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Silver Catalysed Macrocyclic Ether Formation: Crystal Structure of $[(CH_2O)_6Ag_2][Ag][AsF_6]_3$

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Crystals containing the $[(CH_2O)_6Ag_2]^{2+}$ cation, which possesses approximate D_{3d} symmetry with the two silver atoms each co-ordinated by alternate oxygens of a novel twelve membered macrocyclic ether, were isolated from the reaction of $(CH_2O)_3$ with $AgAsF_6$.

Oxymethylene trimer and tetramer are well known,[1] and long chain oligomers are important plastics. We now report the first synthesis of a macrocyclic ether with six alternating carbon and oxygen atoms, in the form of the complex salt $[(CH_2O)_6Ag_2][Ag][AsF_6]_3$, and its structure elucidation by *X*-ray diffraction. We have shown recently that $(CH_2S)_3$ and $(CH_2Se)_3$ react with $AgAsF_6$ in liquid sulphur dioxide to form $[\{(CH_2S)_3\}_5Ag_2][AsF_6]_2[SO_2]$[2] and $[\{(CH_2E)_3\}_2Ag][AsF_6][SO_2]$ (E = S, Se);[3] the analogous reaction of $(CH_2O)_3$ leads however to the unexpected formation of a twelve-membered ring.

A mixture of $AgAsF_6$ (1 mmol) and $(CH_2O)_3$ (2 mmol) was cooled to −186 °C in a Schlenk vessel and liquid SO_2 (25 cm^3) condensed in. After warming slowly to room temperature the mixture was stirred for 20 h in the dark. Extremely hydroscopic colourless crystals formed, which disintegrated if the last traces of SO_2 were removed *in vacuo*. Crystals suitable for *X*-ray diffraction were obtained by recrystallisation from liquid SO_2. The strongest i.r. absorptions were observed at 1328, 1232, 1140, 1010, 930, 700, 555, 522, and 390 cm^{-1} (Nujol mull).

Crystal data:† $C_2H_4AgAsF_6O_2$, $M = 356.8$, cubic, space group $Ia\bar{3}$, $a = 16.376(2)$ Å, $U = 4391.6$ Å^3, $Z = 24$, $D_c = 3.238$ g cm^{-3}. 4799 Diffractometer data [$2\theta_{max} = 45°$, $\mu(\text{Mo-K}_\alpha) = 72.8$ cm^{-1}] were reduced, after Lorentz polarisation and absorption corrections, to 473 unique reflections with $F > 4\sigma(F)$ which were used for all calculations. The three unique heavy atoms were located by a new Patterson interpretation program,[4] and the structure was refined with riding isotropic H and the other atoms anisotropic to R 0.039, R_w 0.041. The two independent silver, the arsenic, and two of the fluorine atoms lie on special positions with site symmetries

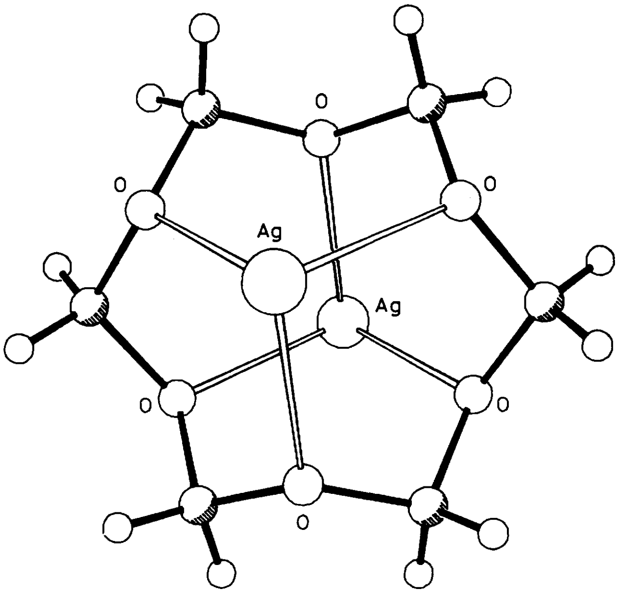

Figure 1. The $[(CH_2O)_6Ag_2]^{2+}$ cation.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23717 (4pp.) from the British Library. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.

3, $\bar{3}$, 2, 2, and 2 respectively; the remaining atoms occupy general sites.

The complex cation (Figure 1) possesses crystallographic $\bar{3}$ (C_{3i}) and approximate local $\bar{3}m$ (D_{3d}) symmetry, and contains two crystallographically equivalent silver atoms, each co-ordinated by alternate oxygen atoms of the twelve-membered $(CH_2O)_6$ ring [Ag–O 2.458(5) Å]. Octahedral co-ordination of each silver atom is completed by three fluorines [Ag–F 2.589(5) Å]. The remaining silver atom is co-ordinated octahedrally by six fluorines [Ag–F 2.655(6) Å] of different $[AsF_6]^-$ anions.

We expect that variations of this reaction will be of use for the preparation of a wide range of macrocyclic ethers.

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