Photochemistry of the Supercomplex obtained on Complexation of the Hexacyanocobaltate(III) Anion by a Polyammonium Macrocyclic Receptor

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Enclosure of $Co(CN)_6{}^{3-}$ into a polyammonium macrocyclic ligand partially hinders the CN^- photoaquation reaction, showing that it may be possible to control and orient the ligand photosubstitution reactions of transition metal complexes by using appropriate receptor molecules.

There have been extensive photochemical and photophysical studies on complexes where a transition metal or lanthanoid ion is enclosed into a macrocyclic ligand in the last few years.[1] We report here results concerning the photochemical behaviour of 'supercomplexes' which are obtained when a transition metal complex is enclosed into a suitable macrocyclic receptor.

Lehn and coworkers[2] have recently synthesized polyammonium macrocycles which are able to form strong complexes with a variety of anions in aqueous solution. In particular they have shown that the fully protonated forms of the $32\text{-}N_8$ and $24\text{-}N_6$ macrocyclic ligands (Figure 1) are able to bind complex anions like $Fe(CN)_6{}^{4-}$, $Ru(CN)_6{}^{4-}$, and $Co(CN)_6{}^{3-}$, to yield species that can be considered as complexes of complexes: the metal ion is complexed by six cyanide ligands and the resultant $M(CN)_6{}^{z-}$ anion is, in its turn, complexed by the polyammonium macrocyclic ligand. We are carrying out a systematic investigation on the photochemical and photophysical behaviour of these supercomplexes, and we report here results obtained from studies of the photochemistry of $Co(CN)_6[32\text{-}N_8H_8]^{5+}$.†

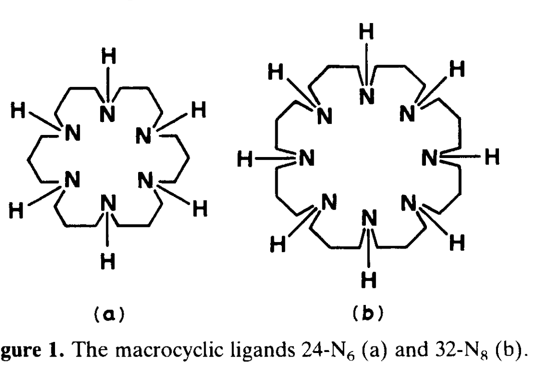

Figure 1. The macrocyclic ligands $24\text{-}N_6$ (a) and $32\text{-}N_8$ (b).

$Co(CN)_6{}^{3-}$ was chosen as the anion for the supercomplex in this study because its photochemical behaviour in aqueous solution is well known and very simple.[3] Excitation with light corresponding to the ligand-field bands (λ_{max}: 260 and 313 nm) leads to a clean aquation reaction (1) with quantum yield 0.31

$$Co(CN)_6{}^{3-} \xrightarrow[H_2O]{h\nu} Co(CN)_5(H_2O)^{2-} + CN^- \quad (1)$$

at 25 °C, independent of the excitation wavelength (254, 313, or 365 nm) and acidity of the solution (pH 2.5—7.5). There are two isosbestic points at 286 and 333 nm throughout the reaction, which has also been used to prepare pure $Co(CN)_5(H_2O)^{2-}$.[4] We have carried out experiments on a 2.0×10^{-3} M solution of $Co(CN)_6{}^{3-}$ containing 0.1 M KCl and 3.0×10^{-3} M HCl (pH 2.5) at 25 °C, using excitation at 313 nm, and we have obtained results in full agreement ($\Phi = 0.30 \pm 0.02$) with those previously reported.[3]

Solutions containing the $Co(CN)_6[32\text{-}N_8H_8]^{5+}$ supercomplex were prepared by adding a stoicheiometric amount of

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† Round and square brackets enclose the ligands which form the first and second co-ordination sphere of the central metal ion, respectively.

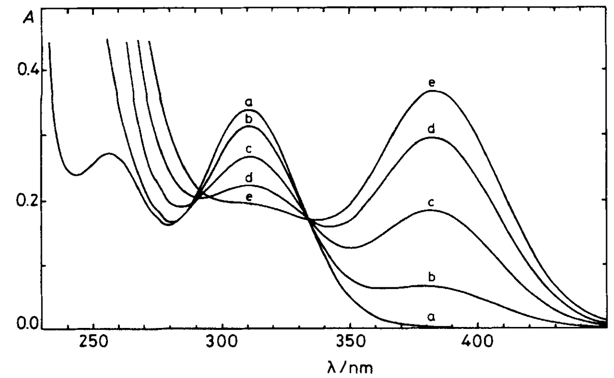

Figure 2. Spectral variations obtained upon irradiation (with 313 nm light) of $Co(CN)_6[32\text{-}N_8H_8]^{5+}$ in aqueous solution containing 3.0×10^{-3} M HCl and 0.1 M KCl. Curves a—e correspond to 0, 30, 105, 225, and 375 min of irradiation, respectively.

solid $(32\text{-}N_8H_8)Cl_8$ to the above solution. Under these conditions, practically 100% complexation is expected on the basis of the stability constant of the supercomplex,[2] the acidity constants of the polyammonium macrocyclic ligand,[2] and the protonation constant of $Co(CN)_6{}^{3-}$.‡ The absorption spectrum of the supercomplex is practically equal to the summation of the spectra of $Co(CN)_6{}^{3-}$ and $32\text{-}N_8H_8{}^{8+}$, except for a more intense absorption below 280 nm.

Excitation of this $Co(CN)_6[32\text{-}N_8H_8]^{5+}$ solution with 313 nm light caused the spectral changes shown in Figure 2. A comparison of the initial spectral changes with those observed upon irradiation of $Co(CN)_6{}^{3-}$ (see *e.g.*, ref. 3) shows that the supercomplex undergoes the same photoaquation as the free complex anion, *i.e.*, reaction (2).

$$Co(CN)_6[32\text{-}N_8H_8]^{5+} \xrightarrow[H_2O]{h\nu} Co(CN)_5(H_2O)[32\text{-}N_8H_8]^{6+} + CN^- \quad (2)$$

The slight red shift of the 'isosbestic point' at *ca.* 285 nm with irradiation time [not observed during the photoreaction of $Co(CN)_6{}^{3-}$] was demonstrated§ to be due to a thermal Cl^- anation of the pentacyanoaquo supercomplex, which is faster than the analogous anation of $Co(CN)_6{}^{3-}$ because of the high positive charge of the supercomplex. The quantum yield of reaction (2) was 0.10 ± 0.01 (average of three experiments), *i.e.* exactly one-third the quantum yield found for the photoaquation reaction (1) of the free complex anion. This result shows that in the supercomplex two-thirds (*i.e.*, four out of six) of the cyanide groups of the first co-ordination sphere cannot dissociate. This suggests that the structure of the supercomplex is of the type represented in Figure 3, where four coplanar CN^- ligands of the first co-ordination sphere are hydrogen-bonded to the ammonium groups of the macrocyclic receptor.[2a]¶ Another inference that can be drawn from this reduction of the quantum yield is that both in the free and complexed $Co(CN)_6{}^{3-}$ complex the effect of light excitation is equally distributed among the six CN^- ligands. This shows that the receptor does not affect the properties of the reactive metal-centred excited state, but simply hinders the escape of the four CN^- ligands, which are hydrogen-bonded to the macrocycle.

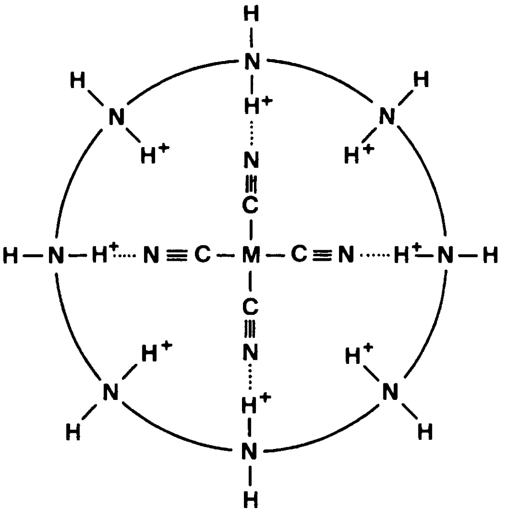

Figure 3. A possible structure for the $Co(CN)_6[32\text{-}N_8H_8]^{5+}$ supercomplex. The two CN^- ligands perpendicular to the plane of the macrocycle are not shown. An alternative structure could involve an eightfold hydrogen-bonding pattern, with the CN^- ligands located between two ammonium sites.[2a]

The result obtained shows that it is possible to protect co-ordination compounds against ligand photodissociation by using appropriate receptors. This method may help to establish the site of ligand release in mixed-ligand complexes, and it could yield information on the way in which a mixed-ligand complex is bonded into a receptor molecule.

Finally, it is worth noting that the anation reaction of the pentacyanoaquo supercomplex is a ligand-substitution process catalysed and oriented by binding to the receptor molecule, and it could represent a useful path for the synthesis of substituted cyano complexes.

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‡ Taken as equal to the second protonation constant of $Fe(CN)_6{}^{4-}$.[5]

§ The displacement is reduced when $KClO_4$ and $HClO_4$ are substituted for KCl and HCl in the irradiated solution.

¶ Space-filling models show that the structure of Figure 3 is a possible one for the supercomplex.