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The preparation and structural characterisation of thiolato anions of bismuth(III) ☆

Jonathan P.H. Charmant, A.H.M. Monowar Jahan, Nicholas C. Norman *, A. Guy Orpen

School of Chemistry, The University of Bristol, Bristol BS8 1TS, UK

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Dedicated to F.G.A. Stone in recognition of his contributions to inorganic chemistry

Abstract

The preparation and structures of the bismuth thiolato anions $[Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)]^-$ and $[Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)_2]^{2-}$ and the halothiolato anions $[Bi_2(SC_6F_5)_6(\mu\text{-}Br)]^-$, $[Bi_2(SC_6F_5)_6(\mu\text{-}Cl)_2]^{2-}$ and $[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]^{2-}$ are described. All compounds have been isolated from reactions between $Bi(SC_6F_5)_3$ and ammonium or phosphonium halides. The basic structural units in the dinuclear species are of two types namely $[Bi_2(SR)_6(\mu\text{-}X)]^-$ and $[Bi_2(SR)_6(\mu\text{-}X)_2]^{2-}$, where X = thiolate or halide. In the former case the single bridging groups occupy an axial site within the disphenoidal (equatorially vacant, trigonal bipyramidal) geometry around the bismuth centres whereas in the latter the two bridging groups occupy *cis* basal sites in square based pyramidal bismuth environments. The trinuclear anion $[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]^{2-}$ has features in common with the basic $[Bi_2(SC_6F_5)_6(\mu\text{-}Br)]^-$ unit.

Keywords: Bismuth(III); Thiolato anions; Halothiolato anions; X-ray crystallography

1. Introduction

Neutral thiolates of bismuth(III), $Bi(SR)_3$, are known from a number of studies together with a range of coordination complexes with neutral two-electron donor ligands, L, of the form $[Bi(SR)_3(L)_{1–3}]$ particularly in the case where $R = C_6F_5$ [1–5]. Thiolato anions result when L is an anionic donor and examples include the species $[AsPh_4][Bi(SC_6F_5)_4]$ [1a], $[Na_2(thf)_4][Bi(SC_6F_5)_5]$ [2] (thf = tetrahydrofuran) and $[K(18\text{-crown-}6)][Bi(SC_6F_5)_3(NCS)]$ [4] the latter two having been characterised crystallographically. More recently, we reported the structure of the compound $[4\text{-picH}][(4\text{-pic})_2H][Bi_3(SC_6F_5)_{11}]$ (4-pic = 4-picoline) incorporating a trinuclear di-anion which also contains bridging thiolates [5]. As part of a more systematic study of the reactivity of the Lewis acidic thiolate $Bi(SC_6F_5)_3$ towards anionic donor ligands, we have examined its reactions with sources of halide ion and describe herein the synthesis and structural characterisation of both homoleptic thiolato anions of bismuth and species which contain halide ions.

2. Results and discussion

The compounds isolated from reactions between $Bi(SC_6F_5)_3$ (**1**) and sources of halide anions are summarised in Eqs. (1)–(4). Compounds **2**–**6** were all characterised by X-ray crystallography, the results of which are described below. Selected bond distance and angle data for all anionic complexes are given in Table 1 and crystallographic data are presented in Table 2. Whilst compounds **4**–**6** contain both thiolate and halide groups

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☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.03.025.

* Corresponding author. Tel.: +44-117-928-7577; fax: +44-117-929-0509.
E-mail address: n.c.norman@bristol.ac.uk (N.C. Norman).

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Table 1
Selected bond distance (Å) and angle (°) data for complexes **2**–**6**

Compounds									
2		**3**		**4**		**5**		**6**	
Bond distance									
Bi(1)–S(1)	2.586(5)	Bi(1)–S(1)	3.154	Bi(1)–S(1)	2.621(4)	Bi(1)–S(1)	2.6708(17)	Bi(1)–S(1)	2.6716(17)
Bi(1)–S(2)	2.549(4)	Bi(1)–S(3)	2.901(3)	Bi(1)–S(2)	2.569(4)	Bi(1)–S(2)	2.567(2)	Bi(1)–S(2)	2.5907(16)
Bi(1)–S(3)	2.655(5)	Bi(1)–S(5)	2.626(3)	Bi(1)–S(3)	2.634(4)	Bi(1)–S(3)	2.6800(18)	Bi(1)–S(3)	2.6012(18)
Bi(1)–S(7)	3.114(4)	Bi(1)–S(6)	2.701(3)	Bi(1)–Br(1)	3.0040(18)	Bi(1)–Cl(1)	2.9190(19)	Bi(1)–Br(1)	3.0956(7)
Bi(1)–S(6)	3.482	Bi(1)–S(8)	2.566(3)	Bi(1)–S(5)	3.426	Bi(1)–Cl(1a)	2.9229(19)	Bi(2)–S(2)	3.482
Bi(2)–S(4)	2.598(4)	Bi(2)–S(1)	2.961(3)	Bi(2)–S(4)	2.604(4)			Bi(2)–S(4)	2.6244(17)
Bi(2)–S(5)	2.643(4)	Bi(2)–S(2)	2.583(3)	Bi(2)–S(5)	2.641(4)			Bi(2)–S(5)	2.6601(16)
Bi(2)–S(6)	2.615(4)	Bi(2)–S(3)	3.160	Bi(2)–S(6)	2.617(4)			Bi(2)–S(6)	2.5852(16)
Bi(2)–S(7)	3.052(3)	Bi(2)–S(4)	2.627(3)	Bi(2)–Br(1)	3.1443(19)			Bi(2)–Br(1)	3.1280(7)
		Bi(2)–S(7)	2.678(3)	Bi(2)–Br(2)	3.533			Bi(2)–Br(2)	3.2400(7)
				Bi(2)–S(11)	3.301			Bi(3)–S(6)	3.455
				Bi(3)–S(7)	2.620(4)			Bi(3)–S(7)	2.6019(19)
				Bi(3)–S(8)	2.651(4)			Bi(3)–S(8)	2.6111(17)
				Bi(3)–S(9)	2.595(4)			Bi(3)–S(9)	2.5830(16)
				Bi(3)–Br(2)	3.1830(18)			Bi(3)–Br(2)	3.1890(7)
				Bi(3)–S(1)	3.197				
				Bi(3)–S(8)	2.646				
				Bi(3)–Br(1)	3.596				
				Bi(4)–S(10)	2.636(4)				
				Bi(4)–S(11)	2.610(4)				
				Bi(4)–S(12)	2.561(4)				
				Bi(4)–Br(2)	3.0163(18)				
				Bi(4)–S(8)	3.461				
Bond angle									
S(3)–Bi(1)–S(7)	157.05(13)	S(1)–Bi(1)–S(5)	168.03	Br(1)–Bi(1)–S(3)	170.20(11)	S(1)–Bi(1)–Cl(1a)	177.29(5)	S(1)–Bi(1)–Br(1)	179.21(4)
S(5)–Bi(2)–S(7)	162.68(12)	S(3)–Bi(1)–S(6)	166.18(8)	Br(1)–Bi(2)–S(6)	169.39(10)	S(3)–Bi(1)–Cl(1)	165.42(6)	Bi(1)–Br(1)–Bi(2)	88.525(18)
Bi(1)–S(7)–Bi(2)	95.92(10)	S(1)–Bi(2)–S(7)	169.58(8)	Br(2)–Bi(3)–S(7)	169.41(10)	Bi(1)–Cl(1)–Bi(1a)	90.54(5)	Br(1)–Bi(2)–S(5)	171.09(4)
S(6)–Bi(1)–S(1)	144.61	S(3)–Bi(2)–S(4)	168.64	Br(2)–Bi(4)–S(10)	169.42(11)			Br(2)–Bi(2)–S(4)	155.09(4)
		Bi(1)–S(1)–Bi(2)	88.88	Bi(1)–Br(1)–Bi(2)	93.78(5)			Bi(2)–Br(2)–Bi(3)	88.633(16)
		Bi(1)–S(3)–Bi(2)	89.84	Bi(3)–Br(2)–Bi(4)	90.50(5)			S(8)–Bi(3)–Br(2)	160.21(5)
				S(5)–Bi(1)–S(1)	146.80				
				S(5)–Bi(1)–S(2)	103.56				
				S(11)–Bi(2)–S(5)	172.50				
				Br(2)–Bi(2)–S(4)	141.69				
				S(1)–Bi(3)–S(8)	165.54				
				Br(1)–Bi(3)–S(9)	141.51				
				S(8)–Bi(4)–S(11)	146.33				
				S(8)–Bi(4)–S(12)	105.55				

Table 2
Crystallographic data for compounds **2**–**6**

	$[PPh_4][Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)]$	$[NEt_4]_2[Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)_2]$	$[PPh_3CH_2CO_2CH_3][Bi_2(SC_6F_5)_6(\mu\text{-}Br)](C_6H_{12})0.50\ (CH_2Cl_2)0.16$	$[PPh_3CH_2Ph]_2[Bi_2(SC_6F_5)_6(\mu\text{-}Cl)_2]$	$[PPh_4]_2[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]$
	2	**3**	**4**	**5**	**6**
Formula	$C_{66}H_{20}Bi_2F_{35}PS_7$	$C_{68}H_{48}Bi_2F_{40}N_2OS_8$	$C_{117.17}H_{47.33}Bi_4Br_2Cl_{0.33}F_{60}O_4P_2S_{12}$	$C_{86}H_{44}Bi_2Cl_2F_{30}P_2S_6$	$C_{102}H_{40}Bi_3Br_2F_{45}P_2S_9$
Molecular weight	2151.17	2343.52	4112.96	2390.37	3257.58
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	15.056(23)	27.1737(11)	13.6346(14)	14.7522(6)	27.7454(6)
b (Å)	15.536(45)	13.7689(6)	16.8210(15)	13.2545(5)	13.5241(3)
c (Å)	15.553(26)	22.4789(9)	30.319(3)	22.4229(10)	30.1460(7)
α (°)	73.96(25)		75.770(9)		
β (°)	88.49(16)	107.010(9)	82.126(7)	104.350(1)	108.86(2)
γ (°)	82.12(13)		89.489(8)		
V (Å^3)	3463.0(6)	8042.6(6)	6674.5(12)	4247.6(3)	10704.4(4)
Z	2	4	2	2	4
D_c (g cm^{-3})	2.063	1.935	2.018	1.869	2.021
μ (Mo Kα)/mm^{-1}	5.447	4.715	6.202	4.498	5.998
Data collected	36516	51816	71078	21873	69701
Unique data (R_{int})	14294 (0.1396)	14164 (0.1080)	30106 (0.0880)	9748 (0.0603)	24470 (0.0518)
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0534, 0.1116	0.0502, 0.1182	0.0321, 0.1106	0.0483, 0.0963	0.0331, 0.0861
(All data)	0.1787, 0.1810	0.1559, 0.1394	0.1031, 0.756	0.1037, 0.1372	0.0694, 0.1190

as anticipated, compounds **2** and **3** are bismuthate anions containing only thiolate groups. Redistribution reactions wherein ligands or groups are exchanged between bismuth centres in solution are not unexpected, however, and have been well documented for aryl bismuth halides in particular see references 6 and 7 and references therein. A considerable range and type of anionic species is therefore possible and factors such as the solvent, the counter-cation, concentration of the reactants in solution and crystallisation processes are likely to have an impact on which particular species are isolated in a manner which is hard to predict. Reactions between **1** and other ammonium and phosphonium halides were carried out although no crystalline materials were isolated

$$\mathrm{Bi(SC_6F_5)_3}\ (\mathbf{1}) + \mathrm{[PPh_4]Br} \rightarrow \mathrm{[PPh_4][Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)]}\ (\mathbf{2}) + \mathrm{[PPh_4]_2[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]}\ (\mathbf{6}) \qquad (1)$$

$$\mathrm{Bi(SC_6F_5)_3}\ (\mathbf{1}) + \mathrm{[NEt_4]Br} \rightarrow \mathrm{[NEt_4]_2[Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)_2]}\ (\mathbf{3}) \qquad (2)$$

$$\mathrm{Bi(SC_6F_5)_3}\ (\mathbf{1}) + \mathrm{[PPh_3CH_2CO_2CH_3]Br} \rightarrow \mathrm{[PPh_3CH_2CO_2CH_3][Bi_2(SC_6F_5)_6(\mu\text{-}Br)]}\ (\mathbf{4}) \qquad (3)$$

$$\mathrm{Bi(SC_6F_5)_3}\ (\mathbf{1}) + \mathrm{[PPh_3CH_2Ph]Cl} \rightarrow \mathrm{[PPh_3CH_2Ph]_2[Bi_2(SC_6F_5)_6(\mu\text{-}Cl)_2]}\ (\mathbf{5}) \qquad (4)$$

Compound **2** comprises the $[\mathrm{PPh_4}]^+$ cation and the dinuclear mono-anion $[\mathrm{Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)}]^-$. The anion is shown in Fig. 1 which reveals two bismuth centres bridged by a single thiolate group. Each bismuth centre is four-coordinate with the expected equatorially vacant, trigonal bipyramidal or disphenoidal geometry in which the bridging thiolate occupies an axial site. The unique thiolate bridges the two bismuth centres fairly symmetrically but with Bi–S bonds [3.052(3) and 3.114(4) Å] significantly longer than any of the terminal Bi–S bonds (Table 1). For the terminal Bi–S distances, equatorial bonds are slightly shorter than axial bonds as expected. The conformations about the S(7)–Bi(1) and S(7)–Bi(2) bonds are noteworthy in that the conformation about the latter bond places S(6) in close proximity to Bi(1) [Bi(1)–S(6) 3.482 Å] such that S(6) lies approximately *trans* to S(1) [S(6)–Bi(1)–S(1) 144.61°] with Bi(1) therefore approaching a five-coordinate geometry. The presence of this semi-bridging thiolate could be viewed as a snapshot along a reaction pathway for thiolate exchange between bismuth centres, the importance of which is highlighted above in relation to the nature of the products isolated in this study. Additional semi-bridging interactions are also seen in some of the structures described below.

Compound **3** comprises the dinuclear di-anion $[\mathrm{Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)_2}]^{2-}$ (Fig. 2) with two $[\mathrm{NEt_4}]^+$ cations and two molecules of thf (tetrahydrofuran) of crystallisation per formula unit. In **3**, two thiolates bridge the one bismuth centres albeit more asymmetrically than in **2** [S(1)–Bi(1) 3.154, S(1)–Bi(2) 2.961(3); S(3)–Bi(1) 2.901(3), S(3)–Bi(2) 3.160 Å]. Each bismuth centre is five-coordinate with a square-based pyramidal geometry in which the bridging thiolates occupy basal sites. All Bi–S distances follow expected trends; the apical bonds are the shortest whilst the Bi–S bonds to the bridging thiolates are longer than the terminal Bi–S bonds in the basal plane. Moreover, the shortest terminal Bi–S bonds are *trans* to the longer bridging bonds. Both apical thiolates lie on the same side of the $\mathrm{Bi_2S_6}$ plane, i.e. a *syn* rather than an *anti* arrangement.

Compound **4** is a salt containing the phosphonium cation $[\mathrm{PPh_3CH_2CO_2CH_3}]^+$ and the mono anion

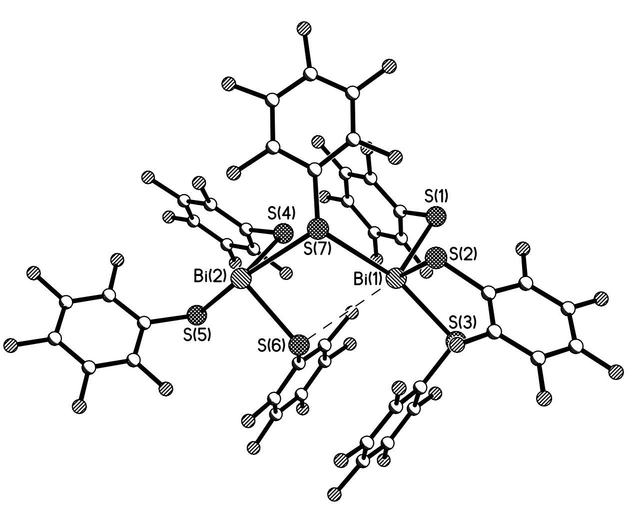


Fig. 1. A view of the dinuclear mono-anion $[\mathrm{Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)}]^-$ in the structure of **2**.

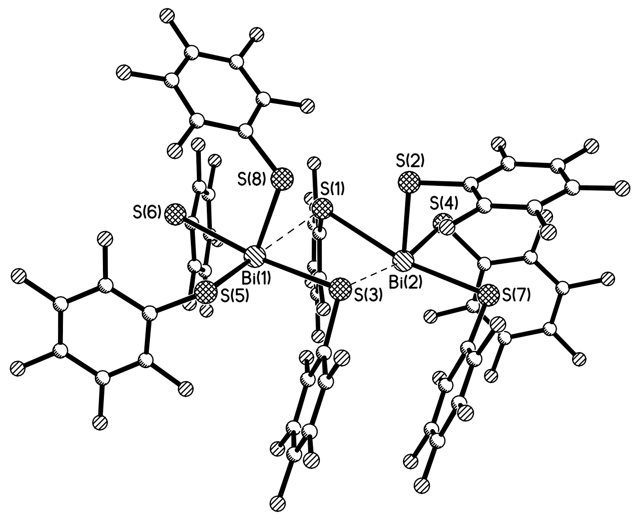


Fig. 2. A view of the dinuclear di-anion $[\mathrm{Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)_2}]^{2-}$ in the structure of **3**.

$[Bi_2(SC_6F_5)_6(\mu\text{-}Br)]^-$ with two of each per asymmetric unit. Each $[Bi_2(SC_6F_5)_6(\mu\text{-}Br)]^-$ anion is superficially similar to the anion in **2** in which the bridging thiolate in **2** is replaced by a bridging bromide in **4**. Geometrically and conformationally, both anions in **4** are similar to each other and to the anion in **2** including the close contact between one bismuth centre and a terminal (or semi-bridging) thiolate sulfur on the other [Bi(1)–S(5) 3.426; Bi(4)–S(8) 3.461 Å]. Unlike in **2**, however, the two anions in **4** are weakly associated into an approximately centrosymmetric dimer through additional long Bi···Br and Bi···S contacts as is evident from Fig. 3; distances and angles associated with these longer interactions are given in Table 1.

Compound **5** contains the crystallographically centrosymmetric di-anion $[Bi_2(SC_6F_5)_6(\mu\text{-}Cl)_2]^{2-}$ (Fig. 4) and triphenylbenzyl phosphonium cations $[PPh_3CH_2{-}Ph]^+$. The $[Bi_2(SC_6F_5)_6(\mu\text{-}Cl)_2]^{2-}$ di-anion resembles the di-anion in **3** with the exception that the chlorines in **5** bridge much more symmetrically [Bi(1)–Cl(1) 2.9190 (19), Bi(1)–Cl(1a) 2.9229(19) Å] than the thiolates in **3** (see above) and that the apical thiolates in **5** adopt an *anti* disposition with respect to the adjoined square-basal planes rather than the *syn* arrangement found in **3**.

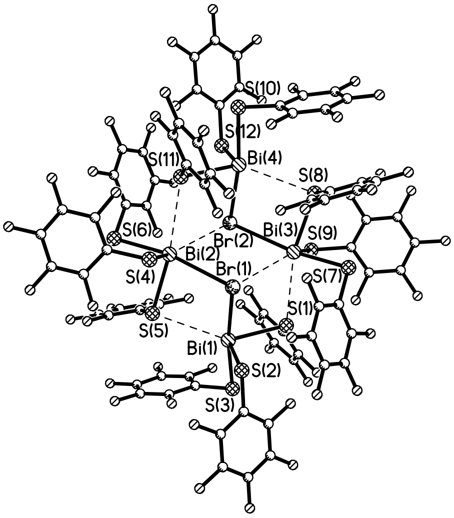


Fig. 3. A view of the dimeric arrangement of $[Bi_2(SC_6F_5)_6(\mu\text{-}Br)]^-$ anions in the structure of **4**.

Compound **6** incorporates the trinuclear di-anion $[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]^{2-}$ (Fig. 5) with associated $[PPh_4]^+$ cations. The structure of the anion $[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]^{2-}$ comprises a central bismuth tristhiolate unit linked to two other bismuth centres by single bridging bromides. The geometry around the central bismuth is square-based pyramidal with the two bromides in mutually *cis* basal sites. Each terminal bismuth centre is four-coordinate with a disphenoidal geometry in which the bromines occupy axial sites. Bi–S bond lengths in **6** follow the expected trends described above (Table 1) and the bromines bridge fairly symmetrically. The Bi(1), Br(1), Bi(2) unit and the Bi(2), Br(2), Bi(3) unit each resemble the basic structure seen in the $[Bi_2(SC_6F_5)_6(\mu\text{-}Br)]^-$ anion in **4** notably in terms of the conformations about the Bi(1)–Br(1) and Bi(3)–Br(2) bonds which place S(2) close to Bi(2) [3.482 Å] and S(6) close to Bi(3) [3.455 Å]. The presence of these two semi-bridging thiolates results in Bi(2) and Bi(3) approaching six- and five-coordination, respectively, as is clear from Fig. 5. The structure of the anion in **6** is closely related to the trinuclear di-anion found in the structure of $[4\text{-picH}][(4\text{-pic})_2H][Bi_3(SC_6F_5)_{11}]$[5] in which the bridging groups are thiolates although conformationally the two structures are rather different and the $[Bi_3(SC_6F_5)_{11}]^{2-}$ anion lacks the semi-bridging thiolates seen in **6**.

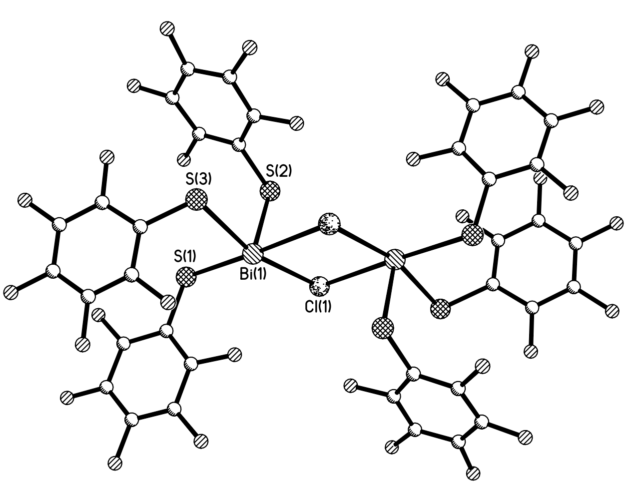


Fig. 4. A view of the crystallographically centrosymmetric dinuclear di-anion $[Bi_2(SC_6F_5)_6(\mu\text{-}Cl)_2]^{2-}$ in the structure of **5**.

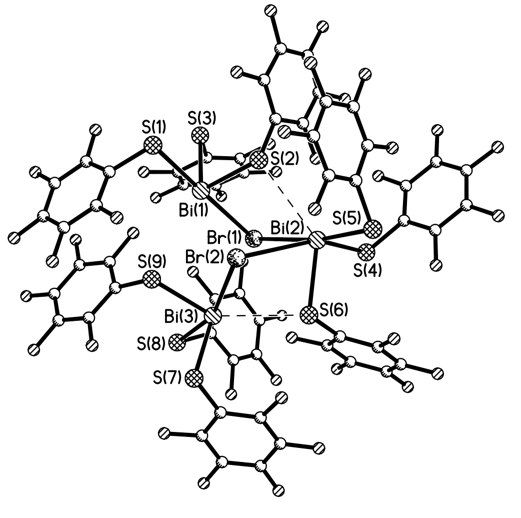
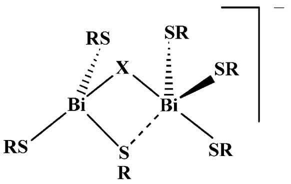
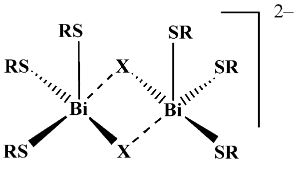


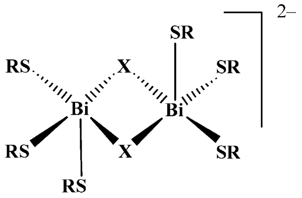
Fig. 5. A view of the trinuclear di-anion $[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]^{2-}$ in the structure of **6**.



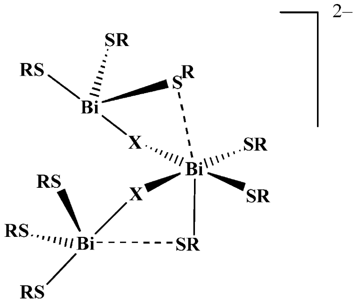
R = C_6F_5: **2**, X = SC_6F_5; **4**, X = Br



R = C_6F_5: **3**, X = SC_6F_5



R = C_6F_5: **5**, X = Cl



R = C_6F_5: **6**, X = Br

Whilst all the structures reported here are different, a number of general structural features are apparent. The basic units are of two types namely $[Bi_2(SR)_6(\mu\text{-}X)]^-$ (this can be taken to include the anion in **6**, see discussion above) and $[Bi_2(SR)_6(\mu\text{-}X)_2]^{2-}$, where X = thiolate or halide. In the former case the single bridging groups occupy an axial site within the disphenoidal geometry around the bismuth centres whereas in the latter the two bridging groups occupy *cis* basal sites in the square based pyramid (apical groups can adopt both *syn* and *anti* arrangements). Semi-bridging thiolates are also encountered in the structures of the type $[Bi_2(SR)_6(\mu\text{-}X)]^-$. A further point to note is that in the structures of **4**–**6** which contain both thiolate and halide groups, it is the halides which bridge rather than the thiolates. A similar situation is found in the alkoxide anion $[Bi_2(O\text{-}2,6\text{-}Me_2C_6H_3)_6(\mu\text{-}Cl)_2]^{2-}$ which is closely related to the structure of the anion in **5**, although in the neutral species $[Bi_2Cl_4(thf)_2(\mu_2\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)_2]$ and $[Bi_2Cl_4\text{-}(thf)_2(\mu_2\text{-}O\text{-}2,4,6\text{-}Me_3C_6H_2)_2]$, it is the alkoxides which bridge in preference to the halides [8]. Finally, we note that if a graph is plotted of all the *trans* related S–Bi–S pairs of distances in the structures reported herein, as well as previously reported structures (Fig. 6), the expected correlation in both distances is observed as discussed in ref. 9, and references therein.

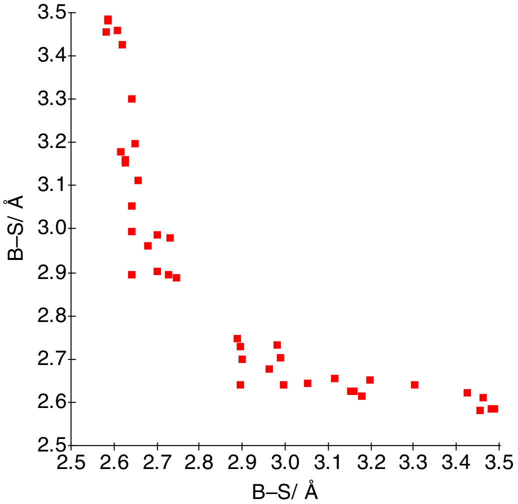


Fig. 6. A plot of *trans* related S–Bi–S distances for bismuth thiolates and thiolato anions.

3. Experimental

3.1. 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 [3].

3.2. Preparations

3.2.1. $[PPh_4][Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)]$ (2) and $[PPh_4]_2[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]$ (6)

A solution of **1** (0.11 g, 0.136 mmol) in CH_2Cl_2 (3 cm^3) was added to solid $[PPh_4]Br$ (0.057 g, 0.136 mmol) affording a clear orange solution. After stirring for 5 min, the solvent volume was reduced by vacuum and hexane (3 cm^3) was added as an overlayer. Solvent diffusion at −30 °C over a period of several days afforded orange crystals of **2** (0.075 g, 45%) and a small crop of yellow crystals of **6**. Difficulties in separating crystals of **2** and **6** prevented satisfactory analytical data from being obtained.

3.2.2. $[NEt_4]_2[Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)_2]\cdot 2thf$ (3)

A filtered solution of $[NEt_4]Br$ (0.05 g, 0.237 mmol) in thf (2 cm^3) was added to a solution of **1** (0.10 g, 0.124 mmol) in thf (3 cm^3). After stirring, hexane (3 cm^3) was added an overlayer. Solvent diffusion at −30 °C over a period of days afforded orange crystals of **3** (0.072 g, 48%). Satisfactory analytical data were not obtained due to facile solvent loss from the crystals.

3.2.3. [$PPh_3CH_2CO_2CH_3$][$Bi_2(SC_6F_5)_6(\mu$-$Br)$] (4)

Compound **1** (0.06 g, 0.074 mmol) and [$PPh_3CH_2CO_2CH_3$]Br (0.025 g, 0.074 mmol) were dissolved in CH_2Cl_2 (3 cm^3) and hexane (3 cm^3) was added an overlayer. Solvent diffusion over a period of days −30 °C afforded orange crystals of **4** (0.043 g, 51%). *Anal.* Calc. for $C_{57}H_{20}Bi_2BrF_{30}O_2PS_6$: C, 33.75; H, 1.00. Found: C, 34.00; H, 1.40%.

3.2.4. [PPh_3CH_2Ph]$_2$[$Bi_2(SC_6F_5)_6(\mu$-$Cl)_2$] (5)

Compound **1** (0.10 g, 0.124 mmol) and [PPh_3CH_2Ph]Cl (0.048 g, 0.124 mmol) were dissolved in CH_2Cl_2 (3 cm^3) and hexane was added as an overlayer. Solvent diffusion over a period of days at −30 °C afforded orange crystals of **5** (0.083 g, 73%). *Anal.* Calc. for $C_{86}H_{44}Bi_2Cl_2F_{30}P_2S_6$: C, 43.20; H, 1.85; Cl, 2.95. Found: C, 43.15; H, 1.80; Cl, 2.70%.

3.3. 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 [10,11] area detector diffractometer using graphite monochromated Mo Kα 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 [12]. In each case hydrogen atom were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} the attached carbon.

Absorption corrections were applied using SADABS [13] and extinction coefficients were refined where appropriate. Non-hydrogen atoms were assigned anisotropic parameters and refined without positional constraints for all structures. In addition to the bismuth containing species, the solid state structure of **4** has a unit cell containing one hexane molecule and two, symmetry related, sites partially occupied by a dichloromethane molecule.

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