

On the Transport and Selective Complexation of Silver(I) by Mixed Thioether–Oxa Crowns. The Single Crystal X-Ray Structures of $[Ag_n([15]aneS_2O_3)_n](PF_6)_n$ and $[Ag_2([15]aneS_2O_3)_3](PF_6)_2$ ($[15]aneS_2O_3 = 1,4,7$ -Trioxa-10,13-dithiacyclopentadecane)

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Reaction of $AgNO_3$ with $[15]aneS_2O_3$ followed by addition of NH_4PF_6 affords the complexes $[Ag_n([15]aneS_2O_3)_n](PF_6)_n$ and $[Ag_2([15]aneS_2O_3)_3](PF_6)_2$; the complex $[Ag_n([15]aneS_2O_3)_n]^{n+}$ is an S-bridged linear-chain polymer of $[Ag([15]aneS_2O_3)]^+$ units with formal $S_2O_3S_{bridge}$ coordination at Ag^I , while the binuclear species $[Ag_2([15]aneS_2O_3)_3]^{2+}$ shows distorted trigonal planar S_3 coordination at Ag^I with long-range interactions to three O-donors at each Ag^I .

The extraction and transport of Ag^I and related heavy metal ions across liquid–liquid interfaces and membranes have been achieved using polyether and polythioether cyclic ionophores.^{1,2} The complexation and transport of Ag^I has focused particularly on the use of mixed S- and O-donor crowns. However, the precise mode of coordination of these mixed-donor macrocycles to Ag^I is unknown, although it was observed that increasing the number of S-donors in the ionophore increased complex stability.^{1,3} Kinetically the S-donors in thioether crowns generally prefer to bind to metal ions in an *exo* manner,⁴ and so it has been assumed that *exo*-coordination of these ligands to Ag^I was occurring *via* binding at the S-donors. Thus, both 1:1 and 2:1 ligand–Ag complexes involving *exo*-coordination have been suggested^{1,3} implying that the ether O-donors are non-bonded. Indeed, *exo*-coordination of mixed S–O crowns has been observed, for example, with Pd^{II} ,⁵ while recent structural studies on Ag^I complexes of thioether macrocycles have confirmed further the affinity of thioether S-donors for soft d^{10} metal ions.⁶ We were interested in defining the precise modes of coordination of mixed S–O crowns to Ag^I , particularly with respect to the role of possible Ag–O(ether) interactions. Very few examples of Ag^I complexes of cyclic ether ligands have been reported,⁷ and, to our knowledge, no examples of Ag^I complexes of mixed S–O crowns have been fully characterised.

Reaction of $AgNO_3$ with one molar equivalent of $[15]aneS_2O_3$ ($[15]aneS_2O_3 = 1,4,7$ -trioxa-10,13-dithiacyclopentadecane) in refluxing $MeOH-H_2O$ (1:1 v/v) followed by addition of NH_4PF_6 affords a white product in high yield. The FAB mass spectrum of the complex shows molecular ion peaks at $M^+ = 359$ and 361 corresponding to

$[^{107}Ag([15]aneS_2O_3)]^+$ and $[^{109}Ag([15]aneS_2O_3)]^+$, respectively. This, together with IR and analytical data, confirmed the empirical formulation $[Ag([15]aneS_2O_3)]PF_6$ for the product. Single crystals of the complex were grown by slow evaporation of a solution of the complex in $MeNO_2$. The single crystal X-ray structure of $[Ag([15]aneS_2O_3)]PF_6^\dagger$ shows (Fig. 1) the complex to be an unusual S-bridged linear-chain polymer with each Ag^I bound to a distorted octahedral $S_2O_3S_{bridge}$ donor set. Each $[15]aneS_2O_3$ is coordinated to one Ag^I centre in an *endo* manner *via* three O-donors and two

[†] Crystal data for: $C_{10}H_{20}AgO_3S_2^+ \cdot PF_6^-$, $M = 505.23$, orthorhombic, space group $Pbca$, $a = 9.8118(4)$, $b = 23.2741(10)$, $c = 14.8501(8)$ Å, $V = 3391.1$ Å³ [from 2θ values of 84 reflections measured at $\pm\omega$ ($2\theta = 30$ – 32°), $\lambda = 0.71073$ Å, $T = 298$ K], $Z = 8$, $D_c = 1.979$ g cm⁻³, $\mu(Mo-K\alpha) = 1.572$ mm⁻¹. A colourless needle ($0.085 \times 0.15 \times 0.77$ mm) was mounted on a Stoe STADI-4 four-circle diffractometer. Data collection at 298 K using Mo-K α X-radiation ($\lambda = 0.71073$ Å), ω – 2θ scans and the learnt-profile method⁸ gave 3404 reflections ($2\theta_{max} 45^\circ$), 2114 unique ($R_{int} 0.076$), of which 1850 with $F \geq 6\sigma(F)$ were used in all calculations. A Patterson synthesis located the Ag and iterative cycles of least-squares refinement and difference Fourier synthesis revealed the remaining non-H atoms. The structure was then refined by the full-matrix least-squares technique (on F), with anisotropic thermal parameters for all fully-occupied non-H atoms; H atoms were included in fixed, calculated positions.⁹ Disorder was identified around C(5) and C(6) but with constraints (C–S 1.83, C–C 1.52, C–O 1.43 Å) applied to bond lengths in the affected region modelling was successful and showed two orientations with occupancies of 0.688(15) and 0.312(15). At final convergence, $R = 0.0383$, $R_w = 0.0632$, $S = 0.827$ for 217 parameters and the final ΔF synthesis showed no $\Delta\rho$ outwith the range 0.70 to -0.67 e Å⁻³.

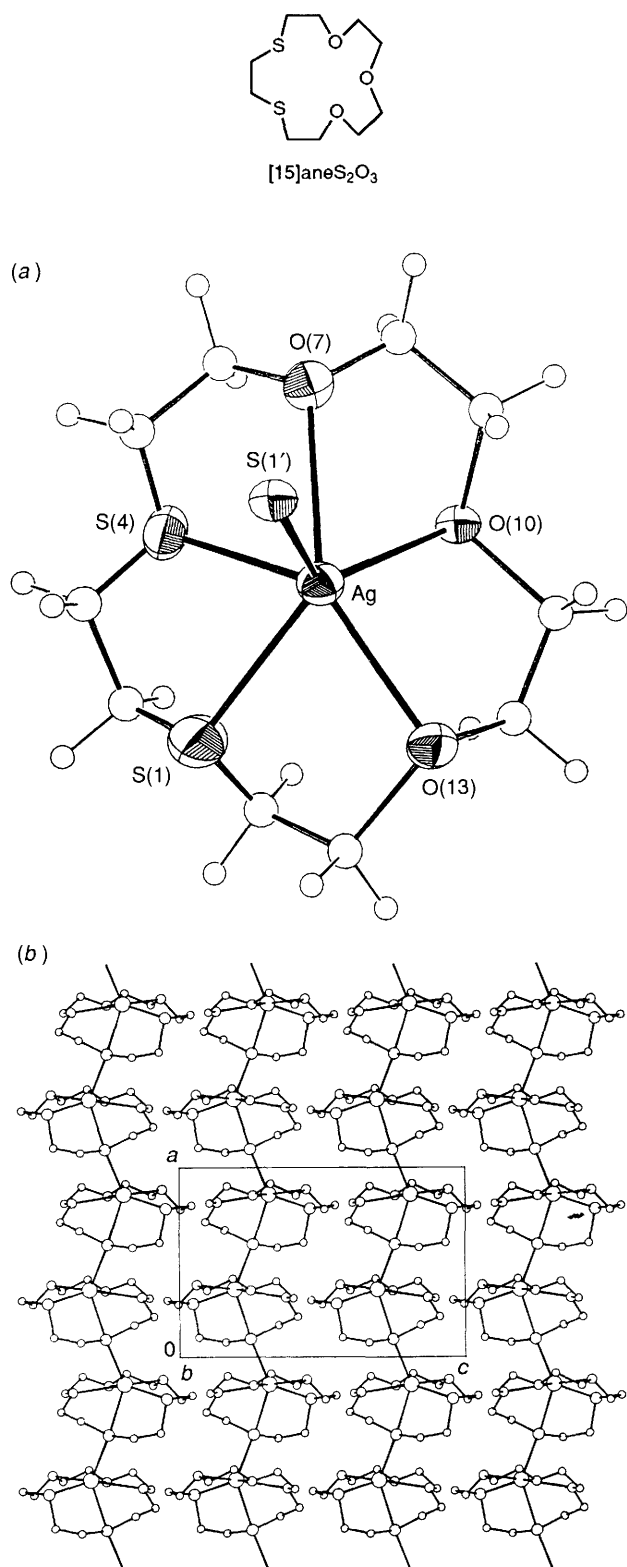


Fig. 1 (a) View of the coordination sphere of the metal ion in $[\text{Ag}([15]\text{aneS}_2\text{O}_3)]^+$ with numbering scheme adopted. (b) Projection of the structure along the b -axis showing linear-chain polymeric chains of $[\text{Ag}([15]\text{aneS}_2\text{O}_3)]^+$ ions. The PF_6^- anions have been omitted for clarity.

S-donors [$\text{Ag}-\text{O}(7) = 2.667(5)$, $\text{Ag}-\text{O}(13) = 2.690(4)$, $\text{Ag}-\text{O}(10) = 2.492(4)$; $\text{Ag}-\text{S}(4) = 2.540(15)$, $\text{Ag}-\text{S}(1) = 2.7996(12)$ Å]. Additionally, one of the S-donors bridges to another $[\text{Ag}([15]\text{aneS}_2\text{O}_3)]^+$ fragment [$\text{Ag}-\text{S}(1') = 2.5951(12)$ Å] to give a polymer chain of formally six coordinated Ag^{I} centres.

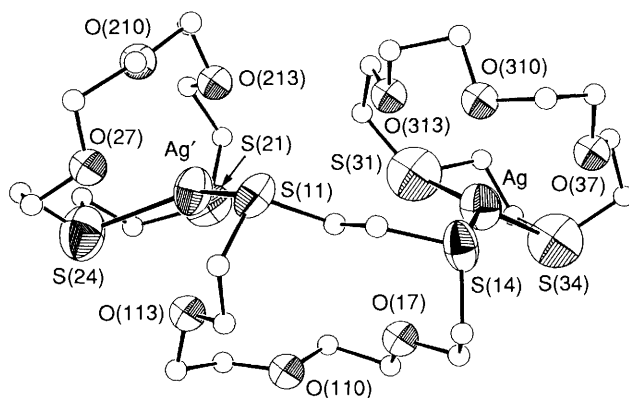


Fig. 2 View of the structure of $[\text{Ag}_2([15]\text{aneS}_2\text{O}_3)_3]^{2+}$ with numbering scheme adopted

The proposed formation of 2 : 1 $[15]\text{aneS}_2\text{O}_3$: Ag complexes also interested us since, assuming that S-binding prevails, the two thioether chelates in the species $[\text{Ag}([15]\text{aneS}_2\text{O}_3)_2]^+$ would be required to span a rather large bite angle to accommodate the expected tetrahedral coordination at Ag^{I} . Repeated attempts to isolate $[\text{Ag}([15]\text{aneS}_2\text{O}_3)]^+$ under a variety of conditions failed in our hands, although this species may well be present in solution. However, using stoichiometries of Ag : $[15]\text{aneS}_2\text{O}_3$ ranging from 1 : 1.5 to 1 : 3 we were able to isolate a highly unusual, and unexpected species $[\text{Ag}_2([15]\text{aneS}_2\text{O}_3)_3](\text{PF}_6)_2$. This formulation was confirmed by elemental analysis, FAB mass spectrometry and by a single crystal X-ray structure determination.[‡] Crystals of $[\text{Ag}_2([15]\text{aneS}_2\text{O}_3)_3](\text{PF}_6)_2$ were obtained by slow evaporation of a solution of the complex in MeNO_2 . Despite the presence of disorder in the macrocyclic rings, it is clear from the X-ray structure (Fig. 2) that each Ag^{I} ion in the cation is bound in a distorted trigonal planar geometry via three thioether donor atoms; two from a terminally bound bidentate macrocycle [$\text{Ag}-\text{S}(31) = 2.579(18)$, $\text{Ag}-\text{S}(34) = 2.604(18)$, $\text{Ag}'-\text{S}(21) = 2.540(6)$, $\text{Ag}'-\text{S}(24) = 2.625(8)$ Å], and one from the bridging $[15]\text{aneS}_2\text{O}_3$ macrocycle [$\text{Ag}-\text{S}(14) = 2.446(6)$, $\text{Ag}'-\text{S}(11) = 2.453(5)$ Å]. Significantly, the O-donors of the terminally bound macrocycles interact at long-range with the Ag^{I} centres [$\text{Ag}\cdots\text{O}(37) = 2.68(3)$, $\text{Ag}\cdots\text{O}(310) = 2.87(4)$, $\text{Ag}\cdots\text{O}(313) = 3.16(3)$, $\text{Ag}'\cdots\text{O}(27)$

[‡] Crystal data for: $\text{C}_{30}\text{H}_{60}\text{Ag}_2\text{O}_9\text{S}_6^{2+} \cdot 2\text{PF}_6^-$, $M = 1262.7$, monoclinic, space group $P2_1/n$, $a = 12.548(6)$, $b = 21.874(11)$, $c = 17.571(9)$ Å, $\beta = 94.359(26)^\circ$, $V = 4809$ Å³ (from 2θ values of 12 centred reflections with $2\theta = 30\text{--}32^\circ$, $\lambda = 0.71073$ Å, $T = 298$ K), $Z = 4$, $D_c = 1.744$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 1.211$ mm^{-1} . A colourless columnar crystal ($0.19 \times 0.25 \times 0.50$ mm) was mounted on a Stöe STADI-4 four-circle diffractometer. Data collection at 298 K using Mo-K α X-radiation ($\lambda = 0.71073$ Å), ω - 2θ scans and the learnt-profile method⁷ gave 5411 unique reflections, ($2\theta_{\text{max}} 45^\circ$), $R_{\text{int}} = 0.031$ of which 3935 with $F \geq 6\sigma(F)$ were used in all calculations. During data reduction a correction for linear isotropic decay (ca. 10%) was made. Following location of the Ag atoms by direct methods,¹⁰ the structure was refined by the full-matrix least-squares technique (on F),⁸ with anisotropic thermal parameters for Ag, P, F and ordered S atoms. One of the $[15]\text{aneS}_2\text{O}_3$ ligands is badly disordered and could only be refined by constraining all its bond lengths and angles and allowing for the presence of two conformations, which after refinement were found to be equally occupied. Although the other two $[15]\text{aneS}_2\text{O}_3$ ligands showed disorder to a lesser extent, it was still necessary to constrain the bond lengths and angles in these groups. The PF_6^- ions exhibited some residual disorder which could not be completely modelled. At final convergence, $R = 0.108$, $S = 5.94$ for 381 parameters and the final ΔF synthesis showed no $\Delta\rho$ outwith the range 1.6 to -1.0 $e \text{ \AA}^{-3}$. For both structures atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

= 3.080(16), Ag'...O(210) = 3.135(19), Ag'...O(213) = 2.855(23) Å]. Ag and Ag' are both displaced out of their local least-squares trigonal S₃ coordination plane by 0.39 Å towards the O-donors of the terminally-bound crowns.

This work confirms that ether O-donation is of relevance in the complexation of Ag^I by mixed S–O-donor ionophores, and that transport of Ag^I by such ligands may occur *via* Ag...O interactions (albeit at long-range in some cases) as well as Ag–S bonding. Further, the isolation of the above complexes confirms the formation of both *exo*- and *endo*-cyclic adducts of Ag^I with [15]aneS₂O₃, and reveals that these systems are not as simple as they may at first appear.

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