In principle, the formation of superoxide could explain the oxygen effect on $\phi_{-Cu(I)}$ for *trans*-$[Co(NH_3)_4(CN)_2]^+$ (see Table IV). Because of its reducing character, superoxide could act as an electron carrier,[48] or "relay", providing another route to the reduction of Co(III). However, the rate constants for the reduction of Co(III) by superoxide are not large, typically being $<10^5$ M^{-1} s^{-1}.[49] Another possibility is that in the case of the cyano complex, O_2 may scavenge a transient Co(II) species which is capable of back-reacting with Cu(II).

Conclusions

The reduction of a variety of Co(III) complexes and molecular oxygen has been observed upon irradiating $[Cu(dmp)_2]^+$ in solution. The results are consistent with the idea that a strongly reducing CT excited state of $[Cu(dmp)_2]^+$ survives to undergo reaction. In general, rather low quantum efficiencies are observed, and several possible sources of inefficiency have been identified. So far and despite several attempts, energy-transfer reactivity has not been detected, perhaps because the rate of energy transfer is not competitive with that of excited-state relaxation. Many important questions about the mechanism of these reactions remain. Flash photolysis studies may provide some of the answers.

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Registry No. $[Cu(dmp)_2]^+$, 21710-12-3; *cis*-$[Co(IDA)_2]^-$, 21718-59-2; *trans*-$[Co(NH_3)_4(CN)_2]^+$, 34902-82-4; $[Co(en)_2bpy]^{3+}$, 48185-94-0; $Co(acac)_3$, 21679-46-9; $[Co(en)_2phen]^{3+}$, 47247-88-1; β-$Co(ala)_3$, 55448-50-5; $[Co(NH_3)_5py]^{3+}$, 31011-67-3; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(NH_3)_5(CN)]^{2+}$, 19529-81-8; O_2, 7782-44-7.

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Stereochemistry of Equatorial Aquation in the Ligand Field Photolysis of *trans*-Dicyanotetraamminechromium(III)

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The photolysis of *trans*-$Cr(NH_3)_4(CN)_2^+$ in acidic aqueous solution at 10 °C results in NH_3 aquation with a wavelength-independent quantum yield of 0.24 throughout the ligand field absorption region. No cyanide is photoreleased (ϕ < 0.005), while the dark reaction is one of exclusive CN^- loss. The photolabilization pattern is discussed in terms of the equatorial antibonding properties of the lowest quartet excited state, $^4B_{2g}$, and is compared with the predictions of the available photolysis models. By ion-exchange separations and subsequent thermal aquation, the photoproduct $Cr(NH_3)_3(H_2O)(CN)_2^+$ is demonstrated to consist of a mixture of 1,6-CN-2-H_2O and 1,2-CN-6-H_2O isomers, in a ca. 2:1 proportion. Equatorial photoaquation is concluded to be partially stereoretentive and partially stereomobile. The consistency of the product nature and distribution with the plausible excited-state mechanisms is examined.

Introduction

Among the various aspects of chromium(III) photosubstitutions, the stereochemistry has long been a point of major interest.[1] The complexes investigated from this point of view are of the general types CrN_5X^{2+} [2-8] and *trans*-CrN_4XY^{z+},[8-20] where N stands for ammonia or amines and X and Y are acido groups. In most of these systems the main photoreaction following ligand field (LF) excitation is displacement of the axial ligands and occurs with complete trans → cis isomerization. Moreover, photosubstitution is efficient only if such a rearrangement is not prevented.[11,14]

Much less stereochemical information exists on equatorial photosolvation. So far, only two species have been found to undergo preferential cleavage of the equatorial Cr–N bonds: *trans*-$Cr(en)_2F_2^+$ [10,18] and *trans*-$Cr(en)_2(CN)_2^+$, reported[21] after completion of this work. Photoproduct identification has been attempted for the former[10,18] but not for the latter.[21] In

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all the other cases, photoinduced bond rupture on the *xy* plane has been observed as a minor reaction mode, accompanying axial photoreactions. The relatively low quantum yields have usually hindered isomeric analysis of equatorial products. The only quantitative account of product distribution concerns CrN_5F^{2+}.[8,22] The available data show that, contrary to an earlier contention of stereorigidity,[15] equatorial photoaquation is at least partially stereomobile.[8,18,22]

The specificity of ligand photorelease has been rationalized by a number of models,[10,23-27] elaborated around Adamson's rules.[28] Theoretical attention has also been devoted to the stereochemistry of axial photolysis[29] and, very recently, has been extended to equatorial processes,[30] although only within a dissociative context.

We have examined the photochemistry of the newly synthesized[31a] *trans*-$Cr(NH_3)_4(CN)_2^+$ ion in acidic aqueous solution. One aim of this study was to obtain specific data on equatorial labilization in order to test the predictions of the various models for a D_{4h} system with π-acceptor ligands, in an unusual excited state. The main purpose, however, was to provide unequivocal information on the stereochemical course of "in-plane" photosubstitutions.

The *trans*-dicyanotetraammine complex is suitable for various reasons. First, as in *trans*-$Cr(en)_2(CN)_2^+$, the extreme spectrochemical position of the apical ligands causes the LF strength to be lower on the *xy* plane, rather than on the *z* axis, and the lowest excited quartet is $^4B_{2g}$, rather than ^4E_g. The $^4B_{2g}$ state is associated with selective population of the $d_{x^2-y^2}$ orbital, and LF band irradiation is expected[23-28] (and found) to produce exclusive equatorial destabilization. Second, the photolysis products constitute reliable indicators of the stereochemistry, since the original coordination site (axial or equatorial) of each type of ligand is univocally identified and the stereochemical ambiguity incurred with acidopentaammines[1] is excluded. Finally, the monodentate equatorial groups (as opposed to polyamines) rule out undue complications in photoproduct characterization.

The present results corroborate and complement the stereochemical indications emerging from a study of the $Cr(NH_3)_5(CN)^{2+}$ ion, previously carried out in this laboratory.[32]

Experimental Section

Materials. *trans*-Dicyanotetraamminechromium(III) perchlorate was synthesized by cyanide anation of *trans*-bis(dimethyl sulfoxide)tetraamminechromium(III) in dimethyl sulfoxide, as reported in detail elsewhere.[31a] Anal. Calcd for $[Cr(NH_3)_4(CN)_2]ClO_4$: Cr, 19.15; NH_3, 25.08; CN, 19.16. Found: Cr, 18.9; NH_3, 25.1; CN, 19.3 ± 0.2. The LF absorption spectrum, illustrated in Figure 1, shows maxima at 440 (ϵ 42.6) and 344 nm (ϵ 41.5). The charge-transfer band (corresponding to a metal-to-ligand transition)[31a,32] is characterized (ϵ values in parentheses) by a succession of shoulders at 250 (155), 240 (610), 231 (1320), 224 (1610), 216.5 (1770), and 209 nm (2530).

Analytical Procedures. Cyanide was determined potentiometrically by an Amel Model 201-CN Sens-Ion electrode, connected to a Radiometer Model PHM 84 research pH meter. Solutions were buffered at pH 12. Standardization plots were obtained in parallel with each analysis, with use of KCN. Separate tests showed that the presence of cyano complexes did not affect the reproducibility, since thermal release of cyanide is negligible in alkaline media.

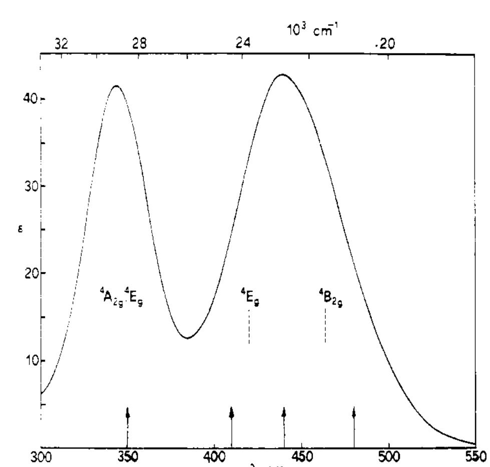

Figure 1. Ligand field absorption spectrum of *trans*-$Cr(NH_3)_4(CN)_2^+$ in 5×10^{-4} M $HClO_4$. The energies of the two lowest spin-allowed transitions are those predicted in ref 42. Arrows indicate irradiation wavelengths.

Ammonia was analyzed by two independent techniques. The first method was based on proton uptake measurements,[33] by means of a glass microelectrode, coupled with the above-mentioned pH meter. The ionic strength was kept constant at 0.04 M by adding sodium perchlorate. Besides NH_3, also cyanide contributes to H_3O^+ neutralization. Thus, the sums of photochemical NH_3 and CN^- resulted from the differences between the moles of acid consumed in the irradiated aliquots and those consumed in the dark samples. Both these quantities were measured as pH changes relative to the pure solvent. Photoproduced NH_3 was then obtained by subtracting the photolytic CN^- amounts, independently determined, from total photolytic proton uptake.

The second procedure consisted of direct monitoring with an Orion Model 95-10, NH_3 sensing electrode. Solutions were brought to ca. pH 13 by adding NaOH prior to measurement. Calibration was performed each time, by using freshly prepared ammonia (NH_4Cl + NaOH) standards. The sensitivities of the two methods were comparable in the 5×10^{-5} – 5×10^{-4} M range, and the results agreed within experimental error.

Ion-exchange separations of the photoproducts were accomplished by means of Sephadex resins, either cationic (SP-C25) in the sodium form or anionic (QAE-A25) in the perchlorate form. Unless otherwise specified in the Results, 2–3 × 1 cm columns were employed. Elution was with sodium perchlorate of various concentrations and pHs. During the chromatographic experiments the columns were kept in a refrigerator (at 2–3 °C) in order to reduce thermal reaction effects. Electronic absorption spectra were recorded with either Shimadzu UV 200S or Cary 17 instruments. Optical densities at specific wavelengths were read with a Beckman DU spectrophotometer.

Photolysis Procedures. The general apparatus was that already described.[9] Irradiation wavelengths were selected by using a Bausch & Lomb high-intensity, grating monochromator. Incident intensities were usually about 5×10^{-9} einstein s^{-1} and were either continuously monitored by a thermopile[9] or determined by the reineckate[34] and ferrioxalate[35] actinometers. Samples of 10-mL volume were photolyzed in 4-cm path length spectrophotometer cells, held in a thermostated compartment at 10.0 ± 0.5 °C, under continuous magnetic stirring. Solutions were ca. 10^{-3} M in *trans*-$Cr(NH_3)_4(CN)_2^+$ and 1.5×10^{-4} M in $HClO_4$, and the ionic strength was adjusted to 0.04 M with $NaClO_4$. At these complex concentrations, light absorption was incomplete, and the absorbed energy was evaluated as described previously.[36] The extent of photoconversion was usually less than

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5%. Analytically suitable amounts of products could thus be obtained, without any interference by inner filter effects and secondary photolysis. Irradiation periods ranged between 20 and 30 min. Under the above conditions, the dark reaction was not negligible, as 2–3% CN^- was released thermally during photolysis. In all cases blank solutions were analyzed in parallel with the photolyzed ones, in order to allow for thermal processes.

When the photoproduct was to be prepared in larger quantities for isomeric analysis, about 40% of the reactant was decomposed. A broad band-pass filter was employed, in order to attain light absorption by a whole LF spectral band of the complex at an higher intensity, without protracting irradiation. The complex concentration was raised to 10^{-2} M for increasing the optical density. No ionic strength was added in this case, both for solubility reasons and for facilitating the chromatographic separations.

Results

Photoaquation Quantum Yields. While a detailed kinetic picture will be the subject of a separate report,[31b] the dark reactivity of *trans*-$Cr(NH_3)_4(CN)_2^+$ was preliminarily explored before proceeding with photochemistry. The thermal behavior consists of acid-catalyzed, stepwise aquation of cyanide. Both reactions are completely stereorigid (eq 1 and 2), as is usually

$$trans\text{-}Cr(NH_3)_4(CN)_2^+ + H_2O \rightarrow trans\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + CN^- \quad (1)$$

$$trans\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + H_2O \rightarrow trans\text{-}Cr(NH_3)_4(H_2O)_2^{3+} + CN^- \quad (2)$$

found for chromium(III) systems in aqueous media.[37,38] The configuration of the final diaquotetraammine complex constitutes the main piece of evidence for the trans structure. This inference is supported by the parallel observation that *cis*-$Cr(NH_3)_4(CN)_2^+$ also aquates with total stereoretention.[31a] The absorption spectra of the two dicyanotetraammine isomers are not different enough to be indicative of the respective geometries, whereas those of the well-known diaquo analogues are fully diagnostic in this respect.[37,39] The *trans*-dicyanotetraammine cation is remarkably inert in neutral or alkaline solutions at room temperature, as indicated by the stability of its absorption spectrum for at least 12 h. In contrast, aquation becomes rapid in acidic media, owing to efficient protonation of the highly basic leaving groups. For example, the second-order rate constant for the acid-assisted reaction path in step 1 is about 0.1 M^{-1} s^{-1} at 25 °C. The successive aquation stage (eq 2) is slower by 3 orders of magnitude.

The conditions for photolysis were chosen so as to simultaneously meet several needs. (i) Because of the scant solubility of the complex as the perchlorate salt, the concentration was kept relatively low (ca. 10^{-3} M), for permitting addition of some ionic strength as $NaClO_4$. (ii) The acidity and the temperature were such as to minimize thermal processes ($k_{obsd} \simeq 5 \times 10^{-6}$ s^{-1} at 10 °C, pH 3.8, and $\mu = 0.04$ M). (iii) Yet, the $HClO_4$ concentration was not too low, in order to ensure the desired precision in proton uptake determinations. (iv) Although at these acidity levels partial deprotonation of the photoaquation products could not be avoided, it was limited to less than 5% (the pK_a value of the photoproduct was estimated to be ca. 5). The usually higher reactivity of hydroxo complexes, with respect to their aquo counterparts, may, in fact, enhance postirradiation effects.

The photolytic behavior is qualitatively and quantitatively the same upon irradiation in the LF range, at any wavelength between 480 and 350 nm. The two LF absorption bands undergo a bathochromic shift, consistent with coordination of H_2O, which is spectrochemically weaker than both NH_3 and CN^-. The spectral evolution (expanded by differential spectrophotometry) presents three isosbestic points at 450, 405, and 353 nm, indicating either a single photoproduct or more products in constant ratios. Progressive proton uptake parallels these changes. Increasing amounts of NH_3 appear in solution. Free cyanide can be entirely attributed to thermal aquation, as no differences are observed between the CN^- concentrations of dark and photolyzed samples. Acid consumption corresponds to the sum of thermal CN^- plus photochemical NH_3, each of these three quantities being independently measured. The only photoinduced reaction is thus ammonia aquation (eq 3).

Table I. Quantum Yields for the Ligand Field Photolysis of *trans*-$Cr(NH_3)_4(CN)_2^+$ in Acid Aqueous Solution at 10 °C

irradiation wavelength,[a] nm	transition[b]	ϕ_{NH_3},[c] mol einstein^{-1}	ϕ_{CN^-},[c] mol einstein^{-1}
480	$^4B_{1g} \rightarrow {}^4B_{2g}$	0.236 ± 0.023 (5)	<0.005 (2)
440	$^4B_{1g} \rightarrow {}^4B_{2g}$, $^4E_g(^4T_{2g})$	0.240 ± 0.015 (7)	<0.005 (3)
410	$^4B_{1g} \rightarrow {}^4E_g(^4T_{2g})$	0.240 ± 0.017 (4)	<0.005 (1)
350	$^4B_{1g} \rightarrow {}^4E_g(^4T_{1g})$, $^4A_{2g}$	0.235 ± 0.008 (6)	<0.005 (2)

[a] Irradiation bands of 14-nm half-width. [b] The tetragonal absorption components overlap; the prevalent excitation is indicated. O_h parent states are in parentheses. [c] Number of runs in parentheses.

$$trans\text{-}Cr(NH_3)_4(CN)_2^+ + H_2O \xrightarrow{h\nu} Cr(NH_3)_3(H_2O)(CN)_2^+ + NH_3 \quad (3)$$

The optical density changes, the moles of acid neutralized (corrected for thermal H^+ uptake), and the amounts of free NH_3 exhibit a linear dependence on the absorbed light quanta, throughout photolysis (usually ca. 5%). The quantum yields for NH_3 photoaquation at various LF excitation wavelengths are collected in Table I.

As mentioned above, no photochemical release of CN^- was ever detected. The upper limits given in Table I for ϕ_{CN^-} are based on the instrumental sensitivity of cyanide analysis.

Isomeric Characterization of the Photolysis Products. Besides *trans*-$Cr(NH_3)_4(CN)_2^+$ (A) and the photogenerated $Cr(NH_3)_3(H_2O)(CN)_2^+$ species (B), the photolysis mixtures contain minor amounts of the thermal aquation product *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ (C). Also, at ca. 40% photoconversion (see Experimental Section), secondary photoproducts such as $Cr(NH_3)_2(H_2O)_2(CN)_2^+$ (D) cannot be ignored. In addition, especially during subsequent handling in acidic media, further aquation of B may give rise to some $Cr(NH_3)_3(H_2O)_2(CN)^{2+}$ (E). Isolation of B from solutions of such a complexity was accomplished by a sequence of ion-exchange experiments, as follows.

Irradiated samples were made ca. 1×10^{-3} M in NaOH, so as to deprotonate all the H_2O ligands. At this pH, A and C are still positively charged, B and E are converted into neutral compounds, and D becomes a negative ion. Elution through the cationic resin with 1×10^{-3} M NaOH moved B, D, and E, while A and C remained adsorbed. The eluates were then passed through the anionic column, and treatment with the same eluant yielded solutions of B and E only, both as hydroxo complexes. Protonation of the latter was restored by adjusting the pH to 3.3 with diluted $HClO_4$ (after cooling with ice, in order to suppress acid-catalyzed CN^- release). Upon acidification, the color turned reversibly from red to yellow, consistent with the higher LF strength of H_2O, relative to OH^-. Subsequent elution through the cation exchanger by means of 2×10^{-2} M $NaClO_4$ at the same pH selectively displaced

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Table II. Ligand Field Absorption Data for Some Chromium(III)-Triammine Complexes in Acid Aqueous Solution

complex	wavelength, nm (ε, M^{-1} cm^{-1}) L$_1$ max	min	L$_2$ max	ϵ_1/ϵ_2	ref
$Cr(NH_3)_3(H_2O)(CN)_2^{+}$ [a]					
photoproduct mixture	450 (43.5 ± 0.5)	393 (18.5 ± 0.5)	351 (39.0 ± 0.5)	1.12	c
1,6-CN-2-H_2O isomer	449 (39 ± 1)	395 (19 ± 1)	351 (41 ± 1)	0.95	c
1,2-CN-6-H_2O isomer	452 (53 ± 1)	391 (17 ± 1)	350 (34 ± 1)	1.56	c
$Cr(NH_3)_3(H_2O)_3^{3+}$ [b]					
aquated photoproducts	504 (26.0 ± 0.5)	432 (9.0 ± 0.5)	376 (26.5 ± 0.5)	0.98	c
meridional isomer (1,2,6)	502[d] (26.3)	432 (9.1)	376 (26.8)[e]	0.98	40, 41
facial isomer (1,2,3)	513 (36.6)		374 (22.6)	1.62	40

[a] In 5 × 10^{-4} M $HClO_4$. [b] In 1 M $HClO_4$. [c] This work. [d] 504 nm in ref 41. [e] ε 26.0 in ref 41.

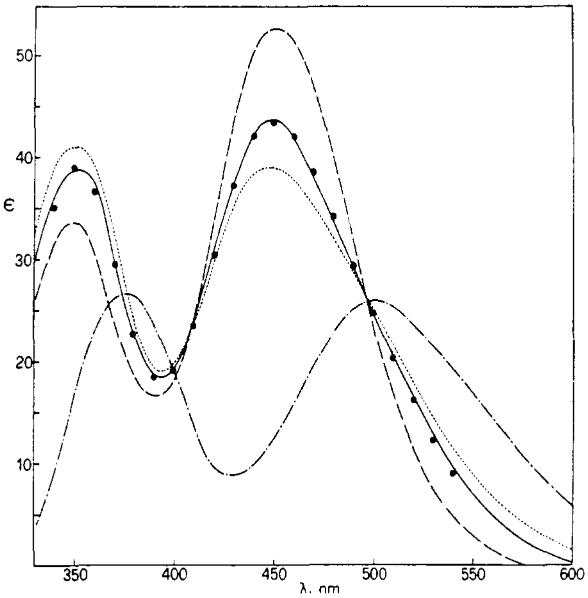


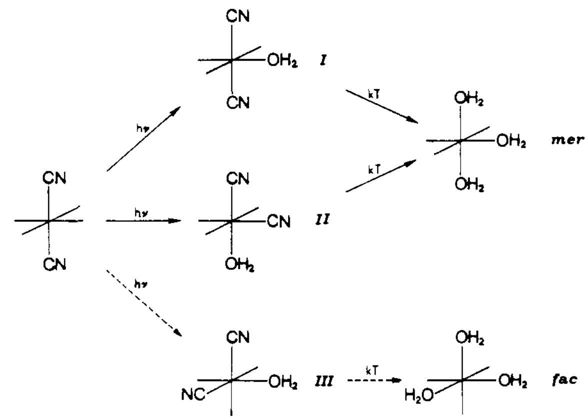
Figure 2. Ligand field absorption spectra of chromium(III) complexes in acid aqueous solution: —, photoproduced mixture of $Cr(NH_3)_3(H_2O)(CN)_2^+$ ions; ···, 1,6-CN-2-H_2O isomer (I); - - -, 1,2-CN-6-H_2O isomer (II); -·-, thermally aquated photoproducts, *mer*-$Cr(NH_3)_3(H_2O)_3^{3+}$. Circles correspond to the calculated absorption for a 70:30 mixture of I and II.

the monopositive B species, whereas the dipositive E ion was completely retained.

Chromium determination in solution led to the absolute absorption spectrum, reported in Figure 2 and in Table II. The wavelengths of the LF maxima are in agreement with coordination of one H_2O ligand. Furthermore, these features match the absorption curves calculated by correlating the difference spectra with the amounts of uncoordinated ammonia during photolysis, assuming loss of one NH_3 group per complex ion. Also, the intense and structured CT band in the UV region, characteristic of bound cyanide,[31a] is unaltered with respect to the reactant.

Three geometric isomers of the $Cr(NH_3)_3(H_2O)(CN)_2^+$ cation are possible, namely, 1,6-CN-2-H_2O (I), 1,2-CN-6-H_2O (II), and 1,2-CN-3-H_2O (III), as illustrated in Scheme I. None of them is known, however. A first step toward structural elucidation of the product(s) was suggested by the availability of absorption data for the complexes obtainable by complete cyanide aquation of I–III. The 1,2,6- and 1,2,3-triaquotriammine ions (*mer*- and *fac*-$Cr(NH_3)_3(H_2O)_3^{3+}$, respectively) have been described in the literature and can be adequately distinguished through their LF spectra.[37,40,41] This analysis rested on the assumption of stereoretention during replacement of CN^- by H_2O. Such a premise seemed correct in the light of the general stereorigidity of chromium(III) aqueous substitutions[37,38] and, more specifically, was justified by the complete retention of configuration observed for aquation of both *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$.[31a]

Scheme I



Acidification of $Cr(NH_3)_3(H_2O)(CN)_2^+$ solutions to about pH 0 accelerates aquation of CN^-, yielding $Cr(NH_3)_3(H_2O)_3^{3+}$ within ca. 3 h at room temperature. The spectrum (again determined by chromium analysis in solution) then remains unaltered over a period of 24 h at room temperature. Its characteristics are given in Figure 2 and in Table II, which includes absorption data for the two known triaquo isomers.[37,40,41] The peak ratios are particularly significant for stereochemical identification. Spectral comparison indicates that only the 1,2,6 (meridional) complex is present. The 1,2,3 (facial) isomer, if any is formed, may be safely estimated to amount to no more than 5%, on the basis of spectrophotometric precision. It follows that possible product III can be ruled out.

So that we could ascertain whether only one or both of the remaining aquodicyano ions are actually photoproduced, samples of B were further adsorbed on a 12 × 0.7 cm cationic column and eluted with 1 × 10^{-2} M $NaClO_4$ at pH 3.3. Essentially complete separation into two bands was achieved. The LF spectra of the two fractions, reported in Figure 2 and in Table II, are very different, both in shape and in intensity, and prove that two species are simultaneously generated. Parallel chromatographic experiments were performed on mixtures of *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$, which are also monopositive and whose structures and polarities are similar to those of I and II. The two couples differ, in fact, by a neutral ligand only: in I the CN^- groups are trans to each other, while in II they are cis. The dicyanotetraammine complexes were also fully separated, and, as expected, the faster moving compound was found to be the nonpolar trans isomer. On these grounds, the first fraction was associated to I and the second one to II. The absorption features confirm such an assignment. The low-energy LF band of I is less intense and less symmetric than that of II, as is usually true for trans–cis pairs.[42] Acid-assisted aquation (at pH ~0) leads

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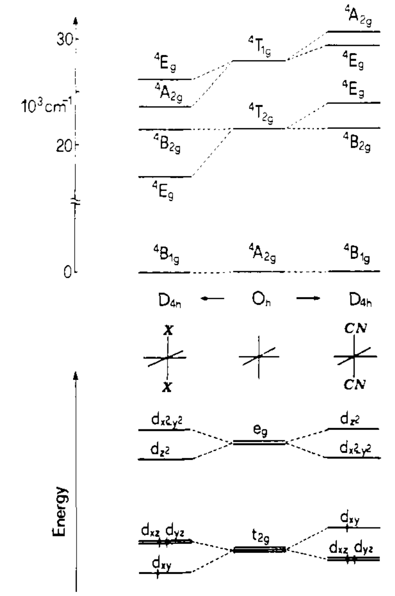

Figure 3. Schematic state and orbital energy-level diagram for *trans*-diacidotetraamminechromium(III) ions. X denotes ligands of lower spectrochemical strength than NH_3 as, for example, Cl^-. Data (upper part) are from ref 42.

to *mer*-$Cr(NH_3)_3(H_2O)_3^{3+}$ in both fractions. The final spectra are identical and coincide with that determined in the aquated mixture.

It should be pointed out that even in the case where *mer*- and *fac*-$Cr(NH_3)_3(H_2O)_3^{3+}$ were unknown, the finding that both photoproducts are converted to the same triaquo isomer would be per se sufficient to infer structures I and II. Moreover, the present results confirm the 1,2,6 isomerism for the $Cr(NH_3)_3(H_2O)_3^{3+}$ cation reported by Caldwell and House,[41] about which there seemed to exist some uncertainty.

The two fractions could not be quantitatively recovered because of a residual, small degree of overlap between the bands and unavoidable thermal aquation during elution, even at 2 °C (this does not interfere, however, as the 2+ charged aquated species are retained). Nevertheless, evaluation of the percentages of I and II was possible, since the spectrum of B could be reproduced by a linear combination of those of the two aquodicyano isomers (Figure 2). The absorption curves of I and II were determined on the core of the respective elution bands. Through five independent sets of determinations the photoproduct mixture was found to consist of 70 ± 10% of the 1,6-CN-2-H_2O species (I) and 30 ± 10% of the 1,2-CN-6-H_2O ion (II). The deviations should be viewed pessimistically, since they allow for the maximum error propagation in the spectra of Table II.

Discussion

Specificity of Photolabilization. In Figure 3 the relevant LF features of *trans*-$Cr(NH_3)_4(CN)_2^+$ are schematically compared with those of other *trans*-$CrN_4X_2^+$ ions. As mentioned above, the orbital and state energy sequence is atypical, owing to the higher spectrochemical strength of CN^-, relative to NH_3. Upon descent to D_{4h} symmetry, the parent O_h states split oppositely to the usual ordering, and the lowest excited quartet is $^4B_{2g}$. The energies of the four spin-allowed transitions from the $^4B_{1g}$ ground state have been anticipated in the literature by LF theory.[42] The spectrum (Figure 1) appears octahedral-like, however, because of the relatively small spacings (2250 and 1200 cm^{-1}, respectively)[42] between the excited components.

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Table III. Ratios of Equatorial to Axial Photoaquation Quantum Yields for *trans*-$CrN_4X_2^{z+}$ Complexes upon Excitation to the Lowest Quartet Excited State, as a Function of Various Parameters

X	Δ^b	$E(^4E_g) - E(^4B_{2g})$,^{c} cm^{-1}	σ_X,^{d} cm^{-1}	% $d_{x^2-y^2}$^{e}	ϕ_N/ϕ_X	ref
Br^- ^{a}	0.72	−4850	5100	9	0.008	17
Cl^-	0.78	−4200	5600	12	0.01	9
H_2O	1.00	−2860	5950	15	<0.06	9
NCS^- ^{a}	1.02	−1915	6400	19	0.6	15
NH_3	1.25	0	7200	25^f	2	g
F^- ^{a}	0.9	−2725	7650	29	10	18
CN^-	1.7	2530	8500	100	>50^h	i

^{a} Equatorial ethylenediamine. ^{b} Spectrochemical parameters relative to H_2O, from ref 45. ^{c} Evaluated as in ref 27. ^{d} Additive angular overlap parameters.[27] ^{e} Population in the lowest quartet excited state (^4E_g for X ≠ CN^-; $^4B_{2g}$ for X = CN^-), calculated according to ref 27. ^{f} For uniformity, the percentage refers only to the ^4E_g component of the $^4T_{2g}$ state in O_h symmetry. The actual $d_{x^2-y^2}$ population of $^4T_{2g}$ is obviously 50% (see also ref 44). ^{g} $Cr(NH_3)_6^{3+}$ is included for comparison, assuming random NH_3 aquation. ^{h} A >30 ratio is reported for *trans*-$Cr(en)_2(CN)_2^+$, in ref 21. ^{i} This work.

The LF excited-state chemistry of the *trans*-dicyanotetraammine cation is extremely selective, in that only NH_3 is photoaquated. The more so, as it differs in quality from the ground-state chemistry, which consists of exclusive CN^- loss. Such a behavior may be related in a simple way to the excited-state electron distribution. The constancy of the quantum yields, extending to the long-wavelength tail of the first LF band, implies efficient conversion to the lower-lying excited state within a spin manifold. Although until recently there seemed to be little doubt about the photochemical preeminence of the lowest quartet,[1] pulsed laser results now indicate that the lowest doublet may also photoreact.[43] According to current thinking, the present photoreaction should proceed entirely from the lowest vibrationally equilibrated quartet, since it is "antithermal" in nature.[43] The $^4B_{1g} \rightarrow {}^4B_{2g}$ transition involves a 45° rotation around the CN–CN axis of the equatorial electron density, resulting in the d_{xz}, d_{yz}, $d_{x^2-y^2}$ configuration. The Cr–N bonds are selectively weakened, as the $d_{x^2-y^2}$ antibonding charge is directed toward the four NH_3 groups. The experimental findings can be examined, more specifically, in light of the available theories.

According to Adamson's rules,[28] ammonia release is expected to dominate, on the grounds that the NH_3–NH_3 axes are those characterized by the lower LF strength.

σ/π-bonding models[10,23–25] predict a decrease of the σ-donor strength on the *xy* plane for the $^4B_{2g}$ state. At the same time π-donor bonds (which are absent for NH_3) would be strengthened. The NH_3 ligands are thus destabilized, while the axial electron density, including π back-bonding to CN^-, should not be modified with respect to the ground state.

The additive angular overlap treatment[27] provides a more quantitative account for NH_3 loss, on the basis of the following calculated bond energies in $^4B_{2g}$: $I^*(Cr–NH_3)$ = 8980 cm^{-1}; $I^*(Cr–CN)$ = 17 550 cm^{-1}. It should be remarked that, among the ligands so far dealt with, CN^- is the only π-acceptor one, i.e., the only group associated with a negative π parameter.

Table III summarizes the ratios of equatorial (ϕ_N) to axial (ϕ_X) photoaquation quantum yields, upon long-wavelength LF irradiation of the *trans*-$CrN_4X_2^{z+}$ species investigated to date. Certain regularities are apparent, as these ratios in general increase with increasing (1) spectrochemical position of X, (2) ^4Eg–$^4B_{2g}$ energy gap, (3) σ-donor ability of X, and (4) $d_{x^2-y^2}$ population in the lowest excited quartet. For X ≠ CN such

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a state is ^4E_g, and point 2 should reflect the involvement of $^4B_{2g}$, that has usually been indicated as the major responsible for in-plane photoreactions. It has also been pointed out that a certain fraction of equatorial ligand release may be attributed to the $d_{x^2-y^2}$ component of the low-lying ^4E_g state;[44] this would be in line with point 4. As has already been discussed,[10] the X = F case fits the σ-bonding order but not the spectrochemical sequence. In addition, the prevalence of amine aquation in the difluoro complex cannot be merely ascribed to the $d_{x^2-y^2}$ component of the lowest excited state, as the d_{z^2} character is intrinsically dominant in ^4E_g; the decisive factor is instead the large Cr–F bond strength in the ground state.[44]

In the extreme case of *trans*-$Cr(NH_3)_4(CN)_2^+$ the predictions based on either LF or bonding criteria coincide. That is, both the exclusive $d_{x^2-y^2}$ population in the lowest excited quartet and the strong σ (and π) bonding of CN^- are concurrent in determining the observed high preference for equatorial photolabilization.

Stereochemistry of Equatorial Photoaquation. Even from qualitative inspection of the photoproducts, two conclusions may be immediately drawn. (1) Equatorial photolysis is stereospecific, in that only two of the three $Cr(NH_3)_3(H_2O)(CN)_2^+$ ions are generated. (2) The photoreaction is in part stereorigid and in part stereomobile. In fact, the two CN^- groups remain trans to each other in one of the two actual isomers (the only possible "*trans*-dicyano" product). Moreover, both products have a meridional configuration; i.e., the missing species is the "*cis*-dicyano" one of facial type. These findings supplement previous reports of partial stereorearrangement for in-plane photosubstitution of CrN_5F^{2+} [8,22] and *trans*-$Cr(en)_2F_2^+$ ions[18] and help one to understand the stereochemical behavior of $Cr(NH_3)_5(CN)^{2+}$ [32] (vide infra).

It is worthwhile to note that the procedure adopted for stereochemical identification would be hardly possible starting from the analogous ethylenediamine complex. The $Cr(en)(enH)(H_2O)_3^{3+}$ isomers are not characterized,[37] and their tendency to lose the one-ended enH ligand would bring about complications. Also, the final aquated product $Cr(en)(H_2O)_4^{3+}$ would not allow distinction between meridional and facial photoproduct configurations.

In regard to the quantitative aspect, unfortunately, the product ratio bears some uncertainty arising from analytical complexity. Yet, the stereoretentive photoproduct was found to be predominant (ca. $^2/_3$) well beyond error limits, and it appears possible to discuss the congruence of the geometries and of the relative amounts of products with the more plausible mechanisms.

As far as dissociative photoreaction paths are concerned, it seems proper to compare the results with the Vanquickenborne–Ceulemans model that has recently been applied to equatorial photosolvation.[30] This theory envisages for the $^4B_{2g}$ state a trigonal-bipyramid intermediate with the CN^- ligands still in axial position, obtained by the allowed process of NH_3–Cr–NH_3 bending after NH_3 departure. Solvent entry in the plane would exclusively lead to the 1,6-CN-2-H_2O isomer. If also the ^4E_g state were photoactive, CN–Cr–CN bending would generate a bipyramid with both cyanides on the equatorial plane, in its first excited state, $^4A_1$. Electronic selection rules would permit coordination of water trans to one of the CN^- groups (i.e., along the original z axis), forming the 1,2-CN-6-H_2O complex. $^4A_1$ may also decay to the $^4B_2$ ground state of the bipyramid, which is expected to add H_2O in a different way (i.e., between the cyanide groups), to yield more 1,6-CN-2-H_2O species.

While the observed isomers are definitely those expected from the above analysis, the model would justify formation of the 1,2-CN-6-H_2O species only on the rather drastic assumption that a considerable fraction of the excited complex react from ^4E_g. Ammonia labilization is predicted in the latter state also, but with less discrimination over cyanide than in $^4B_{2g}$ (I^*(Cr–NH_3) = 11 230 cm^{-1}; I^*(Cr–CN) = 11 940 cm^{-1}).[27]

It should be stressed that ^4E is indeed the lowest excited quartet for CrN_5F^{2+} and *trans*-$Cr(en)_2F_2^+$,[44] so that formation of two photoproducts[8,18] is accommodated in those cases.[30] Here the lowest excited level is $^4B_{2g}$, and that the photoreaction proceeds mostly, if not exclusively, from this state is suggested by (i) the constancy of the NH_3 quantum yields, (ii) the constancy of the product ratio, and (iii) the absence of CN^- photorelease. Although population of ^4E_g by thermal equilibrium may not be disregarded in principle, a ^4E_g–$^4B_{2g}$ energy difference corresponding to 11–12kT at room temperature[27,42] implies a negligible equilibrium amount of ^4E_g molecules. Even with assumption of a smaller gap between the thermally equilibrated states, an unlikely ^4E_g fraction of at least 30% would be required to fit the experimental data. In conclusion, the dissociative LF approach does not seem able to account for the observed stereochemistry.

For consideration of this matter within an associative (or concerted) framework, a pentagonal bipyramid with axial cyanides is postulated. Relaxation of the $^4B_{2g}$ state to this structure should be facilitated by the invariance, with respect to the ground state, of the d_{xz} and d_{yz} charge around the CN–CN axis and by mutual repulsion of the CN^- ligands. The $d_{xy} \rightarrow d_{x^2-y^2}$ migration would allow in-plane expansion of coordination by lowering the electron density on the equatorial edges. Solvent entry cis to the leaving NH_3 group would result in the 1,6-CN-2-H_2O product only. Water access, however, is more likely to occur trans to the departing ligand.[14] Statistical trans attack would lead to a 1:1 ratio of 1,6-CN-2-H_2O and 1,2-CN-6-H_2O isomers; if solvent coordination were limited to the equatorial plane, exclusive formation of the 1,6-CN-2-H_2O species would follow. In this context, the observed product proportion may be explained by preferential association on the equatorial plane, favored by the vacancy of the d_{xy} orbital in conjunction with repulsion from the d_{xz} and d_{yz} clouds and from the apical CN^- groups.

A significant comparison is possible between the present results and the previously reported photostereochemistry of $Cr(NH_3)_5(CN)^{2+}$.[32] LF excitation of the latter complex gives rise to a 2:1 ratio of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, with wavelength-independent quantum yields. Keeping in mind that the monocyano and the *trans*-dicyano ions differ by one axial ligand, the *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ product may be regarded as the analogue of the 1,6-CN-2-H_2O one (where H_2O is cis to both cyanides) and, likewise, a parallel may be drawn between *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ and the 1,2-CN-6-H_2O species (where H_2O is trans to one of the CN^- groups). For both systems the product distribution would be substantially the same within error limits, suggesting that, despite the different ligand composition and ^4E–$^4B_2$ separation, the same mechanism (regardless its dissociative or associative nature) is operative. This may be taken to indicate that the involvement of ^4E is highly improbable even for $Cr(NH_3)_5(CN)^{2+}$, in which the energy difference between the lowest excited quartets is half of that occurring in *trans*-$Cr(NH_3)_4(CN)_2^+$.[42] Like all pentaammines, cyanopentaamminechromium(III) is stereochemically not unequivocal.[1,32] Thus, the above analogy may cast some light on the photolabilization pattern of $Cr(NH_3)_5(CN)^{2+}$, by implying a largely equatorial NH_3 photorelease.

A further remark is that the absence of the 1,2-CN-3-H_2O (facial) isomer among the photoproducts excludes either five-

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or seven-coordinate intermediates having one apical and one equatorial CN^-. Some angular motions during vibrational relaxation of the excited state are therefore definitely precluded. This limitation may again depend on the fact that in the $^4B_{2g}$ state the electron density along the z axis is unchanged relatively to the ground state and preserves rigidity in the CN–CN direction.

In conclusion, although dissociative mechanisms cannot be completely ruled out, the present stereochemical findings seem more compatible with either associative or concerted pathways. This view is in agreement with earlier mechanistic results[14] and with solvent-dependence studies[46,47] on other chromium(III) cations.

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Registry No. *trans*-$Cr(NH_3)_4(CN)_2^+$, 76299-50-8; $Cr(NH_3)_3(H_2O)(CN)_2^+$ (isomer I), 76299-51-9; $Cr(NH_3)_3(H_2O)(CN)_2^+$ (isomer II), 76333-25-0; *mer*-$Cr(NH_3)_3(H_2O)_3^{3+}$, 23774-35-8.

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Laser-Flash-Induced Dissociation and Recombination of Aqueous Pentacyano(2-methylpyrazine)ferrate(II) ion

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Metal-to-ligand charge transfer (MLCT) excitation of pentacyano(2-methylpyrazine)ferrate(II) ion in solution has been investigated, employing pulsed laser light of wavelengths 440–530 nm. Bleaching of the MLCT absorption due to loss of the heterocycle occurs in less than 20 ns. In the presence of excess heterocycle the starting material is regenerated via two intermediates, characterized by their substitution kinetics. One of the intermediates is the ion pentacyanoaquaferrate(II), for which the rates of recombination with 2-methylpyrazine were measured in the concentration range $0.0025\ M \leq [2\text{-Mepyr}] \leq 9.6$ M. The rate law for the process when $[2\text{-Mepyr}] \leq 1$ M is rate = $k_f[Fe(CN)_5OH_2^{3-}][2\text{-Mepyr}]$ ($k_f = 475 \pm 25\ M^{-1}\ s^{-1}$, 25 °C, $\mu = 0.1$ M LiTFMS, $\Delta H^* = 16.0 \pm 0.3$ kcal/mol, $\Delta S^* = 7.7 \pm 1$ cal mol^{-1} deg^{-1}). The rate of this reaction is independent of pH in the range $6.6 \leq pH \leq 11.4$. At $[2\text{-Mepyr}] > 1$ M the apparent order in that reagent's concentration increases markedly. The second intermediate decays via a much smaller absorbance change than the first and exhibits a tendency toward rate saturation in its substitution kinetics. This species is identified tentatively as the sterically hindered N-1 isomer of pentacyano(2-methylpyrazine)ferrate(II).

Introduction

Irradiation of metal-to-ligand charge-transfer (MLCT) bands has been shown to labilize the ligand L, an aromatic N heterocycle, in complexes of the type $Ru(NH_3)_5L^{2+}$,[1] $W(CO)_5L$,[2] and $Fe(CN)_5L^{3-}$.[3] All of these are low-spin, d^6, octahedral species which are inert to substitution in their ground states.

A great deal of work has been undertaken to conceptualize the events leading to loss of the ligand L.[1-7] The primary MLCT* excited states are described as reduced ligand/oxidized metal species which should not be especially reactive to substitution during their short (probably less than 10^{-9} s) lifetimes. However, the complexes possess low-lying excited ligand field states (LF*) which should be strongly labilizing.[6] Thus, various workers have invoked internal conversion of MLCT* to LF* to explain observations of moderately efficient photosubstitution. Strong support is given to these arguments by the fact that the quantum yield for labilization of L, Φ_L, is diminished substantially in cases where $E(\text{MLCT*}) < E(\text{LF*})$.[1-3]

Rather less attention has been focused upon the events which follow ejection of L from the complex, although flash photolysis studies of the ruthenium(II) ammines have been reported recently.[7] In the present work we discuss the substitution kinetics of two intermediates formed in aqueous 2-methylpyrazine (2-Mepyr) solution after flash MLCT photolysis of $Fe(CN)_5(2\text{-Mepyr})^{3-}$. The speed of the photolysis technique permitted investigation at concentrations of 2-Mepyr up to 9.6 M. At high concentrations of the ligand, the rate of water replacement in the ion $Fe(CN)_5OH_2^{3-}$, which is one of the intermediates, is accelerated markedly.

Experimental Section

Materials. The pentacyanoferrate(II) complexes were prepared as solid sodium salts according to published methods and characterized by their visible spectra.[8] Stock solutions of the complexes were diluted to desired concentrations with lithium trifluoromethylsulfonate (LiTFMS) solution and excess free ligand. Except for the pH-dependence experiments, no buffers were added and the pH was allowed to vary in the range 6–8. Removal of dissolved oxygen by deaerating the solutions with argon gas was shown not to affect the kinetics. *N*-Methyl-4,4′-bipyridinium iodide was synthesized by adding an excess of 4,4′-bipyridine to methyl iodide in benzene solution. Ligands 2-methylpyrazine, isonicotinamide, and 4,4′-bipyridine were purchased from Aldrich Chemical Co. The first of these was used as supplied while the second and third were purified, respectively, by recrystallization from water or benzene. Water was triply distilled.

Measurements. Most of the flash measurements were made with a dye laser system that has been described previously.[9] The untuned broad-band output of coumarin dye (~440 nm) was employed with

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