Molecular Association in a Silver(I) Complex of a Planar Macrocyclic Ligand. *X*-Ray Crystal Structure of a Binuclear Silver(I) Complex

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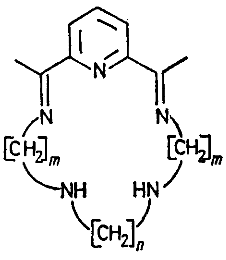
Summary In the dimeric complex $[Ag(2,3,2\text{-}N_5)]_2(ClO_4)_2$, two near-planar $[Ag(2,3,2\text{-}N_5)]^+$ cations are associated in a face-to-face fashion such that each metal ion interacts axially [at 2·748(10) Å] with one trigonally hybridised and co-ordinatively saturated nitrogen atom of the other macrocycle, the co-ordination geometry about each metal ion being pentagonal pyramidal.

We have recently described the structures of a number of metal complexes of the quinquedentate 'N_5' macrocyclic ligands (I), (II), and (III).[1] Most commonly these have pentagonal bipyramidal structures with the macrocyclic donors defining the pentagonal plane and the axial positions occupied by monodentate anions or solvent molecules.[1] In exceptional cases one or both of the axial positions may be unoccupied leading, respectively, to structures based on the pentagonal pyramid and the pentagonal plane.[2] We now describe a binuclear Ag^I complex in which one axial site of each almost planar macrocyclic unit is occupied by a nitrogen donor of the other macrocycle.

The orange diamagnetic complex $[Ag(2,3,2\text{-}N_5)]_2(ClO_4)_2$ was prepared from 2,6-diacetylpyridine and 1,9-diamino-3,7-diazanonane in methanol by a template method similar to those described previously. Satisfactory chemical analysis was obtained and i.r., u.v.–visible, and ^1H n.m.r. spectra confirmed that ring closure had occurred during the synthesis. Crystal data were collected on a G.E.XRD 5 diffractometer. $[Ag(2,3,2\text{-}N_5)]_2(ClO_4)_2$, $C_{32}H_{50}Ag_2Cl_2N_{10}O_8$, $M = 989·4$, monoclinic, $a = 12·154(8)$, $b = 20·650(9)$, $c = 16·461(8)$ Å, $\beta = 110·11(8)°$, $U = 3879.4$ Å^3, $Z = 4$, $D_m = 1·68(2)$ g cm^{-3}, $D_c = 1·69$ g cm^{-3}, Mo-K_α radiation, space group $I2/c$, 2066 independent reflections above background ($2\theta < 50°$) were used in the full-matrix least-squares refinement to R 0·066.†



(I) $m = n = 2$ (2,2,2-N_5)
(II) $m = 2$, $n = 3$ (2,3,2-N_5)
(III) $m = 3$; $n = 2$ (3,2,3-N_5)

The structure of the dimeric cation $[Ag(2,3,2\text{-}N_5)]_2^{2+}$ which has crystallographically imposed C_2 geometry is shown in Figure 1.‡ Each metal atom is bonded to the five

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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.

‡ Both perchlorate anions in the asymmetric unit are disordered.

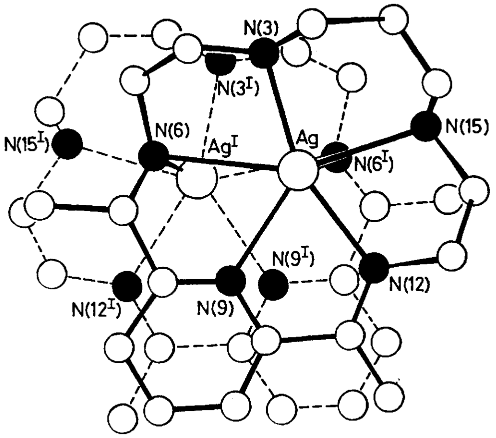

FIGURE 1. The $[\mathrm{Ag}(2,3,2\text{-}\mathrm{N}_5)]_2^{2+}$ dimer. Bonds in the two macrocycles are distinguished as full and dotted lines, respectively. The dimer is projected on to the AgN_5 equatorial plane of the top macrocycle.

nitrogen atoms of one (2,3,2-N_5) macrocycle in the expected manner but the two Ag(2,3,2-N_5) units are linked *via* axial Ag–N(6$^{\mathrm{I}}$) contacts of 2·748(10) Å, a distance only just longer than the Ag–N_{eq} bond lengths (Figure 2). The macrocycle is not very much distorted by the dimer formation except that Ag and N(6) are pulled towards the C_2 axis lying, respectively, 0·59 and 0·88 Å above the N_4 plane. Despite this, the maximum deviation of a contributing atom from the AgN_5 least-squares plane is 0·45 Å. The geometry of the co-ordination sphere is thus a relatively undistorted pentagonal pyramid.

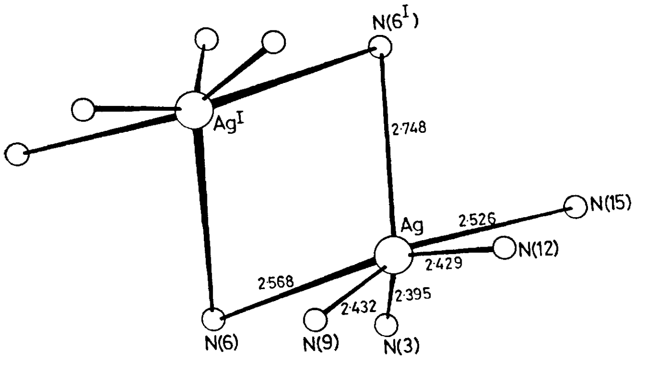

FIGURE 2. Bridging of the two AgN_5 equatorial planes in the dimer, viewed down the C_2 axis.

The question of principal chemical interest posed by this structure is the nature of the interaction between the two macrocycle units in the dimer since the axially positioned imino N(6) atoms appear to have no residual σ co-ordinating capacity, in that N(6)–C(7) has double bond length 1·29(2) Å and the arrangement around N(6) is more closely planar than tetrahedral (angles totalling 347·8°). There are no significant differences in the molecular dimensions about N(6) and the corresponding N(12) atom. While it is probable that $\mathrm{Ag}^{+}\cdots\mathrm{N}(6^{\mathrm{I}})^{\delta-}$ ion-dipole forces contribute to the associative interaction, purely coulombic forces are unlikely to be dominant because of the 'soft' nature of the Ag$^{\mathrm{I}}$ ion and because the ClO_4^- anions would provide a more effective negative axial field, as observed in other cases.[3]

We therefore suggest that a major source of the bonding between the two halves of the dimer has its origin in the delocalised π-systems of the two macrocycles.[4] The angle between the unsaturated parts of the two macrocycles is 11·9° and the closest contact is 3·25 Å for $\mathrm{C}(23)\cdots\mathrm{C}(23^{\mathrm{I}})$. In view of the short Ag–N(6$^{\mathrm{I}}$) distance it is likely that an important part of this interaction is a donation of π-electron density to the metal ion, analogous to that occurring in π-complexes of Ag$^{\mathrm{I}}$ with alkenes.[5] If this is the case, it might be considered that a more favourable overlap would result if the N(6$^{\mathrm{I}}$)–C(7$^{\mathrm{I}}$) bond, rather than the N(6$^{\mathrm{I}}$) atom, was associated with the Ag atom. However, molecular models show that such an arrangement brings the two pyridine rings closer to an eclipsed relationship. In fact, as shown in Figure 1, the two pyridine rings are displaced from each other by just under a ring diameter and form a staggered relationship with an unsaturated five-membered ring in the other macrocycle. This is similar to the kind of staggered arrangement predicted by Mulliken[6] to maximise π-donor–π-acceptor interactions in lamellar aromatic systems. A second possible reason for the N(6$^{\mathrm{I}}$) rather than the mid-point of N(6$^{\mathrm{I}}$)–C(7$^{\mathrm{I}}$) lying close to Ag may be the occurrence of weak $\mathrm{Ag}\cdots\mathrm{Ag}$ bonding since in so doing the metal atoms are brought closer together. The observed $\mathrm{Ag}\cdots\mathrm{Ag}$ distance of 3·177(1) Å is among the shortest contacts reported for Ag$^{\mathrm{I}}$ compounds (2·88 Å in silver metal) but there does not appear to be any agreement as to what constitutes a bonding distance in these compounds.[7] Thus the observed relationship of one macrocycle with respect to the other is almost certainly a compromise between different optimum bonding requirements in different parts of the complex. Dispersion forces will of course also contribute.

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