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Photochemistry of supramolecular species involving anionic coordination compounds and polyammonium macrocyclic receptors

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Abstract

Polyammonium macrocyclic receptors can bind anionic coordination compounds, namely those containing cyanide ligands. The driving force to maintain the adduct is essentially the coulombic attraction, but the possibility of formation of hydrogen bonds is also important to define the geometry of the structure. The second coordination sphere that results from the binding of the polyammonium macrocycle can change several physico-chemical properties of the metal coordination compound, such as spectroscopic, redox and photophysical properties as well as the photochemical reactivity. These changes permit to infer, in some favourable cases, details of the supramolecular structure in solution.

Keywords: Polyammonium macrocycles; Anion coordination; Second coordination sphere; Supramolecular photochemistry; Supramolecular photophysics

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1. Introduction

In recent years the study of supramolecular chemistry has grown very rapidly. There are several reasons for that, namely the continuous search for new chemical functions and the need to fill the gap which separates chemistry from biology [1–4]. On the framework of supramolecular chemistry, the effects of the second coordination sphere in some physico-chemical properties of anionic coordination compounds are described in this work, with particular emphasis on the interaction with light. The second coordination sphere is obtained through the binding between the anionic coordination compound, and positively charged polyammonium macrocycles. This supramolecular structure is maintained, not only by electrostatic attraction, but also by formation of hydrogen bonds involving appropriate ligands (e.g. cyanides) and the protonated nitrogens of the macrocycle. One interesting aspect of these supramolecular structures is the existence of a certain degree of molecular recognition of the receptors towards some substrates, as well as the possibility of modification of some physico-chemical properties and reactivity.

2. Polyammonium macrocyclic receptors as a second coordination sphere

2.1. Photochemical reactivity and structure

2.1.1. Supercomplexation with $K_3[Co(CN)_6]$: structural effects

The first photochemical study concerning the enclosure of a coordination compound into a polyammonium macrocyclic ligand was reported for the complex $[Co(CN)_6]^{3-}$ [5,6]. This coordination compound was chosen because its photochemical behaviour in aqueous solution and in absence of macrocycle is well known and very simple [7]. The stability constants of the supercomplexes between $[Co(CN)_6]^{3-}$ and polyammonium macrocyclic receptors are generally high and solutions containing equimolar concentrations of both components can be considered as forming ca. 100% of supercomplex [8–12]. Excitation in the d-d absorption bands (260 and 313 nm) of free $[Co(CN)_6]^{3-}$ leads to a clean photosubstitution of the cyanide ligand with a quantum yield of 0.30, Eq. (1).

$$[Co(CN)_6]^{3-} \underset{H_2O}{\overset{h\nu}{\rightarrow}} [Co(CN)_5(H_2O)]^{2-} + CN^- \qquad (1)$$

In the presence of one or more equivalents of the macrocycles reported in Fig. 1, the absorption spectra of the supercomplex is practically equal to the summation of the spectra of their components. This behaviour is quite general because, as we will see through this work, the d–d absorption bands of the supercomplex are not usually changed in their position and intensity.

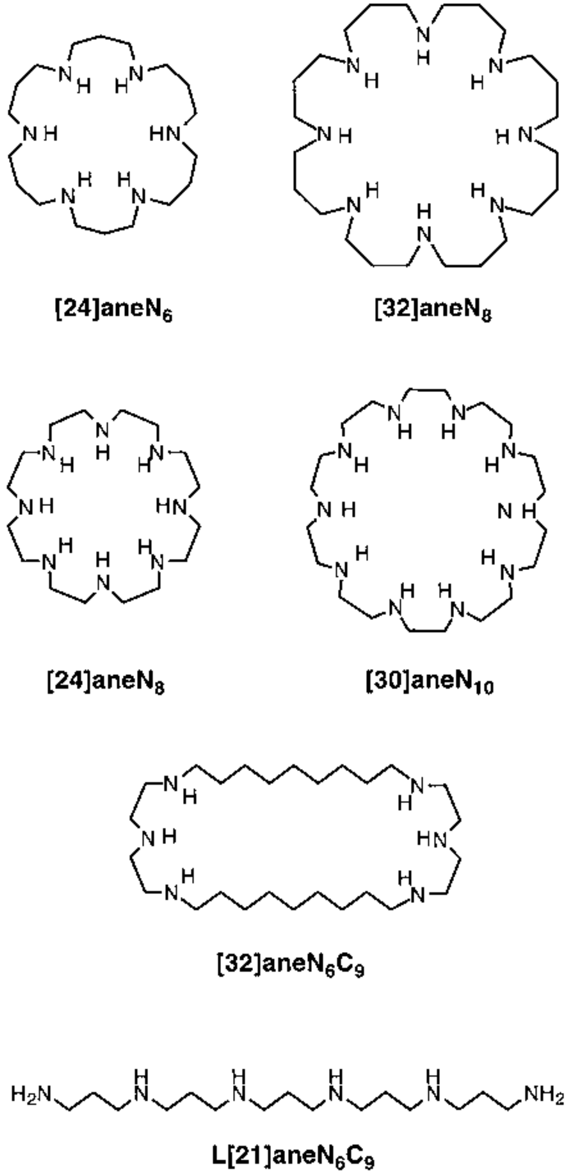
The photoaquation reaction, Eq. (1), carried out in the presence of the macrocycles is qualitatively identical to the photoaquation of the free complex, the same isosbestic points being maintained. However, there is an important quantitative difference: the quantum yield of the photosubstitution reaction is decreased by a factor of: (i) 3 in the case of the supercomplexes with macrocycles containing 32 atoms; (ii) 2 if the macrocycle possesses 30 atoms or less and (iii) 1.5 in the case of the linear polyammonium ligand (Table 1).

These results were interpreted on the basis of the following premises: (i) in both free and complexed $[Co(CN)_6]^{3-}$ the effect of light excitation is equally distributed among the six CN^- ligands; (ii) four CN^- ligands out of six are involved in hydrogen bonding with the protonated nitrogens of the macrocycle containing 32 atoms and are thus prevented to escape, explaining the reduction of the photoaquation by a factor of 3; (iii) in the case of the macrocycles with 30 or less atoms, three out of six cyanide ligands are involved in hydrogen bonding, and only two cyanide ligands are involved in the case of the linear polyammonium receptor.

The macrocyclic receptors reported in Fig. 1 are different in their charge and dimensions. The charge seems to have no effect. As an example, both $[24]aneN_8H_8^{8+}$ and $[24]aneN_6H_6^{6+}$ reduce the photoaquation by the same amount. According to the CPK models it can be shown that in the case of a macrocycle containing 32 atoms, the dimension of the macrocycle allows the formation of four hydrogen bonds while in the case of the smaller macrocycles only three hydrogen bonds can take place.

The results of the photochemical reactivity were used to infer some details about the structure of the supercomplex in solution. In the case of the macrocycles containing from 24 to 30 atoms there is no ambiguity and the hydrogen bonding seems to involve three ammonium groups of the macrocycle and three cyanide ligands positioned on a face of the octaedron. However, in the case of $[32]aneN_8H_8^{8+}$, two different structures are possible: (a) '*belt*'; (b) '*boat*', see Fig. 2.

In the first case, only the four equatorial cyanide ligands participate, while in the second case three equatorial and one axial cyanide ligands are involved in hydrogen bonding. Some controversy has arisen from which of the configurations is adopted by the supercomplex in solution. In the case of the macrocycle $[30]aneN_{10}H_{10}^{10+}$ there is evidence that in both solid state [9,12] and solution [13,14] the coordination compound does not reside in the cavity. However, Bencini et al. have found that the equilibrium constants for the formation of the adducts of $[Co(CN)_6]^{3-}$ with equally protonated forms of [27]aneN_9, [30]aneN_{10}, [33]aneN_{11} and [36]aneN_{12} (which should decrease with increasing ring dimension) are unexpectedly high in the case of 33-atom receptor [12]. Furthermore, the association constants of



[24]aneN_6 **[32]aneN_8**

[24]aneN_8 **[30]aneN_{10}**

[32]aneN_6C_9

L[21]aneN_6C_9

Fig. 1. Polyaza macrocyclic receptors: in [*m*]aneN_n, *m* stands for the number of atoms in the cycle and *n* for the number of nitrogens; the exception is the linear receptor L[21]aneN_6.

Table 1
Quantum yields for photoaquation of $[Co(CN)_6]^{3-}$ and of its supercomplexes with polyammonium macrocycles[a]

	pH	Φ_0	Φ	Φ_0/Φ
$[Co(CN)_6]^{3-}$	1.0	0.33		
	1.2–5.0	0.30		
$\{[Co(CN)_6]\cdot[24]aneN_6H_6\}^{3+}$	2.5		0.15	2
$\{[Co(CN)_6]\cdot[24]aneN_8H_7\}^{4+}$	2.5		0.15	2
$\{[Co(CN)_6]\cdot[24]aneN_8H_8\}^{5+}$	1.0		0.16	2
$\{[Co(CN)_6]\cdot[30]aneN_{10}H_{10}\}^{7+}$	2.3		0.14	2
$\{[Co(CN)_6]\cdot[32]aneN_6H_6C_9\}^{5+}$	1.2		0.11	3
$\{[Co(CN)_6]\cdot[32]aneN_8H_8\}^{5+}$	2.5		0.10	3
$\{[Co(CN)_6]\cdot L[21]aneN_6H_6\}^{3+}$	2.5		0.22 ± 0.01	1.4

[a] $[[Co(CN)_6]^{3-}]=2.0\times10^{-3}$ M; $[\text{macrocycle}]=2.0\times10^{-3}$ M, except for $[24]aneN_6H_6^{6+}$, 4.0×10^{-3} M and $L[21]aneN_6H_6^{6+}$, 6.0×10^{-3} M; $NaClO_4$ 0.1 M [6,13].

$[Co(CN)_6]^{3-}$ with 6-protonated forms of $[24]aneN_6$, $[32]aneN_6$–C_7 and $[38]aneN_6$–C_{10} ($\log K=3.9$, 5.4 and 3.5, respectively) show a peak for the 32-atom ring [15]. These results suggest that the 'belt' structure is adopted by the supercomplex in solution.

2.1.2. Supercomplexation with $[Co(CN)_5(H_2O)]^{2-}$. 'Belt' structure

More evidence for the '*belt*' structure was obtained through the study of the photochemical and thermal reactivity of the photoproduct $[Co(CN)_5(H_2O)]^{2-}$ [16]. In the presence of excess bromide, a thermal anation to produce $[Co(CN)_5Br]^{3-}$ occurs (40°C, pH 1.0), its rate constant being increased by the presence of the macrocycle $[32]aneN_8H_8{}^{8+}$. According to this result the ligand water seems not to be involved in the binding with the macrocycle.

$$[Co(CN)_5(H_2O)]^{2-}\xrightarrow[H_2O]{h\nu}[Co(CN)_4(H_2O_2)]^{-}+CN^{-} \tag{2}$$

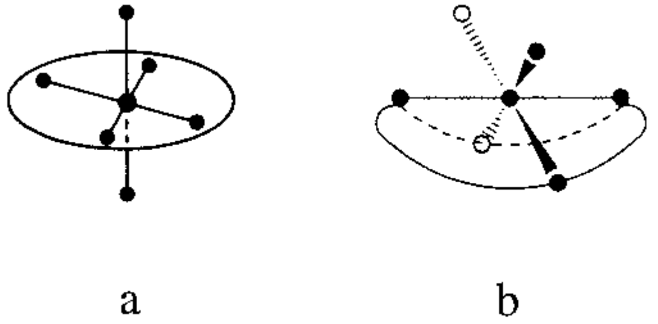


Fig. 2. The '*belt*' (a) and '*boat*' (b) structures in solution for supercomplexes involving polyammonium macrocycles that bind four ligands of an octahedral anionic metal transition complex [16].

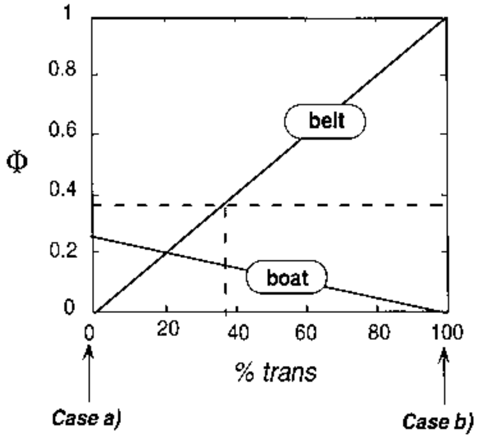


Fig. 3. Predicted quantum yield, Φ, for Eq. (2) according to the fraction of light absorbed by the ligands *trans* to H_2O in $[Co(CN)_5(H_2O)]^{2-}$, for each structure of Fig. 2.

The photoreaction of free $[Co(CN)_5(H_2O)]^{2-}$, Eq. (2), is much less efficient than the previous example with a quantum yield of $\Phi = 0.003$ at 313 nm and pH 1.0. Addition of the macrocycle $[32]aneN_8H_8{}^{8+}$ reduces the quantum yield approximately threefold: $\Phi/\Phi_0 = 0.36 \pm 0.02$, where Φ and Φ_0 correspond to the quantum yield in presence and in absence of the macrocyclic receptor, respectively. As in the previous example, the absorption spectra is practically not affected by the presence of the macrocycle.

In which concerns the photoreaction, there is now the possibility of light excitation not to be equally distributed among the five CN^- ligands. Two extreme cases could be considered: (a) exclusive *cis*-substitution; (b) exclusive *trans*-substitution, see Fig. 3. At this point we can predict (as in the case of the first photosubstitution) the rates between the quantum yields in the presence and absence of the macrocycle. In case (a), the 'belt' structure should completely quench the photoaquation while the '*boat*' structure should reduce the quantum yield to 1/4 of the initial value. In case (b), the '*belt*' structure should not affect the photoaquation while the '*boat*' structure should completely quench the process.

Actually it can not be predicted how the excitation light is distributed among the *cis* and *trans* cyanide ligands. Considering all of these possibilities, i.e. that the *trans* cyanide can get from 0% (100% to the *cis* cyanides) to 100% (0% to the *cis* cyanides) of the excitation light, the following expressions account for the predicted ratio of quantum yields,

$$\frac{\Phi}{\Phi_0} = x \times 1 + (1 - x) \times 0 \qquad \text{'belt' structure} \tag{3}$$

$$\frac{\Phi}{\Phi_0} = x \times 0 + (1 - x) \times \frac{1}{4} \qquad \text{'belt' structure} \tag{4}$$

where x is the molar fraction of the light that is absorbed by the *trans* cyanide. The experimental ratio is 0.36 ± 0.02 which allows to conclude not only that the '*belt*' structure is predicted (see Fig. 3), but also that the excitation light is distributed ca. 36% for the *trans* cyanide and the remaining 64% for the equatorial plane containing the four *cis* cyanides. These conclusions are only valid for the excitation wavelength of 313 nm and are in agreement with the results of Wrighton and Bredesen [17]. These authors verified that the quantum yield for cyanide release in $[Co(CN)_5(H_2O)]^{2-}$ depends on the irradiation wavelength ($\Phi = 0.003$ at 313 nm and 0.001 at 366 nm). At 313 nm, the main absorption band was assigned [17,18] to a transition that populates essentially the $d_{x^2-y^2}$ orbital, labilizing the equatorial cyanides, while at 366 nm the trans cyanide is more labilized.

In conclusion, by means of supercomplexation, information about the supercomplex structure in solution as well the photosubstitution mechanisms in $[Co(CN)_5(H_2O)]^{2-}$ can be obtained.

2.1.3. Coulombic effects

2.1.3.1. Supercomplexation with $K_3[Co(CN)_5Br]$. The next example of the effects of supercomplexation concerns the photoaquation of the complex $K_3[Co(CN)_5Br]$, Eq. (5).

$$[Co(CN)_5Br]^{3-} \xrightarrow[H_2O]{h\nu} [Co(CN)_5(H_2O)]^{2-} \tag{5}$$

As in the previous examples, addition of the macrocycle practically does not change the absorption spectra but the quantum yield of the photoreaction is reduced in the presence of $[24]aneN_6H_6{}^{6+}$, $[24]aneN_8H_8{}^{8+}$ and $[32]aneN_8H_8{}^{8+}$, Table 2 [19]. It appears that: (i) the photoaquation of $[Co(CN)_5Br]^{3-}$ is quenched much more than that of $[Co(CN)_6]^{3-}$, or $[Co(CN)_5(H_2O)]^{2-}$ and (ii) the order of the quenching ability of the three receptors on $[Co(CN)_5Br]^{3-}$ parallels their ionic charge rather than their dimensions. The quenching of $[Co(CN)_5Br]^{3-}$ photoreaction is therefore ascribed to the positive charge of the adduct between complex and receptor, which increases the rate of the back recombination between Br^- and $[Co(CN)_5]^{2-}$ formed in the primary photodissociation step. The question now is: why is this effect not observed when the leaving ligand is cyanide? The answer is probably found on the fact that the pK_a of hydrogen cyanide is 9.31 (25°C) [20]. At

Table 2
Quantum yields for photoaquation of $[Co(CN)_5Br]^{3-}$ and of its supercomplexes with polyammonium macrocycles[a]

	pH	Φ_0	Φ	Φ_0/Φ
$[Co(CN)_5Br]^{3-}$	1.0–4.7	0.23		
$\{[Co(CN)_5Br] \cdot [24]aneN_6H_6\}^{3+}$	3.1		0.05	4
$\{[Co(CN)_5Br] \cdot [24]aneN_8H_8\}^{5+}$	1.0		0.015	16
$\{[Co(CN)_5Br] \cdot [32]aneN_8H_8\}^{5+}$	3.1		0.02	12

[a] $[[Co(CN)_5Br]^{3-}] = 1 \times 10^{-3}$ M, [macrocycle] $= 2 \times 10^{-3}$ M [19].

the pH values used to carry out the photoaquations (acidic pH, in order to ensure the fully protonation of the macrocycles), the free cyanide ligand is immediately protonated explaining the absence of charge effects.

2.1.3.2. The $[Co(EDTA)]^{-} \cdot I^{-}$ system. Photoinduced electron transfer can occur between iodide and $Co(EDTA)^{-}$, Eq. (6). This system exhibits an ion–pair charge transfer band (IPCT) in spite of the same signal of the charges of its components [21,22].

$$[Co(EDTA)]^{-} \cdot I^{-} \xrightarrow[I^{-}]{hv} [Co(EDTA)]^{2-} + I_3^{-} \tag{6}$$

Absorption of light by the IPCT band gives rise to a photo-induced electron transfer from the iodide to the Co(III) complex with production of iodine (I_3^{-}) and $[Co^{II}(EDTA)]^{2-}$. In the presence of polyammonium macrocycles, the association constant between $[Co(EDTA)]^{-}$ and I^{-} is increased, but no effect is found on the photochemical reactivity. This effect can be easily explained when considering for example the supercomplex $\{[Co(EDTA)] \cdot [32]aneN_8H_8\}^{7+}$ which has a very high net positive charge that favours the association constant of ion–pair formation with iodide. However, in the electron transfer reaction, the leaving group is the uncharged iodine radical, $I^{\bullet}$, that is not affected by the supercomplex positive charge, leading to unchanged quantum yield.

2.1.4. Supercomplexation with $K_3[Cr(CN)_6]$ and $K_2[Cr(CN)_5(H_2O)]$. Control of the thermal and photochemical aquation: more evidence for the 'belt' structure

The hexacyanochromate(III) ion undergoes a photoaquation reaction analogous to that of $[Co(CN)_6]^{3-}$, Eq. (7), but unlike the cobalt complex, it also exhibits a thermal aquation reaction, Eq. (8), complicated by numerous secondary processes involving additional loss of cyanide ligands. The thermal aquation rate constant and the photoaquation quantum yield of $[Cr(CN)_6]^{3-}$ are reduced by a factor of 40 and 3, respectively, when the complex forms a 1:1 adduct with $[32]aneN_8H_8{}^{8+}$, Table 3. The decrease on photoaquation quantum yield is identical to that previously found for the similar adduct with $[Co(CN)_6]^{3-}$ and most probably the supercomplex possesses the same 'belt' structure, Fig. 2(a). On the other hand, the same macrocycle has practically no effect on the photoaquation of $[Cr(CN)_5(H_2O)]^{2-}$, Eq. (9), and a very small effect on the thermal reaction of this complex, Eq. (10), actually considered as a slow-fast, two-step process, Eqs. (10a, b) [23].

$$[Cr(CN)_6]^{3-} + H_3O^{+} \xrightarrow{hv} [Cr(CN)_5(H_2O)]^{2-} + HCN \tag{7}$$

$$[Cr(CN)_6]^{3-} + H_3O^{+} \xrightarrow{k_1} [Cr(CN)_5(H_2O)]^{2-} + HCN \tag{8}$$

$$[Cr(CN)_5(H_2O)]^{2-} + 2H_3O^{+} \xrightarrow{hv} fac - [Cr(CN)_3(H_2O)_3] + 2HCN \tag{9}$$

$$[Cr(CN)_5(H_2O)]^{3-} + 2H_3O^{+} \rightarrow fac - [Cr(CN)_3(H_2O)_3] + 2HCN \tag{10}$$

$$[Cr(CN)_5(H_2O)]^{2-} + H_3O^{+} \xrightarrow[slow]{k_2} [Cr(CN)_4(H_2O)_2]^{-} + HCN \tag{10a}$$

$$[Cr(CN)_4(H_2O)_2]^{-} + H_3O^{+} \xrightarrow[fast]{} fac - [Cr(CN)_3(H_2O)_3] + HCN \tag{10b}$$

Table 3
Pseudo first-order rate constants and quantum yields for thermal and photochemical (313 and 366 nm) aquation of $[Cr(CN)_6]^{3-}$ and $[Cr(CN)_5(H_2O)]^{2-}$ and of its supercomplexes with $[32]aneN_8H_8{}^{8+}$ [23]

	k_1/s^{-1} [a]	k_2/s^{-1} [a]	Φ_0 [b]	Φ [b]	Φ_0/Φ
$[Cr(CN)_6]^{3-}$	$(2.8 \pm 0.3) \times 10^{-3}$		0.12 ± 0.01		
$\{[Cr(CN)_6] \cdot [32]aneN_8H_8\}^{5+}$ [c]	$(6.6 \pm 1.3) \times 10^{-5}$			0.04 ± 0.01	3
$[Cr(CN)_5(H_2O)]^{2-}$		$(6.5 \pm 0.3) \times 10^{-3}$	0.029 ± 0.001		
$\{[Cr(CN)_5(H_2O)] \cdot [24]aneN_8H_8\}^{6+}$ [d]		$(2.8 \pm 0.6) \times 10^{-3}$		0.030 ± 0.003	1

[a] pH 1.0.
[b] pH 14.3.
[c] $[[Cr(CN)_6]^{3-}] = 3.0 \times 10^{-3}$ M, $[\text{macrocycle}] = 3.6 \times 10^{-3}$ M.
[d] $[[Cr(CN)_5(H_2O)]^{2-}] = 3.0 \times 10^{-3}$ M, $[\text{macrocycle}] = 3.6 \times 10^{-3}$ M.

In the light of the thermal reactivity, the photoaquation of the aquapentacyanochromate(III) ion can be viewed as a sequence of a primary photochemical release of one CN^- ligand, followed by the very rapid thermal loss of a second CN^- group (Eq. (10b)). The quantum yield of Eq. (9), measured by the appearance of *fac*-$[Cr(CN)_3(H_2O)_3]$, is not affected by the macrocycle, in spite of the fact that the steric hindrance to the photodissociation of a hydrogen-bound CN^- ligand, observed in the $\{[32]aneN_8H_8 \cdot [Cr(CN)_6]\}^{5+}$ adduct, is also expected for $\{[32]aneN_8H_8 \cdot [Cr(CN)_5(H_2O)]\}^{6+}$. It must be noted however that, unlike $[Cr(CN)_6]^{3-}$, the five cyanide ligands of $[Cr(CN)_5(H_2O)]^{2-}$ are no longer photochemically equivalent. According to the Vanquickenborn–Ceulemans model for chromium(III) photolysis [24–26], regarded as a reliable standard, and using the σ and π AOM parameters of the CN^- and H_2O ligands, the bond energies in the $^4E_2$ state (i.e. the lowest quartet recognized as the principally photoreactive state) are evaluated as: 8200 (H_2O), 9800 (axial CN^-) and 14750 cm^{-1} (equatorial CN^-). The model anticipates that the main photolysis mode of the pentacyano complex is H_2O photoexchange (undetected [23]) which would account for the relatively low quantum yield of CN^- loss, while the less efficient CN^- photoaquation mainly concerns the ligand *trans* to H_2O. In this framework, the invariance of the quantum yield in the presence of the macrocycle is consistent with the 'belt' structure, which leaves such CN^- ligand free from hydrogen bonding. This hypothesis could appear in contrast with the *fac* geometry of the final product $[Cr(CN)_3(H_2O)_3]$; however, because of the general stereomobility of the photosubstitution reactions of CrL_5X^{n-} complexes, the photorelease of the axial CN^- ligand from $\{[32]aneN_8H_8 \cdot [Cr(CN)_5(H_2O)]\}^{6+}$ would likely be accompanied by a steric rearrangement leading to a 'boat'-shaped adduct of the *cis*-diaquo complex. Because of its structure and the small negative charge of the complex, this adduct is supposed to undergo rapid partial dissociation of the macrocycle, which in turn facilitates the secondary thermal aquation process.

The drastic reduction of thermal aquation of $[Cr(CN)_6]^{3-}$ in the presence of the macrocycle can be explained by considering that this reaction proceeds mainly through a H^+ catalysed two-step mechanism consisting of a rapid protonation equilibrium,

$$[Cr(CN)_6]^{3-} + H^+ \overset{K_p}{\leftrightarrows} [Cr(CN)_5(CNH)]^{2-} \qquad (11)$$

followed by aquation of the protonated species:

$$[Cr(CN)_5(CNH)]^{2-} \underset{H_2O}{\rightarrow} [Cr(CN)_5(H_2O)_2]^{2-} + HCN \qquad (12)$$

In the presence of the macrocycle the overall ionic charge changes from -3 to $+5$ and thus the cyanide ligands are expected to be far less basic in the adduct than in the free complex and to be less inclined to substitution through the H^+ catalysed mechanism.

The absence of $[Cr(CN)_5(H_2O)]^{2-}$ among the adduct aquation products requires the rate constant for Eq. (10a), k_2, to exceed that of Eq. (8), k_1. In effect, while Eq. (8) is reduced by a factor of 40, Eq. (10a) is only slightly affected. This is consistent with the observation that coordinated water molecules contribute to the overall reactivity of the aquo–cyano complexes of Cr(III), by either assisting the detachment of the protonated CN^- ligand in the second step of the proton-assisted path or originating a pH-independent path through intramolecular proton transfer from H_2O to a CN^- ligand. The positive charge of the macrocycle is expected to increase the rate constant of the H^+ assisted path or to promote a pH independent path. Either or both of these factors can compensate the obvious decrease of the protonation constant. On the basis of our results, however, it is impossible to discriminate between the two suggested effects.

2.2. Electrochemistry

The effect of polyammonium macrocyles on the electrochemical properties was described for the $[Fe(CN)_6]^{3-/4-}$ [9,11,27–29] and $[Ru(CN)_6]^{3-/4-}$ [27,28] complexes. In both cases it was demonstrated by cyclic voltammetry that these compounds are strongly affected by the structure of the receptor and by its degree of protonation. The anodic oxidation potential becomes more positive, respectively by $+130$ and $+165$ mV for the supercomplex $\{[32]aneN_8H_8 \cdot [Fe(CN)_6]\}^{4+}$, and $\{[32]aneN_8H_8 \cdot [Ru(CN)_6]\}^{4+}$. The increased difficulty in oxidyzing these complexes in the presence of macrocyle was attributed to the electrostatic nature of the interactions involved in the supercomplexation processes. The most stable supercomplexes are those formed between the most charged species. For this reason the supercomplexes with Fe(II) and Ru(II) are more stabilized and consequently the oxidation processes take place at more anodic potentials.

Actually the effect of charge is probably not the only factor to take into account, as can be concluded by the cyclic voltammetry study of the $\{[32]aneN_8H_8\cdot[Ru(bpy)(CN)_4]\}^{6+}$ adduct [30]. In aqueous solution, a reversible oxidation wave of $[Ru(bpy)(CN)_4]^{2-}$ at +0.80 V versus SCE was not appreciably shifted upon addition of one equivalent of $[32]aneN_8H_8{}^{8+}$. In acetonitrile, a reversible oxidation wave at +0.27 V versus SCE and a reversible reduction wave at −1.95 V versus SCE observed for the free complex are shifted respectively to +1.0 and −1.58 V (cathodic peak, poorly reversible). This behaviour was attributed to the extremely solvatochromic properties of this complex. The mechanism of solvatochromism is similar to that of supercomplex formation, being based on the second-sphere donor-acceptor interactions at the cyanides. Thus in water strong hydrogen bonding to the cyanides already withdraws charge from the metal and the redox potential remains unchanged while in acetonitrile supercomplexation reduces the charge density on the metal, shifting the Ru(III)/Ru(II) potential to substantially more positive values. For more details see below.

2.3. Intermolecular electron transfer

2.3.1. The $[Fe(CN)_6]^{3-}\cdot I^-$ system

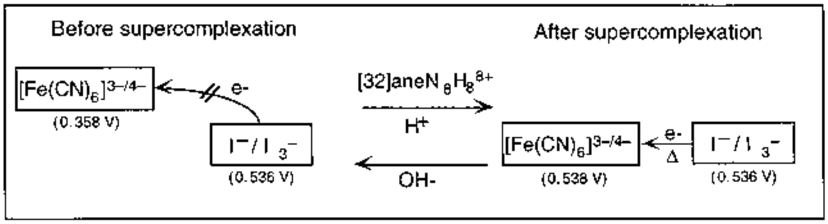
The effect of the supercomplexation in the oxidation potential was used to promote electron transfer between $[Fe(CN)_6]^{3-}$ and iodide [31]. In the absence of macrocycle, the standard reduction potential of $[Fe(CN)_6]^{3-}$ is $E° = 0.358$ V and the electron transfer reaction from I^- ($E° = 0.536$ V) to Fe(III) complex is thermodinamically unfavourable. In the presence of $[32]aneN_8H_8{}^{8+}$ (acidic medium), the redox potential of the coordination compound is increased by 0.180 V and thus the electron transfer becomes essentially isoergonic, allowing the formation of measurable amounts of the electron transfer products, I_3^- and Fe(II) supercomplex, Eq. (13), Fig. 4(a).

$$2\{[Fe(CN)_6]\cdot[32]aneN_8H_8\}^{5+} + 3I^- \rightleftarrows 2\{[Fe(CN)_6]\cdot[32]aneN_8H_8\}^{4+} + I_3^- \tag{13}$$

This system may be viewed as pH controlled on/off switch. In basic medium, the supercomplex dissociates and the back electron transfer from Fe(II) to I_3^- becomes thermodinamically allowed. Successive cycles of electron transfer in the direct and reverse direction can thus be performed by a sequential addition of acid and base, Fig. 4(a).

The equilibrium that is reached in acidic medium can be perturbed by light. Irradiation of a solution that contains the equilibrium concentrations of the redox pairs, $[32]aneN_8H_8^{8+}\cdot[Fe(CN)_6]^{3-/4-}$, and I_3^-/I^-, gives rise to the formation of more I_3^-. The formation of iodine occurs during the lifetime of the pulse (20 ms) and the back reaction follows a first order kinetics with a lifetime that is dependent on the temperature (ca. 8 min at 25°C), Fig. 4(b). The system behaves as a reversible *photochromic system*.

a) pH controlled on/off switch



b) reversible photochromic system

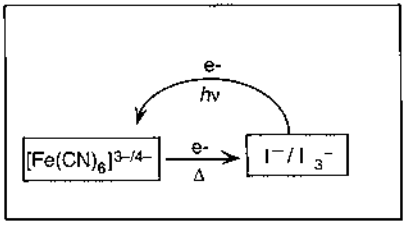


Fig. 4. Schematic representation of the thermal (a) and photochemical (b) reactivity of the system $[Fe(CN)_6]^{3-} + I^-$ in the presence of the polyammonium macrocycle $[32]aneN_8H_8^{8+}$.

2.4. Proton transfer

As a result of the high positive charge of polyammonium macrocycles, supercomplexation usually involves electron density withdrawing from the metal complex. This fact can be used to modify the acid–base properties of metal complexes containing protonable ligands.

The complex $[Co(CN)_5(HSO_3)]^{3-}$ has a pK_a of 4.0 corresponding to the acid–base equilibrium described by Eq. (14). The presence of a LMCT transition $\sigma(SO_3) \rightarrow d_z2$ allows an easy determination of the pK_a by UV-vis spectrophotometry. In what reactivity is concerned, the complex is quite stable thermally but reacts photochemically according to Eqs. (15) and (16), Table 4.

Table 4
Maximum absorption wavelength corresponding to the LMCT band ($\sigma(SO_3) \rightarrow d_z2$) and photoaquation quantum yields ($\lambda_{exc} = 313$ nm) for the complexes $[Co(CN)_5(SO_3)]^{4-}$ and $[Co(CN)_5(HSO_3)]^{3-}$ and for some of their supercomplexes with polyammonium macrocycles, $T = 25°C$

	pH	λ_{max}/nm	Φ
$[Co(CN)_5(HSO_3)]^{3-}$	1.1–2.5	248	0.40+0.05
$[Co(CN)_5(SO_3)]^{4-}$	5.5–6.5	265	0.85+0.09
$\{[Co(CN)_5(SO_3)] \cdot [24]aneN_8H_8\}^{4+}$	1.0–3.1	253	0.05+0.01
$\{[Co(CN)_5(SO_3)] \cdot [30]aneN_{10}H_{10}\}^{6+}$	1.0–1.3	256	0.12+0.03
$\{[Co(CN)_5(SO_3)] \cdot [32]aneN_8H_8\}^{4+}$	1.0–3.1	264	0.45+0.09
$\{[Co(CN)_5(HSO_3)] \cdot [32]aneN_8H_8\}^{5+}$	4 M $HClO_4$	248	0.40+0.05

$$[Co(CN)_5(HSO_3)]^{3-} \rightleftarrows [Co(CN)_5(SO_3)]^{4-} + H_3O^+ \tag{14}$$

$$[Co(CN)_5(HSO_3)]^{3-} \xrightarrow[H_2O]{h\nu\ (313\ nm)} [Co(CN)_5(H_2O)]^{2-} + HSO_3^- \tag{15}$$

$$[Co(CN)_5(SO_3)]^{4-} \xrightarrow[H_2O]{h\nu\ (313\ nm)} [Co(CN)_5(H_2O)]^{2-} + SO_3^{2-} \tag{16}$$

Addition of the polyammonium macrocycles $[24]aneN_8H_8{}^{8+}$, $[30]aneN_{10}H_{10}^{10+}$ and $[32]aneN_8H_8{}^{8+}$ to acidic solutions of the complex causes bathocromic shifts of the LMCT band relatively to the free complex at the same pH (acidic form), Table 4 [14]. These data suggests that the hydrogenosulfite ligand has an intermediate degree of protonation in the supercomplexes with $[24]aneN_8H_8{}^{8+}$ and $[30]aneN_{10}H_{10}^{10+}$ while in the supercomplex with $[32]aneN_8H_8{}^{8+}$ it becomes totally deprotonated. Charge withdrawal from the complex by the positively charged macrocycle reflects then on a lowering of the basicity of the hydrogenosulfite ligand leading to deprotonation. The sulfite ligand is able to participate in hydrogen bonding with the ammonium groups of the macrocycles causing the observed bathochromic shifts. A metal center with four cyanide ligands in equatorial positions seems to fit very well the size of macrocycles with 32 [16,23] or 33 [12] atoms which explains why the sulfite ligand is essentially free from hydrogen bonding in the supercomplex $\{[Co(CN)_5(SO_3)]\cdot[32]aneN_8H_8\}^{4+}$.

The pK_as of the supercomplexes obtained by spectrophotometric titrations support this interpretation: pK_a ca. 0.5 for $\{[Co(CN)_5(HSO_3)]\cdot[32]aneN_8H_8\}^{5+}$, $pK_a < 0$ for $\{[Co(CN)_5(HSO_3)]\cdot[30]aneN_{10}H_{10}\}^{7+}$ and $pK_a < -0.5$ for $\{[Co(CN)_5(HSO_3)]\cdot[24]aneN_8H_8\}^{5+}$. They further indicate, in accordance with the bathochromic shifts observed, that the $[24]aneN_8H_8{}^{8+}$ macrocycle meets the stereochemical requirements for hydrogen bonding to the sulfite ligand better than the $[30]aneN_{10}H_{10}^{10+}$ macrocycle.

The supercomplexes exhibit the same qualitative photochemical reactivity as the free complex. However, the quantum yields are lower, Table 4, as would be expected from the participation of the sulfite ligand in hydrogen bonding (*stereochemical limitation*) and from the electrostatic attraction between the leaving sulfite and the positively charged macrocycle (*coulombic effect*).

Taking together spectroscopic data, acid–base behaviour and photochemical reactivity (stereochemical and coulombic effects) it is possible to obtain structural information about the supercomplexes in solution: in the supercomplexes with $[24]aneN_8H_8{}^{8+}$ and $[30]aneN_{10}H_{10}^{10+}$, a structure involving two cyanides and the sulfite in hydrogen bonding with the macrocycle must prevail; in the supercomplex with $[32]aneN_8H_8{}^{8+}$, structure (a) of Fig. 2 should prevail, involving the four equatorial cyanides.

2.5. Photophysics

The photophysical properties of a metal complex can be strongly modified through second-sphere interactions [1,32,33]. An emissive complex containing cyanide ligands was chosen, $[Ru(bpy)(CN)_4]^{2-}$, which proved to change widely its properties upon supercomplexation with the polyammonium macrocycle $[32]aneN_8H_8{}^{8+}$, Table 5 [30].

Table 5
Spectroscopic, photophysical and redox properties of $[Ru(bpy)(CN)_4]^{2-}$[a] and of the supercomplex $\{[Ru(bpy)(CN)_4]\cdot[32]aneN_8H_8\}^{6+}$[b] in aqueous solution and in acetonitrile

	$[Ru(bpy)(CN)_4]^{2-}$		$\{[Ru(bpy)(CN)_4]\cdot[32]aneN_8H_8\}^{6+}$	
	H_2O	CH_3CN	H_2O	CH_3CN
λ_{max}^{abs}/nm	400	535	398	374
λ_{max}^{abs}/nm	610	790	ca. 610	640
Φ_e	0.0068	0.0003	0.012	0.022
τ/ns	101	7	180	330
E^{ox}/V[c]	+0.78	+0.27	ca. +0.80	+1.0
E^{red}/V[d]	–	−1.95	–	−1.58[e]

[a] Deaerated solution [35,37].
[b] Deaerated solution [30].
[c] $E_{1/2}$ vs. SCE; Ru(II) → Ru(III).
[d] $E_{1/2}$ vs. SCE; (bpy) → $(bpy)^-$.
[e] All reversible waves, except this one.

The spectroscopic, redox and photophysical properties of $[Ru(bpy)(CN)_4]^{2-}$ are extremely solvent dependent due to second-sphere donor–acceptor interactions involving the cyanide ligands [34,35]. The most important feature of the absorption spectrum is a metal-to-ligand charge transfer (MLCT) band, which shifts to higher energy in solvents that can form hydrogen bonds with the cyanides, Table 5. Charge withdrawal due to this kind of second-sphere interactions reflects also in the redox behaviour, leading to anodic shifts in the Ru(II) → Ru(III) oxidation wave and in the bpy → bpy^- reduction wave. The photophysical behaviour is characterized by an increase in the MLCT excited state lifetime and in the emission quantum yield when such interactions are present (energy-gap law [34]).

Addition of the polyammonium macrocycle $[32]aneN_8H_8{}^{8+}$ to aqueous solutions of $[Ru(bpy)(CN)_4]^{2-}$ does not substantially modify neither the MLCT maximum nor the redox behaviour, since the cyanides were already involved in hydrogen bonding with water. Supercomplex formation is however evidenced by an increase in both emission quantum yield and lifetime, Table 5. In acetonitrile, supercomplexation shows up visually as a sharp change in color, from deep violet to yellow, leading also to changes in redox potentials and to an increase in emission quantum yield and lifetime [30].

The remarkable changes brought up by supercomplexation suggest that the cyanides are involved in hydrogen bonding with the macrocycle. In this case, the supercomplex structure in solution should correspond to a 'boat' rearrangement, Fig. 5. This hypothesis is consistent with NMR data, both in water and acetonitrile [30].

The excited state redox properties of $[Ru(bpy)(CN)_4]^{2-}$, and thus its excited state reactivity towards electron transfer quenchers, can in principle be modified upon supercomplexation, since changes in ground state redox properties and excited state energies were observed. In this particular supercomplex, there is a parallel shift in both properties and the thermodynamics for excited state reactivity of the supercomplex does not differ substantially from that of the free complex. But the kinetics may change since there is a reverse in the overall charge (changing from -2 to $+6$) and the supercomplex still retains hydrogen bonding capability. Addition of the negatively charged electron acceptor $[Rh(dcb)_3]^{3-}$ (dcb=4,4′-dicarboxy-2,2′-bipyridine) to aqueous solutions of the supercomplex led to a partial reversal of the lifetime changes, indicating that a three species adduct formed. However, even if $\Delta G°$ is ca. -0.70 eV, no quenching was observed. This behaviour has been attributed to the detailed structure of the supercomplex-quencher adduct, in which the macrocycle acts as an insulating spacer between the two reactants [30]. This opens the possibility to design excited state reactants with built-in receptor capability.

The ability of $[32]aneN_8H_8{}^{8+}$ macrocycle to interact with polynuclear complex species is being investigated. Preliminary results [36] show that with the rod-like, all *trans* $[CN–Cr(cyclam)–CN–Ru(CN)_4–NC–Cr(cyclam)–CN]$ complex, a very stable 1:1 adduct is formed, despite the neutral overall charge of the complex. The interaction substantially modifies the MMCT (Ru(II) → Cr(III)) spectroscopy of the complex and its Cr(III) based photophysics. This study opens interesting possibilities for 'rotaxane-type' systems based on supercomplex formation.

3. Conclusions

The thermal and photochemical reactivity of coordination compounds can be greatly modified by formation of a second coordination sphere that results from the binding of a polyammonium macrocycle. Examples of ligand substitution, redox and acid–base reactions have been given that exemplify such modifications. The

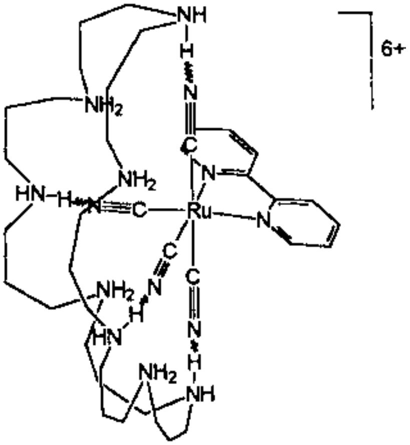


Fig. 5. Proposed structure for the supercomplex $\{[Ru(bpy)(CN)_4]\cdot[32]aneN_8H_8\}^{6+}$ in acetonitrile solution [30].

second coordination sphere also permits the tuning of some photophysical properties such as light emission and excited-state reactivity towards external quenchers. Formation of these adducts only occurs at acidic pH values, and thus the formation/destruction of the supexcomplex structure can be controlled by pH changes. In suitably designed systems, pH and/or light operated photochemical molecular devices based on supercomplexes can be envisioned.

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