra on a JEOL FX90Q spectrometer referenced to $CFCl_3$. The compounds $BiCl_3$ and $SbCl_3$ (99.9%), thiols and other reagents were procured commercially and used without further purification.

Table 6 Atomic positional parameters (× 10^4) for compound **16**

Atom	*x*	*y*	*z*
Mo(1)	2954(1)	1966(1)	2589(1)
Mo(2)	3421(1)	6854(1)	3727(1)
Bi	2620(1)	4728(1)	2377(1)
S	5831(3)	4781(2)	1685(1)
O(11)	1207(7)	3261(5)	4010(2)
O(12)	7442(6)	3134(5)	2816(3)
O(13)	5359(8)	730(5)	3819(3)
O(21)	6020(6)	4649(4)	4254(2)
O(22)	5624(6)	8031(4)	2599(2)
O(23)	7026(6)	8591(5)	4788(2)
F(312)	8611(6)	6953(5)	1453(2)
F(313)	7895(7)	8637(5)	531(2)
F(314)	1280(7)	6743(6)	−237(3)
F(315)	4207(7)	8572(4)	−302(2)
F(316)	1955(7)	4990(5)	646(2)
C(11)	1868(8)	2850(6)	3480(3)
C(12)	5759(9)	2782(6)	2727(3)
C(13)	4438(10)	1162(6)	3367(3)
C(21)	5070(8)	5415(6)	4025(3)
C(22)	4831(8)	7530(5)	3002(3)
C(23)	5729(8)	7944(6)	4397(3)
C(111)	1889(12)	1499(8)	1304(3)
C(112)	124(11)	1556(7)	1641(4)
C(113)	70(11)	541(7)	2029(4)
C(114)	1793(13)	−173(7)	1944(4)
C(115)	2929(13)	423(9)	1481(4)
C(211)	178(9)	7470(9)	3368(4)
C(212)	1088(10)	8425(7)	3957(5)
C(213)	1454(10)	7858(10)	4573(4)
C(214)	715(10)	6528(9)	4359(4)
C(215)	−67(9)	6299(7)	3620(4)
C(311)	5308(9)	5914(6)	1102(3)
C(312)	6770(9)	6873(7)	1045(3)
C(313)	6432(10)	7743(6)	577(3)
C(314)	3090(11)	6796(8)	188(4)
C(315)	4577(11)	7705(6)	143(3)
C(316)	3481(10)	5900(7)	647(3)

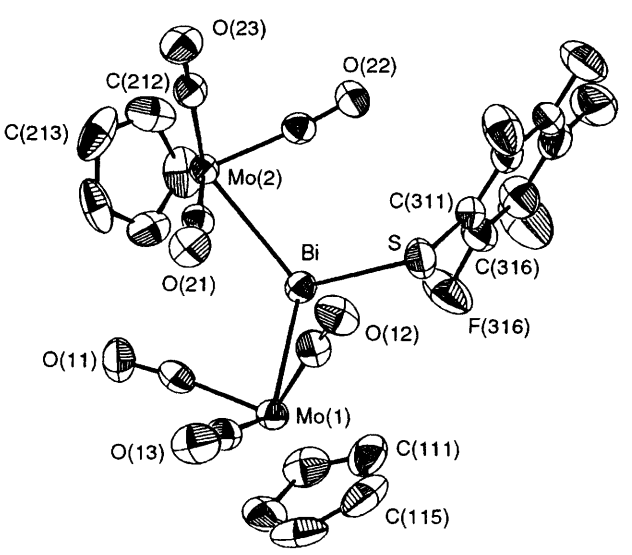

Fig. 5 Molecular structure of compound **16** showing the atom numbering scheme. Atoms are drawn as 50% probability ellipsoids. The structure of **17** is isomorphous

Preparations.—$Bi(SC_6F_5)_3$ **2**. The compound HSC_6F_5 (0.273 cm^3, 2.044 mmol) was added to a solution of $BiPh_3$ (0.300 g, 0.681 mmol) in toluene (40.0 cm^3) and the resulting reaction mixture then refluxed for 96 h during which time it turned from colourless to orange. After this time the solution was filtered through Celite and hexanes (40 cm^3) were added as an overlayer. Solvent diffusion over several days at −30 °C

Table 7 Atomic positional parameters (× 10^4) for compound **17**

Atom	x	y	z
W(1)	2947(1)	1958(1)	2594(1)
W(2)	3422(1)	6849(1)	3729(1)
Bi	2581(1)	4717(1)	2379(1)
S	5809(6)	4800(3)	1686(2)
O(11)	1229(15)	3249(11)	4023(6)
O(12)	7460(13)	3177(10)	2814(7)
O(13)	5369(18)	720(10)	3829(6)
O(21)	6013(13)	4649(9)	4265(5)
O(22)	5603(14)	8058(9)	2594(5)
O(23)	7088(12)	8567(10)	4794(6)
F(312)	8634(14)	6965(11)	1452(6)
F(313)	7947(20)	8639(12)	525(6)
F(314)	1281(17)	6767(15)	−240(7)
F(315)	4210(20)	8570(10)	−321(6)
F(316)	1958(17)	4971(14)	636(7)
C(11)	1870(18)	2848(12)	3491(8)
C(12)	5743(18)	2789(13)	2718(6)
C(13)	4485(22)	1178(13)	3382(9)
C(21)	5091(15)	5435(12)	4037(6)
C(22)	4845(15)	7541(12)	3011(7)
C(23)	5795(17)	7950(12)	4402(7)
C(111)	1850(28)	1508(17)	1323(8)
C(112)	114(22)	1563(15)	1668(8)
C(113)	−2(24)	516(16)	2058(10)
C(114)	1721(30)	−200(13)	1950(9)
C(115)	2857(27)	401(22)	1496(10)
C(211)	120(20)	7391(22)	3372(10)
C(212)	1097(23)	8378(14)	3965(14)
C(213)	1459(19)	7870(22)	4559(8)
C(214)	780(23)	6563(21)	4396(10)
C(215)	−43(17)	6277(14)	3670(9)
C(311)	5300(21)	5932(13)	1092(7)
C(312)	6794(23)	6880(15)	1032(8)
C(313)	6462(28)	7757(16)	571(9)
C(314)	3074(29)	6813(21)	173(10)
C(315)	4560(27)	7712(14)	145(8)
C(316)	3468(23)	5898(15)	637(8)

afforded large orange crystals of **2** (0.386 g, 70%) (Found: C, 26.75. $C_{18}BiF_{15}S_3$ requires C, 26.80%). ^{19}F NMR (C_6D_6, reference $CFCl_3$): δ −131.1 (m, 6 F, $F^{2,6}$ of C_6F_5), −154.5 (m, 3 F, F^4 of C_6F_5) and −162.5 (m, 6 F, $F^{3,5}$ of C_6F_5).

$Bi(SC_6H_3Me_2\text{-}2,6)_3$ **5**. A solution of Na[SC_6H_3Me-2,6], prepared by sodium reduction of the thiol $HSC_6H_3Me_2$-2,6 (0.443 cm^3, 3.330 mmol), in thf (10 cm^3) was added to a stirred solution of $BiCl_3$ (0.350 g, 1.110 mmol) in thf (15 cm^3) which resulted in an immediate change from colourless to dark purple. Stirring was continued for 1 h after which time all volatiles were removed by vacuum. The crude solid was then redissolved in hexanes (50 cm^3) and filtered through Celite which afforded an orange solution. Cooling to −30 °C afforded an orange fluffy solid after about 12 h (0.537 g, 78%) (Found: C, 46.30; H, 4.40. $C_{24}H_{27}BiS_3$ requires C, 46.45; H, 4.40%). NMR (CD_2Cl_2): ^1H, δ 7.05 (m, 6 H, $H^{3,5}$ of $C_6\mathit{H}_3Me_2$, J = 7.5), 6.85 (m, 3 H, H^4 of $C_6\mathit{H}_3Me_2$, J = 7.5 Hz) and 2.40 (s, 18 H, 2,6-$\mathit{Me}_2C_6H_3$); $^{13}C\text{-}\{^1H\}$, δ 143.8 (s, *ipso*-C of $C_6H_3Me_2$), 142.7 (s, $C^{2,6}$ of $\mathit{C}_6H_3Me_2$), 134.2 (s, $C^{3,5}$ of $\mathit{C}_6H_3Me_2$), 131.7 (s, C^4 of $\mathit{C}_6H_3Me_2$) and 22.7 (s, 2,6-$\mathit{Me}_2C_6H_3$).

$Bi(SC_6H_3Me_2\text{-}3,5)_3$ **6**. Compound **6** was prepared in a similar manner to that described for **5** using $BiCl_3$ (0.540 g, 1.713 mmol) and $HSC_6H_3Me_2$-3,5 (0.70 cm^3, 5.140 mmol). Extraction and crystallisation from CH_2Cl_2 (40 cm^3) cooled to −30 °C afforded an orange fluffy solid after about 12 h (0.526 g, 49%) (Found: C, 46.15; H, 3.95. $C_{24}H_{27}BiS_3$ requires C, 46.45; H, 4.40%). NMR (C_6D_6): ^1H, δ 7.35 (s, 6 H, $H^{2,6}$ of $C_6\mathit{H}_3Me_2$), 6.75 (s, 3 H, H^4 of $C_6\mathit{H}_3Me_2$) and 2.25 (s, 18 H, 3,5-$\mathit{Me}_2C_6H_3$); $^{13}C\text{-}\{^1H\}$, δ 138.7 (s, *ipso*-C of $C_6H_3Me_2$), 134.3 (s, $C^{2,6}$ of $\mathit{C}_6H_3Me_2$), 134.1 (s, $C^{3,5}$ of $C_6H_3Me_2$), 130.2 (s, C^4 of $\mathit{C}_6H_3Me_2$) and 21.8 (s, 3,5-$\mathit{Me}_2C_6H_3$).

$Bi(SC_6H_4Me\text{-}4)_3$ **4**. Compound **4** was also prepared in a similar manner to that described for **5** using HSC_6H_4Me-4 (0.354 g, 2.854 mmol) and $BiCl_3$ (0.300 g, 0.951 mmol). Extraction of the crude reaction mixture with Et_2O (20 cm^3) and filtration through Celite gave an orange solution. The solvent volume was then reduced to about 10 cm^3 and hexanes (20 cm^3) were added as an overlayer. Solvent diffusion over a period of 24 h at −30 °C afforded **4** as an orange fluffy solid (0.340 g, 62%) (Found: C, 41.90; H, 3.10. $C_{21}H_{21}BiS_3$ requires C, 43.60; H, 3.65%). ^1H NMR (C_6D_6): δ 7.60 (d, 6 H, $H^{2,6}$ of $C_6\mathit{H}_4Me$, J = 8.0), 7.10 (d, 6 H, $H^{3,5}$ of $C_6\mathit{H}_4Me$, J = 8.0 Hz) and 2.40 (s, 9 H, 4-$\mathit{Me}C_6H_4$).

$Sb(SC_6H_3Me_2\text{-}3,5)_3$ **15**. A solution of Na[$SC_6H_3Me_2$-3,5], prepared by sodium reduction of the thiol $HSC_6H_3Me_2$-3,5 (0.537 cm^3, 3.946 mmol), in thf (10 cm^3) was added to a solution of $SbCl_3$ (0.300 g, 1.315 mmol) in thf (10 cm^3) which resulted in an immediate change from colourless to yellow. The mixture was allowed to stir for a further hour after which time all volatiles were removed by vacuum resulting in a yellow oil. This crude reaction product was redissolved in Et_2O (30 cm^3) and filtered through Celite resulting in a pale yellow solution. Hexanes (50 cm^3) were then added as an overlayer and solvent diffusion over a period of days at −30 °C afforded yellow crystals of **15** (0.453 g, 65%) (Found: C, 54.35; H, 4.95. $C_{24}H_{27}S_3Sb$ requires C, 54.05; H, 5.10%). NMR (C_6D_6): ^1H, δ 7.45 (s, 6 H, $H^{2,6}$ of $C_6\mathit{H}_3Me_2$), 6.85 (s, 3 H, H^4 of $C_6\mathit{H}_3Me_2$) and 2.20 (s, 18 H, 3,5-$\mathit{Me}_2C_6H_3$); $^{13}C\text{-}\{^1H\}$, δ 138.6 (s, *ipso*-C of $\mathit{C}_6H_3Me_2$), 133.0 (s, $C^{2,6}$ of $C_6H_3Me_2$), 132.3 (s, $C^{3,5}$ of $\mathit{C}_6H_3Me_2$), 129.6 (s, C^4 of $\mathit{C}_6H_3Me_2$) and 20.8 (s, 3,5-$\mathit{Me}_2C_6H_3$).

$Sb(SC_6H_4Me\text{-}4)_3$ **14**. Compound **14** was prepared using the same method as that described for **15** using HSC_6H_4Me-4 (0.490 g, 3.946 mmol) and $SbCl_3$ (0.300 g, 1.315 mmol). Extraction of the crude reaction mixture in hexanes and crystallisation by cooling to −30 °C afforded yellow crystals of **14** (0.328 g, 51 %) (Found: C, 50.35; H, 3.95. $C_{21}H_{21}S_3Sb$ requires C, 51.35; H, 4.30%). NMR (C_6D_6): ^1H, δ 7.70 (d, 6 H, $H^{2,6}$ of $C_6\mathit{H}_4Me$, J = 8.0), 7.00 (d, 6 H, $H^{3,5}$ of $C_6\mathit{H}_4Me$, J = 8.0 Hz) and 2.20 (s, 9 H, 4-$\mathit{Me}C_6H_3$); $^{13}C\text{-}\{^1H\}$, δ 137.6 (s, *ipso*-C of C_6H_4Me), 135.4 (s, $C^{2,6}$ of C_6H_4Me), 130.0 (s, $C^{3,5}$ of C_6H_4Me), 129.0 (s, C^4 of C_6H_4Me) and 20.6 (s, 4-$\mathit{Me}C_6H_4$).

$[Bi(SC_6F_5)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **16**. A red solution of $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$[25] (0.198 g, 0.209 mmol) in thf (20 cm^3) was added to a stirred orange solution of $Bi(SC_6F_5)_3$ (0.085 g, 0.105 mmol) in thf (10 cm^3) which resulted in an immediate change to dark green. The solution was stirred for a further hour, after which time all volatiles were removed by vacuum. The crude product was then redissolved in CH_2Cl_2 (30 cm^3) and filtered through Celite affording a clear green solution over which hexanes (40 cm^3) were layered. Solvent diffusion over a period of days at −30 °C afforded dark green-black crystals of **16** (0.208 g, 74%) (Found: C, 29.25; H, 0.75. $C_{22}H_{10}BiF_5Mo_2O_6S$ requires C, 29.40; H, 1.10%). ^1H NMR (CD_2Cl_2): δ 5.50 (s, 10 H, C_5H_5). Infrared ν(CO) (thf solution, CaF_2 cells): 2039w, 2010s, 1979m and 1921s (br).

$[Bi(SC_6F_5)\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **17**. Compound **17** was prepared by the same method as that described for **16** using $[Bi\{W(CO)_3(\eta\text{-}C_5H_5)\}_3]$[25] (0.465 g, 0.385 mmol) and $Bi(SC_6F_5)_3$ (0.155 g, 0.193 mmol). Solvent diffusion over a period of days at −30 °C afforded dark green crystals of **17** (0.347 g, 56%) (Found: C, 23.85; H, 0.70. $C_{22}H_{10}BiF_5O_6SW_2$ requires C, 24.60; H, 0.95%). ^1H NMR (CD_2Cl_2): δ 5.50 (s, 10 H, C_5H_5). Infrared ν(CO) (thf solution, CaF_2 cells): 2033w, 2006s, 1973m and 1914s (br).

X-Ray Crystallography.—Crystallographic data and details of the data-collection procedures and structure refinement for all structures are presented in Table 8. The following section deals with the structure of compound **14**; details for **15**–**17** where different are given in parentheses. Data were collected on a Stoe-Siemens diffractometer using on-line profile fitting[27] with all machine-control calculations performed using Stoe

Table 8 Crystallographic and structure solution data for compounds **14**–**17**

	14	**15**	**16**	**17**
Compound formula	$C_{21}H_{21}S_3Sb$	$C_{24}H_{27}S_3Sb$	$C_{22}H_{10}BiF_5Mo_2O_6S$	$C_{22}H_{10}BiF_5O_6SW_2$
M_r	491.31	533.39	898.22	1074.04
Space group	$P2_1$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
a/Å	10.1872(13)	10.989(3)	6.6764(4)	6.6410(5)
b/Å	10.3112(11)	24.981(6)	10.2702(6)	10.2732(11)
c/Å	10.1904(14)	8.955(3)	18.6163(12)	18.576(2)
α/°			101.159(5)	101.099(8)
β/°	91.46(2)	98.54(4)	98.372(5)	98.511(8)
γ/°			92.470(5)	93.115(8)
U/Å^3	1070.1(2)	2431.0(12)	1235.7(1)	1225.5(2)
θ range for cell/°	10.88–12.37	10.15–11.71	17.7–20.8	17.7–20.8
Z	2	4	2	2
D_c/g cm^{-3}	1.525	1.457	2.414	2.911
$F(000)$	492	1080	836	964
μ(Mo-Kα)/mm^{-1}	1.583	1.400	8.262	16.687
T/K	160(2)	160(2)	292(2)	292(2)
Scan mode	ω–θ	ω–θ	θ–2θ	θ–2θ
θ range/°	2.79–25.00	2.82–24.00	2.30–25.00	2.50–25.00
Crystal size/mm	0.35 × 0.12 × 0.10	0.36 × 0.13 × 0.09	0.56 × 0.13 × 0.05	0.50 × 0.20 × 0.05
Range of transmission coefficients	0.704–0.766	0.786–0.943	0.810–1.340	0.254–0.807
No. of data collected	6295	3834	4761	4537
No. of unique data	3759	3798	4351	4278
hkl ranges	−12 to 12, −12 to 12, −12 to 12	−12 to 12, −28 to 0, −10 to 10	0–7, −12 to 12, −22 to 21	−7 to 7, −12 to 0, −21 to 22
R_{merge}	0.0154	0.0272	0.0260	0.0355
No. of refined parameters	229	259	334	334
Weighting parameters, a and b	0.0256, 0.2226	0.0250, 4.7262	0.0412, 0	0.0952, 0
Final R ('observed' data)[a]	0.0176 (3701)	0.0330 (2818)	0.0261	0.0410
Final R' (all data)[b]	0.0437	0.0997	0.0648	0.1198
Goodness of fit, S[c]	1.057	1.087	1.019	1.022
Maximum/minimum largest remaining feature in electron-density map/e Å^{-3}	+0.59, −0.22	+0.62, −0.56	+1.17, −0.87	+2.00, −2.29
Maximum shift/e.s.d. in last cycle	0.001	0.001	0.001	0.001
Absolute structure parameter	−0.005(14)	—	—	—

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections having $F_o^2 > 2\sigma(F_o^2)$ ('observed' reflections). [b] $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all unique data. [c] On F^2 values for all data.

DIF4 software (Enraf-Nonius Turbo-CAD4 diffractometer running under CAD4-Express software for **16** and **17**) and with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Accurate unit-cell parameters were determined from setting angles of 36 (33 for **15**, 25 for **16** and **17**) selected reflections. Standard reflections were measured every hour (2 h for **16** and **17**) during data collection, and a 0.5% (1.5 for **15**, 5 for **16**, 8% for **17**) decrease in intensities was noted and a correction applied. Corrections were applied for Lorentz-polarisation effects and for absorption semiempirically from ψ scans (DIFABS[28] for **16**). The variation of standard reflections was also used, together with normal counting statistics, to estimate standard deviations of intensities for **14** and **15**.

All programs used were members of the SHELX family (SHELXS 86, SHELXL 93 and SHELXTL/PC[29]). The structure was solved using heavy-atom methods (direct methods for **15** and **16**, the atomic positions in **16** for the isostructural **17**). Subsequent difference syntheses gave all other non-H atomic positions. Least-squares refinement was based on F^2 values for all measured reflections except for any flagged for potential systematic errors. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined with a riding model for positions and isotropic displacement parameters. The weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where P is $(F_o^2 + 2F_c^2)/3$. The absolute structure (polar axis direction) of **14** was determined using the enantiopole parameter as defined by Flack.[30]

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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