Charge effects on the photochemistry of the $Co(EDTA)^- \cdot I^-$ system in the presence of polyammonium macrocyclic receptors

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Abstract

The effects of polyammonium macrocycles on the spectroscopic and photochemical properties of the $Co(EDTA)^- \cdot I^-$ ion-pair have been investigated. The addition of a macrocycle to aqueous solutions containing $Co(EDTA)^-$ and I^- causes an increase of the absorbance in the region of the ion-pair charge-transfer band, as well as an increase of the quantum yield for the intramolecular photooxidation reduction of the ion-pair. Both these effects are mainly, if not only, due to an increase of the association constant between $Co(EDTA)^-$ and I^-, caused by the positive charge of the macrocycle bound to the complex. On the contrary no change was observed on the intrinsic photoreactivity of the excited ion-pair. This last result is discussed in comparison with the effects already observed on the ligand photodissociation of MC excited states of Co(III) cyanide complexes.

Introduction

Polyammonium macrocycles are known [1–5] to form 1:1 supramolecular adducts with several anionic coordination compounds. In the case of $Co(CN)_6^{3-}$ and $Co(CN)_5Br^{3-}$, the photochemical behaviour of these adducts was also investigated [6–8], and it has been found that the interaction with the macrocycle does not affect the nature of the photoreaction of the parent complex (namely, ligand photoaquation), but causes a decrease of its quantum yield.

In order to extend similar studies to photoreactions of different nature, we have investigated the photochemical behaviour of aqueous solutions of the $Co(EDTA)^- \cdot I^-$ ion-pair in the presence of the protonated forms of the polyaza macrocycles 1,5,9,13,17,21-hexaazacyclotetraeicosane (hereafter called [24]ane-N_6), 1,5,9,13,17,21,25,29-octaazacyclodotriacontane ([32]ane-N_8) or 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane ([30]ane-N_{10}), which are shown in Fig. 1. $Co(EDTA)^- \cdot I^-$ is in fact known [9, 10] to undergo an intramolecular photooxidation reduction upon excitation into the ion-pair charge-transfer (IPCT) absorption band; the photoreaction consists of the homolytic cleavage of the complex–I^- bond in the IPCT excited state of the ion-pair

$$Co^{III}(EDTA)^- \cdot I^- \xrightarrow{h\nu(IPCT)} Co^{II}(EDTA)^{2-} \cdot I^\cdot \qquad (1)$$

followed by secondary processes which lead to $Co(EDTA)^{2-}$ and I_3^- as final products.

Experimental

K[Co(EDTA)] was prepared following the method of Dwyer *et al.* [11]. The polyammonium macrocycles were prepared and used as chloride salts. [24]ane-N_6 and [32]ane-N_8 were synthesized as described in ref. 12, except that the starting material was 1,3-propanediamine instead of 3,3′-diaminodipropylamine. [30]ane-N_{10} was prepared as described in ref. 13. All the other chemicals were of reagent grade.

Electronic absorption spectra were recorded on a Shimadzu UV 160 spectrophotometer.

Light excitation at 313 nm was isolated from the emission of a medium pressure mercury lamp (Müller Elektronik Optik) by means of an interference filter (Oriel P/N 56410). The intensity of the light incident on the reaction cell (2.7×10^{-7} Einstein min^{-1}) was measured by means of ferrioxalate actinometry [14].

All the experiments were carried out at room temperature on acidic ($HClO_4$) aqueous solutions containing

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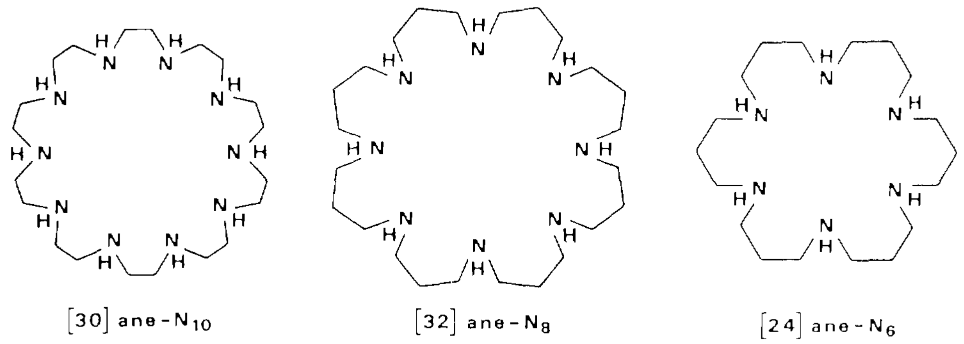

Fig. 1. The polyaza macrocycles [30]ane-N_{10}, [32]ane-N_8 and [24]ane-N_6.

K[Co(EDTA)] (1.0×10^{-3} M), KI (0–0.10 M) and the macrocycle (2×10^{-3} to 4×10^{-3} M). The analytical procedure for the quantum yield determination is described in ref. 9.

Results

It is known [9, 10] that a new absorption around 300 nm appears in the spectrum of Co(EDTA)$^-$ upon addition of I$^-$ (Fig. 2). This new absorption was identified [9] as a charge-transfer transition (IPCT) within the ion-pair that the two ions are able to form in spite of the fact that they are like charged.

$$\mathrm{Co(EDTA)^-} + \mathrm{I^-} \overset{K_{ip}}{\rightleftharpoons} \mathrm{Co(EDTA)^-} \cdot \mathrm{I^-} \qquad (2)$$

An independent evaluation of the association constant, K_{ip}, and of the molar absorption coefficient of the ion-pair, ϵ_{ip}, cannot be achieved [10] in this case from absorbance measurements by means of the usual Benesi–Hildebrand equation [15], because K_{ip} is by far too small and the product $K_{ip}\times[\mathrm{I^-}]_0$ is much less than 1 at all the attainable initial concentrations of I$^-$, $[\mathrm{I^-}]_0$. However, it has been observed [10] that, in similar situations, the equilibrium concentration of the ion-pair is much less than the initial concentrations of the parent ions and thus, provided that the initial concentration of I$^-$ exceeds that of Co(EDTA)$^-$, the following approximate equations hold

$$[\mathrm{IP}] = K_{ip}[\mathrm{Co}]_0[\mathrm{I^-}]_0 \qquad (3)$$

$$A = \epsilon_0[\mathrm{Co}]_0 + \epsilon_{ip}K_{ip}[\mathrm{Co}]_0[\mathrm{I^-}]_0 \qquad (4)$$

where [IP] is the equilibrium concentration of the ion-pair, $[\mathrm{Co}]_0$ the initial concentration of Co(EDTA)$^-$, A the absorbance of the solution, and ϵ_0 the molar absorption coefficient of 'free' Co(EDTA)$^-$. According to eqn. (4) and in agreement with a previous report [10], we have found that the ratio $A/[\mathrm{Co}]_0$ increases linearly with $[\mathrm{I^-}]_0$ (Fig. 3); the value of the slope of this line, which is equal to the product $\epsilon_{ip}K_{ip}$, is 451 dm^6 mol^{-2} cm^{-1} at 313 nm for a 1.0×10^{-3} M solution of Co(EDTA)$^-$, in a very good agreement with the value previously obtained [10] for a more concentrated solution.

The addition of polyammonium macrocycles (which have a negligible light absorption above 280 nm) to an acidic solution containing Co(EDTA)$^-$ has no effect on the absorbance around 300 nm in the absence of I$^-$, while it causes an increase of the absorbance when I$^-$ is present (Fig. 2 and Table 1); the absorbance exhibits again a linear dependence on $[\mathrm{I^-}]_0$ but, as shown in Fig. 3, the slope is larger than that obtained in the absence of the macrocycle. The values of the slopes of similar plots obtained at 313 nm for solutions containing [24]ane-N_6, [32]ane-N_8 or [30]ane-N_{10} are summarized in column 4 of Table 1.

313 nm excitation of solutions containing Co(EDTA)$^-$ and I$^-$ leads [9, 10] to the following overall photoreaction

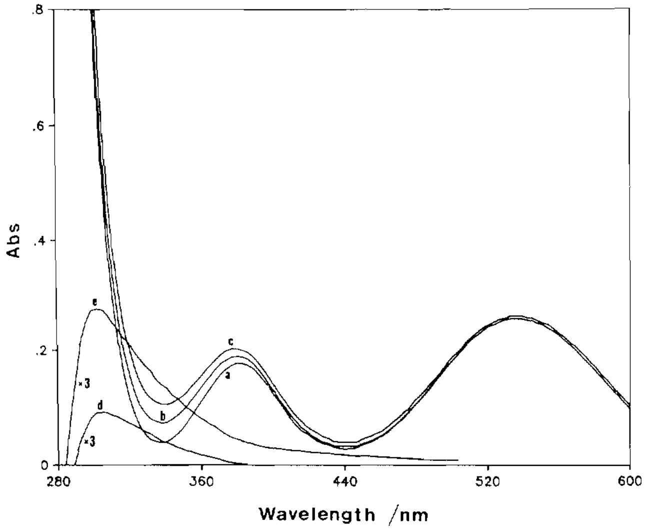

Fig. 2. Electronic absorption spectra of a 1.0×10^{-3} M solution of Co(EDTA)$^-$: a, alone; b, in the presence of 0.10 M I$^-$; c, in the presence of 0.10 M I$^-$ and 2.0×10^{-3} M [32]ane-N_8; d, absorbance difference between spectra b and a; e, absorbance difference between spectra c and a. (I$^-$ and [32]ane-N_8 have negligible absorption above 280 nm.)

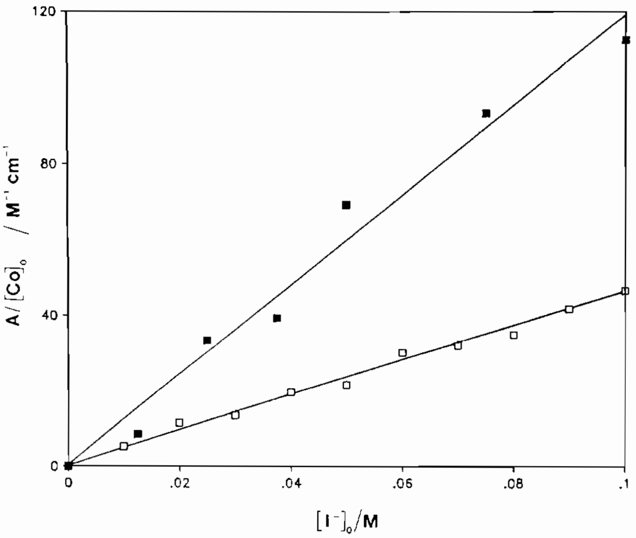

Fig. 3. Values of $A/[Co]_0$ at 313 nm, for a 1.0×10^{-3} M solution of $Co(EDTA)^-$, as a function of I^- concentration, in the absence of macrocycles (□) and in the presence of 2.0×10^{-3} M [30]ane-N_{10} (■).

$$2Co(EDTA)^- + 3I^- \xrightarrow{h\nu} 2Co(EDTA)^{2-} + I_3^- \qquad (5)$$

The quantum yield of I_3^- formation, Φ_{obs}, calculated on the basis of the total amount of light absorbed by the solution (i.e. the light absorbed by both the ion-pair and the 'free' $Co(EDTA)^-$) and reported in the first row of Table 1, is in good agreement with the values previously obtained [9] at a different pH.

The same photoreaction has been obtained upon 313 nm excitation in the presence of the polyammonium macrocycles listed above, but the values of Φ_{obs} (rows 2–5 of Table 1) are higher than those in the absence of the organic molecules.

Discussion

The results reported above and summarized in Table 1 clearly show that the addition of a polyammonium macrocycle to a solution containing $Co(EDTA)^-$ and I^- causes an increase of both the absorbance of the solution in the region of the IPCT band and the experimental quantum yield, Φ_{obs}, of I_3^- production. Both these results are evidences for an interaction between the macrocycle and $Co(EDTA)^-$ or I^-. Since the values of association constants [1, 5] indicate that the formation of adducts between these macrocycles and I^- is negligible in the experimental conditions used, we conclude that a macrocycle–$Co(EDTA)^-$ adduct, hereafter called $PM\text{–}Co^{x+}$, is present in our systems, which therefore contain four species absorbing 313 nm light: $Co(EDTA)^-$, $PM\text{–}Co^{x+}$, and the ion-pairs $Co(EDTA)^-\cdot I^-$ and $PM\text{–}Co^{x+}\cdot I^-$*. The concentrations of these species are related to each other by the equilibria (2), (6) and (7).

$$Co(EDTA)^- + \text{macrocycle} \overset{K_m}{\rightleftharpoons} PM\text{–}Co^{x+} \qquad (6)$$

$$PM\text{–}Co^{x+} + I^- \overset{K'_{ip}}{\rightleftharpoons} PM\text{–}Co^{x+}\cdot I^- \qquad (7)$$

The association constant for the ion-pairing between $PM\text{–}Co^{x+}$ and I^-, K'_{ip}, is obviously expected to be larger than the constant of the simple $Co(EDTA)^-\cdot I^-$ion-pair, K_{ip}, as a consequence of the large positive charge carried on by the protonated form of the macrocycle. Setting $[Co(EDTA)^-] = \alpha\times[Co]_0$ and

TABLE 1. Effect of polyammonium macrocycles on the photochemistry of $Co(EDTA)^-\cdot I^-$ [a]

Macrocycle	pH	A[b]	$\epsilon_{ip}K_{ip}$ [b,c]	Φ_{obs} [d]	φ[e]	Charge[f]
	2.6	0.274	451	0.056	0.34	
[24]ane-N_6 (2.0×10^{-3} M)	2.6	0.312	830	0.077	0.30	6
[32]ane-N_8 (2.0×10^{-3} M)	2.6	0.318	890	0.089	0.32	8
[32]ane-N_8 (4.0×10^{-3} M)	2.6	0.368	1390	0.139	0.36	8
[30]ane-N_{10} (2.0×10^{-3} M)	2.0	0.340	1110	0.117	0.35	9.5

[a] $[Co(EDTA)^-] = 1.0\times10^{-3}$ M; $[I^-] = 0.10$ M; excitation at 313 nm. [b] At 313 nm. [c] The dimensions are $dm^6\ mol^{-2}\ cm^{-1}$. [d] Quantum yield of I_3^- formation based on the total light absorbed by the solution; uncertainty: ±0.005. [e] Average 'true' quantum yield of I_3^- formation calculated by means of eqn. (12); uncertainty: ±0.03. [f] Ionic charge of the macrocycle at the pH of the solution, calculated using the reported [12, 13] values of pK_a.

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*A comparison of rows 3 and 4 in Table 1 shows that only a fraction of $Co(EDTA)^-$ has formed an adduct with the macrocycle, at least for the lower concentration of the macrocycle; the same might also occur in the case of the other two macrocycles.

$[\text{PM–Co}^{x+}] = \beta \times [\text{Co}]_0$ *, the absorbance of the solution is given by

$$A = \epsilon_0\alpha[\text{Co}]_0 + \epsilon'_0\beta[\text{Co}]_0 + \epsilon_{\text{ip}}K_{\text{ip}}\alpha[\text{Co}]_0[\text{I}^-]_0 + \epsilon'_{\text{ip}}K'_{\text{ip}}\beta[\text{Co}]_0[\text{I}^-]_0 \qquad (8)$$

where ϵ'_0 and ϵ'_{ip} are the molar extinction coefficients of PM–Co^{x+} and $\text{PM–Co}^{x+}\cdot\text{I}^-$, respectively. Taking into account that:

(i) $\epsilon_0 = \epsilon'_0$, since macrocycles have no effect on the absorbance of Co(EDTA)^- in the absence of I^-;

(ii) the linearity of the A vs. $[\text{I}^-]_0$ plots indicate that α and β are practically independent of $[\text{I}^-]_0$, in the limits of our experimental conditions;

(iii) in our experimental conditions, $[\text{I}^-] \approx [\text{I}^-]_0$; eqn. (8) can be rearranged to

$$A = \epsilon_0[\text{Co}]_0 + \{\epsilon_{\text{ip}}K_{\text{ip}}\alpha + \epsilon'_{\text{ip}}K'_{\text{ip}}(1-\alpha)\}[\text{Co}]_0[\text{I}^-]_0 \qquad (9)$$

This equation reduces to eqn. (4) in the absence of macrocycles ($\alpha = 1$), and implies analogous approximations, namely $[\text{Co(EDTA)}^-] + [\text{PM–Co}^{x+}] \approx [\text{Co}]_0$ at all the experimental conditions, $K_{\text{ip}}[\text{I}^-]_0 \ll 1$, $K'_{\text{ip}}[\text{I}^-]_0 \ll 1$.

Equation (9) shows that the slopes of the $A/[\text{Co}]_0$ versus $[\text{I}^-]_0$ plots are weighed averages of the products $\epsilon_{\text{ip}}K_{\text{ip}}$ and $\epsilon'_{\text{ip}}K'_{\text{ip}}$.

$$\overline{\epsilon_{\text{ip}}K_{\text{ip}}} = \epsilon_{\text{ip}}K_{\text{ip}}\alpha + \epsilon'_{\text{ip}}K'_{\text{ip}}(1-\alpha) \qquad (10)$$

The values of $\overline{\epsilon_{\text{ip}}K_{\text{ip}}}$ are collected in Table 1: since $\alpha = 1$ at $[\text{macrocycle}]_0 = 0$ and it obviously decreases with increasing [macrocycle], an inspection of the trend of $\overline{\epsilon_{\text{ip}}K_{\text{ip}}}$ in Table 1 clearly indicates that $\epsilon'_{\text{ip}}K'_{\text{ip}} > \epsilon_{\text{ip}}K_{\text{ip}}$. The already discussed inequality $K'_{\text{ip}} > K_{\text{ip}}$ obviously gives a major contribution to this result, and the fact that the trend of the $\overline{\epsilon_{\text{ip}}K_{\text{ip}}}$ values parallels that of the ionic charge of the macrocycles (last column in Table 1) corroborates this view. Since in the present conditions, it is impossible to evaluate ϵ_{ip} and ϵ'_{ip} independently by means of spectrophotometric measurements, the possibility that these terms give a minor contribution to the change of $\overline{\epsilon_{\text{ip}}K_{\text{ip}}}$ cannot be discarded; however, the photochemical results discussed below suggest that the IPCT excited states of $\text{Co(EDTA)}^-\cdot\text{I}^-$ and $\text{PM–Co}^{x+}\cdot\text{I}^-$ ion-pairs have quite similar spectroscopic properties.

In the absence of a macrocycle, the observed photochemical reaction only originates [9, 10] from the IPCT excited state of $\text{Co(EDTA)}^-\cdot\text{I}^-$ ion-pair, while 'free' Co(EDTA)^- is photoinert; a similar difference can be safely assumed to occur between $\text{PM–Co}^{x+}\cdot\text{I}^-$ and PM–Co^{x+}. Therefore, the change of Φ_{obs} caused by the addition of a macrocycle can be ascribed to a change in the repartition of the absorbed light between photoactive and photoinert species and/or to a different intrinsic photoreactivity of the two ion-pairs, $\text{PM–Co}^{x+}\cdot\text{I}^-$ and $\text{Co(EDTA)}^-\cdot\text{I}^-$; these photoreactivities are measured by the 'true' quantum yields of the photoreaction of the photoactive ion-pairs, φ for $\text{Co(EDTA)}^-\cdot\text{I}^-$ and φ' for $\text{PM–Co}^{x+}\cdot\text{I}^-$, i.e. the ratios between the amount of I_3^- formed and the amount of light absorbed by each ion-pair.

Whenever eqn. (4) holds, the relation between Φ_{obs} and φ in the absence of macrocycles is given [10] by

$$\Phi_{\text{obs}} \times \frac{A}{\epsilon_{\text{ip}}K_{\text{ip}}[\text{Co}]_0[\text{I}^-]_0} = \varphi \qquad (11)$$

where the symbols used have the meanings stated above. The value of φ calculated by means of this equation is shown in column 6, row 1 of Table 1. In the presence of a macrocycle, the analogy of eqn. (11) is

$$\Phi_{\text{obs}} \frac{A}{\overline{\epsilon_{\text{ip}}K_{\text{ip}}}[\text{Co}]_0[\text{I}^-]_0} = \varphi\frac{\epsilon_{\text{ip}}K_{\text{ip}}\alpha}{\overline{\epsilon_{\text{ip}}K_{\text{ip}}}} + \varphi'\frac{\epsilon'_{\text{ip}}K'_{\text{ip}}(1-\alpha)}{\overline{\epsilon_{\text{ip}}K_{\text{ip}}}} \qquad (12)$$

the right side of which is a weighed average of φ and φ'

$$\bar{\varphi} = \varphi\gamma + \varphi'(1-\gamma) \qquad (13)$$

where $\gamma = \epsilon_{\text{ip}}K_{\text{ip}}\alpha/\overline{\epsilon_{\text{ip}}K_{\text{ip}}}$. Values of $\bar{\varphi}$ have been calculated by means of eqn. (12) for all of our experiments in the presence of a macrocycle, and are reported in Table 1: they are practically equal to each other and also equal to φ obtained in the absence of macrocycles. Since α and thus γ depend on $[\text{macrocycle}]_0$, this result clearly demonstrates that $\varphi = \varphi'$ within experimental error, i.e., that $\text{PM–Co}^{x+}\cdot\text{I}^-$ and $\text{Co(EDTA)}^-\cdot\text{I}^-$ have the same 'true' quantum yield, and thus the same intrinsic photoreactivity. In other words, our results show that the addition of a macrocycle increases the relative production of excited ion-pairs under light excitation, but it does not affect their fate.

This result is quite different from the effects that the same polyammonium macrocycles have on the photochemical reactions of Co(CN)_6^{3-} and $\text{Co(CN)}_5\text{Br}^{3-}$ [6–8]

$$\text{Co(CN)}_5\text{X}^{3-} \xrightarrow{h\nu,\ \text{H}_2\text{O}} \text{Co(CN)}_5\text{H}_2\text{O}^{2-} + \text{X}^- \qquad (14)$$

X = CN, Br

which originate from a dissociative metal-centered (MC) excited state of the complex: no change in the MC absorption spectrum was in fact observed, but the quantum yield of the photoreaction was strongly reduced. These complexes form adducts of defined molecular structure with the macrocycles, in which some CN^- ligands are hydrogen-bound to ammonium groups;

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*At $[\text{I}^-]_0 = 0$, it is obviously $\alpha + \beta = 1$; moreover, $\alpha = 1$ for $[\text{macrocycle}] = 0$ and it decreases with increasing macrocycle concentration. At $[\text{I}^-]_0 > 0$, $\alpha + \beta < 1$ and both these terms decrease with increasing $[\text{I}^-]_0$.

in these supramolecular structures, the photophysical and photochemical properties of the reacting excited state of the complex remain unchanged at 'spectroscopic' Co–X distances but, when Co–X bonds are temporarily broken by light excitation the X^- ligand is restrained to escape out of the coordination sphere because of steric limitations, hydrogen bonding (for $X=CN$), or coulombic interaction (for $X=Br$) with the macrocycle.

The photochemistry of the $Co(EDTA)^- \cdot I^-$ ion-pair proceeds through the following main mechanism [9, 10]

$$Co^{III}(EDTA)^- \cdot I^- \xrightarrow{h\nu(IPCT)} Co^{II}(EDTA)^{2-} \cdot I^{\bullet} \text{ (excitation)} \qquad (15)$$

$$Co^{II}(EDTA)^{2-} \cdot I^{\bullet} \rightarrow \begin{cases} Co^{III}(EDTA)^{-} \cdot I^{-} & (16) \\ \text{(backbonding)} & \\ Co^{II}(EDTA)^{2-} + I^{\bullet} & (17) \\ \text{(dissociation)} & \end{cases}$$

$$I^{\bullet} \longrightarrow \ldots \ \ldots \longrightarrow I_3^- \qquad (18)$$

and an analogous mechanism is quite probably operative for the $PM\text{–}Co^{x+} \cdot I^-$ ion-pair. The equality $\varphi = \varphi'$ indicates that the dissociation

$$PM\text{–}Co^{(x-1)+} \cdot I^{\bullet} \longrightarrow PM\text{–}Co^{(x-1)+} + I^{\bullet} \qquad (19)$$

has the same efficiency as step (17), i.e. that the dissociation of the $I^{\bullet}$ radical from the Co(II) complex is not affected by the presence of the macrocycle. The lack of a 'long distance' shielding effect by the macrocycles, analogous to that described above for the photochemistry of cyanide complexes, can be easily explained by considering that:

(i) the macrocycle is quite probably bound to the EDTA ligand and thus it leaves unshielded the pocket in the first coordination sphere, through which the iodide ion approaches to and the iodine radical goes away from the metal ion;

(ii) the leaving iodine radical does not interact with the macrocycle through hydrogen bonding;

(iii) the positive charge of the bound macrocycle cannot affect the diffusion of the uncharged $I^{\bullet}$ radical into the bulk, even if it promotes the approach of I^- to the metal ion.

Modification of photodissociative processes of coordination compounds by means of adduct formation with polyammonium macrocycles seems therefore to depend on the nature of the leaving particle.

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