Crown Thioether Chemistry: Synthesis and Characterisation of Bis(1,4,7-trithiacyclononane)silver(I) Trifluoromethanesulphonate, an Octahedral Homoleptic Thioether Complex of Ag^I Showing Unusually Facile Oxidation

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1,4,7-Trithiacyclononane (9S3) reacts with soluble silver(I) salts to form $[Ag(9S3)_2]^+$, a monomeric complex that has a distorted octahedral structure and is readily oxidised to the silver(II) complex.

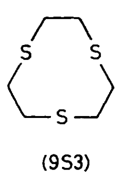
Earlier studies have shown that crown thioether ligands such as 1,4,7-trithiacyclononane (9S3) and 1,4,7,10,13,16-hexathiacyclo-octadecane (18S6) often impose novel electronic properties on transition metal ions.[1,2] For example, ligands of this class can facilitate access to uncommon oxidation states, as in the mononuclear rhodium(II) complex $[Rh(9S3)_2]^{2+}$.[3] Prompted by the possibility of unusual redox behaviour, and the well-known affinity of silver for thioether ligands, we have examined the reaction of the tridentate crown 9S3 with silver(I). In general, complexes of silver(I) exhibit a preference for linear two-co-ordination and, occasionally, tetrahedral four-co-ordination. Higher co-ordination numbers may be enforced by polydentate macrocyclic ligands but such complexes generally show irregular geometries and ambiguous co-ordination numbers due to poor 'fit' between metal ion and ligand.[4,5] On the other hand, 9S3 is uniquely well suited conformationally[6] to co-ordinate to a trigonal face, and for this reason it generally enforces octahedral co-ordination in $[M(9S3)_2]^{n+}$ complexes (*vide infra*). We report here the preparation, structure, and redox chemistry of $[Ag(9S3)_2](CF_3SO_3)$, the first homoleptic hexathioether complex of silver.

While reaction of one equivalent of 9S3 with silver trifluoromethanesulphonate in methanol gives $Ag(9S3)(CF_3SO_3)$, two equivalents of 9S3 give a white precipitate of $[Ag(9S3)_2](CF_3SO_3)$ in 50% yield. Conductivity measurements indicate that both of these complexes are 1 : 1 electrolytes in nitromethane solution. Recrystallisation of $[Ag(9S3)_2](CF_3SO_3)$ from methanol at 0 °C affords crystals suitable for diffraction studies.[†]

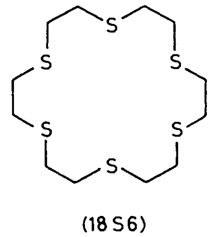
In the centrosymmetric $[Ag(9S3)_2]^+$ cation (Figure 1), the silver atom is sandwiched between the two 9S3 ligands to yield a six-co-ordinate complex with Ag–S distances ranging from 2.696(2) to 2.753(1) Å. While these distances are comparable with those in, *e.g.*, $[Ag_2(1,3,5\text{-trithiane})_5]^{2+}$ (which contains both four- and five-co-ordinate silver),[7] they exceed by *ca.* 0.2 Å the longest M–S distances so far reported for a 9S3 complex. The Ag co-ordination sphere deviates from octahedral geometry (idealised symmetry: D_{3d}) by virtue of a severe trigonal elongation, which manifests itself most clearly in the large difference between chelating and non-chelating *cis*-S–Ag–S angles [which have average values of 79.98(3) and 100.02(3)°, respectively].

Cyclic voltammetry of $[Ag(9S3)_2]^+$ (in $MeNO_2$ containing 0.1 M NEt_4BF_4 at a platinum wire electrode) shows a reversible oxidation wave at +1.30 V *vs.* normal hydrogen electrode (N.H.E.) ($\Delta E_p = 106$ mV at $v = 500$ mV s^{-1}). At slower scan rates the anodic current exceeds the cathodic owing to a rapid chemical reaction of the oxidised species. On electrolysis at 1.5 V *vs.* N.H.E. the oxidation product is visible as a transient blue coloration near the cathode.

E.s.r. spectroscopy confirms that oxidation yields a paramagnetic product. Chemical oxidation of $[Ag(9S3)_2]^+$ with Ce^{IV} (in MeOH) affords a deep blue solution that is stable at



(9S3)



(18S6)

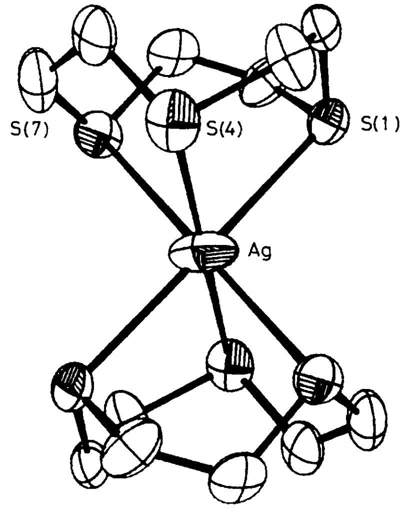


Figure 1. ORTEP drawing of the $[Ag(9S3)_2]^+$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity). Ligand atoms are numbered sequentially around the ring [S(1), C(2), *etc.*].

[†] *Crystal data:* $C_{13}H_{24}S_7F_3O_3Ag$, $M = 617.7$, orthorhombic, space group *Pnam* (a non-standard setting of *Pnma*; an attempt to refine the structure in space group $Pna2_1$ was unsuccessful), $a = 7.884(2)$, $b = 12.396(5)$, $c = 23.546(7)$ Å, $U = 2300.97$ Å^3, $Z = 4$, $D_c = 1.783$, $D_m = 1.78$ g cm^{-3} by flotation. A crystal of dimensions 0.5 × 0.3 × 0.2 mm was sealed in an *X*-ray capillary and mounted on an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation (0.71069 Å). 4726 reflections with $2\theta \leqslant 60°$ were measured. Three standard reflections were measured every hour and showed no decay. Calculations were performed with the CRYSTALS crystallographic programs on a VAX 11/750 computer, with atomic scattering factors from the usual source. An empirical absorption correction was applied. The S atoms were found from a three-dimensional Patterson map and the remaining atoms found by Fourier syntheses. All hydrogen atoms were located and refined with a group isotropic thermal parameter. Full-matrix least-squares refinement based on 1601 data with $F^2 > 3\sigma(F^2)$ converged to $R = 3.96\%$ ($R_w = 3.75\%$) for 122 parameters. The large anisotropic temperature factors associated with the trifluoromethanesulphonate anion and the location of the highest peak in the final difference map [1.6 eÅ^{-3} close to O(12)] suggest that the anion shows slight disorder. 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.

−70 °C but not at room temperature. At 149 K this solution exhibits an isotropic e.s.r. signal (g = 2.03) without resolved hyperfine splitting. The absence of ^{107,109}Ag hyperfine splitting (^{107}Ag: I = 1/2, 51.4%; ^{109}Ag: I = 1/2, 48.6%) may derive from the small nuclear magnetic moments of these isotopes (−0.1130 and −0.1299 nuclear magnetons, respectively), in conjunction with the substantial linewidth of the signal (50 G; 1 G = 10^{-4} T). These observations are consistent with formation of $[Ag(9S3)_2]^{2+}$, although they do not allow rigorous identification of the silver ion as the location of the odd electron. In this connection we note that free 9S3 and the monoadduct $[Ag(9S3)]^+$ are not electroactive below 1.65 V and 2.0 V *vs.* N.H.E., respectively.

The structural and electrochemical properties warrant further comment. The attainment here of a regular six-co-ordinate geometry contrasts with structurally characterised complexes of silver with other thioether ligands, which are either two-co-ordinate[8] or have polymeric structures with irregular geometries.[7,9,10] It apparently results from the unique combination of electronic and conformational properties of the 9S3 ligand. Electronically the strong interaction between Ag and thioether groups favours high co-ordination numbers. Conformational factors reinforce this electronic effect. Thus, the ligand torsional angles in $[Ag(9S3)_2]^+$ match those of the free ligand (within 2°) more closely than do those in any of the previously characterised $[M(9S3)_2]^{n+}$ (M = Fe^{II},[11] Co^{II},[12] Co^{III},[13] Ni^{II},[12] Cu^{II},[12] Ru^{II},[14] Rh^{III}[3]) complexes. This conservation of conformation reflects the rigidity of 9S3, and (in this case) the lack of strong stereochemical preferences of the d^{10} Ag$^+$ ion in complexes of high co-ordination number. Thus electronic and conformational factors combine to overcome the general preference of Ag^I for lower co-ordination numbers.

The ligand also plays an instrumental role in the unusual electrochemistry. Although thioether co-ordination usually stabilises *low* oxidation states,[15] this complex is readily oxidised. The oxidation is noteworthy for its relatively low potential (1.31 V *vs.* N.H.E.; *cf.* $E°(Ag^{2+/+})$ = 1.98 V[16]) and for its reversibility, both of which are unusual in Ag$^{II/I}$ electrochemistry. Presumably the relatively high co-ordination number enhances the 'electron-richness' of the metal. As a consequence, the $[Ag(9S3)_2]^{2+/+}$ potential is low compared to those of silver complexes with lower co-ordination number. Furthermore, the ligand facilitates reversible interconversion of the mono- and di-cation by providing a co-ordination environment that is compatible with both oxidation states. This is in sharp contrast to examples of stabilisation of Ag^{II} by other macrocyclic ligands such as cyclam.[17,18] In such cases the Ag^I complex is unobserved because disproportionation occurs in the presence of the ligand to generate metallic silver and the Ag^{II} complex.

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