

Supramolecular interactions between $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ and polyammonium macrocyclic receptors

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The acid–base properties as well as the photochemical reactivity of the co-ordination compound $\text{K}_4[\text{Co}(\text{CN})_5(\text{SO}_3)]$ in the presence of three polyammonium macrocyclic receptors were studied in aqueous solution. The $\text{p}K_a$ of the free complex (3.9) (sulfite deprotonation) changed to $\text{p}K_a < 0.5$ upon complexation with the receptors. The quantum yield for sulfite photoaquation of the free complex in the basic form ($\Phi = 0.85 \pm 0.09$) decreased to 0.05 ± 0.01 , 0.12 ± 0.03 and 0.45 ± 0.09 in the presence of $[\text{24}]ane\text{N}_8\text{H}_8^{8+}$, $[\text{30}]ane\text{N}_{10}\text{H}_{10}^{10+}$ and $[\text{32}]ane\text{N}_8\text{H}_8^{8+}$, respectively. For the acidic form of the free complex ($\Phi = 0.40 \pm 0.05$) the quantum yield was not affected by supercomplexation with $[\text{32}]ane\text{N}_8\text{H}_8^{8+}$. For the adducts formed from the other two macrocyclic receptors it was not possible to evaluate the quantum yields of the acidic forms, because protonation was not complete even at very high proton concentrations. The results were interpreted in terms of second-sphere interactions involving hydrogen bonding between the complex and the macrocycles. In the case of $[\text{32}]ane\text{N}_8\text{H}_8^{8+}$, the experimental results are compatible with a structure in which the cyanides are involved in hydrogen bonding but the sulfite ligand is not. In the two other supercomplexes the sulfite ligand seems to be involved in hydrogen bonding.

The study of the supramolecular species obtained by an appropriate assembly of transition-metal complexes with polyammonium macrocyclic receptors has been subjected to an increasing interest.^{1–8} The ‘supercomplexes’ thus formed are species in which the macrocyclic receptor is non-covalently bound to the complex in a second co-ordination sphere, mainly by coulombic interactions and/or hydrogen bonding. The assembly can confer new physicochemical properties to the complex, namely modifying redox potentials, electronic absorption and emission spectra, thermal and photochemical reactivity. These modifications may also depend on (and thus provide information about) the geometrical structure of the adduct; for example, the thermal and photochemical reactivity of the ligands directly involved in second-sphere bonding are expected to be much more affected by the macrocycle than those of the other ligands.^{9–13}

In this work we are presenting the study of the supercomplexes formed between the pentacyanosulfitecobaltate(III) complex ion and some polyammonium macrocyclic receptors of different charge and dimensions shown in Fig. 1. This complex ion was chosen because it contains two different ligands, having both basic properties and being able to form hydrogen bonds with the macrocycle. The study of the effect of the macrocycle on the acid–base properties of $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$, as well as on its thermal and photochemical reactivity could in fact provide structural information on the supercomplexes thus formed.

Results and Discussion

Acid–base behaviour and photochemistry of the complex

The absorption spectrum of $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ in its basic form has been described previously in the literature^{14–18} and is composed of a weak absorption band centered at 333 nm, assigned to a $d\pi \rightarrow \pi^*(\text{CN})$ transition, and a more intense band with a maximum at 265 nm, identified as a charge transfer from the sulfite ligand to the metal, $\sigma(\text{SO}_3) \rightarrow d_z^2$, Fig. 2. According to Chen *et al.*,¹⁶ this complex participates in a single acid–base

equilibrium with $\text{p}K_a = 4$. The protonated ligand is likely to be the sulfite because it is known that the cyanide ligands are extremely acidic and can only be protonated at very high proton concentrations.¹⁹ The protonation of the sulfite ligand gives rise to the complex $\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$ which can essentially be distinguished from its basic parent by an hypsochromic shift of 15 nm on the charge-transfer band ($\sigma(\text{SO}_3) \rightarrow d_z^2$, Fig. 2). This shift reflects the decrease of charge density on the sulfite ligand upon protonation. Table 1 summarizes the data of the absorption spectra. From a spectrophotometric titration, Fig. 3, a $\text{p}K_a$ value of 3.9 was obtained, in good agreement with the previously reported value.¹⁶

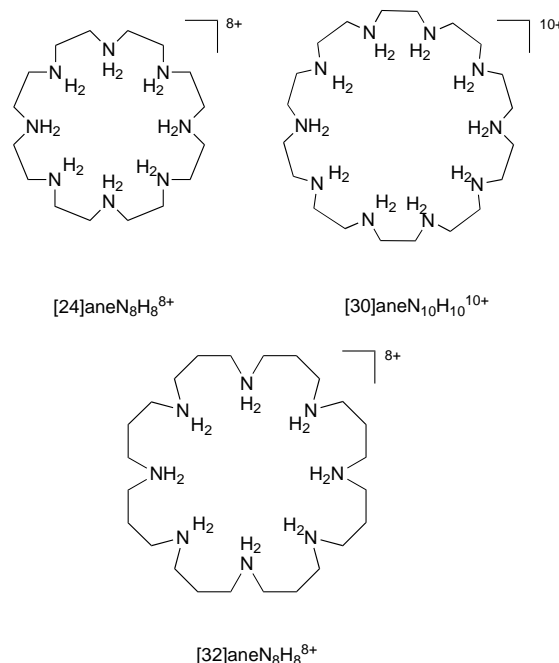


Fig. 1 Polyammonium macrocycles $[m]ane\text{N}_n\text{H}_n^{n+}$ used in this work (m stands for the number of atoms in the cycle and n for the number of nitrogens and protons)

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Table 1 Absorption bands of the complexes $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ and $\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$ in water

$\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$		$\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$		Assignment*
λ/nm	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	λ/nm	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	
333	431	333	277	${}^1\text{A}_1 \rightarrow {}^1\text{E}_g$
265	17 380	250	15 260	$\sigma(\text{SO}_3) \rightarrow \text{d}_z$
≈ 199	11 600	202	13 980	$\text{d}\pi \rightarrow \pi^*(\text{CN})$

* According to Miskowski and Gray.¹⁴

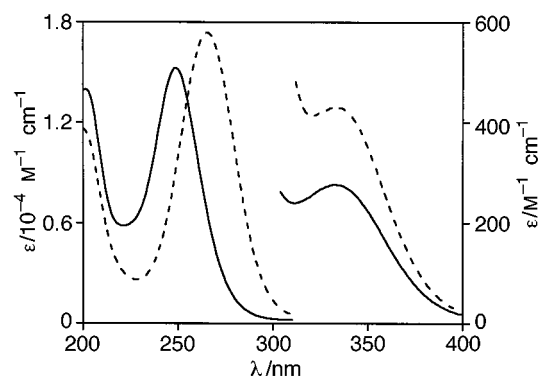


Fig. 2 Absorption spectra of the complexes $\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$ (—, acidic form) and $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ (---, basic form), at pH 2.1 and 8.2, respectively

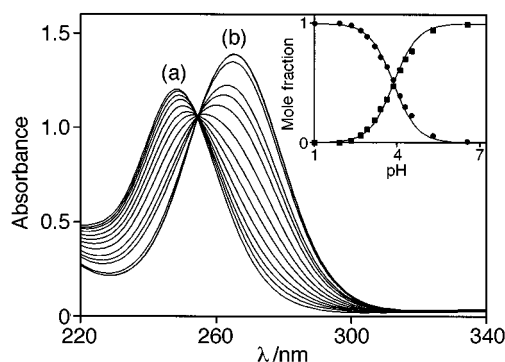
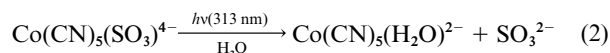
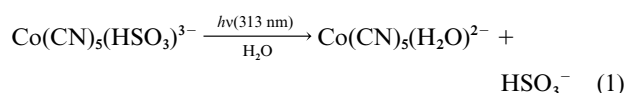


Fig. 3 Absorption spectra of $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ aqueous solution (1.0×10^{-4} M) with varying pH: 1.01 (a); 2.34, 2.68, 3.18, 3.41, 3.63, 3.86, 4.11, 4.30, 4.52, 5.30, 6.54, 7.90 (b). Inset: fitting of the spectrophotometric titration, with $\text{p}K_a = 3.9$

Irradiation of acidic or basic aqueous solutions of pentacyanosulfitecobaltate(III) gives rise to spectral variations that indicate formation of the photoproduct pentacyanoaquaocobaltate(III), Fig. 4. The presence of isosbestic points indicates that the following clean reactions, equations (1) and (2), are



occurring and the final spectrum is in accordance with published data for $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$.¹⁴

The quantum yield for the photoaquation reaction was calculated as a function of pH. At the extreme pH values, the quantum yield is 0.40 ± 0.05 and 0.85 ± 0.09 at pH = 1.0 (acidic form) and at pH = 7.0 (basic form), respectively. In general, the observed quantum yield, Φ_{obs} , at any pH value is given by equation (3), where Φ_A and Φ_{AH} are, respectively, the quantum

$$\Phi_{\text{obs}} = \beta_{\text{obs}}\Phi_A + (1 - \beta_{\text{obs}})\Phi_{\text{HA}} \quad (3)$$

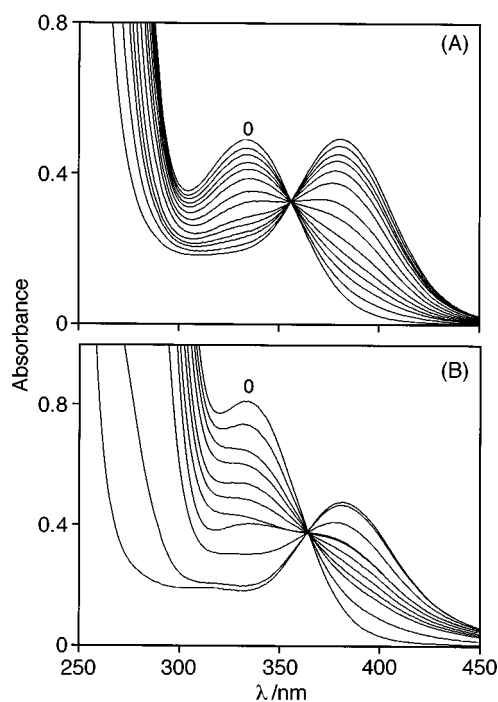


Fig. 4 Spectral variations upon 313 nm irradiation (25 °C) of the complex: (A), $\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$ (2.0×10^{-3} M) at pH 1.0 for the following times: 0 (0), 10, 20, 30, 40, 55, 80, 105, 145, 175, 210, 240, 300 and 360 min; (B), $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ (2.0×10^{-3} M) at pH 5.0 for the following times: 0 (0), 10, 30, 40, 55, 70, 90, 120, 200 and 360 min

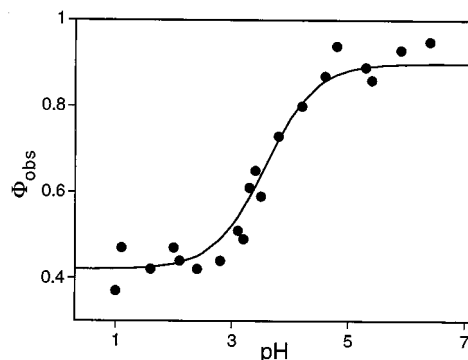


Fig. 5 Experimental (●) pH dependence of $\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$ and $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ photoaquation quantum yields (Φ_{obs}) upon 313 nm irradiation, fitted (—) through equations (3) and (4)

yields of the basic and acidic forms and β_{obs} is the fraction of the absorbance of the basic species defined by equation (4);

$$\beta_{\text{obs}} = \frac{\epsilon_A[\text{A}]}{\epsilon_{\text{AH}}[\text{AH}] + \epsilon_A[\text{A}]} = \frac{(\epsilon_A/\epsilon_{\text{AH}})K_a}{(\epsilon_A/\epsilon_{\text{AH}})K_a + [\text{H}^+]} \quad (4)$$

ϵ_A and ϵ_{AH} are the molar absorption coefficients at 313 nm, of the basic and acidic forms, respectively.

Inspection of equation (3) indicates that the observed quantum yield, Φ_{obs} , depends on the proton concentration through the function β_{obs} . The representation of Φ_{obs} as a function of pH is a titration curve with an inflection point at $\text{p}K_a(\text{obs}) = \text{p}[K_a - (\epsilon_A/\epsilon_{\text{AH}})] = 3.55$, Fig. 5. This value can be compared with 3.62, calculated from the molar absorption coefficients of the acidic [$\epsilon_{\text{AH}}(313\text{ nm}) = 240\text{ M}^{-1}\text{cm}^{-1}$] and basic [$\epsilon_A(313\text{ nm}) = 460\text{ M}^{-1}\text{cm}^{-1}$] species and the acidity constant. The calculation of the quantum yield for the photoaquation reaction was performed upon correction for the fraction of the light effectively absorbed by the reagent. However, a different behaviour depending on the pH was observed. At pH < 3.5, the plots of the corrected absorbance (380 nm) as a function of the irradiation time are straight lines, but for pH > 3.5 a negative deviation is observed

Table 2 Maximum absorption wavelength corresponding to the LMCT band ($\sigma(\text{SO}_3) \rightarrow d_z$) and photoaquation quantum yields ($\lambda_{\text{exc}} = 313 \text{ nm}$) for the complexes $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ and $\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$ and for some of their supercomplexes with polyammonium macrocycles, $T = 25 \text{ }^\circ\text{C}$

	pH	$\lambda_{\text{max}}/\text{nm}$	Φ
$\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$	1.1–2.5	248	0.40 ± 0.05
$\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$	5.5–6.5	265	0.85 ± 0.09
$[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [24]\text{aneN}_8\text{H}_8]^{4+}$	1.0–3.1	253	0.05 ± 0.01
$[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [30]\text{aneN}_{10}\text{H}_{10}]^{6+}$	1.0–1.3	256	0.12 ± 0.03
$[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [32]\text{aneN}_8\text{H}_8]^{4+}$	1.0–3.5	264	0.45 ± 0.09
$[\text{Co}(\text{CN})_5(\text{HSO}_3) \cdot [32]\text{aneN}_8\text{H}_8]^{5+}$	4 M HClO_4	248	0.40 ± 0.05

which increases with increasing irradiation time. This behaviour can be explained by the existence of a thermal back reaction that increases as long as the concentration of HSO_3^- or SO_3^{2-} increases. This hypothesis was confirmed by carrying out the photoaquation in the presence of Na_2SO_3 . At pH 6.4 and $[\text{Na}_2\text{SO}_3]$ of 1.0×10^{-3} and $2.0 \times 10^{-3} \text{ M}$ the quantum yield is reduced by 30 and 46%, respectively, in comparison with the photoaquation in the absence of Na_2SO_3 . At pH 1.0 and $[\text{Na}_2\text{SO}_3]$ of $1.0 \times 10^{-3} \text{ M}$, only 6% reduction was observed. Due to the existence of this effect, calculation of the photoaquation quantum yield at $\text{pH} > 3.5$ was performed using the correct absorbance values obtained from extrapolation for the initial time.

According to the Förster cycle^{20,21} the excited state $\text{p}K_a^*$ is -0.8 . This means that the excited acidic species is a very strong acid and that, from the thermodynamic point of view, the formation of an excited base is likely all over the working pH range (1 to 7). However, the fact that equation (3) is obeyed is an evidence that the excited-state proton transfer is not efficient.

The difference in the photoreactivities of the two acid–base forms of the complex could be due to a difference in the efficiency of conversion of the CT excited state produced by irradiation to the reactive d–d state.

Formation, acid–base and photochemical behaviour of the supercomplex

Addition of polyammonium macrocycles to acidic solutions of the complex in a 1:1 ratio gives rise to spectral modifications indicating formation of adducts. The most relevant difference occurs on the position of the LMCT band ($\sigma(\text{SO}_3) \rightarrow d_z$), see Table 2. Formation of supercomplexes between polyammonium macrocycles and negatively charged transition-metal cyanocomplexes was previously observed to occur in aqueous solutions with large association constants.^{4,6,22–24} For supercomplex formation between the complexes $\text{Co}(\text{CN})_5(\text{HSO}_3)^{3-}$ and $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ with the polyammonium macrocycles used here, association constants of $\approx 10^6$ and $\approx 10^8 \text{ M}^{-1}$, respectively, are expected which leads to $>95\%$ supercomplexes in solution with the concentrations used. Addition of excess macrocycle causes no additional spectral changes, which is evidence for a 1:1 stoichiometry of the supercomplexes.

The supercomplexation causes a bathochromic shift of the $\sigma(\text{SO}_3) \rightarrow d_z$ absorption band of the complex, with respect to the free complex at the same pH (acidic form). In the case of the adduct with $[32]\text{aneN}_8\text{H}_8^{8+}$, the shift (14 nm) is almost the same as that observed between the acidic and basic forms of the free complex. In other words, the absorption spectrum of the adduct $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [32]\text{aneN}_8\text{H}_8]^{4+}$ (pH 1.0) is practically coincident with the absorption spectrum of $\text{Co}(\text{CN})_5(\text{SO}_3)^{4-}$ (pH > 3.5), which means that supercomplexation involves deprotonation of the hydrogensulfite ligand. Acidification of the supercomplex causes a blue shift of the LMCT band, indicating that protonation only occurs at very acidic pH values; a $\text{p}K_a \approx 0.5$ can be estimated for the supercomplex, and the pos-

ition of the maximum of its band in 2 M HCl is coincident with the maximum of the acidic form of the free complex. This result indicates that supercomplexation does not change the absorption spectra of both forms of the free complex, and that the variations observed are due to different $\text{p}K_a$ values in the absence and presence of the macrocycle. A similar negligible effect on the absorption spectra of the co-ordination compound upon supercomplexation with polyammonium macrocycles was previously observed for hexacyanocobaltate(III),^{9–11} pentacyanoaquacobaltate(III),¹² hexacyanochromate(III) and pentacyanoaquachromate(III).¹³ The difference between $\text{p}K_a \approx 0.5$ (supercomplex) and 3.9 (free complex) can be attributed to the positive charge of the macrocycle, which reduces the charge density on the ligands and on the metal center. An analogous effect of the charge of the macrocycle was previously reported for similar adducts,¹² and in other cases an anodic shift of the redox potential of the metal upon supercomplexation was also observed.^{4,8,23–27} Unfortunately, the instability of the reduced form of our complex prevented us from performing electrochemical experiments.

On the other hand, the positions of the LMCT maxima of the supercomplexes with $[24]\text{aneN}_8\text{H}_8^{8+}$ and $[30]\text{aneN}_{10}\text{H}_{10}^{10+}$, located between the maxima of the acidic and basic forms of the free complex, are indicative of an intermediate degree of protonation of the sulfite ligand in the supercomplexes, suggesting that the ligand is involved in hydrogen bonding with the ammonium groups of the macrocycle. Acidification of the $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [24]\text{aneN}_8\text{H}_8]^{4+}$ and $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [30]\text{aneN}_{10}\text{H}_{10}]^{6+}$ supercomplexes causes a blue shift of the LMCT band in extremely acidic media, so that a $\text{p}K_a$ value can not be accurately measured. However, the spectra in concentrated HClO_4 are almost coincident with that of the acidic form of the free complex, indicating that in these extreme conditions the sulfite ligand of the supercomplex protonates. The fact that, in these two supercomplexes, the protonation occurs at higher proton concentrations compared with the $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [32]\text{aneN}_8\text{H}_8]^{4+}$ supercomplex, is additional evidence for considering the sulfite ligand being involved in hydrogen bonding within the $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [24]\text{aneN}_8\text{H}_8]^{4+}$ and $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [30]\text{aneN}_{10}\text{H}_{10}]^{6+}$ supercomplexes.

The spectral variations that result from irradiation of the supercomplexes are in general similar to those observed in the absence of the macrocycle, indicating that the photoproduct is again the pentacyanoaquacobaltate(III), see Fig. 6. The quantum yields for the photoaquation of the supercomplexes are shown in Table 2. Inspection of this table indicates that the quantum yields for photoaquation in the supercomplexes $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [24]\text{aneN}_8\text{H}_8]^{4+}$ ($\Phi = 0.05$) and $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [30]\text{aneN}_{10}\text{H}_{10}]^{6+}$ ($\Phi = 0.12$) are reduced several times in comparison with the basic form of the free complex ($\Phi = 0.85$). For the supercomplex $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [32]\text{aneN}_8\text{H}_8]^{4+}$, the photoaquation quantum yield ($\Phi = 0.45$) is only about one half than that of the free complex.

These results parallel the spectral changes described above, as far as the degree of participation of the sulfite ligand in hydrogen bonding with the macrocycles is concerned. The large decrease of the quantum yield observed in the supercomplexes with $[24]\text{aneN}_8\text{H}_8^{8+}$ and $[30]\text{aneN}_{10}\text{H}_{10}^{10+}$ can only be attributed to a *steric limitation* to ligand detachment caused by the macrocycle, and so it implies that the sulfite is involved in the hydrogen bonds. The fact that the decrease is more pronounced in the supercomplex with $[24]\text{aneN}_8\text{H}_8^{8+}$ suggests that the sulfite is more tightly hydrogen bonded to this macrocycle than to $[30]\text{aneN}_{10}\text{H}_{10}^{10+}$, as already indicated by the spectral shifts of Table 2. The relatively small decrease of the quantum yield observed in $[\text{Co}(\text{CN})_5(\text{SO}_3) \cdot [32]\text{aneN}_8\text{H}_8]^{4+}$ is clear evidence that in this case the sulfite ligand is not involved in hydrogen bonding, and it can only be attributed to a *coulombic effect* caused by the positive charge of the macrocycle. Such an effect is also expected to be present in the supercomplexes with

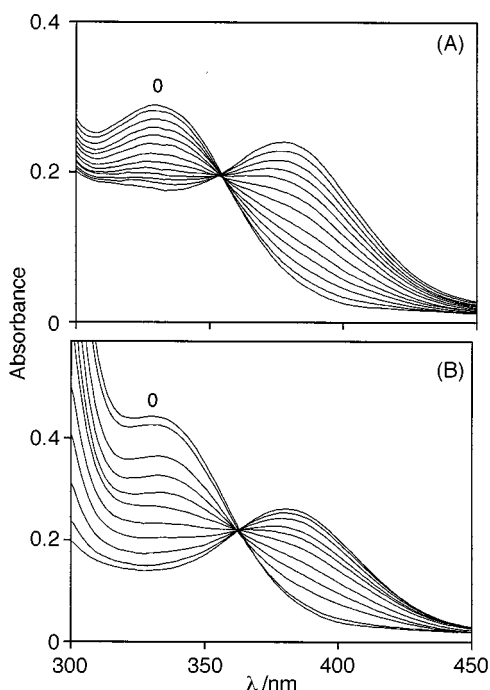


Fig. 6 Spectral variations upon 313 nm irradiation (25 °C) of aqueous solutions containing: (A) $K_4[Co(CN)_5(SO_3)]$ (1.0×10^{-3} M) and $[32]aneN_8H_8^{8+} \cdot 8HCl$ (2.0×10^{-3} M) in $HClO_4$ (4 M) (nominal pH -0.6), for the following times: 0 (0), 6, 14, 23, 33, 45, 60, 75, 90, 105, 120, 140 and 160 min; (B) $K_4[Co(CN)_5(SO_3)]$ (1.0×10^{-3} M) and $[32]aneN_8H_8^{8+} \cdot 8HCl$ (2.0×10^{-3} M) at pH 3.5, for the following times: 0 (0), 2, 5, 10, 17, 25, 35, 45, 55, 70, 90, 110 and 140 min

$[24]aneN_8H_8^{8+}$ and $[30]aneN_{10}H_{10}^{10+}$, but it is overcome by the larger steric effect.

In the light of the results obtained for the adducts between these macrocycles and other cyano complexes, the qualitative differences between the spectral and photochemical properties of the adducts of $Co(CN)_5(SO_3)^{4-}$ with $[24]aneN_8H_8^{8+}$ and $[30]aneN_{10}H_{10}^{10+}$ on one side and that with $[32]aneN_8H_8^{8+}$ on the other can be ascribed to the different dimensions of the macrocycles. In fact, the photochemical behaviour of the adducts of $Co(CN)_6^{3-}$ clearly indicates¹¹ that the two smaller macrocycles can only interact with three adjacent ligands of the complex, while $[32]aneN_8H_8^{8+}$ is sufficiently large to bind four CN^- ligands; in addition, the behaviour of $Co(CN)_5(H_2O)^{2-12}$ and $Cr(CN)_5(H_2O)^{2-13}$ with this last macrocycle strongly suggests that the CN^- ligands involved in the hydrogen bonds are the equatorial ones, giving rise to a 'belt' structure of the adduct, probably because of a favorable geometrical relationship between the NH^+ groups and the ligands. Since the adducts of $Co(CN)_5(SO_3)^{4-}$ have quite probably similar geometries, the results obtained in this work with $[24]aneN_8H_8^{8+}$ and $[30]aneN_{10}H_{10}^{10+}$ suggest that these macrocycles form hydrogen bonds with the SO_3^{2-} and two CN^- ligands rather than with three CN^- ; the lack of a similar preference for SO_3^{2-} in the case of $[32]aneN_8H_8^{8+}$ can be explained by the large size of the sulfite ion, so that the macrocycle cannot encircle a diameter of the complex containing one sulfite and three CN^- , but only one containing four CN^- ligands. Space filling models have confirmed this hypothesis.

Photophysical data on complexes derived from $Ru(bpy)_2(CN)_4^{2-}$ ($bpy = 2,2'$ -bipyridine) show that an increase in the MLCT excited state energy caused by second-sphere donor-acceptor interactions (solvent effects, protonation, super-complexation with polyammonium macrocycles, substitution of cyanide with methyl isocyanide) is always accompanied by an increase in the excited-state lifetime.^{28,29} This result has been attributed mainly to the energy-gap law.²⁸ The complex $Co(CN)_5(SO_3)^{4-}$ is luminescent only in rigid matrices³⁰ and its lifetime can not be accessed in solution by luminescence. How-

ever, based on the above results, it can be expected that super-complexation of $Co(CN)_5(SO_3)^{4-}$ would lead to an increase in the excited-state lifetime. In the supercomplex with $[32]aneN_8H_8^{8+}$, the photoaquation quantum yields are equal in the acidic and basic forms within the experimental error and thus do not follow the ground-state pK_a , contrary to what happens in the free complex. Since pK_a^* is expected to be lower than -0.8 , this would suggest that the excited state lives long enough to equilibrate between the two acid-base forms, so that the observed quantum yield would always originate from the excited basic form, $[Co(CN)_5(SO_3) \cdot [32]aneN_8H_8^{8+}]^*$.

Experimental

CAUTION: Care must be exercised in handling cyanide compounds. All operations should be performed in a well ventilated hood.

$K_4[Co(CN)_5(SO_3)]$

This complex was prepared according to the method of Fujita and Shimura,¹⁷ which involves substitution of Br^- by SO_3^{2-} in $K_3[Co(CN)_5Br]$. The UV/VIS absorption spectrum presents maxima at 265 nm ($\epsilon = 17\,380\, M^{-1}\, cm^{-1}$) and 333 nm ($\epsilon = 431\, M^{-1}\, cm^{-1}$) above pH = 6 [basic form, $Co(CN)_5(SO_3)^{4-}$], in good agreement with the published literature data.^{14,16,18} The complex $K_3[Co(CN)_5Br]$ was synthesized according to ref. 31.

Polyammonium macrocycles

The macrocycle 1,5,9,13,17,21,25,29-octaazacyclodotriacontane ($[32]aneN_8$) was synthesized following a reported method,³² except that propane-1,3-diamine was used as a starting material in place of 3,3'-diaminodipropylamine. The macrocycles 1,4,7,10,13,16,19,22-octaazacyclotetrasocane ($[24]aneN_8$) and 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane ($[30]aneN_{10}$) were synthesized according to the methods reported in refs. 33 and 34, respectively. All three macrocycles were prepared and used as their hydrochlorides.

Procedures

All reagents used were of analytical grade. Aqueous solutions of appropriate concentrations of NaOH and $HClO_4$ were used for pH adjustment. All measurements were made at 25 °C. Spectrophotometric titrations were carried out in 1.0×10^{-4} M aqueous solutions of the complex. When present, the macrocycle had the concentration of 1.1×10^{-4} M. Photochemical experiments were carried out in 5.0×10^{-4} or 1.0×10^{-3} M aqueous solutions of the complex and, when present, the macrocycle had concentrations of 5.0×10^{-4} , 1.0×10^{-3} or 2.0×10^{-3} M. Electronic absorption spectra were run on a Lambda 6 Perkin-Elmer spectrophotometer.

Photolyses at 313 nm were performed using a Müller Elektronic Optic (Germany) irradiation lamp. Light at 313 nm was isolated by means of a $K_2Cr_2O_7$ alkaline solution or an Oriel P/N 56410 interference filter. The light intensity, measured by ferrioxalate actinometry³⁵ and/or by the known quantum yield (0.31) of $K_3[Co(CN)_6]$ monophotoaquation,³⁶ was of the order of 10^{-7} Einstein min^{-1} . The photolyses were performed on 3.0 ml of solution in a conventional spectrophotometric cell (1 cm optical path) and were followed by UV/VIS spectrophotometry.

Quantum yields were calculated by monitoring the absorbances at 313 and 380 nm with irradiation time. The absorbances were corrected for the fraction of light absorbed only by the reactive species. For pH < 3.5, linear $\Delta A_{380\, nm}$ vs. time plots were obtained. For pH > 3.5 the same plots show a negative deviation (see Results and Discussion section) and the quantum yield was calculated from the slope tangent at the initial time.

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References

- 1 V. Balzani, N. Sabbatini and F. Scandola, *Chem. Rev.*, 1986, **86**, 319.
- 2 V. Balzani, R. Ballardini, M. T. Gandolfi and L. Prodi, in *Supramolecular Photochemistry of Coordination Compounds: Ion-Pairs and Host-Guest Systems*, eds. H. J. Schneider and H. Dürr, VCH, Weinheim, 1991, p. 371.
- 3 L. Moggi and M. F. Manfrin, in *Photochemistry and Photophysics of Supramolecular Systems Containing Anions*, eds. A. Bianchi, K. Bowman-James and E. Garcia-España, Wiley-VCH, Weinheim, 1997, p. 321.
- 4 A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1987, **26**, 3902.
- 5 A. Bianchi, M. Micheloni and P. Paoletti, *Pure Appl. Chem.*, 1988, **60**, 525.
- 6 A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, M. Micheloni, J. A. Ramirez, P. Paoletti and P. Paoli, *Inorg. Chem.*, 1992, **31**, 1902.
- 7 J. M. Lehn, in *Photophysical and Photochemical Aspects of Supramolecular Chemistry*, ed. V. Balzani, Reidel, Dordrecht, 1987, p. 29.
- 8 M. W. Hosseini, in *Preorganization of the Second Coordination Sphere*, eds. A. F. Williams, C. Floriani and A. E. Merbach, VCH, Weinheim, 1992, p. 333.
- 9 M. F. Manfrin, N. Sabbatini, L. Moggi, V. Balzani, M. W. Hosseini and J. M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1984, 555.
- 10 M. F. Manfrin, L. Moggi, V. Castelvetro, V. Balzani, M. W. Hosseini and J. M. Lehn, *J. Am. Chem. Soc.*, 1985, **107**, 6888.
- 11 F. Pina, L. Moggi, M. F. Manfrin, V. Balzani, M. W. Hosseini and J. M. Lehn, *Gazz. Chim. Ital.*, 1989, **119**, 65.
- 12 A. J. Parola and F. Pina, *J. Photochem. Photobiol. A*, 1992, **66**, 337.
- 13 J. Sotomayor, A. J. Parola, F. Pina, E. Zinato, P. Riccieri, M. F. Manfrin and L. Moggi, *Inorg. Chem.*, 1995, **34**, 6532.
- 14 V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, 1975, **14**, 401.
- 15 N. Maki, *Inorg. Chem.*, 1974, **13**, 2180.
- 16 H. H. Chen, M. S. Tsao, R. W. Gaver, P. H. Tewari and W. K. Wilmarth, *Inorg. Chem.*, 1966, **5**, 1913.
- 17 J. Fujita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 1281.
- 18 J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.
- 19 J. Jordan and G. J. Ewing, *Inorg. Chem.*, 1962, **1**, 587.
- 20 T. Förster, *Z. Elektrochem.*, 1950, **54**, 42.
- 21 C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968, p. 332.
- 22 B. Dietrich, M. W. Hosseini, J. M. Lehn and R. B. Sessions, *J. Am. Chem. Soc.*, 1981, **103**, 1282.
- 23 E. Garcia-España, M. Micheloni, P. Paoletti and A. Bianchi, *Inorg. Chim. Acta*, 1985, **102**, L9.
- 24 J. Aragó, A. Bencini, A. Bianchi, A. Domenech and E. Garcia-España, *J. Chem. Soc., Dalton Trans.*, 1992, 319.
- 25 F. Peter, M. Gross, M. W. Hosseini, J. M. Lehn and R. B. Sessions, *J. Chem. Soc., Chem. Commun.*, 1981, 1067.
- 26 F. Peter, M. Gross, M. W. Hosseini and J. M. Lehn, *J. Electroanal. Chem. Interfacial Electrochem.*, 1983, **144**, 279.
- 27 M. A. Rampi, M. T. Indelli, F. Scandola, F. Pina and A. J. Parola, *Inorg. Chem.*, 1996, **35**, 3355.
- 28 C. A. Bignozzi, C. Chiorboli, M. T. Indelli, M. A. R. Scandola, G. Varani and F. Scandola, *J. Am. Chem. Soc.*, 1986, **108**, 7872.
- 29 M. T. Indelli, C. A. Bignozzi, A. Marconi and F. Scandola, *J. Am. Chem. Soc.*, 1988, **110**, 7381.
- 30 B. Loeb and F. Zuloaga, *J. Phys. Chem.*, 1977, **81**, 59.
- 31 A. W. Adamson, *J. Am. Chem. Soc.*, 1956, **78**, 4260.
- 32 B. Dietrich, M. W. Hosseini, J. M. Lehn and R. B. Sessions, *Helv. Chim. Acta*, 1983, **66**, 1262.
- 33 A. Bianchi, S. Mangani, M. Micheloni, V. Nanini, P. Orioli, P. Paoletti and B. Seghi, *Inorg. Chem.*, 1985, **24**, 1182.
- 34 A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1987, **26**, 1243.
- 35 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.
- 36 L. Moggi, F. Bolletta, V. Balzani and F. Scandola, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2589.

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