$\{Ag_5[\mu_2\text{-}S\text{-}(CH_2)_3\text{-}NHMe_2]_3[\mu_2\text{-}S\text{-}(CH_2)_3\text{-}NMe_2]_3\}^{2+}$, the First Thiolate Complex of a Metal with Trigonal Bipyramido-M_5-trigonal Prismo-S_6 Polyhedral Stereochemistry

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The synthesis and structure of $\{Ag_5[\mu_2\text{-}S\text{-}(CH_2)_3\text{-}NHMe_2]_3[\mu_2\text{-}S\text{-}(CH_2)_3\text{-}NMe_2]_3\}(ClO_4)_2$; the Ag_5S_6 core of the cage cation provides the only known case of an $[M_x(SR)_y]$ aggregate that can be described as a trigonal bipyramid of metal atoms enclosed within a regular trigonal prism of doubly bridging thiolate ligands.

Recent reports,[1—3] which include the relevant structural patterns found in metal thiolate complexes, show clearly the renewed interest in the metal complex chemistry of thiolates, mainly because of their biological significance. The preponderance of cage structures over monometallic and non-molecular compounds in $[M_x(SR)_y]$ aggregates[1] is shown particularly well by Cu^I and Ag^I (ref. 4) and can be rationalized in terms of the solubility of the complex species. Idealization of the structures found for $[Cu_4(SR)_6]^{2-}$,[5,6] $[Cu_5(SR)_6]^-$,[4] $[M_5(SR)_7]^{2-}$ ($M = Cu^I, Ag^I$,[7] and $[Ag_6(SR)_8]_p{}^{2p-}$ ($p = 1,2$),[8] have suggested topological relationships between the cage and metal polyhedra.[1]

While studying solution equilibria[9] between Ag^I and 3-dimethylaminopropane-1-thiol, which essentially behaves as a monofunctional thiolate ligand, we isolated several solid complexes.[10] We report here the synthesis and the structure of $\{Ag_5[S(CH_2)_3NMe_2]_3[S(CH_2)_3NHMe_2]_3\}(ClO_4)_2$, the Ag_5S_6 core of the cation being the first example of a bipyramido-M_5-trigonal prismo-S_6 polyhedral stereochemistry. The coexistence of protonated and unprotonated amine groups in γ-mercaptoamine complexes, as the stoicheiometry of some soluble species had already suggested,[10] is also shown here for the first time.

The pale yellow pentanuclear cage compound was obtained as crystals from solutions containing $AgClO_4$ and the ligand (ligand to metal mole ratio, 2—3 : 1) in a water–methanol mixture (1 : 5). Elemental analyses agreed well with the expected $Ag_5C_{30}N_6S_6Cl_2O_8H_{75}$. The i.r. spectrum was characterized by the absence of the band associated with a weak N-H-X ($X = ClO_4^-, BPh_4^-$) hydrogen bond (*ca.* 3100 cm^{-1}), by very weak absorptions at 2780 and 1380 cm^{-1}, which appear very clearly when the ligand is neither protonated nor co-ordinated,[11] and by a broad band centred at 2250 cm^{-1}. The crystal and molecular structure, determined by *X*-ray crystallography,† consists of $[Ag_5(SR)_3(SRH)_3]^{2+}$ cations (Figure 1) and somewhat disordered ClO_4^- anions. There is no evidence for cation–cation interaction.

The molecular cage cation, $[Ag_5(SR)_3(SRH)_3]^{2+}$, contains six doubly-bridging thiolate ligands, leading to trigonal planar co-ordination (Figure 2) for the silver atoms which are related by a two-fold axis [S(1)–Ag(1)–S(1′) 119.7°, Ag(1)–S(1) 2.508

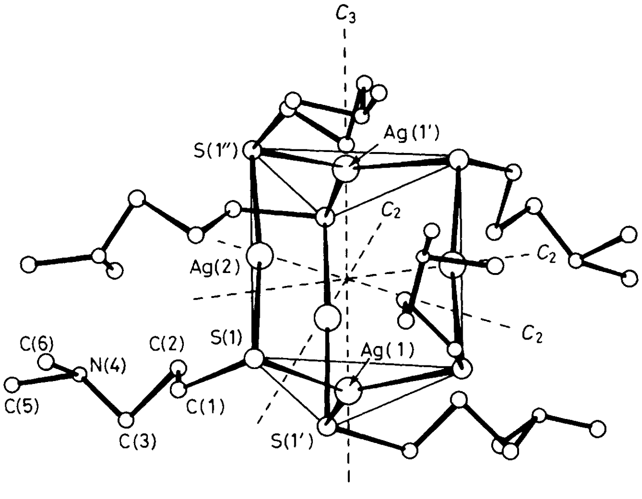

Figure 1. Structure of the pentanuclear $\{Ag_5[\mu_2\text{-}S\text{-}(CH_2)_3NHMe_2]_3[\mu_2\text{-}S(CH_2)_3NMe_2]_3\}^{2+}$ cation. H atoms have been omitted.

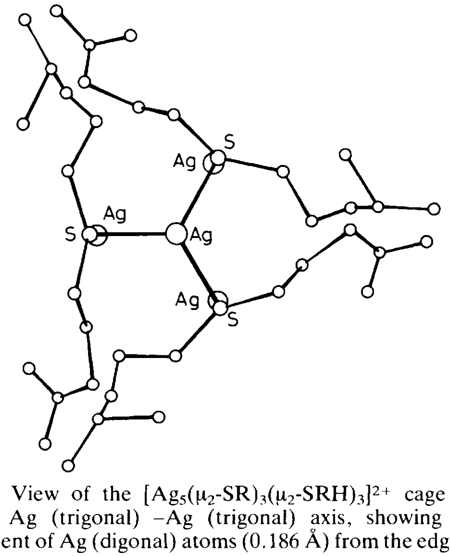

Figure 2. View of the $[Ag_5(\mu_2\text{-}SR)_3(\mu_2\text{-}SRH)_3]^{2+}$ cage along the threefold Ag (trigonal) –Ag (trigonal) axis, showing the slight displacement of Ag (digonal) atoms (0.186 Å) from the edges of the S_6 prism. H atoms have been omitted.

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† *Crystal data.* $C_{30}H_{75}Ag_5Cl_2N_6O_8S_6$, $M = 1450.61$, hexagonal, space group $P6_322$, $a = 13.630(2)$, $c = 16.078(3)$ Å, $Z = 2$, $D_c = 1.283$ g cm^{-3}, μ (Mo–K_α) = 19.33 cm^{-1}, $2\theta_{max.} = 50°$, crystal dimensions 0.1 × 0.1 × 0.15 mm. 2134 measured reflections including 1385 observed reflections with $I \geqslant 2.5\,\sigma(I)$ were collected using a Philips PW-1100 four circle diffractometer, Mo-K_α radiation, graphite monochromator, ω-scan technique, scan width 0.8°, scan speed 0.03° s^{-1}, 288 K, empirical absorption corrections. The structure was solved by direct methods and refined by full-matrix least-squares to give $R = 0.054$ and R_w 0.057 using MULTAN84 and SHELX76, respectively. The minimized function was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma(F_o)]^{-1}$. The chlorine atoms of the ClO_4^- anions are disordered on the three-fold axes, with an occupancy factor of 0.5 (determined by peak of difference synthesis). Oxygen and hydrogen atoms were not located. Attempts to define a model in order to locate oxygen atoms have not been successful, which suggests a spherical behaviour for these ions. Both enantiomers were refined and final atomic co-ordinates are given for those with lowest *R* value.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Å; Ag(1) is displaced out of the S_3 co-ordination plane by 0.148 Å], and digonal linear co-ordination for the three other silver atoms which are related by a three-fold axis [S(1)–Ag(2)–S(1″) 170.7°, Ag(2)–S(1) 2.289 Å]. Ag(2) atoms are displaced 0.186 Å from the edges of the S_6 prism towards the centroid of the cage and the dihedral angle between the plane defined by Ag(1)–Ag(1′)–S(1″) and S(1)–Ag(1)–Ag(1′) is 0.3°.

The most important feature of this structure is the unprecedented M_5S_6 core in which the M_5 polyhedron is a trigonal bipyramid and the S_6 polyhedron a trigonal prism. The only structures previously reported for M_5S_6 cores are those of $[Cu_5(SBu^t)_6]^-$, described as a trigonal bipyramido-Cu_5-trigonal antiprismo-S_6 (antiprismatic twist angle *ca.* 50°), and $[Ag_5(SBu^t)_6]^-$ described as isostructural with the Cu analogue.[4]

Two other notable structural features are (i) the observed distances between silver atoms of the same cage cation [Ag(1)–Ag(2) 3.357, Ag(2)–Ag(2′) 4.015 Å] and that of two consecutive silver atoms of different cages on the three-fold axis [Ag(1)–Ag(1i) 3.181 Å], which indicate no interaction between the silver atoms of different cages, and (ii) the intracage N–N distance between pairs of ligands diagonally opposed in the faces of the S_6 prism [N(4)–N(4′) 3.258 Å], which is within the range given in the literature for N–H–N hydrogen bond interactions.[12,13]

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