The Synthesis and Single-crystal X-Ray Structure of the Tetranuclear Silver(I) Complex $\{[Ag_2([18]aneS_2O_4)_2]_2\}(PF_6)_4$ ($[18]aneS_2O_4$ = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane)

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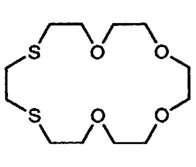
Reaction of $AgNO_3$ with $[18]aneS_2O_4$ ($[18]aneS_2O_4$ = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane) affords a 1 : 1 complex, the single-crystal X-ray structure of which confirms the formation of binuclear $[Ag_2([18]aneS_2O_4)_2]^{2+}$ dications; these dications are linked in pairs by a long S···S interaction to give an overall tetranuclear structure.

It has been shown previously that stepwise substitution of S-atoms for the O-atoms in cyclic crown ethers drastically changes the complexation properties of the macrocyclic ligand.[1] Thus, on replacing O-donor atoms with thioether S-atoms, the affinity of crown ionophores for group 1 and 2 metal ions decreases while affinity towards transition-metal complexes increases. This has led to the study of mixed O/S- and homoleptic S-donor ionophores as extraction and transport agents for heavy precious metal ions such as Ag^I.[2] We are currently investigating the structural properties of complexes between d- and p-block metal ions with saturated mixed O/S-donor ionophores[3,4] and are particularly interested in determining the mode(s) of coordination of these extractants with metal ions. We have found that these ligands tend to bind to platinum metal ions[3] in an *exo* manner *via* the thioether S donors, the O donors showing no significant interactions with the metal. There are few reports of complexation of Ag^I by O-donor ether macrocycles[4,5] and we wished to ascertain the extent of Ag–O interactions in large ring S/O donor complexes with Ag^I. We report herein the synthesis and structure of an unusual tetranuclear complex of Ag^I with $[18]aneS_2O_4$.



$[18]aneS_2O_4$

The reaction of $AgNO_3$ with $[18]aneS_2O_4$[6] in a 1 : 1 molar ratio in MeOH–H_2O followed by addition of NH_4PF_6 affords colourless crystals of a product of stoichiometry $[Ag([18]aneS_2O_4)]^+PF_6^-$. Spectroscopic and analytical data are consistent with the formulation of a 1 : 1 Ag^I–$[18]aneS_2O_4$ complex. FAB mass spectrometry shows peaks at *m/z* 953 with the correct isotopic distribution assigned to $[Ag_2([18]aneS_2O_4)_2PF_6]^+$ suggesting a dimeric structure in the solid state. Additionally, a peak is observed at *m/z* 1761 with the correct isotopic distribution assigned to a tetranuclear species $\{[Ag_4([18]aneS_2O_4)_4](PF_6)\}^+$. In order to confirm the nature of this product, a single-crystal X-ray structure determination was undertaken.

The single-crystal X-ray structure of the complex shows† (Fig. 1) an unusual dimeric $[Ag_2([18]aneS_2O_4)_2]^{2+}$ cation with Ag(1) bound to two S and one O donors of one macrocycle and to an S donor of another, Ag(1)–S(1) 2.698(3), Ag(1)–S(4) 2.556(3), Ag(1)–O(13) 2.564(7) and Ag(1)–S(24) 2.5214(24) Å, giving an overall tetrahedral geometry at Ag(1). The second metal ion, Ag(2), adopts a different and far more complicated stereochemistry. It is bound to two O and two S donors in one macrocycle and to an O donor of the other, Ag(2)–O(7) 2.661(6), Ag(2)–S(21) 2.555(3), Ag(2)–S(24) 2.7057(24), Ag(2)–O(30) 2.458(7), Ag(2)–O(33) 2.649(9) Å. The overall coordination geometry at Ag(1) and Ag(2) cannot be described in simple terms because the 'free' donor atoms

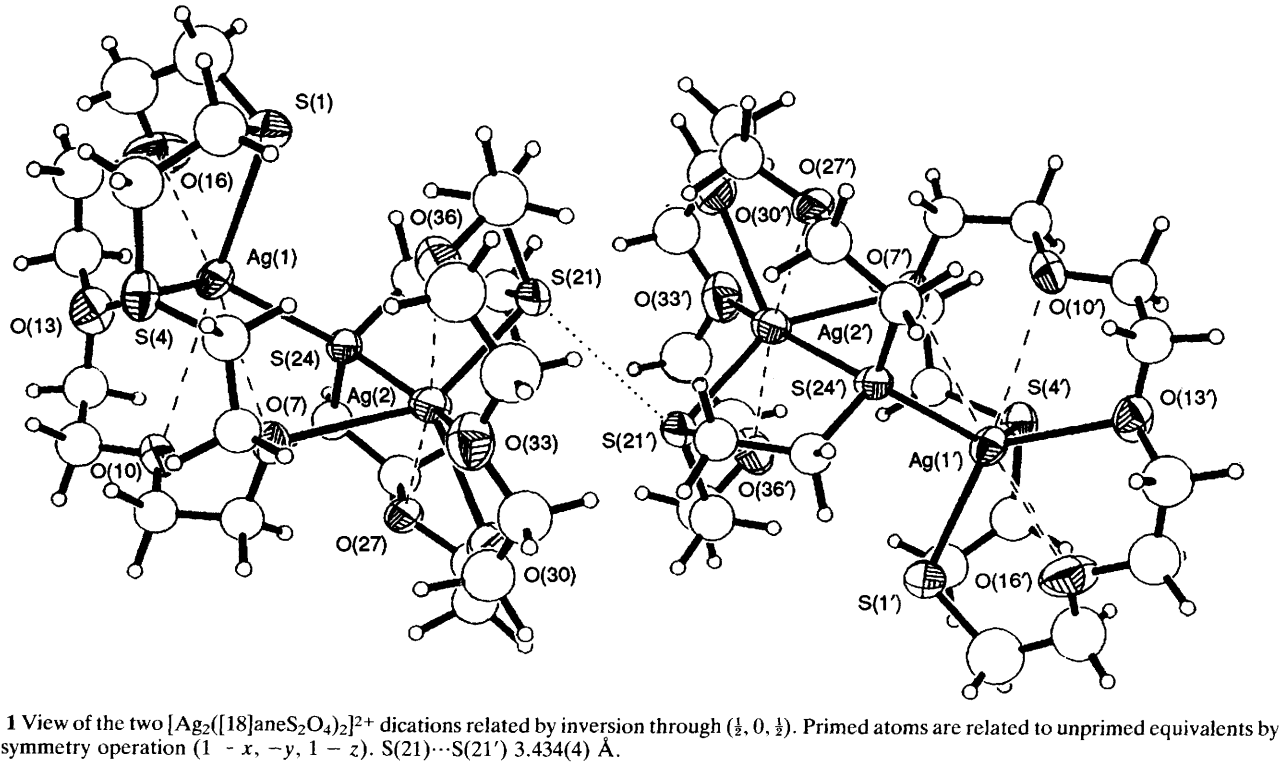


Fig. 1 View of the two $[Ag_2([18]aneS_2O_4)_2]^{2+}$ dications related by inversion through $(\frac{1}{2}, 0, \frac{1}{2})$. Primed atoms are related to unprimed equivalents by the symmetry operation $(1 - x, -y, 1 - z)$. S(21)···S(21') 3.434(4) Å.

show long-range interactions, $Ag(1)\cdots O(7)$ 3.371(5), $Ag(1)\cdots O(10)$ 3.097(6), $Ag(1)\cdots O(16)$ 2.712(11), $Ag(2)\cdots O(27)$ 2.873(6), $Ag(2)\cdots O(36)$ 2.905(8) Å. It is therefore clear that substantial $Ag\cdots O$ interactions are involved in the complexation of Ag^I. The $Ag(1)\cdots Ag(2)$ distance is 4.214(1) Å. Interestingly, the metal-free macrocycle $[18]aneS_2O_4$ adopts a conformation in which the S atoms lie in *exo*-positions with the cavity occupied by the ethylene bridge between the two sulfur atoms.[7] Thus, on complexation to Ag^I the conformation of the ligand alters dramatically and this suggests that introduction of stereochemical constraints in the form of bulky or rigid groups might enhance (or at least alter) the selectivity of the macrocycle. The related homoleptic thioether complex $[Ag_2([15]aneS_5)_2]^{2+}$ shows an asymmetrically bridged structure with Ag–S 2.529(3), 2.608(4), 2.558(4), 2.623(5) and 2.716(5) Å; $Ag\cdots S$(bridge) 2.537(3) and 2.486(3) Å,[8] while $[Ag([18]aneS_6)]^+$ shows an octahedral structure with Ag–S 2.6665(12) and 2.7813(10) Å.[9]

However, the most unusual feature of the solid-state structure of $[Ag_2([18]aneS_2O_4)_2]^{2+}$ is the presence of an $S\cdots S$ interaction with a symmetry-related second dication giving an overall tetranuclear structure (Fig. 1). The two dications lie on opposite sides of a crystallographic inversion centre with an $S(21)\cdots S(21')$ separation of 3.434(4) Å, less than twice the van der Waals radius of sulfur (3.70 Å). $S\cdots S$ interactions in radical cations and sulfonium species have been observed previously in cyclic and noncyclic species,[10] although this is the first example, to our knowledge, of apparent $S\cdots S$ interaction in cyclic crown complexes.

The above results indicate that the complexation and transport of metal ions such as Ag^+ by mixed thioether/oxy crown ethers is not a simple process. We have now defined the involvement not only of terminal and bridging Ag–S bonding, but of terminal and bridging Ag–O bonding or interactions, and the subsequent formation of oligomer and cluster species *via* long-range $S\cdots S$ interaction. The role of these types of $S\cdots S$ interactions in related systems is under investigation.

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Footnote

† *Crystal data* for $C_{24}H_{48}Ag_2O_8S_4{}^{2+}2PF_6{}^-$, $M = 1098.4$, monoclinic, space group $P2_1/c$, $a = 18.1728(20)$, $b = 11.0751(10)$, $c = 20.0893(14)$ Å, $\beta = 93.327(10)°$, $V = 4036.5$ Å^3 [from 2θ values of 40 reflections measured at $\pm\omega$ ($2\theta = 30$–$32°$, $\lambda = 0.71073$ Å), $T = 298$ K], $Z = 4$, $D_c = 1.807$ g cm^{-3}, μ(Mo-Kα) = 1.332 mm^{-1}. A colourless tablet (0.51 × 0.51 × 0.23 mm) was mounted on a Stoë Stadi-4 four-circle diffractometer. Data collection using Mo-Kα X-radiation, ω–2θ scans and the learnt-profile method (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22) gave 6972 reflections ($2\theta_{max}$ 45°), 5041 unique (R_{int} 0.023), of which 4412 with $F \geqslant 4\sigma(F)$ were used in all calculations. A Patterson synthesis was used to locate the two silver atoms, from which point the structure was developed by iterative cycles of least-squares refinement and difference Fourier synthesis. The structure was refined by full-matrix least squares (on F) with anisotropic thermal parameters for Ag, S, P, O and fully occupied F atoms. Disorder modelling was required for one $PF_6{}^-$ group (three orientations for equatorial F atoms) and in the O(16)–C(17)–C(18) region. Outside the disorder region, H atoms were included in fixed, calculated positions (SHELX-76: G. M. Sheldrick, University of Cambridge, 1976). At final convergence, $R = 0.0635$, $R_w = 0.0877$, $S = 1.307$ for 355 parameters and the final ΔF synthesis showed no feature above 0.90 eÅ^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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