Ammoniumthiolatobismuth halides: a new thiolate bonding environment for Bi^{III} as an alternative to metathesis and chelation

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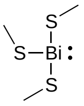
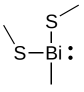
Synthesis, isolation and characterization of the first monothiolatobismuth complexes are contrary to the prominent thiophilicity, the tendency towards maximum metathesis and the extensive chelation chemistry of bismuth.

The coordination chemistry of the heavier p block elements is diverse due primarily to the potential for both covalent and coordinative bonding, the access of coordination numbers up to nine, and facile ligand exchange in solution. Despite the rapid developments in the chemistry of bismuth resulting from demonstrated bioactivity[1] and the need for viable synthetic approaches to new materials,[2] systematic assessments of coordinative environments for bismuth still require the identification, characterization and classification of numerous structural possibilities. Thiobismuth derivatives are perhaps the most extensively studied series of bismuth compounds owing to their high thermal and reactive stability, and include complexes of thiolato,[3,4] dithiocarboxylato derivatives,[5] thione[6] and thioether[7] ligands. Numerous examples of multithiolato compounds (**1** and **2**) have been structurally characterized, but monothiolato complexes of type **3** have only been postulated on the basis of spectroscopic data.[8]


1a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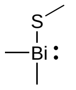
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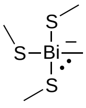
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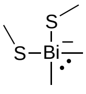
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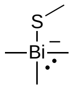
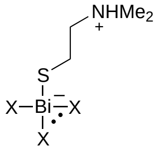
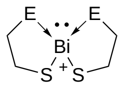

3b

Here we describe the isolation and characterization† of ammoniumthiolatobismuth halides **4**, which are formed in high yield independent of stoichiometry in the reactions of $HSC_2H_4NMe_2HX$ with either $Bi(NO_3)_3$ or BiX_3 (X = Cl **a**, Br **b**). An X-ray crystallographic study of **4a** (Fig. 1) confirms the empirical formula and the pendant ammoniumethanethiolato moiety. The one-dimensional spirocyclic polymeric array, typical of bismuth halides,[4,9] is due to association of the bismuth centres by alternating chlorine and sulfur coordinative bridges, imposing a near octahedral, six-coordinate environment for bismuth. The two $Bi–Cl_{terminal}$ bonds [2.615(4), 2.636(3) Å] are predictably shorter than the $Bi–Cl_{bridging}$ bonds [2.776(4), 3.001(4) Å], and the Bi–S bond [2.669(3) Å] which is *trans* to the $Bi–Cl_{bridging}$ bonds is significantly shorter than that which is *trans* to the $Bi–Cl_{terminal}$ [2.927(3) Å] bond. These comparisons can be interpreted in terms of the bismuth centre engaging four covalent bonds (three to chlorine and one to sulfur) and two bridging coordinative bonds (one to chlorine and one to sulfur), which presumably dissociate on solvation to give the monomer in solution.

Although observation of a monothiolatobismuth environment of type **3b** in derivatives of **4** is contrary to the prominent thiophilicity of bismuth and the tendency towards maximum metathesis (which gives bonding environments **1** and **2**),[4,10–12] the quantitative halogenation of bismuth in the reaction of $Bi(NO_3)_3$ with $HSC_2H_4NMe_2HX$ implies that derivatives of **4** are thermodynamically favoured. In addition, formation of **4** contrasts the extensive chelation chemistry of bismuth, and specifically the reaction of aminoethanethiol (the conjugate base of $HSC_2H_4NH_3X$) with $Bi(NO_3)_3$ in acetic acid, which gives **5a** $(NO_3)\cdot H_2O$ as the result of a double metathesis.[12] We conclude that the thiophilicity of Bi^{3+} is greater than that of BiX_3 (X = Cl, Br), and the higher basicity of the halide ligands restricts thiolation. Interestingly, $Bi(NO_3)_3$ and BiX_3 react with mercaptoethanol ($HSCH_2CH_2OH$) to give **5b** by virtue of bisthiolation,[10,11] implying that the higher protic basicity of the amine inhibits the chelation which is observed for the hydroxythiolate.


4a X = Cl
b X = Br


5a E = NH_2
b E = OH

Derivatives of **4**, as the first examples of bonding type **3b**, represent a fundamental missing link in the developing chemistry of bismuth, and their thermodynamically favoured formation bodes well for efficient and systematic assessment of a potentially extensive new direction, including anions of the type $[X_3BiSR]^-$, which we are currently examining.

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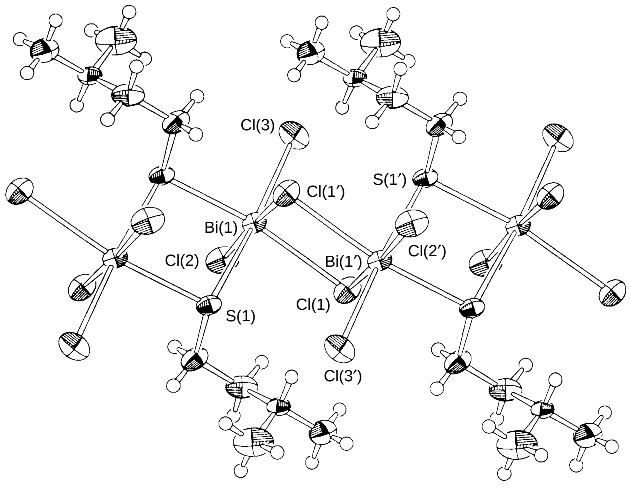

Fig. 1 Crystallographic view of **4a**. Selected bond lengths (Å) and angles (°): Bi(1)–Cl(1′) 2.776(4), Bi(1)–Cl(2) 2.615(4), Bi(1)–Cl(3) 2.636(3), Bi(1)–Cl(1) 3.001(4), Bi(1)–S(1) 2.927(3), Bi(1)–S(1′) 2.669(3); Cl(1)–Bi(1)-Cl(1′) 85.31(10), Cl(1)–Bi(1)–Cl(2) 92.3(1), Cl(1)–Bi(1)–Cl(3) 100.2(1), Cl(1)–Bi(1)–S(1) 84.64(10), Cl(1)–Bi(1)–S(1′) 170.5(1).

Footnotes and References

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† BiX_3 (6.6 mmol) in THF (50 ml) added to $HSC_2H_4NMe_2HX$ (13.3 mmol) in ethanol (125 ml), or $Bi(NO_3)_3{\cdot}5H_2O$ (5.0 mmol) with $HSC_2H_4NMe_2HX$ (15.0 mmol) in H_2O (14 ml) and glacial acetic acid (6 ml), each give a yellow precipitate. **4a**: yield from $BiCl_3$, 97%. Anal. Calc.: C, 11.42; H, 2.62; N, 3.33%; Found: C, 11.98; H, 2.77; N, 3.42%; yield from $Bi(NO_3)_3{\cdot}5H_2O$, 67%. Anal. Found: C, 11.52; H, 2.64; N, 3.42%; 205 °C (decomp.); IR (ν/cm^{-1}): 303w, 335m, 411w, 513w, 662w, 722m, 756w, 835w, 885w, 926s, 967w, 1011m, 1035w, 1048w, 1117w, 1149w, 1211w, 1226w, 1256w, 1305w, 1404w, 1429m. Raman (cm^{-1}): 107vs, 127vs, 172s, 220s (sh), 247vs, 334s, 412w, 446w, 514w, 663m, 757m, 885w, 927w, 967w, 1011w, 1037w, 1050w, 1213w, 1229w, 1258w, 1305w, 1365w, 1385m, 1431m, 1451m, 2896w (sh), 2939s (sh), 2955s, 2991m, 3020m, 3032m. ^{1}H NMR [$(CD_3)_2SO$]; δ 2.77s, 3.30 (t, br), 4.98 (s, br), 9.02 (s, br). ^{13}C NMR [$(CD_3)_2SO$], δ 23.2, 42.7, 60.8. Recrystallized (needle-like) from water by slow evaporation for 3–12 d, yield: 2.4%. Anal. Found: C, 11.57; H, 2.79; N, 3.32; consistent Raman and decomparison temperature. *Crystal data*: $C_4H_{11}BiCl_3NS$, M = 420.54, monoclinic, space group $P2_1/c$, a = 6.850(2), b = 13.977(2), c = 11.720(1) Å, β = 106.14(1)°, U = 1077.8(4) Å^3, D_c = 2.591 g cm^{-3}, Z = 4, λ(Mo-Kα) = 404.11 cm^{-1}, 1842 collected reflections, 1688 unique reflections, $2\theta_{max}$ = 120.2°, R = 0.044, R_w = 0.050 (Cu-Kα radiation, λ = 1.541 78 Å, T = 23.0 °C). All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu-Kα radiation and a 12 kW rotating anode generator. The structure was solved by direct methods and refined by full-matrix least-squares techniques using 1417 reflections with $I > 3.00\sigma(I)$. The non-hydrogen atoms were refined anisotropically. A final difference-Fourier map yielded maximum and minimum peaks of 2.48 and -2.73 e Å^{-3}, respectively. CCDC 182/657.

4b: yield from $BiBr_3$, >95%. Anal. Calc.: C, 8.67; H, 2.00; N, 2.53; Found: C, 9.19; H, 2.07; N, 2.57%; yield from $Bi(NO_3)_3{\cdot}5H_2O$, 90%. Anal. Found: C, 8.94; H, 2.04; N, 2.62%; 195 °C (decomp.). IR (ν/cm^{-1}) (Nujol): 513s, 588m, 658w, 721w, 752w (sh), 774s, 834m (br), 866m, 893w, 922m, 965w, 1007m, 1031w, 1045w, 1117w, 1145w, 1180m, 1226w (sh), 1256w (sh), 1321s, 1340m, 1425w (sh), 1513vs, 1570vs, 1623vs, 1639w (sh), 3402vs (br). Raman (cm^{-1}): 75vs, 101m, 119vs, 144m, 162vs, 210vs, 300w, 328s, 408w, 444w, 513m, 660m, 753m, 878m, 924w, 967w, 1008w, 1033m, 1045w (sh), 1117w, 1147w, 1212w, 1227w, 1257w, 1302w, 1359m, 1377m, 1394w, 1427m, 1451m, 1464w, 1475w (sh), 2841w (br), 2893w, 2932w (sh), 2947s, 2960s, 2983w, 3020m, 3074w (br). ^{1}H NMR [$(CD_3)_2SO$], δ 2.78 (s), 3.30 (s, br), 5.04 (s, br), 8.99 (s, br). ^{13}C NMR [$(CD_3)_2SO$], δ 24.2, 42.7, 60.9.

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