Bismuth(III) thioether chemistry: the synthesis and structure of $[Bi_4Cl_{12}(MeSCH_2CH_2CH_2SMe)_4]_n{\cdot}nH_2O$, a highly unusual network involving Bi_4Cl_4 rings and bridging dithioether ligands

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The structure of $[Bi_4Cl_{12}(MeSCH_2CH_2CH_2SMe)_4]_n{\cdot}nH_2O$ involves $Bi_4Cl_{12}(\eta^1\text{-}MeSCH_2CH_2CH_2SMe)_4$ tetrameric units which are linked by bridging dithioether ligands to give a three-dimensional polymeric network; the Bi_4Cl_4 core is an eight-membered heterocycle which adopts an open cradle conformation.

With the exception of complexes with phosphine and amine ligands,[1,2] the coordination chemistry of the heavier p-block elements such as bismuth is rather poorly developed. A small number of Bi^{III} complexes involving macrocyclic thioethers has been described, including $[BiCl_3([9]aneS_3)]$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane),[3] $[BiCl_3([12]aneS_4)]$ ($[12]aneS_4$ = 1,4,7,10-tetrathiacyclododecane)[4] and $[BiCl_3([18]aneS_6)]$ ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane).[5] Macrocyclic ligands however offer enhanced binding properties over acyclic ligands, are conformationally less flexible than their acyclic counterparts and often exhibit different binding modes. Structural studies have shown that these macrocyclic Bi species are discrete molecular entities, with coordination numbers varying from six to nine. As part of our investigation into thio-, seleno- and telluro-ether complexes with p-block elements we report here the preparation and structure of a very unusual Bi^{III} compound $[Bi_4Cl_{12}(MeSCH_2CH_2CH_2SMe)_4]_n{\cdot}nH_2O$. Other than the macrocyclic compounds described above, the only structurally characterised Bi^{III} thioether complex is $[Bi_2I_8(SMe_2)_2][SMe_3]_2$.[6]

Reaction of $BiCl_3$ with 1 mol equiv. of $MeSCH_2CH_2CH_2SMe$ in CH_2Cl_2 affords a light yellow solution. Following filtration and concentration of the solution, the flask was left to stand for several days during which yellow crystals of a compound with the formula $[BiCl_3(MeSCH_2CH_2CH_2SMe)]{\cdot}H_2O$ were isolated in *ca.* 20% yield. The IR spectrum shows the presence of the dithioether, as well as several peaks in the range 300–230 cm^{-1} assigned to Bi–Cl stretching vibrations. Microanalyses are also consistent with the above formulation. Traces of moisture in the CH_2Cl_2 probably account for the associated water. A single crystal X-ray structure determination† revealed a three-dimensional polymeric network with the structural formula $[Bi_4Cl_{12}(MeSCH_2CH_2CH_2SMe)_4]_n{\cdot}nH_2O$. The structure involves $Bi_4Cl_{12}(MeSCH_2CH_2CH_2SMe)_4$ tetrameric units (related by crystallographic $\bar{4}$ symmetry) which are linked by bridging dithioether ligands to give a three-dimensional polymeric network [Fig. 1(a) and (b)]. Each Bi^{III} ion is therefore coordinated to two terminal Cl atoms, Bi–Cl(2) 2.538(7), Bi–Cl(3) 2.533(7) Å, two μ_2 bridging Cl atoms, Bi–Cl(1) 2.913(7), Bi–Cl(1*) 2.969(6) Å, and two S-donors from different bridging dithioether ligands, Bi–S(1) 2.857(7), Bi–S(2*) 2.977(7) Å. The geometry at each Bi atom therefore approximates to a severely distorted octahedron, with an open triangular face which we assume is occupied by the Bi lone pair. The μ_2-bridging Bi–Cl distances are much longer than the terminal distances and are themselves only slightly different, hence an alternative description is that the structure comprises of $[BiCl_2(\eta^1\text{-}MeSCH_2CH_2CH_2SMe)_2]^+$ cations loosely associated into tetramers through interactions with chloride anions, Cl(1) and Cl(1*). There are additional long range, weak interactions which link the μ_2-bridging Cl atoms to Bi centres across the Bi_4Cl_4 ring, forming a pseudo-cuboid arrangement, $Bi{\cdots}Cl(1^*)$ 3.268(7) Å. This interaction is significantly longer than one would expect for a genuine μ_3-bridging Cl.[7] The

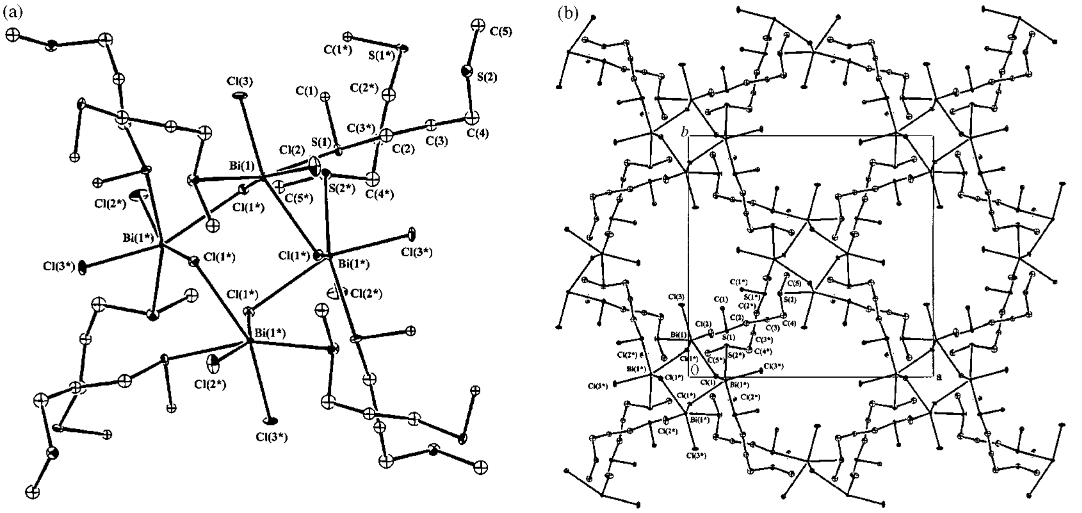

Fig. 1 (*a*) View of a portion of the $[Bi_4Cl_{12}(MeSCH_2CH_2CH_2SMe)_4]_n$ structure with the numbering scheme adopted (H atoms are omitted for clarity and atoms marked with an asterisk are related by a crystallographic $\bar{4}$ operation). Selected bond lengths (Å): Bi–Cl(1) 2.913(7), Bi–Cl(2) 2.538(7), Bi–Cl(3) 2.533(7), Bi–S(1) 2.857(7), Bi–S(2*) 2.977(7) Å. (*b*) View down the *c*-axis of the three-dimensional polymer, illustrating the channels running through the structure.

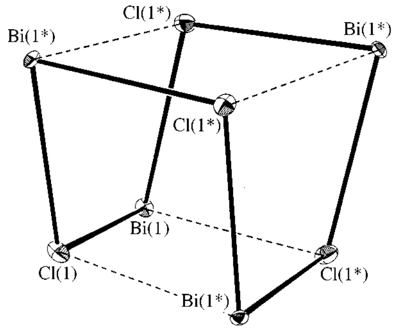

Fig. 2 View of the Bi_4Cl_4 core, illustrating the open cradle conformation. The dashed lines indicate the secondary Bi···Cl interactions.

Bi_4Cl_4 core forms an eight-membered heterocyclic ring which, as a result of the weak Bi···Cl interactions adopts an open cradle conformation (Fig. 2). The secondary Bi···Cl(1*) interaction is in the general direction of the void assumed to be occupied by the lone pair, but not in the direction of the maximum electron density. This behaviour is commonly observed in Bi^{III} and Sb^{III} chemistry.[8]

Bismuth halides often form compounds incorporating partially condensed Bi_4X_4 polyhedra,[7] however, the open cradle or pseudo-cuboid arrangement adopted in the title compound is very unusual. The Bi–S and Bi–$Cl_{terminal}$ bond lengths are similar to those observed in the reported macrocyclic thioether complexes of Bi^{III}, *e.g.* seven-coordinate [$BiCl_3$([12]aneS_4)] [Bi–S 2.987(3)–3.072(3), Bi–Cl 2.569(4)–2.575(3) Å] and nine-coordinate [$BiCl_3$([18]aneS_6)] [Bi–S 3.146(4)–3.225(4), Bi–Cl 2.607(4) Å]. The polymeric network arises due to incorporation of bridging $MeSCH_2CH_2CH_2SMe$ ligands. We have shown previously that this and other related group 16 donor ligands can bind to Cu^I and Ag^I centres and in a small number of cases also yield complex polymeric arrays, although quite different in detail from the title compound.[9]

Further work is underway to establish whether this highly unexpected structural motif is replicated in other Bi^{III} complexes with group 16 donor ligands, and to understand the factors which influence the assembly of supramolecular arrays of this type.

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Notes and References

† *Crystal data* for $C_5H_{12}BiCl_3S_2\cdot H_2O$, M = 469.62, tetragonal, space group $P\bar{4}2_1c$, a = 16.440(10), c = 11.843(7) Å, V = 3200 $Å^3$, Z = 8, D_c = 1.949 g cm^{-3}, μ(Mo-Kα) = 117.26 cm^{-1}. A pale yellow block (0.40 × 0.35 × 0.10 mm) grown by slow evaporation of a solution of the compound in CH_2Cl_2 was mounted on a Rigaku AFC7S four-circle diffractometer. Data collection at 150 K using Mo-Kα X-radiation (λ = 0.710 73 Å), gave 1668 unique reflections of which 1183 with $F \geqslant 4\sigma(F)$ were used in all calculations. The structure was solved using direct methods[10] and developed by iterative cycles of least-squares refinement[11] and difference Fourier synthesis which revealed a $BiCl_3(MeSCH_2CH_2CH_2SMe)$ unit and a water molecule in the asymmetric unit. Crystallographic $\bar{4}$ symmetry generates the tetrameric unit and the three-dimensional array. The data were corrected for absorption using DIFABS[12] with the model at isotropic convergence (max., min. transmission factors = 1.000, 0.309, respectively). Some of the C atoms in the ligand backbone show quite high thermal motion, although alternative sites could not be identified, hence these were refined isotropically. Anisotropic thermal parameters were refined for the Bi, Cl and S atoms and H atoms associated with the dithioether were included in fixed, calculated positions (the H atoms associated with the H_2O solvent molecule were not located). At final convergence, R = 0.050, R_w = 0.066, S = 1.80 for 79 parameters. CCDC 182/1002.

Satisfactory spectroscopic and analytical data were obtained.

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