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THE STRUCTURES OF BOTH THE KINETIC AND THE THERMODYNAMIC ISOMERS OF 1,4,8,11-TETRAAZACYCLOTETRADECANESILVER(II) PERCHLORATE AS DETERMINED BY X-RAY ANALYSES

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The title compound obtained initially from the reaction mixture has a basket type configuration, but successive slow recrystallizations from weakly acidic aqueous solution resulted in structural isomerization to a thermodynamically more stable structure.

Kinetically controlled structural isomerism was found with the title silver(II) complex, $[AgL](ClO_4)_2$. Reaction of silver(I) perchlorate with the titled tetraaza fourteen-membered macrocyclic ligand (L) produces red-orange needles of $[AgL](ClO_4)_2$.[1] Slow recrystallization of the compound from 0.001 mol dm^{-3} perchloric acid solution gave a small amount of yellow block crystals along with a large amount of needles. Successive slow recrystallizations resulted in an increase in the amount of the yellow blocks. With successive recrystallizations, the color of the needles turned gradually orange from red-orange. Elemental analyses for both the needle and block crystals gave satisfactory results. The structures of the two types of crystals were determined by X-ray diffractometry.

Crystal Data.[2] The needle crystal : orthorhombic, Pbnm, a = 13.024(2), b = 14.510(1), c = 9.594(1) Å, U = 1813.1(3) Å^3, Z = 4, D_c = 1.87, D_m = 1.86 g cm^{-3}, R = 0.039 for 2159 independent reflections (2θ < 65°) ; the block crystal[3] : triclinic, P$\bar{1}$, a = 8.647(2), b = 8.794(2), c = 8.056(1) Å, α = 67.26(1), β = 117.53(1), γ = 122.92(1)°, U = 448.4(2) Å^3, Z = 1, D_c = 1.89, D_m = 1.88 g cm^{-3}, R = 0.026 for 3851 independent reflections (2θ < 70°).

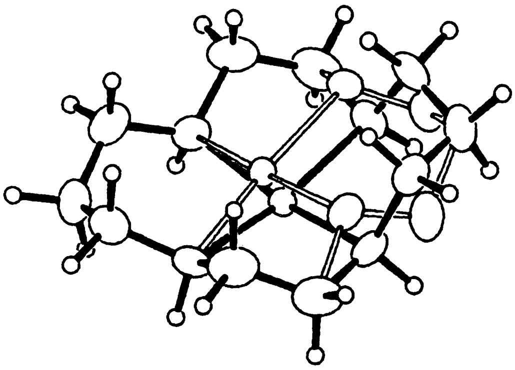

Figure 1.
Two disordered isomeric structures of $[AgL]^{2+}$ in the needle crystal.

The needle crystal consists of $[AgL](ClO_4)_2$ having two disordered isomeric structures (Figure 1). The main component (75 %)[4] has a basket configuration[5] (type 1) shown in Figure 2. The total stereochemistry of the minor component (25 %)[4] was essentially the same as that in Figure 3, which illustrates the structure found in the block crystal (type 2). In each crystal, the silver is surrounded by a square planar array of nitrogen atoms. In the needle crystal, no axial interaction was found and the silver in the type 1 structure is displaced 0.24 Å below the plane defined by the four nitrogens. On the other hand, in the block crystal, the silver sits in the N_4 plane and weak axial interactions with perchlorate oxygens result in a distorted octahedral coordination in which Ag-O is 2.788(2) Å.

As shown in Figure 4, electronic absorption spectra of the needles (curve 1) and the blocks (curve 2) are clearly different. In 0.01 mol dm^{-3} $HClO_4$, the spectrum of the type 2 complex (curve 2) remained unchanged at least three months in the dark at room temperature. On the other hand, the spectrum of the needles (curve 1) changed gradually with a decrease in the intensity (5.5 % decrease for initial 24 h) and the solution after three months showed almost the same spectral

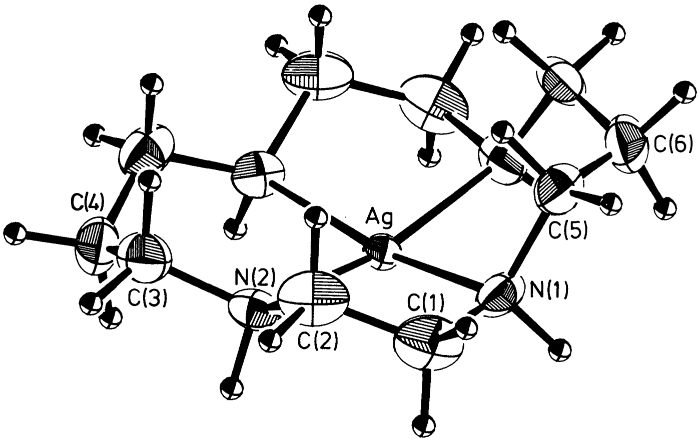

Figure 2. A perspective view of $[AgL]^{2+}$ in the main component of the two disordered structures in the needle crystal (Type 1 structure). The silver sits in a crystallographic mirror plane bisecting the two six-membered chelate rings. The Ag-N distances average 2.192(11) Å.

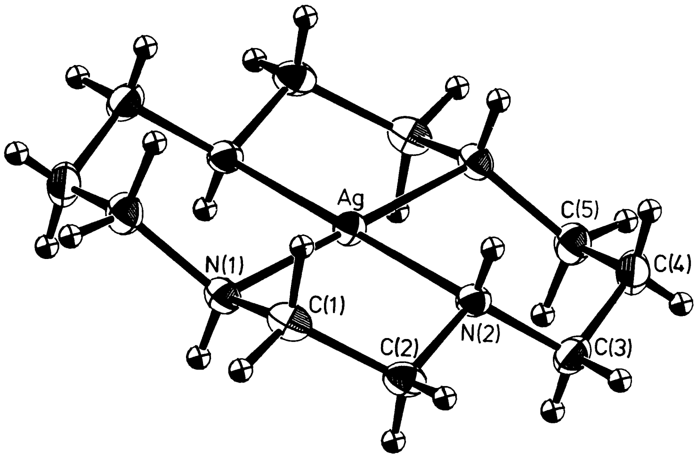

Figure 3. A perspective view of $[AgL]^{2+}$ in the block crystal (Type 2 structure). The silver sits on a crystallographic center of symmetry. The Ag-N distances average 2.158(2) Å.

pattern as the curve 2 spectrum. Taking into consideration the presence of 25 % type 2 complex in the needle crystal, the spectrum observed after three months indicates that 69 % of the type 1 complex decomposed and 31 % were converted to the type 2 complex. In 0.001 mol dm^{-3} NaOH solution, the spectrum of the type 2 complex lost slowly the intensity and the solution after 1 d became almost transparent with disappearance of the absorption bands around 330 nm, black precipitates (probably silver oxide) being deposited. On the other hand, the spectrum of the needles in 0.001 mol dm^{-3} NaOH changed rapidly with a decrease in the intensity to become almost the same as the spectrum 2 in Figure 4 after 2 h. This spectrum indicates that more than 64 % of the type 1 complex in the needles were converted to the type 2 complex under this condition.

These observations show clearly that the type 1 complex isomerizes to the type 2 complex in solution, although the compound decomposes under certain conditions.

Esr spectra of the needles and blocks in frozen 0.01 mol dm^{-3} $HClO_4$ solutions at 77 °K were very similar to each other and were essentially the same as the reported one.[1)]

The color change of the needles from red-orange to orange upon recrystallization may be caused by a decrease in the relative amount of the basket type structure. The relative amount of yellow blocks isolated increased with successive recrystallizations. The analogous silver(II) complex with the hexamethyl derivative of the ligand (L) has been reported to have the type 2 structure.[6)] These facts along with the solution behavior indicate that the type 2 structure is thermody-

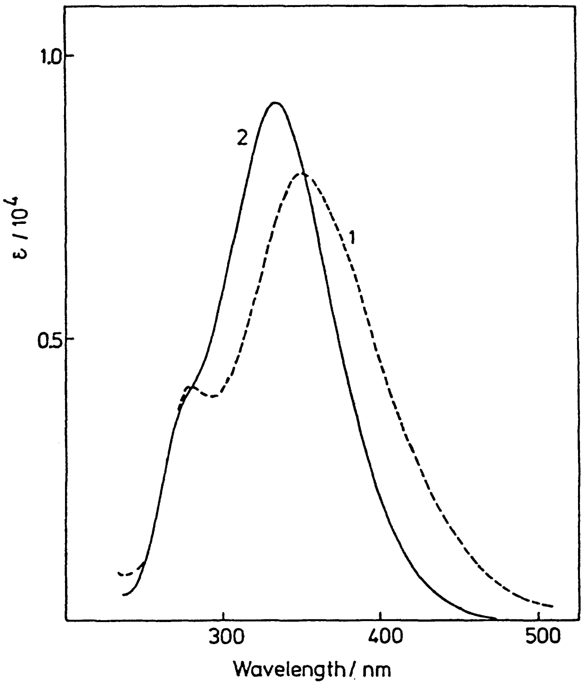

Figure 4.
Electronic absorption spectra of $[AgL](ClO_4)_2$ in 0.01 mol dm^{-3} $HClO_4$: Curve 1, the needle crystals; Curve 2, the block crystals. The spectra were measured immediately after sample dissolution.

namically more stable. However, the basket type structure would be favored for the formation of the silver(II) complex, since the complex formation reaction proceeds *via* disproportionation of Ag(I)[1)] and the basket type structure can provide a large vacant site for the reaction. It is most reasonable to consider the observed basket type stereochemistry to be a result of kinetic control. The ligand (L) forms type 2 complexes with the smaller first transition metal ions[7)] but type 1 complexes with larger ions such as Hg^{2+}.[8)] Since the radius of Ag^{2+} (0.89 Å)[9)] is intermediate, both the structure types could be isolated. The type 1 is kinetically formed initially while the type 2 structure is clearly the thermodynamically more stable isomer.

References

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