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COMMUNICATION

BISMUTH(III) THIOLATES: SYNTHESES AND THE STRUCTURES OF A NEUTRAL THIOLATE AND A THIOLATO ANION

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Abstract—The synthesis of a range of bismuth(III) arenethiolates and a thiolato anion are described together with two X-ray crystal structure determinations of SC_6F_5 derivatives.

The presence of bismuth in one of the classes of copper oxide based superconductors with some of the highest T_c values[1] has led to a resurgence of interest in the preparation and characterisation of bismuth(III) amides[2] and alkoxides[3] in view of their potential use in sol–gel or MOCVD synthetic routes to these materials. In contrast, the chemistry of bismuth(III) thiolates, $Bi(SR)_3$, remains largely undeveloped in spite of their potential use as solution or vapour phase precursors to bismuth(III) sulfide and related compounds, which are important as photovoltaic materials. The only compounds reported to date of which we are aware, are $Bi(SPh)_3$ (**1**),[4] $Bi(SC_6F_5)_3$ (**2**),[5] $Bi(S\text{-}o\text{-}CO_2MeC_6H_4)_3$,[4b] $Bi(SEt)_3$,[6] $Bi(Sbenzyl)_3$,[6] $Bi(SCH_2CH_2OH)_3$,[6] $Bi(SBu^t)_3$,[7] $Bi(S\text{-}4\text{-}FC_6H_4)_3$[8] and $Bi(S\text{-}2,4,6\text{-}Bu^t_3C_6H_2)_3$ (**3**),[9] many of which are not well characterised; only **3** has been characterised by X-ray crystallography.[9] Herein, we report the synthesis of a range of bismuth(III) arenethiolates and a bismuth(III) thiolato anion together with crystal structure determinations of examples of each containing the SC_6F_5 group.

Whilst a few synthetic routes to bismuth(III) thiolates have been described,[4–9] a convenient and high yield route (typical yields range from 50–85%) to the complexes $Bi(SR)_3$ (**1**, R = Ph; **4**, R = 4-Me-C_6H_4; **5**, R = 2,6-Me_2-C_6H_3; **6**, R = 3,5-Me_2-C_6H_3) involves the reaction between $BiCl_3$ and three equivalents of NaSR in thf followed by solvent removal *in vacuo*, extraction in hexane (**5**), Et_2O (**1** and **4**) or CH_2Cl_2 (**6**), filtration and low temperature crystallisation (using a hexane overlayer in the case of **1**, **4** and **6**).[†] Complexes **4**–**6** afforded feathery orange crystals unsuitable for X-ray crystallography, but seemingly well formed X-ray quality orange crystals of **1** were obtained from hexane at −30°C. A preliminary analysis of X-ray data collected for **1** (two data sets) shows that the repeat motif is a $Bi(SPh)_3$ unit with similar geometrical parameters to that found for **3**. There are no short intermolecular Bi ··· S contacts, but there are some close S ··· S contacts along the short crystallographic *b* axis. However, there is a possibility that

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[†] Satisfactory analytical and spectroscopic data were obtained for all new compounds.

this arises from an artefact of pseudosymmetry associated with the bismuth atoms, and hence we will defer a full description of the structure to a later publication.

In contrast to the above, the reaction between $BiCl_3$ and three equivalents of $NaSC_6F_5$ in thf afforded, after work up similar to that described above for **5**, orange crystals not of the expected product, **2**, but of an ionic compound identified by X-ray crystallography[‡] as $[Na_2(thf)_4][Bi(SC_6F_5)_5]$ (**7**).[†] A view of the $[Bi(SC_6F_5)_5]^{2-}$ anion in **7** is shown in Fig. 1. The structure comprises a bismuth atom bonded to five SC_6F_5 groups with a square-based pyramidal coordination geometry. Of the five Bi—S bond lengths, the shortest is the apical bond [Bi—S(5) 2.609(10) Å] with the basal bonds being some 0.1–0.3 Å longer (the shorter of these *trans* to the longer ones); none of the interbond angles deviate significantly from 90 or 180°. In addition to this primary coordination sphere, a close contact exists between the bismuth centre and one of the fluorine atoms [Bi $\cdots$ F(416) 2.94 Å] such that this interaction is *trans* to the apical Bi—S bond; all other Bi $\cdots$ F contacts are greater than 4.0 Å. The Bi—S bond lengths may be compared with those in **3** which average 2.559 Å,[9] slightly less than in **7** presumably resulting from the lower coordination number in **3**. The only previous report of a thiolato anion of bismuth(III) is the complex $[Ph_4As][Bi(SC_6F_5)_4]$[5a] although no structural details for this complex are available. Analogous halogenoanions of bismuth are well known[10] but no examples of simple amido, $[Bi(NR_2)_{3+x}]^{x-}$, or alkoxide, $[Bi(OR)_{3+x}]^{x-}$, anions have yet been described.

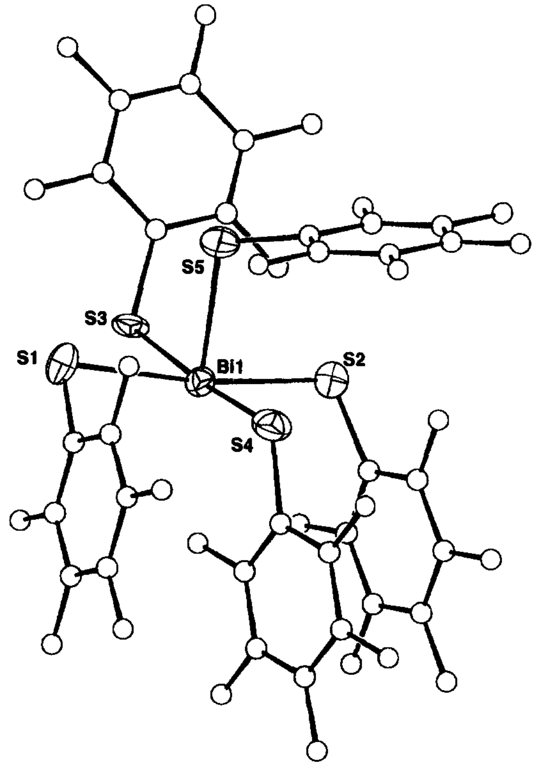

Fig. 1. A view of the structure of the $[Bi(SC_6F_5)_5]^{2-}$ anion in **7**. Thermal ellipsoids are drawn at the 20% level. Selected bond lengths (Å) and angles (°): Bi—S(1) 2.988(9), Bi—S(2) 2.703(9), Bi—S(3) 2.889(9), Bi—S(4) 2.746(10), Bi—S(5) 2.609(10); S(1)—Bi—S(2) 172.0(3), S(1)—Bi—S(3) 92.2(3), S(1)—Bi—S(4) 88.7(3), S(1)—Bi—S(5) 83.7(3), S(2)—Bi—S(3) 89.0(3), S(2)—Bi—S(4) 89.6(3), S(2)—Bi—S(5) 88.6(3), S(3)—Bi—S(4) 175.7(3), S(3)—Bi—S(5) 84.7(3), S(4)—Bi—S(5) 91.2(3).

The isolation of a thiolato anion in the reaction between $BiCl_3$ and $NaSC_6F_5$ is presumably a consequence of the greater Lewis acidity of the bismuth centre when bonded to the electron withdrawing SC_6F_5 groups. The neutral tristhiolate compound **2** can, however, be prepared in high yield from the

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[‡] *Crystal data for* **7**: $C_{46}H_{32}BiF_{25}Na_2O_4S_5$, $M = 1538.97$, monoclinic, space group $P2_1/n$, $a = 15.061(3)$, $b = 19.714(6)$, $c = 19.987(6)$ Å, $\beta = 108.89(2)°$, $U = 5615(3)$ Å^3, $Z = 4$, $D_c = 1.82$ g cm^{-3}, $\mu = 34.44$ cm^{-1}, (Mo-K_α radiation, $\lambda = 0.71069$ Å) $F(000) = 3000$; Final $R = 0.094$, $R' = 0.070$ for 202 parameters, including anisotropic thermal parameters for Bi, F and Na atoms [C_6F_5 groups were refined as rigid groups (C—C 1.395, C—F 1.35 Å, angles 120°), thf molecules were refined as rigid pentagons (C—C and C—O 1.45 Å), no hydrogen atoms were included in the structure factor calculations] by refinement on F from 7011 unique data ($2\theta_{max} = 44.4°$) with $I > 2\sigma(I)$ measured at 298 K on an Enraf-Nonius Turbo CAD4 diffractometer and corrected for absorption; weighting scheme $w = [\sigma^2(F_o)]^{-1}$ with $\sigma(F_o)$ estimated from counting statistics.

Crystal data for **2**: $C_{18}BiF_{15}S_3$, $M = 806.34$, monoclinic, space group $P2_1/c$, $a = 14.4151(9)$, $b = 10.3870(10)$, $c = 14.5680(10)$ Å, $\beta = 102.572(5)°$, $U = 2129.0(3)$ Å^3, $Z = 4$, $D_c = 2.516$ g cm^{-3}, $\mu = 87.13$ cm^{-1}, (Mo-K_α radiation, $\lambda = 0.71069$ Å) $F(000) = 1496$; Final $R = 0.0300$, $R' = 0.0696$ for 334 parameters, including anisotropic thermal parameters for all atoms by refinement on F^2 from 3731 unique data ($2\theta_{max} = 50°$) measured at 293 K on an Enraf-Nonius Turbo CAD4 diffractometer and corrected for absorption and anomalous dispersion; weighting scheme $w = [\sigma^2(F_o)^2 + (0.0474P)^2]^{-1}$ where $P = [F_o^2/3 + 2F_c^2/3]$ with $\sigma(F_o)^2$ estimated from counting statistics.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

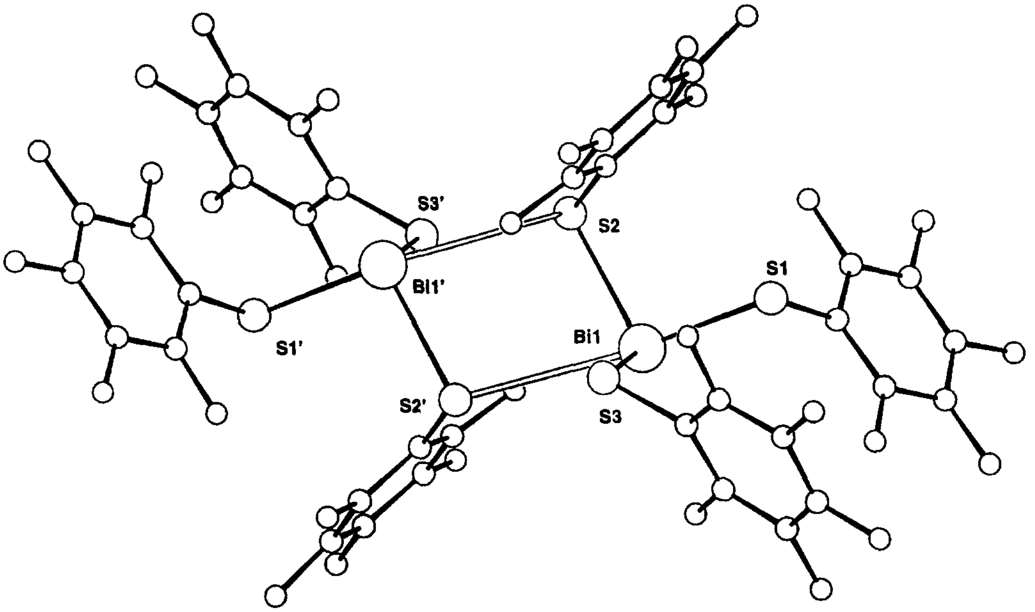

Fig. 2. A view of the structure of **2**. Atoms are drawn as circles of arbitrary radius. Selected bond lengths (Å) and angles (°): Bi—S(1) 2.532(2), Bi—S(2) 2.584(2), Bi—S(3) 2.540(2), Bi—S(2′) 3.323(2); S(1)—Bi—S(2) 96.51(6), S(1)—Bi—S(3) 87.57(5), S(2)—Bi—S(3) 92.76(6), S(1)—Bi—S(2′) 158.05(6), S(2)—Bi—S(2′) 77.05(6), S(3)—Bi—S(2′) 72.01(6). Primed atoms are related to unprimed atoms by the symmetry operation $-x$, $-y$, $-z$.

reaction between $BiPh_3$ and three equivalents of HSC_6F_5 in refluxing toluene (4 days). Subsequent low temperature crystallisation of the reaction solution (after reduction of the solvent volume) afforded (in high yield) orange crystals of **2**, one of which was examined by X-ray crystallography,‡ the results of which are shown in Fig. 2. The structure comprises a loosely bound dimer (crystallographically centrosymmetric) in which each bismuth centre adopts a four-coordinate, disphenoidal geometry with three short Bi—S bonds [Bi—S(1) 2.532(2), Bi—S(2) 2.584(2), Bi—S(3) 2.540(2) Å] and a longer contact [Bi···S(2′) 3.323(2) Å] approximately *trans* to the Bi—S(1) bond [S(1)—Bi—S(2′) 158.05(6)°]. This geometry results in a slight lengthening of the Bi—S(1) bond relative to the terminal Bi—S(3) bond presumably resulting from population of the Bi—S(1) σ^*-orbital by the S(2′) lone pair in this secondary bonding interaction.[11]

It is interesting to compare the structure of **2** with the analogous bismuth alkoxide complex $Bi(OC_6F_5)_3$ (**8**) prepared similarly from $BiPh_3$ and three HOC_6F_5.[3f,g,h] In general, bismuth alkoxides are not monomeric unless the alkoxide groups are sterically demanding, as in $Bi(O\text{-}2,6\text{-}Me_2C_6H_3)_3$,[3a] or as a result of solvent coordination, e.g. in $[Bi(OSiPh_3)_3(thf)_3]$.[3d] Thus, the structure of **8** in crystals obtained from toluene is found to be dimeric, i.e. $[\{Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)(toluene)\}_2]$ (two crystalline forms, both crystallographically centrosymmetric), which therefore provides for an interesting comparison with the structure of **2**. For example, the Bi—O—Bi bridges in **8** [2.210(8) *vs* 2.571(7), difference (Δ) = 0.361 Å and 2.168(7) *vs* 2.5553(9), Δ = 0.3873 Å for the two crystalline forms] are considerably more symmetric than the Bi—S—Bi bridges in **2** [2.532(2) *vs* 3.323(2), Δ = 0.791 Å]; furthermore, in **8** (both forms) there is a molecule of toluene coordinated (albeit loosely) to the bismuth centres which is absent in **2** even though crystallisation is from this solvent. Both of these factors suggest a greater degree of Lewis acidity for the bismuth centre in **8** *vs* **2** possibly arising from the larger electronegativity difference associated with the Bi—O *vs* the Bi—S bonds.§ Mono-

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§ Whilst electronegativity differences would appear to provide a satisfactory explanation for these observations, they clearly do not in the case of many bismuth halide compounds, where it is generally observed that Bi—I—Bi bridges are more symmetric than Bi—Cl—Bi bridges (with Bi—Br—Bi bridges intermediate). These matters are addressed in ref. 11 and we will return to this subject in more detail in a future publication.

meric and hence more soluble and volatile compounds are therefore likely for bismuth(III) thiolates in comparison with bismuth(III) alkoxides without the necessity for sterically demanding groups.

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REFERENCES

1. P. Majewski, *Adv. Mater.* 1994, **6**, 460.
2. C. J. Carmalt, N. A. Compton, R. J. Errington, G. A. Fisher, I. Moenandar and N. C. Norman, *Inorg. Synth.* 1994, **31**, in press, and references cited therein.
3. (a) W. J. Evans, J. H. Hain and J. W. Ziller, *J. Chem. Soc., Chem. Commun.* 1989, 1628; (b) M. A. Matchett, M. Y. Chiang and W. E. Buhro, *Inorg. Chem.* 1990, **29**, 360; (c) M.-C. Massiani, R. Papiernik, L. G. Hubert-Pfalzgraf and J.-C. Daran, *J. Chem. Soc., Chem. Commun.* 1990, 301; (d) M.-C. Massiani, R. Papiernik, L. G. Hubert-Pfalzgraf and J.-C. Daran, *Polyhedron* 1991, **10**, 437; (e) A. Haaland, H. P. Verne, H. V. Volden, R. Papiernik and L. G. Hubert-Pfalzgraf, *Acta Chem. Scand.* 1993, **47**, 1043; (f) C. M. Jones, M. D. Burkart and K. H. Whitmire, *Angew. Chem., Int. Ed. Engl.* 1992, **31**, 451; (g) C. M. Jones, M. D. Burkart, R. E. Bachman, D. L. Serra, S.-J. Hwu and K. H. Whitmire, *Inorg. Chem.* 1993, **32**, 5136; (h) K. H. Whitmire, C. M. Jones, M. D. Burkhart, J. C. Hutchinson and A. L. McKnight, *Mat. Res. Soc. Symp. Proc.* 1992, **271**, 149.
4. (a) M. E. Peach, *J. Inorg. Nucl. Chem.* 1979, **41**, 1392. and references cited therein; (b) H. Gilman and H. L. Yale, *J. Am. Chem. Soc.* 1951, **73**, 2880.
5. (a) M. Muller, R. J. H. Clark and R. S. Nyholm, *Transition Met. Chem.* 1978, **3**, 369; (b) M. E. Peach, *Can. J. Chem.* 1968, **46**, 2699.
6. M. Wieber and U. Baudis, *Z. Anorg. Allg. Chem.* 1976, **423**, 47.
7. A. F. Jansen, O. C. Vaidya and C. J. Willis, *J. Inorg. Nucl. Chem.* 1981, **43**, 1469.
8. S. C. Hergett and M. E. Peach, *J. Fluorine Chem.* 1988, **38**, 367.
9. D. A. Atwood, A. H. Cowley, R. D. Hernandez, R. A. Jones, L. L. Rand, S. G. Bott and J. L. Atwood, *Inorg. Chem.* 1993, **32**, 2972.
10. G. A. Fisher and N. C. Norman, *Adv. Inorg. Chem.* 1994, **41**, 233.
11. N. C. Norman, *Phosphorus Sulfur* 1994, **87**, 167, and references cited therein.