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Control of the Thermal and Photochemical Aquation of the Hexacyanochromate(III) and Aquapentacyanochromate(III) Ions by Formation of a Supramolecular Structure with [32]ane-N_8

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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 the protonated form of the polyaza macrocycle [32]ane-N_8. On the other hand, the same macrocycle has practically no effect on the photoaquation of $[Cr(CN)_5(H_2O)]^{2-}$ and a very small effect on the thermal reaction of this complex. These results are discussed in relation to the thermal and photochemical reaction mechanisms and to the steric configuration of the adducts between complexes and macrocycle.

Introduction

Control of the reactivity of transition-metal complexes can be achieved by their inclusion into supramolecular structures involving appropriate macrocyclic receptors.[1] In the case of cyanide complexes, the protonated forms of polyaza macrocycles were found to be good receptors;[2] we have already investigated[3−6] the thermal and photochemical properties of adducts formed by these macrocycles and the hexacyanocobaltate(III) ion and its derivatives, and found that the receptor affects the reactivity of these complexes through steric or charge effects.

The hexacyanochromate(III) ion undergoes a photoaquation reaction[7−9] analogous to that of $[Co(CN)_6]^{3-}$, but unlike the cobalt complex, it also exhibits a thermal aquation reaction complicated by numerous secondary processes.[10−14] It appears, therefore, of interest to study these aquations in the presence of polyaza macrocycles, in order to compare the effects of the receptors on the thermal and photochemical processes and to obtain additional information on the reaction mechanisms as well as on the interaction between complex and macrocycle. In this paper we report the results of a study of the reactions in aqueous solutions of $[Cr(CN)_6]^{3-}$ and its first aquation product, $[Cr(CN)_5(H_2O)]^{2-}$, in the presence of the macrocycle 1,5,9,13,17,21,25,29-octaazacyclodotriacontane, [32]ane-N_8.

Experimental Section

Caution! Care must be exercised in handling cyanide compounds. All operations should be performed in a well-ventilated hood.

$K_3[Cr(CN)_6]$. This complex was prepared by reaction of chromium(III) acetate with KCN in aqueous solution in the presence of activated charcoal, according to a standard procedure.[15]

$K_3[Cr(CN)_5(OH)]\cdot 2H_2O$. It was realized that, by the same procedure, shorter reaction times (heating for 20−30 min rather than 60−90 min) led to mixtures of $[Cr(CN)_5(OH)]^{3-}$ and $[Cr(CN)_6]^{3-}$, besides minor quantities of other Cr-CN species. Addition to the filtered reaction mixture of an equal volume of 0.5 M potassium acetate in ethanol and cooling in a freezer, precipitated an orange solid that was collected by filtration and washed with ethanol. The crude product (1.5 g) was redissolved in a minimum volume (2−3 mL) of H_2O and eluted with water through a 35 × 1.5 cm column of Sephadex G15 gel filtration resin. While a brown residue remained at the top of the column, the moving solution separated into three bands consisting mainly of $[Cr(CN)_3(H_2O)_3]$ (yellow), $[Cr(CN)_5(OH)]^{3-}$ (orange), and $[Cr(CN)_6]^{3-}$ (yellow), in order of recovery and as identified spectrophotometrically. The second fraction (*ca.* 15 mL) was slowly treated with 30 mL of 0.5 M ethanolic potassium acetate and kept overnight

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in a refrigerator. The orange-yellow precipitate (1.0 g) was filtered off, washed with ethanol and vacuum dried. This material was further purified by at least two more fractionations through the G15 resin: only the core of the spreading band was collected, showing an intensity ratio of 1.6 between the two ligand-field spectral maxima (the discarded side fractions exhibited lower ratios). After the volume was reduced to less than 1 mL in a KOH desiccator, the complex salt was separated by addition of ethanol and washed and dried as above.

The Cr content (14.5 ± 0.1%) is consistent with the occurrence of 2 molecules of H_2O of crystallization (calcd 14.7%) at variance with the single molecule reported by Sakabe.[16] The ligand-field absorption spectrum presents maxima at 436 nm (ϵ = 118 cm^{-1} M^{-1}) and 368 nm (ϵ = 73 cm^{-1} M^{-1}, shoulder) in alkaline solution (pH 12) and at 428 nm (ϵ = 110 cm^{-1} M^{-1}) and 334 nm (ϵ = 50.4 cm^{-1} M^{-1}) in acid solution (pH 4.7), in good agreement with the literature data presented only graphically.[11,16] Acid titration indicates 1 equiv of base per mole of complex, with a pK_a of 8.6, close to the previously reported values.[11,17] The protonated (aqua) form cannot be obtained as a solid salt.

[32]ane-N$_8$. The macrocycle 1,5,9,13,17,21,25,29-octaazacyclodotriacontane was synthesised following a reported method,[18] except that 1,3-propanediamine was used as starting material in place of 3,3'-diaminodipropylamine. The compound was prepared and used as its hydrochloride, [32]ane-N_8·8HCl.

Procedures. Thermal and photochemical experiments were carried out on aqueous solutions of the complex (3 × 10^{-3} mol dm^{-3}) at 25 °C. The concentration of the macrocycle, if present, was either 1.2 or 3.0 times that of the complex. Thermal reaction studies were made at pH 1.0 ($HClO_4$) and pH 4.3 (acetate buffer, 10^{-3} M), and photochemical experiments at pH 4.3 or 6.0 (phosphate buffer, 10^{-3} M). The macrocycle remains totally protonated up to pH 6 and, under these experimental conditions, interacts weakly with the acetate and phosphate ions.[2a]

Photolysis were performed using a Xe–Hg lamp. Light of 313 or 366 nm was isolated by means of a K_2CrO_4 solution or an Oriel P/N 564309 BAGT glass filter, respectively. The light intensity, measured by ferrioxalate actinometry,[19] was of the order of 10^{-7} einstein min^{-1} at both wavelengths.

UV–visible absorption spectra were recorded with a Lambda-6 Perkin-Elmer spectrophotometer and a Hewlett-Packard 8452A diode-array instrument. The concentrations of the aqua–cyano complexes obtained at various reaction times as photochemical or thermal products (see below) were evaluated by simultaneous analysis of absorbance values at several wavelengths, using the extinction coefficients of *fac*-$[Cr(CN)_3(H_2O)_3]$ and its aquation products published elsewhere.[20] Pure solution samples of the tricyano complex were isolated chromatographically in the course of the above-described preparation, and the literature spectral data were confirmed by Cr analysis. Due to the large difference in ligand field strength between CN^- and H_2O, the absorption spectra of the various aqua-cyano complexes of Cr(III) are sufficiently different to allow a satisfactory determination.

Kinetic constants were calculated from the time-dependence of these concentrations using the ROK computer program.[21]

Results

Thermal Aquation. In aqueous solution, $[Cr(CN)_6]^{3-}$ is known[10,11] to undergo acid-catalyzed, consecutive ligand substitution reactions, leading to $[Cr(H_2O)_6]^{3+}$ as the final product. Four intermediate products have been observed by means of spectrophotometric measurements and chromatographic separations: the first was originally identified[10,20] as $[Cr(CN)_4(H_2O)_2]^-$, but later studies demonstrated[17] that it consists of $[Cr(CN)_5(H_2O)]^{2-}$; the other intermediates observed[10] were $[Cr(CN)_3(H_2O)_3]$, $[Cr(CN)_2(H_2O)_4]^+$, and $[Cr(CN)(H_2O)_5]^{2+}$. For $[Cr(CN)_3(H_2O)_3]$ and $[Cr(CN)_2(H_2O)_4]^+$, only one isomer (assigned as *fac* and *cis*, respectively) was observed.[10,20] The thermal behavior of $[Cr(CN)_6]^{3-}$ is therefore represented by the following reaction sequence:

$$[Cr(CN)_6]^{3-} + H_3O^+ \rightarrow [Cr(CN)_5(H_2O)]^{2-} + HCN \quad (1)$$

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

$$fac\text{-}[Cr(CN)_3(H_2O)_3] + H_3O^+ \rightarrow cis\text{-}[Cr(CN)_2(H_2O)_4]^+ + HCN \quad (3)$$

$$cis\text{-}[Cr(CN)_2(H_2O)_4]^+ + H_3O^+ \rightarrow [Cr(CN)(H_2O)_5]^{2+} + HCN \quad (4)$$

$$[Cr(CN)(H_2O)_5]^{2+} + H_3O^+ \rightarrow [Cr(H_2O)_6]^{3+} + HCN \quad (5)$$

Reaction 2 must actually be considered as a slow–fast, two-step process:

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

$$[Cr(CN)_4(H_2O)_2]^- + H_3O^+ \xrightarrow{\text{fast}} fac\text{-}[Cr(CN)_3(H_2O)_3] + HCN \quad (2b)$$

The spectral changes obtained in the present study for the overall reaction of $[Cr(CN)_6]^{3-}$ at pH 1.0 are shown in parts A and B of Figure 1; the absorbance values at various times confirm the proposed sequence, since they can be satisfactorily fitted by appropriate mixtures of the above-mentioned species.

Concentrations of these species at various reaction times are summarized in parts C and D of Figure 1. It is clearly seen that reactions 1 and 2 occur in a time scale much shorter than that of the subsequent reactions, as had already been observed.[10] From the time dependence of the concentrations it should be possible, in principle, to evaluate the pseudo-first-order (at constant acidity) rate constants for reactions 1–5. We have, however, found that a satisfactory fit of the experimental data of Figure 1C at relatively long reaction times could only be obtained by taking into account the back reactions, *i.e.*, the substitution of H_2O by CN^- in the aqua complexes. In addition, reliable values for the rate constants of reactions 3–5 could not be calculated because of the large uncertainty on the concentrations of $[Cr(CN)_2(H_2O)_4]^+$ and subsequent products. Rate constant values at 25 ° C for reaction 1 (k_1), its reverse (k_{-1}), and reaction 2 (k_2, which is actually the rate constant for step 2a) are summarized in Table 1.

The thermal reaction of $[Cr(CN)_6]^{3-}$ at pH 4.3 is much slower, as expected, but shows the same qualitative trend as at pH 1.0. The values of k_1, k_{-1}, and k_2 at this pH are also summarized in Table 1.

The spectral changes caused by the thermal aquation of pure $[Cr(CN)_5(H_2O)]^{2-}$ at a pH of either 1.0 or 4.3, are characterized by an isosbestic point at 445 nm, which corresponds to the crossing point between the absorption spectra of $[Cr(CN)_5(H_2O)]^{2-}$ and *fac*-$[Cr(CN)_3(H_2O)_3]$. At pH 1.0, the isosbestic point is maintained until the reactant is almost completely converted into the product, while at pH 4.3, it disappears before conversion is complete. The rate constants for the observed

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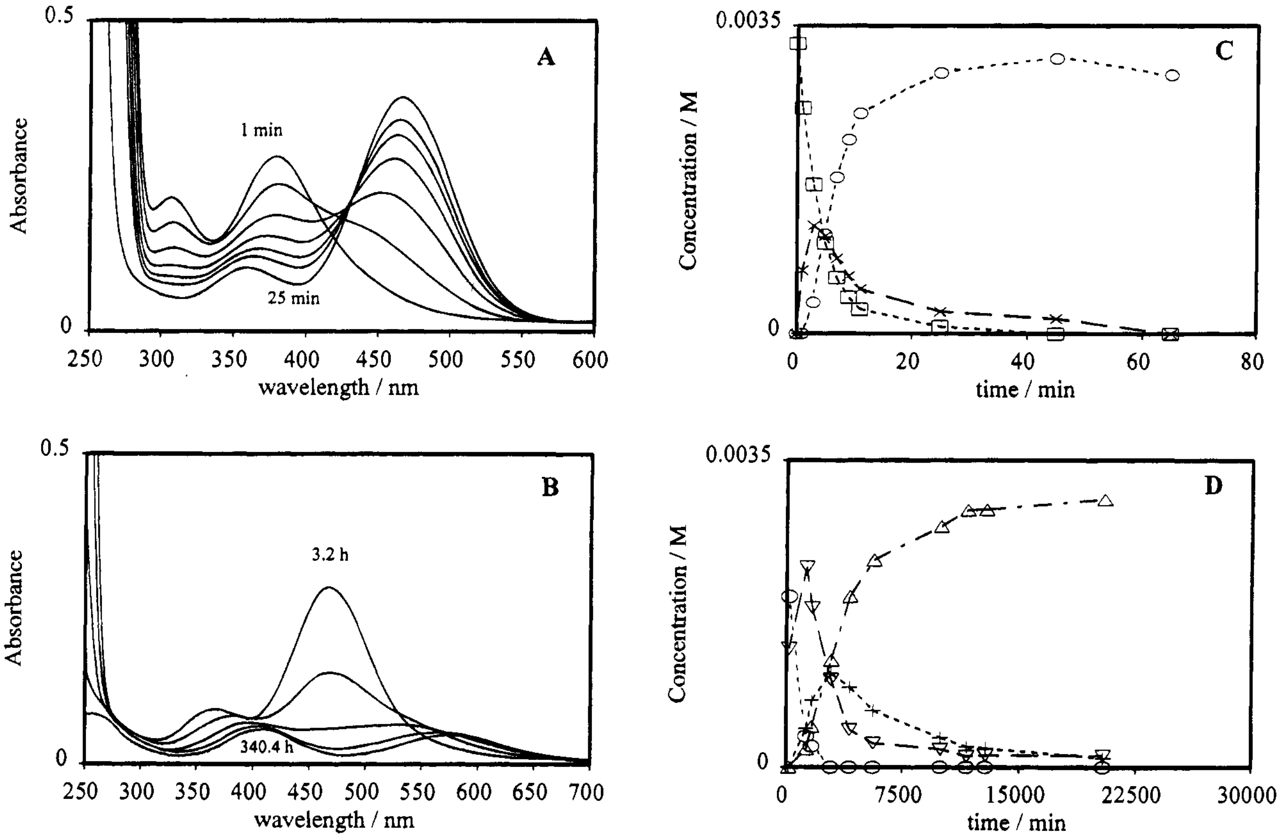

Figure 1. Thermal reactions of aqueous 3.3 × 10^{-3} M $[Cr(CN)_6]^{3-}$ at pH 1.0 and 25 ° C: (A) absorption spectrum after 1, 3, 5, 7, 9, 11, and 25 min; (B) same as part A after 3.2, 21.8, 48.5, 93.5, and 340.4 h; (C) time–concentration plots of $[Cr(CN)_6]^{3-}$ and its products, □ = $[Cr(CN)_6]^{3-}$, × = $[Cr(CN)_5(H_2O)]^{2-}$, and ○ = $[Cr(CN)_3(H_2O)_3]$, where the uncertainty on the concentrations is 3%, 3%, and 5%, respectively; (D) same as part C for longer time periods, ○ = $[Cr(CN)_3(H_2O)_3]$; ▽ = $[Cr(CN)_2(H_2O)_4]^+$, + = $[Cr(CN)(H_2O)_5]^{2+}$, and △ = $[Cr(H_2O)_6]^{3+}$, where the uncertainty on the concentrations is 7%, 30%, 30%, and 30%, respectively. Dashed lines in parts C and D are interpolations of the experimental points, for a better visualization of the concentration trends.

Table 1. Pseudo-First-Order Rate Constants and Quantum Yields for the Thermal and Photochemical Aquation Reactions of the Hexacyanochromate(III) and the Aquapentacyanochromate(III) Ions in Aqueous Solutions at 25 °C[a]

	no $[32]ane-N_8H_8^{8+}$		3.6 × 10^{-3} M $[32]ane-N_8H_8^{8+}$	
	pH 1.0	pH 4.3	pH 1.0	pH 4.3
k_1/s^{-1}	$(2.8 \pm 0.3) \times 10^{-3}$	$(2.3 \pm 0.5) \times 10^{-6}$	$(6.6 \pm 1.3) \times 10^{-5}$ [b]	$<3 \times 10^{-7}$
$k_{-1}/M^{-1}s^{-1}$	$(4.5 \pm 0.9) \times 10^{-2}$	$(1.0 \pm 0.2) \times 10^{-3}$		
k_2/s^{-1} [c]	$(7.5 \pm 1.5) \times 10^{-3}$	$(2.6 \pm 0.8) \times 10^{-5}$	$>2 \times 10^{-3}$	
k_2/s^{-1} [d]	$(6.5 \pm 1.3) \times 10^{-3}$	$(1.4 \pm 0.4) \times 10^{-5}$	$(2.8 \pm 0.6) \times 10^{-3}$	$(2.5 \pm 0.8) \times 10^{-5}$
Φ_1/mol einstein^{-1}		0.12 ± 0.01 [e]		0.04 ± 0.01
Φ_2/mol einstein^{-1}		0.029 ± 0.001		0.03 ± 0.003

[a] Complex concentration: 3 × 10^{-3} M. Each entry is the average of at least three independent determinations. [b] Same result in the presence of 9 × 10^{-3} M $[32]ane-N_8H_8^{8+}$. [c] From experiments with $[Cr(CN)_6]^{3-}$. [d] From experiments with $[Cr(CN)_5(H_2O)]^{2-}$. [e] Same value at pH 6.

primary process, reaction 2, are reported as k_2 in Table 1 and are fairly close to the values obtained by analysis of the spectral evolution during $[Cr(CN)_6]^{3-}$ aquation.

Thermal Aquation in the Presence of [32]ane-N$_8$. Addition of $[32]ane-N_8H_8^{8+}$ (20% or 200% excess) to solutions of $[Cr(CN)_6]^{3-}$ or $[Cr(CN)_5(H_2O)]^{2-}$ causes no change in the initial absorption spectra of both complexes above 300 nm.

The spectral evolution observed during aquation of $[Cr(CN)_6]^{3-}$ at pH 1.0 in the presence of 20% excess of $[32]ane-N_8H_8^{8+}$ is shown in Figure 2A. It denotes large changes in the reaction sequence induced by the macrocycle. An isosbestic point is, in fact, maintained for at least 100 min at 418 nm, which corresponds to the crossing point between the absorption spectra of $[Cr(CN)_6]^{3-}$ and *fac*-$[Cr(CN)_3(H_2O)_3]$. Consistently, the analysis of the absorption values (Figure 2B) reveals that *fac*-$[Cr(CN)_3(H_2O)_3]$ is the only reaction product in the same time range; no spectrophotometrically detectable amounts of $[Cr(CN)_5(H_2O)]^{2-}$ and $[Cr(CN)_4(H_2O)_2]^-$ were observed. At longer times, reactions 3–5 also occur.

The pseudo-first-order rate constant for the disappearance of $[Cr(CN)_6]^{3-}$ and the formation of *fac*-$[Cr(CN)_3(H_2O)_3]$

$$[Cr(CN)_6]^{3-} + 3H_3O^+ \xrightarrow{[32]ane-N_8H_8^{8+}} fac\text{-}[Cr(CN)_3(H_2O)_3] + 3HCN \quad (6)$$

is $(6.6 \pm 1.3) \times 10^{-5}$ s^{-1}. An increase of the concentration of the macrocycle up to 3 times that of $[Cr(CN)_6]^{3-}$ has no effect on both the qualitative behavior of the complex and the value of the rate constant.

For pH values higher than 4, the thermal reaction in the presence of the macrocycle is unappreciable, no spectral variations being observed after one day in the dark ($k < 3 \times 10^{-7}$ s^{-1}).

In contrast with the $[Cr(CN)_6]^{3-}$ system, addition of [32]ane-

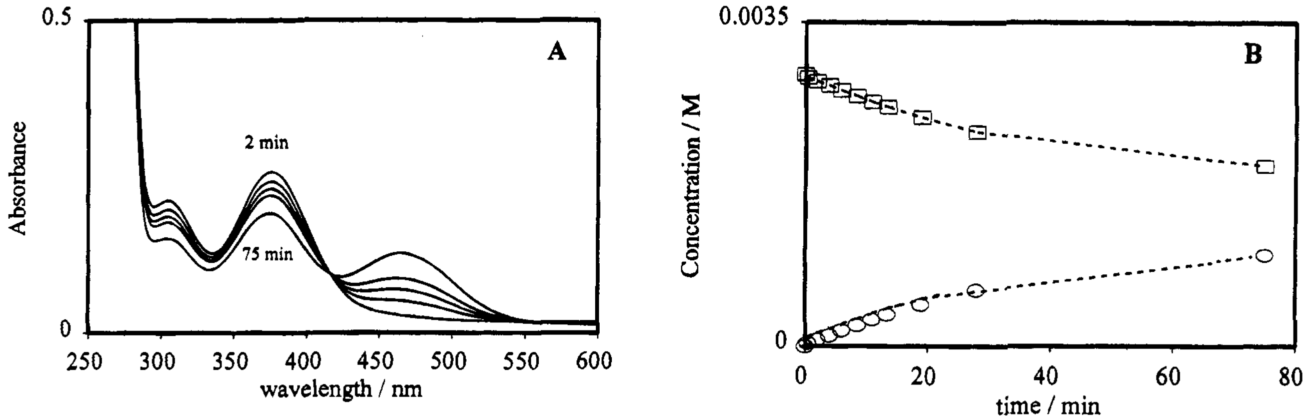

Figure 2. Thermal reactions of aqueous 3.0 × 10^{-3} M $[Cr(CN)_6]^{3-}$ at pH 1.0 and 25 ° C in the presence 20% excess [32]ane-$N_8H_8^{8+}$: (A) absorption spectrum after 2, 11, 19, 28, and 75 min; (B) time–concentration plots of $[Cr(CN)_6]^{3-}$ and its product, □ = $[Cr(CN)_6]^{3-}$ and ○ = $[Cr(CN)_3(H_2O)_3]$, where the uncertainty on the concentrations is 5% and 5%, respectively. Dashed lines in part B are interpolations of the experimental points, for a better visualization of the concentration trends.

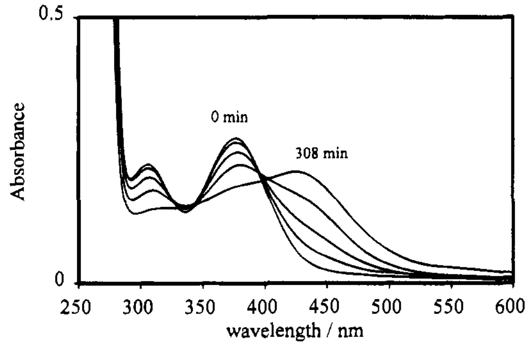

Figure 3. Absorption spectrum of a 3.0 × 10^{-3} M $[Cr(CN)_6]^{3-}$ solution at pH 4.3 and room temperature after 0, 25, 70, 150, and 308 min of irradiation at 313 nm.

$N_8H_8^{8+}$ to $[Cr(CN)_5(H_2O)]^{2-}$ at pH 1.0 and 4.3 does not modify the nature of the thermal reaction of the complex and has little effect on the rate constants, which are reported in Table 1, as k_2.

Photochemical Aquation. The photochemical behavior of $[Cr(CN)_6]^{3-}$ in aqueous solution upon excitation in the ligand field bands (λ > 295 nm) has already been investigated under a variety of conditions.[7-9] The primary photoreaction corresponds to the first step of the thermal aquation:

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

For long irradiation periods, secondary thermal and/or photochemical aquation reactions have also been observed. The quantum yield of reaction 7 is about 0.1, virtually independent of the pH and the excitation wavelength.

A typical series of spectral changes recorded in this study by irradiating (313 nm) $[Cr(CN)_6]^{3-}$ at pH 4.3 is shown in Figure 3. Isosbestic points at about 325, 345, and 395 nm are maintained during the first 100 min of irradiation (more than 30% reaction), which roughly correspond to the crossing points between the absorption spectra of $[Cr(CN)_6]^{3-}$ and $[Cr(CN)_5(H_2O)]^{2-}$. A quantum yield $\Phi_1 = 0.12 \pm 0.01$ for reaction 7 is calculated from the spectral changes that occur prior to loss of the isosbestic behavior. This value is independent of the irradiation wavelength (313 nm or 366 nm) and the pH (4.3–6.0). At longer irradiation times, *fac*-$[Cr(CN)_3(H_2O)_3]$ and its aquation products are also present in the solutions. Therefore, our experiments completely confirm the previous results.

When the irradiation of $[Cr(CN)_6]^{3-}$ is performed in the presence of [32]ane-$N_8H_8^{8+}$ (20% excess), quite similar spectral changes are observed, but Φ_1 is reduced to 0.04 ± 0.01.

The spectral variations induced by 366-nm irradiation of aqueous samples of $[Cr(CN)_5(H_2O)]^{2-}$ at pH 4.3 are the same as in the first thermal reaction stages of the complex: an isosbestic point at 445 nm is maintained for about 100 min of irradiation. *fac*-$[Cr(CN)_3(H_2O)_3]$ is therefore the first observable photoreaction product:

$$[Cr(CN)_5(H_2O)]^{2-} + 2H_3O^+ \xrightarrow{h\nu} fac\text{-}[Cr(CN)_3(H_2O)_3] + 2HCN \quad (8)$$

The quantum yield of this reaction, calculated up to a maximum of 10% conversion, is reported as Φ_2 in Table 1. Its value is of the same magnitude of that (0.04) previously obtained[9] under slightly different experimental conditions. Addition of [32]ane-$N_8H_8^{8+}$ (20% excess) has no effect on the nature of the photoreaction and, within experimental error, on its quantum yield.

Discussion

Polyammonium macrocycles are known[2] to form 1:1 adducts with anionic cyano complexes of transition metals by means of multiple hydrogen bonds between CN^- ligands and ammonium groups. Our results obtained with different macrocycle concentrations (Table 1) indicate that $[Co(CN)_6]^{3-}$ is completely bound to the macrocycle under our experimental conditions. This is in good agreement with analogous conclusions based on photochemical experiments carried out under similar conditions on $[Co(CN)_6]^{3-}$ [3c] and $[Co(CN)_5(H_2O)]^{2-}$,[6] as well as with the published values of association constants;[22] therefore, the same conclusion can be confidently extended to $[Cr(CN)_5(H_2O)]^{2-}$. All the adducts used in this work are characterized by a high positive overall ionic charge and by a firmly bound second coordination sphere, constituted by the macrocycle.

Our results clearly show that the formation of an adduct with [32]ane-$N_8H_8^{8+}$ "quenches" both the thermal and photochemical reactivities of $[Cr(CN)_6]^{3-}$, although to very different extents. A very small effect is instead observed on the thermal aquation of $[Cr(CN)_5(H_2O)]^{2-}$, while the photoreaction of this complex is not affected at all.

Photoreactions. The photoaquation quantum yield of $[Cr(CN)_6]^{3-}$ (reaction 7) is three times smaller for the [32]ane-$N_8H_8^{8+}$–$[Cr(CN)_6]^{3-}$ adduct than for the free complex; this factor is equal to that previously found with $[Co(CN)_6]^{3-}$ [3] and $[Co(CN)_5(H_2O)]^{2-}$.[6] In the case of $[Co(CN)_6]^{3-}$, studies with

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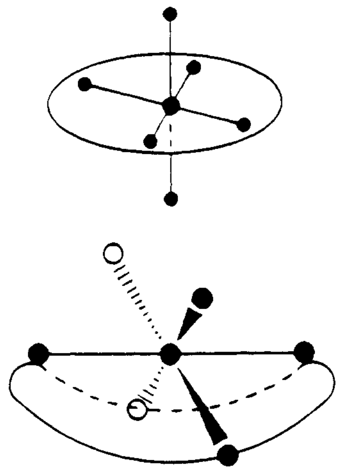

Figure 4. Possible arrangements for the supramolecular adduct of $[Cr(CN)_6]^{3-}$ and $[32]ane\text{-}N_8H_8^{8+}$.

various polyaza macrocycles having different ionic charge and/or size have led to the conclusion that the quantum yield reduction is due to steric effects which prevent the CN^- ligands hydrogen-bound to the receptor from escaping the coordination sphere. The same explanation can straightforwardly be advanced for the photoaquation of $[Cr(CN)_6]^{3-}$, which implies that four hydrogen bonds between CN^- ligands and ammonium groups are present in the $[32]ane\text{-}N_8H_8^{8+}\text{–}[Cr(CN)_6]^{3-}$ adduct. This is in agreement with the possible structures of the adduct inferred from space-filling models, schematically shown in Figure 4.

In the light of the thermal reactivity, eq 2, the observed photoreaction of $[Cr(CN)_5(H_2O)]^{2-}$ (reaction 8) can be viewed as a sequence of a primary photochemical release of one CN^- ligand

$$[Cr(CN)_5(H_2O)]^{2-} + H_3O^+ \xrightarrow{h\nu} [Cr(CN)_4(H_2O)_2]^- + HCN \quad (9)$$

followed by the very rapid thermal loss of a second CN^- group (reaction 2b). The quantum yield of reaction 9, equal to that for 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 $[32]ane\text{-}N_8H_8^{8+}\text{–}[Cr(CN)_6]^{3-}$ adduct, is also expected for $[32]ane\text{-}N_8H_8^{8+}\text{–}[Cr(CN)_5(H_2O)]^{2-}$. It must be noted however that, unlike $[Cr(CN)_6]^{3-}$, the five CN^- ligands of $[Cr(CN)_5(H_2O)]^{2-}$ are no longer photochemically equivalent. According to the Vanquickenborne–Ceulemans model for chromium(III) photolysis[23] 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 state (*i.e.*, the lowest excited quartet recognized as the principally photoreactive state) are evaluated as: 8200 (H_2O), 9800 (axial CN^-), and 14750 cm^{-1} (equatorial CN^-).[24] By the way, the model anticipates that the main photolysis mode of the pentacyano complex is H_2O photoexchange (undetected in this study) 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 (Figure 4) for the $[32]ane\text{-}N_8H_8^{8+}\text{–}[Cr(CN)_5(H_2O)]^{2-}$ adduct, which leaves such a CN^- ligand free from hydrogen bonding. A "belt" structure has already been suggested[6] for the analogous Co(III) adduct in order to explain its photochemical properties. 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 complexes,[23c] the photorelease of the axial CN^- ligand from $[32]ane\text{-}N_8H_8^{8+}\text{–}[Cr(CN)_5(H_2O)]^{2-}$ 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.

Thermal Reactions. The aquation of $[Cr(CN)_6]^{3-}$ in the presence of $[32]ane\text{-}N_8H_8^{8+}$, reaction 6, leads to *fac*-$[Cr(CN)_3(H_2O)_3]$ as the first observable product. The absence of detectable amounts of $[Cr(CN)_5(H_2O)]^{2-}$ among the products can be accounted for in a way similar to that suggested for the absence of $[Cr(CN)_4(H_2O)_2]^-$ in the thermal reaction of the free complex, *i.e.*, by considering reaction 6 as a sequence of three one-ligand aquation stages (reactions 1, 2a, and 2b), the first being the rate determining step. Accordingly, the measured rate constants actually quantify step 1: they have been, therefore, entered as k_1 in Table 1.

Inspection of Table 1 shows that the ratio between the k_1 values for free $[Cr(CN)_6]^{3-}$ and the $[32]ane\text{-}N_8H_8^{8+}\text{-}[Cr(CN)_6]^{3-}$ adduct is larger than 40, at pH 1.[25] Such a drastic reduction of k_1 cannot be ascribed to the steric limitations thought to be responsible for the quenching of the $[Cr(CN)_6]^{3-}$ photoaquation. A satisfactory explanation can be found keeping in mind that the thermal aquation proceeds mainly through a H^+-catalyzed, two-step mechanism[10] consisting of a rapid protonation equilibrium

$$[Cr(CN)_6]^{3-} + H^+ \overset{K_p}{\rightleftharpoons} [Cr(CN)_5(CNH)]^{2-} \quad (10)$$

followed by aquation of the protonated species:

$$[Cr(CN)_5(CNH)]^{2-} \xrightarrow[H_2O]{k_r} [Cr(CN)_5(H_2O)]^{2-} + HCN \quad (11)$$

According to this scheme, the protonation constant K_p and the rate constant k_r are related to the experimental, pseudo-first-order rate constant k_1 by eq 12,

$$k_1 = \frac{k_r K_p [H^+]}{1 + K_p [H^+]} \quad (12)$$

and the literature values of K_p and k_r for the free complex[10] are in fair agreement with the values of k_1 reported in Table 1. Since on going from $[Cr(CN)_6]^{3-}$ to $[32]ane\text{-}N_8H_8^{8+}\text{–}[Cr(CN)_6]^{3-}$ the overall ionic charge changes from −3 to +5, the CN^- ligands are expected to be by far less basic (*i.e.*, to have a lower K_p value) in the adduct than in the free complex and, thus, to be less inclined to substitution through the H^+-catalyzed mechanism.

An additional limitation of steric nature to the release of the hydrogen-bound CN^- ligands cannot be excluded, in principle, also in the thermal aquation of $[32]ane\text{-}N_8H_8^{8+}\text{–}[Cr(CN)_6]^{3-}$. This effect, however, would certainly be obscured by the more pronounced effect of the ionic charge on the protonation of the complex.

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[23] Vanquickenborne, L. G.; Ceulemans, A.: (a) *J. Am. Chem. Soc.* **1977**, *99*, 2208; (b) *Inorg. Chem.* **1979**, *18*, 897; (c) *Coord. Chem. Rev.* **1983**, *48*, 157.

[24] Riccieri, P.; Zinato, E. *Inorg. Chem.* **1990**, *29*, 5035.

[25] At pH 4.3, only a lower limit of 8 could be established for this ratio, because of the slowness of the reaction.

The absence of $[Cr(CN)_5(H_2O)]^{2-}$ among the adduct aquation products requires a rate constant for reaction 2a, k_2, greatly exceeding k_1. Actually, on the basis of the spectrophotometric detectability of $[Cr(CN)_5(H_2O)]^{2-}$, a lower limit of 2×10^{-3} s^{-1} is evaluated for k_2 from the kinetic data of [32]ane-$N_8H_8^{8+}$–$[Cr(CN)_6]^{3-}$ at pH 1.0. This is very close to the value directly obtained from the kinetics of [32]ane-$N_8H_8^{8+}$–$[Cr(CN)_5(H_2O)]^{2-}$ at the same pH.

At first sight, a macrocycle-induced drop of k_2 even larger than that of k_1 might be expected, since, like $[Cr(CN)_6]^{3-}$, free $[Cr(CN)_5(H_2O)]^{2-}$ aquates through an acid-assisted path,[10] and moreover, the substituted ligands are those *cis* to H_2O (*i.e.*, the equatorial ones).[10] In contrast with this expectation, Table 1 shows that k_2 only decreases by a factor as small as 2–3 on going from $[Cr(CN)_5(H_2O)]^{2-}$ to [32]ane-$N_8H_8^{8+}$–$[Cr(CN)_5(H_2O)]^{2-}$ at pH 1.0, and is practically unchanged at pH 4.3. In addition, two peculiar trends emerge from Table 1: (i) k_2 is larger than k_1 under all conditions, but more markedly at pH 4.3, and (ii) the acidity has a larger effect on k_1 than on k_2. These observations are consistent with the suggestion[10,12–14] that the coordinated water molecule(s) 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,[10,12] or originating a pH-independent path through intramolecular proton transfer from a H_2O to a CN^- ligand.[14] The importance of both these contributions is expected to be enhanced by the increase of the acidity of the H_2O ligands, which is known[12] to parallel the decrease of the negative charge (or the increase of the positive charge) of the complex. In the light of these considerations, the lack of a massive effect of [32]ane-$N_8H_8^{8+}$ on the rate constant k_2 for aquation of $[Cr(CN)_5(H_2O)]^{2-}$ can be related to the large positive charge of the receptor, which is expected to increase k_r in the H^+-assisted path and/or to promote a pH-independent path. Either or both of these factors can compensate the obvious decrease of the protonation constant K_p. On the basis of our results, however, it is impossible to discriminate between the two suggested effects.

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