and $AgNO_3$ solutions by X-ray scattering and, although the pertinent region of the radial distribution curve was somewhat obscured by other atom–atom distances, concluded that $Ag^+(aq)$ has two coordinated water molecules with Ag–O distances of 2.41 Å in $AgClO_4$ and 2.45 Å in $AgNO_3$ solutions. There is no information about the structures of hydrolyzed silver(I) species. As with mercury(II), the slope of the solid line in Figure 10 for silver(I) is that expected from the correlation between *B*, C, and electronegativity found for "normal" octahedral/tetrahedral complexes.

Thallium(III) might be expected to behave in the same way as mercury(II) and silver(I), but it does not. Instead, the $Tl(OH)_3(aq)$ species is reported to be much more stable than expected from the correlations found in this work, whereas $TlOH^{2+}$, $Tl(OH)_2^+$, and $Tl(OH)_4^-$ behave normally.

Tin(II), Beryllium(II), and Palladium(II)

In the correlation between *B* and electronegativity shown in Figure 4, it can be seen that beryllium(II), mercury(II), palladium(II), and tin(II) do not behave in the same fashion as other divalent metal ions.[41] All four are more acidic than one would expect on the basis of electronegativity. The reason for the high acidity of mercury(II) was shown above to be due to the unusual stability of "linear" $H_2O–Hg–OH^+$. The high acidity of beryllium(II) and palladium(II) is probably due to the small number of water molecules in the primary coordination sphere. In an octahedral complex there are twelve hydrogen atoms to help carry part of the positive charge. In tetrahedral $Be^{2+}(aq)$ and square-planar $Pd^{2+}(aq)$, however, there are only eight hydrogen atoms, so each hydrogen must carry a somewhat larger portion of the charge. The larger the relative positive charge on a hydrogen atom the more easily it ionizes.

In some of its crystalline compounds tin(II) is three-coordinated.[42a] For example, $SnCl_2(OH_2)$ and $SnCl_3^-$ have a trigonal-pyramidal structure with two unshared electrons at the apex. It is suggested that aqueous tin(II) has the same structure, and therefore, as in the cases of beryllium and palladium, the small number of hydrogen atoms available to help carry the positive charge leads to greater acidity. Johansson and Ohtaki[43] have studied the X-ray scattering of 3 M tin(II) solutions, both in acidic solution and after hydrolysis. They found that $Sn^{2+}(aq)$ has between two and three coordinated water molecules in the inner coordination sphere at 2.3 Å. There is a second peak in the radial distribution curve at 2.8 Å that may be due to a second group of more weakly bound water molecules. Upon hydrolysis, only minor changes were observed in the first hydration sphere. Also in support of the proposed structure of aqueous tin(II), note that even in the most basic solutions complexes with more than three hydroxide ions have not been detected.[44] However, discrete $Sn(OH)_6^{4-}$ ions occur[42b] in crystalline $K_4[Sn(OH)_6]$.

Conclusion

The results described above highlight two major deficiencies in the present state of knowledge about aqueous hydroxy complexes. First, it is apparent that there are still many hydroxide complexes, especially polynuclear complexes, that have not yet been detected. The correlations developed here should be of considerable help in deciding what species to look for and deciding in what pH region they might be found. Second, it appears that equilibria between different structural forms of the same species will turn out to be a rather widespread phenomenon among aqueous hydroxy complexes. For example, one would expect that the species $Al(OH)_2^+$ will be found to be present in a tetrahedral form and as octahedral cis and trans isomers. From the little evidence now available it appears that the free energy difference between the different structural forms is generally small.

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Contribution from the Dipartimento di Chimica,
Università di Perugia, 06100 Perugia, Italy

Photostereochemistry of the *cis*-Dicyanotetraamminechromium(III) Ion

PIETRO RICCIERI and EDOARDO ZINATO*

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Upon ligand field excitation in acid aqueous solution, *cis*-$Cr(NH_3)_4(CN)_2^+$ undergoes simultaneous aquation of NH_3 and CN^-, the former being predominant over the latter by 1 order of magnitude. The quantum yields and their ratios are wavelength dependent. The product of NH_3 release, $Cr(NH_3)_3(H_2O)(CN)_2^+$, was isolated by ion-exchange chromatography and demonstrated to consist of a mixture of 1,2-CN-3-H_2O and 1,2-CN-6-H_2O isomers, the proportion of which varies from ca. 2:1 to ca. 1:1 on passing from the first to the second ligand field band. The major reaction is that expected for the lowest excited quartet, ^4E in D_{4h} approximation, by various photolysis models. The product configurations are also consistent with prevalent ^4E reaction, in terms of currently proposed mechanisms, either dissociative (symmetry restricted) or associative (edge displacement). The complexity of the system does not allow a satisfactory interpretation of the wavelength dependence.

Introduction

The stereochemistry of photosubstitutions of chromium(III) acidoamines upon ligand field (LF) excitation continues to draw both experimental[1-5] and theoretical[6,7] attention. The systems studied in this regard have been mostly of the types CrN_5X^{z+} and *trans*-CrN_4XY^{z+} (N = NH_3 or amines; X, Y = anionic groups of H_2O). Despite this interest, the photochemistry of *cis*-CrN_4XY^{z+} ions has been investigated partially

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and occasionally,[4,8-16] and only for *cis*-$Cr(NH_3)_4F_2^+$ has the isomeric distribution of photoproducts been reported.[4] The main reason is, perhaps, that the presence of both "axial" and "equatorial" Cr–N bonds and the general stereomobility of chromium(III) photolyses[1,2] introduce uncertainties in the interpretation of photolabilization patterns. In addition, some, or even all, of the possible products of N solvation (there are four CrN_3SXY^{z+} isomers, where S = solvent) are often unknown, so that any stereochemical conclusion is precluded.

The recent preparation of *cis*-$Cr(NH_3)_4(CN)_2^+$[17] and the knowledge of two of the three $Cr(NH_3)_3(H_2O)(CN)_2^+$ isomers gained in our previous study of *trans*-$Cr(NH_3)_4(CN)_2^+$[3] offered an opportunity of gathering photostereochemical information for an atypical *cis*-diacidotetraammine. The higher spectrochemical strength of CN^-, relative to NH_3, gives rise to an uncommon energy-level ordering, such that the photochemically important, lowest excited quartet is here ^4E (in D_{4h} approximation; vide infra), instead of $^4B_2$.[18]

The findings for the two dicyano complexes complement each other and provide a homogeneous test of the current models for the photolabilization[19-23] and the photostereochemistry[6,7] of chromium(III).

Experimental Section

Materials. *cis*-Dicyanotetraamminechromium(III) perchlorate was prepared by cyanide anation of *cis*-bis(dimethyl sulfoxide)tetraamminechromium(III) in dimethyl sulfoxide, followed by chromatographic separation from the trans isomer, as already described.[17] The maxima of the LF absorption spectrum occur at 436 (ϵ 49.0) and 342 nm (ϵ 37.6), and the minimum between is at 379 nm (ϵ 14.0).[17]

***mer*- and *fac*-triaquotriamminechromium(III)** ions were obtained[24] in solution by aquation in 1 M $HClO_4$ of *trans*- and *cis*-diaquotetraamminechromium(III), respectively,[25] and subsequent ion-exchange purification, according to reported procedures.[24] The LF absorption features (given in Table II) agreed with the data in the literature.[24]

All other chemicals employed were of reagent grade.

Analytical Procedures. Uncoordinated ligands were determined potentiometrically: cyanide by an Amel Model 201-CN Sens-Ion electrode and ammonia by an Orion Model 95-10 selective electrode, both coupled with a Radiometer Model PHM 84 research pH meter. Measurements were usually carried out on the same photolyzed aliquot, to which a 0.5-mL portion of 0.6 M NaOH was previously added, both for raising the pH to ca. 13 and for ensuring a constant ionic strength of 0.1 M. Calibration plots were obtained in parallel with each set of determinations, by using freshly prepared CN^- or NH_3 (NH_4Cl + NaOH) standards. In alkaline medium, both the reactant and the photoproducts were found to be stable enough to avoid interference with analyses. The chromium content of solution samples was measured spectrophotometrically at 374 nm (ϵ 4760) after decomposition and oxidation to chromate by alkaline hydrogen peroxide.

Chromatographic analyses of the photoproducts were performed by means of Sephadex resins, either cationic (SP-C25) in the sodium form or anionic (QAE-A25) in the perchlorate form. For separation of complexes of different charge, 2–3 × 1 cm columns proved sufficient, and elution was with 5×10^{-4} M $HClO_4$ or 1×10^{-3} M NaOH, depending on the need of having the aquo complexes in their protonated or deprotonated forms, respectively. Isomeric discrimination instead required 20–25 × 0.7 cm columns and elution with 0.1 M $NaClO_4$ at pH 3.3. Samples were processed after ascertaining the spectrophotometric purity of blanks in the 300–600-nm absorption range. Whenever the pH of an aliquot was modified by addition of acid or base, the operation was followed potentiometrically, and the solutions were cooled. During the experiments involving prolonged elutions, the columns were kept in a refrigerator (at 2–3 °C), in order to minimize thermal decomposition.

Absorbances at specific wavelengths were measured by a Beckman DU spectrophotometer, while electronic absorption spectra were recorded by a Cary 17 instrument. For isomeric analysis, the chromatographic fractions of the photoproducts were subjected to thermal aquation, and their LF absorption curves were fitted by linear combinations of known spectra (see Results). A least-squares minimization procedure was applied, by use of an HP 9825 B desk computer, connected with a plotter, which allowed direct reading from the spectrophotometer charts and possible base-line corrections. This analysis could be thus routinely extended over 50–120 different wavelengths, spanning different absorption intervals, when necessary. A check of the quality of the results was provided by comparison of the chromium concentrations evaluated by the fitting, with the values experimentally determined by chemical analysis of the samples. The two independent data generally agreed within ±3%.

Photolysis Procedures. The irradiation setup has already been described.[13] Light intensities were usually about 5×10^{-9} einstein s^{-1} and were monitored by a thermopile, which was calibrated by Reineckate actinometry.[26]

For quantum yield measurements, samples of 2.5-mL volumes were photolyzed in 1-cm path length spectrophotometer cells, thermostated at 20.0 ± 0.5 °C, and magnetically stirred. Solutions were ca. 5×10^{-3} M in *cis*-$Cr(NH_3)_4(CN)_2^+$ and 5×10^{-4} M in $HClO_4$. The ionic strength was brought to 0.10 M by adding $NaClO_4$. Incident light was partially transmitted, and the absorbed quanta were evaluated as reported elsewhere.[27] Photolysis times were 10–20 min, depending on the irradiation wavelength, and the extent of conversion was always less than 5%, in order to rule out inner-filter effects and secondary photoprocesses. At the above pH the dark reaction is sufficiently slow (vide infra) to exclude analytical complications. At any rate, analyses were simultaneously performed on blank and photolyzed samples, so that the thermal reactivity was always taken into account.

In order to obtain larger amounts of products for chromatographic analysis, solutions were made 1.5×10^{-2} M in *cis*-$Cr(NH_3)_4(CN)_2^+$ and 5×10^{-3} M in $HClO_4$, and about 25% of the complex was photoaquated. No ionic strength was added, to avoid interference in the ion-exchange separations. So as to enable absorption by either the first or the second LF band at a higher intensity without prolonging irradiation, an AH-6 lamp was used. Instead of a monochromator, Corning glass filter combinations were employed for light selection.

Results

Quantum Yields. In the dark, *cis*-$Cr(NH_3)_4(CN)_2^+$ undergoes stepwise aquation of CN^-, with complete retention of configuration, as is true for the trans isomer.[17] Both these cations are fairly inert in neutral or alkaline medium, as cyanide loss occurs largely through acid-assisted reaction paths. For the cis isomer, second-order rate constants at 25 °C were estimated to be ca. 5×10^{-3} M^{-1} s^{-1} for both the first and the second aquation steps.[17] Thus, in 5×10^{-4} M $HClO_4$, no more than 0.5% of the complex decomposes thermally during photolysis. Additionally, at this pH the photoaquation products are >99% in their protonated forms (pK_a values of chromium(III)–monoaquo complexes are in the 5.0–5.5 range),[28]

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Table I. Photoaquation Quantum Yields and Product Proportions for the Ligand Field Photolysis of *cis*-$Cr(NH_3)_4(CN)_2^+$ in Acid Aqueous Solution at 20 °C

irradiation wavelength,[a] nm	state[b]	ϕ_{NH_3},[c] mol einstein^{-1}	ϕ_{CN^-},[c] mol einstein^{-1}	% of products 1,2-CN-6-H_2O (II)	% of products 1,2-CN-3-H_2O (III)
480	$^4E(^4T_{2g})$	0.25 ± 0.01 (2)	0.010 ± 0.002 (2)		
435	$^4E(^4T_{2g})$, $^4B_2$	0.26 ± 0.02 (5)	0.022 ± 0.005 (5)	34 ± 5	66 ± 5[d]
405	$^4B_2$	0.30 ± 0.01 (3)	0.020 ± 0.005 (3)		
350	$^4A_2$, $^4E(^4T_{1g})$	0.24 ± 0.01 (3)	0.015 ± 0.003 (3)	45 ± 4	55 ± 4[e]

[a] Irradiation bands of 14-nm half-width. [b] The D_{4h} absorption components overlap; the prevalent excitation is indicated. O_h parent states are in parentheses. [c] Number of runs in parentheses. [d] Irradiation band is centered at 450 nm and is of 70-nm half-width (CS 5-57 and CS 3-75 filters). [e] Irradiation band is centered at 360 nm and is of 50-nm half-width (CS 7-39 filter).

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[b]	447 (47.0 ± 0.5)	389 (18.0 ± 0.5)	350 (36.0 ± 0.5)	1.31	*d*
1,2-CN-3-H_2O isomer	445 (44 ± 1)	388 (19 ± 1)	350 (37 ± 1)	1.19	*d*
1,2-CN-6-H_2O isomer	452 (53 ± 1)	391 (17 ± 1)	350 (34 ± 1)	1.56	3, *d*
$Cr(NH_3)_3(H_2O)_3^{3+}$ [c]					
aquated photoproducts[b]	511 (33.2 ± 0.5)	430 (7.0 ± 0.5)	375 (24.0 ± 0.5)	1.38	*d*
facial isomer (1,2,3)	513 (36.6)	430 (6.2)	374 (22.6)	1.62	24, *d*
meridional isomer (1,2,6)	502 (26.3)	430 (8.9)	376 (26.8)	0.98	24, *d*

[a] In 5 × 10^{-4} M $HClO_4$. [b] Upon irradiation at 450 nm. [c] In 1 M $HClO_4$. [d] This work.

which are usually more stable than their hydroxo analogues.

Irradiation in the LF region induces a progressive red shift of the spectrum, consistent with coordination of H_2O, which is spectrochemically lower than NH_3 and CN^-. The persistence of isosbestic points at 349, 394, and 447 nm, throughout photolysis (normally less than 5%), denotes formation of constant ratios of products. Determination of uncoordinated ligands indicates simultaneous photorelease of both NH_3 and CN^-, with a large predominance of the former. At constant light intensity, the LF spectral changes, as well as generation of free ligands, follow zero-order kinetics. Postirradiation effects are excluded by the spectral stability of photolyzed samples for several hours. Table I summarizes the quantum yields for ammonia and cyanide photoaquations at different excitation energies.

Isomeric Distribution of Products. The major constituents of photolyzed solutions are the reactant (A^+) and one or more $Cr(NH_3)_3(H_2O)(CN)_2^+$ photoproducts (B^+). Thermal and photochemical losses of CN^- give rise to minor concentrations of $Cr(NH_3)_4(H_2O)(CN)^{2+}$, either cis or trans ($C^{2+}$). In addition, at ca. 25% decomposition, secondary photolysis generates nonnegligible amounts of $Cr(NH_3)_2(H_2O)_2(CN)_2^+$ (D^+), NH_3 photorelease being always predominant. Finally, during the subsequent treatments at pH 3.3, further aquation of B^+ may produce some $Cr(NH_3)_3(H_2O)_2(CN)^{2+}$ (E^{2+}). The chromatographic approach for isolation and characterization of B^+ was essentially that devised earlier for the *trans*-$Cr(NH_3)_4(CN)_2^+$ system[3] and consisted of combining deprotonation and reprotonation of the aquo complexes with successive elutions through either cationic or anionic exchangers.

Irradiated mixtures were brought to pH 11.0, at which the charges of the various complexes are as follows: A^+, B^0, C^+, D^-, and E^0. Elution through a cationic column by 1 × 10^{-3} M NaOH led to retention of unreacted A^+ (that was successively recovered) and of C^+. The eluate was then passed, at the same pH, through the anionic resin that retained D^-. The solution containing B^0 and E^0 was acidified to pH 3.3 to restore B^+ and E^{2+}, so that further elution through the cation exchanger by 0.02 M $NaClO_4$ at pH 3.3 yielded B^+, while E^{2+} remained adsorbed.

The LF absorption spectrum of the dicyanoaquo photoproduct(s), quantified by chromium analysis in solution, is reported in Figure 1. The long-wavelength maximum is shifted to the red by 11 nm, with respect to the parent dicyano complex, in conformity with the presence of one H_2O ligand in the coordination sphere.

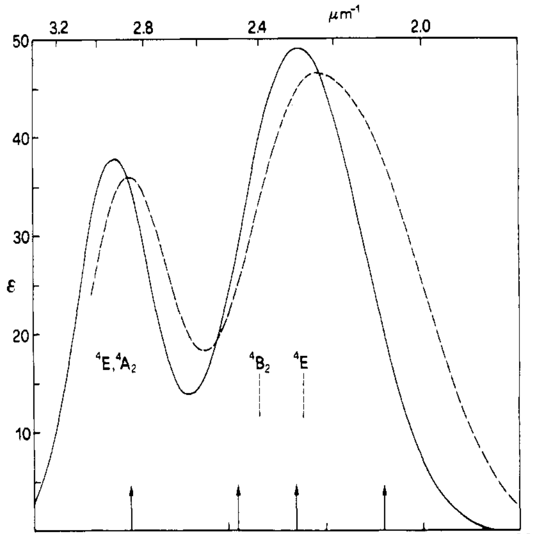

Figure 1. Ligand field absorption spectra in 5 × 10^{-4} M $HClO_4$: solid line, *cis*-$Cr(NH_3)_4(CN)_2^+$; broken line, mixture of $Cr(NH_3)_3(H_2O)(CN)_2^+$ isomers, produced upon 450-nm irradiation. The energies of the two lowest spin-allowed transitions (in D_{4h} approximation) are those predicted in ref 18. Arrows indicate excitation wavelengths.

Qualitative and quantitative isomeric characterization of $Cr(NH_3)_3(H_2O)(CN)_2^+$ was accomplished by two complementary experiments: (1) thermal aquation of cyanide, which is expected to be entirely stereorigid, on the grounds of the stereoretentivity observed in general for chromium(III) substitutions in water[28,29] and in particular for acid hydrolysis of *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$;[17] (2) cation-exchange chromatography, which in our previous study allowed full separation of "*trans*-" from "*cis*-dicyano" (monoaquotriammine) ions.[3]

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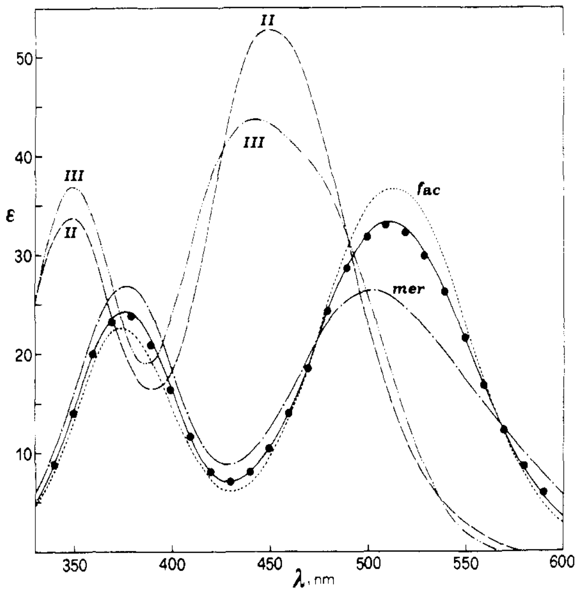


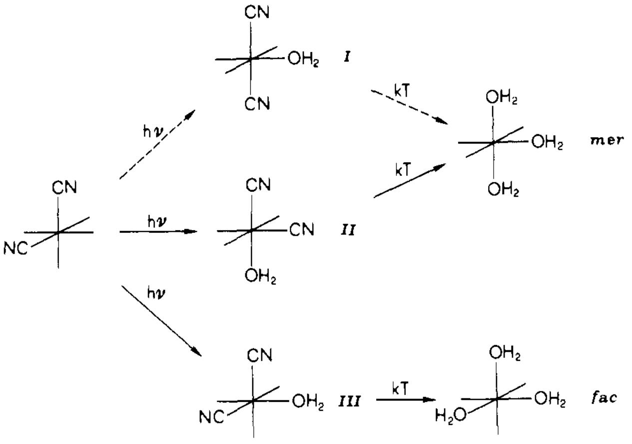
Figure 2. Ligand field absorption spectra of chromium(III)–triammine complexes in acid aqueous solution: – –, 1,2-CN-6-H_2O (II); – ·· –, 1,2-CN-3-H_2O (III); – · –, 1,2,6-H_2O (*mer*); ···, 1,2,3-H_2O (*fac*); —, mixture of thermally aquated photoproducts, $Cr(NH_3)_3(H_2O)_3^{3+}$ (upon 450-nm irradiation). Circles correspond to the calculated absorption for a 1:2 ratio of *mer* and *fac* isomers.

In 1 M $HClO_4$, conversion of the photoproduct(s) into the corresponding $Cr(NH_3)_3(H_2O)_3^{3+}$ cation(s) is complete in 3–4 h at room temperature, and these species are then stable for at least 12 h. The absorption features of the aquated products are intermediate between those of pure *mer*- and *fac*-$Cr(NH_3)_3(H_2O)_3^{3+}$.[24] The LF spectral differences between the two triaquotriammine complexes (see Table II and Figure 2) are large enough to permit evaluation of their proportion in the mixtures. The isomer distribution was determined upon irradiation of either LF band. Five independent experiments were performed for each type of excitation, and the results of least-squares analyses are reported in Table I.

There are three geometric isomers of $Cr(NH_3)_3(H_2O)(CN)_2^+$. Two of them, namely, 1,6-CN-2-H_2O (I) and 1,2-CN-6-H_2O (II) have a meridional configuration, with the cyanide groups either trans (I) or cis (II) to each other, and have already been isolated and identified.[3] The 1,2-CN-3-H_2O complex (III), which is also "*cis*-dicyano", is the only possible facial isomer and is unknown. Stereoretentive aquation[3,17,28,29] implies that the fraction of *fac*-$Cr(NH_3)_3(H_2O)_3^{3+}$ reflects that of III in the photoproduced mixtures.

Regarding *mer*-$Cr(NH_3)_3(H_2O)_3^{3+}$, in order to find out whether it originates from only one or from both of the meridional dicyanoaquo ions, solutions of B^+ were eluted through cationic columns of 20–25-cm length. The yellow band was always displaced without being split. In parallel experiments with solutions of I and II, obtained by photolyzing *trans*-$Cr(NH_3)_4(CN)_2^+$, a 12-cm column proved sufficient for a complete separation of these two isomers, as the nonpolar "*trans*-dicyano" species (I) moved more rapidly than the polar "*cis*-dicyano" one (II).[3] The present lack of chromatographic discrimination, even through a path twice as long, rules out the presence of I, with an estimated uncertainty of 5%. Some fractioning of the two "*cis*-dicyano" species did occur, however, since the absolute LF spectra of various portions of the band were somewhat different. Optical density measurements after aquation of these portions indicated that III is the slower moving complex. This finding is in agreement with literature observations[4,24] that facial isomers generally elute at smaller rates than the meridional ones, the dipole moments being larger for the former than for the latter.

Scheme I



In conclusion, as is summarized in Scheme I, the major products of the LF photolysis of *cis*-$Cr(NH_3)_4(CN)_2^+$ are both "*cis*-dicyano"–aquotriammines, with a facial (III) to meridional (II) ratio varying from ca. 2:1 to ca. 1:1, on passing from the first to the second LF band. Analyses of the absorbances of their mixtures by use of the absorption data previously obtained for II[3] yielded the spectrum of III, reported in Figure 2 and in Table II. It may be noticed that the spectral differences between II and III are not as pronounced as those between I and II,[3] as may be expected on the basis of the same (cis) relative position for the strong-field ligands.

Discussion

Excited-State Labilization. LF excitation of *cis*-$Cr(NH_3)_4(CN)_2^+$ leads to substitution of both types of ligand. The "antithermal" reaction mode, ammonia loss, predominates over cyanide aquation by 1 order of magnitude. The NH_3 and CN^- quantum yields, as well as their ratios, are wavelength dependent. These variations, together with the wavelength dependence of the photoproduct proportion, indicate that more than one excited state is photoactive. The photochemical relevance of the quartet states is now widely accepted, especially for antithermal processes,[1,2] although for some systems doublet-state reaction appears to be an important path.[30,31] In line with current thinking, and in order to make a homogeneous comparison with other chromium(III) acidoamines, the present findings are first discussed in terms of quartet reactivity.

By simple LF theory, *cis*-$Cr(NH_3)_4X_2^+$ complexes, which strictly belong to C_{2v} symmetry, may be approximately regarded as D_{4h}.[18,19] For X = CN, the unique NH_3–NH_3 (z) axis is characterized by the weaker field, while the two NH_3–CN axes define an equatorial (xy) plane of higher average spectrochemical strength. The lowest component of the split $^4T_{2g}$ octahedral state is here ^4E rather than $^4B_2$: a situation that is reversed with respect to all other known *cis*-diacidotetraammines. The $^4B_2$–^4E energy separation is 0.13 μm^{-1}, or half of that occurring in *trans*-$Cr(NH_3)_4(CN)_2^+$,[18] and no splitting is observable in the LF absorption spectrum.[17]

The major photoreaction is consistent with that predicted by all the available photolysis models for ^4E [$(d_{xz}, d_{yz})(d_{xy})$ (80.5% d_{z^2}, 19.5% $d_{x^2-y^2}$)],[23] on the common grounds of selective bond weakening along the z (NH_3–NH_3) axis. Various developments of this basic idea focus on different aspects: (a) the lower LF strength in this direction;[19] (b) an axial decrease of the σ-donor ability (no π effects should be considered for NH_3);[20–22] (c) a smaller excited-state binding energy for axial

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NH_3 (0.86 μm^{-1}) than for equatorial NH_3 (1.19 μm^{-1}) and CN^- (1.45 μm^{-1}), as evaluated by the additive angular overlap treatment (the σ and π equatorial parameters are taken as the average of the values for NH_3 and CN^-).[23] This "axial" labilization behavior is quite opposite to the "equatorial" one, expected for the lowest excited quartet ($^4B_2$) of *cis*-$CrN_4X_2^+$ ions with X $\neq$ CN. The relatively efficient photoaquation of the acido groups observed when X = Cl[14] fits this pattern.

In the above context, the wavelength dependences may be justified by some involvement of the higher $^4B_2$ state $[(d_{xz})(d_{yz})(d_{x^2-y^2})]$, associated with an antibonding charge distribution on the *xy* plane. More or less direct evidence for at least two photoreactive quartets has been obtained in several other instances.[1,2] The thermally equilibrated $^4B_2$ and ^4E states may be produced in varying proportions by relaxation from the corresponding Franck–Condon states (which are simultaneously populated, due to the spectral overlap), or even by conversion of upper quartets. In addition, the relatively small $^4B_2$–^4E energy gap may allow some thermal interconversion between these two states. The many variables involved and the indistinguishability of axial and equatorial NH_3 hinder any detailed assessment. Yet the small, but finite, ϕ_{CN^-} value at 480 nm (where excitation is mainly to ^4E), its increase at shorter wavelengths within the first LF band, and the trend of the ϕ_{CN^-}/ϕ_{NH_3} ratio are consistent with this picture. The Vanquickenborne–Ceulemans model[23] provides an estimate of the bond energies in $^4B_2$ also: 1.44 μm^{-1} for axial NH_3; 0.90 and 1.09 μm^{-1} for equatorial NH_3 and CN^-, respectively. Even though NH_3 labilization should again predominate, the small discrimination between the "equatorial" ligands may account for some CN^- photorelease.

A study of en and CN^- photoaquation has been recently reported for the analogous *cis*-$Cr(en)_2(CN)_2^+$ ion.[15] While the photoreactivity was found to be qualitatively similar to the present one, analytical difficulties obscured quantum yield changes and led to a probable overestimate of ϕ_{CN^-}.[15] Our results confirm the wavelength dependence and show that the actual ϕ_{CN^-} values may be much smaller than the published ones.

The main difference between *cis*- and *trans*-$Cr(NH_3)_4(CN)_2^+$ [3] is that the latter undergoes exclusive NH_3 loss (equatorial bond rupture only) with a constant quantum yield and a constant product ratio throughout the LF region. As already pointed out,[3] this constancy suggests a negligible participation of the higher excited quartet, in agreement with a ^4E–$^4B_2$ energy separation larger for the trans than for the cis isomer.

An alternative explanation for CN^- release would be labilization in the lowest doublet. This state was proposed to react in a "thermal" fashion, that is, as the ground state, on the basis of an orbital population similar to that of the transition state for the dark processes.[32] It was further proposed that, whenever such chemical deactivation occurs, it largely controls the rate of disappearance of the doublet and, hence, the phosphorescence lifetime in room-temperature solution.[31,32] The data available for mixed-ligand complexes led to an empirical rule, stating that emission is expected to be relatively short-lived (less than 1 μs), i.e., determined by chemical reaction, if the ligand substituted thermally lies on the weak-field axis.[32] In *cis*-$Cr(NH_3)_4(CN)_2^+$ the cyanide groups lie on strong-field axes and, consistently, the phosphorescence lifetime in aqueous solution at 20 °C is 25 μs, or relatively long, as that of other chromium(III) cyanoammines.[33] To the extent that the above rule applies in predicting the photoreactivity, CN^- aquation in the doublet state should then be unimportant.

Stereochemistry of Ammonia Photoaquation. Like the trans complex, *cis*-$Cr(NH_3)_4(CN)_2^+$ undergoes stereoselective NH_3 photoaquation, in that only two of the three $Cr(NH_3)_3(H_2O)(CN)_2^+$ isomers are produced. It should be noticed that the isomeric pairs are different in the two systems: for *trans*-$Cr(NH_3)_4(CN)_2^+$ both products are meridional, i.e., 1,6-CN-2-H_2O (trans-*mer*) and 1,2-CN-6-H_2O (cis-*mer*), while for *cis*-$Cr(NH_3)_4(CN)_2^+$ they are "*cis*-dicyano", namely, 1,2-CN-3-H_2O (cis-*fac*) and 1,2-CN-6-H_2O (cis-*mer*). The retention of the cis position for the CN^- groups makes it impossible to establish whether or not the customary stereomobility of chromium(III) photolyses[1,2] is operative in the present case.

The *cis*-dicyanotetraammine ion is not, in principle, fully unambiguous from a stereochemical point of view, as NH_3 may be released from either "axial" or "equatorial" sites. However, the consistency of the quantum yield pattern with a predominant ^4E axial labilization and the complementarity with the trans system enable comparison of the isomerism and the distribution of photoproducts with some mechanistic predictions. So as to supplement our previous discussion on the photostereochemistry of *trans*-$Cr(NH_3)_4(CN)_2^+$,[3] the results are analyzed in terms of the Vanquickenborne–Ceulemans theory[6,7] and of an edge-displacement mechanism,[2–4] which are presently recognized as the more plausible dissociative and associative models, respectively.

The dissociative treatment[6,7,34,35] predicts for the lower lying ^4E state (axially antibonding in D_{4h} approximation) a trigonal-bipyramid intermediate with one axial and one equatorial CN^-, generated by symmetry-restricted NH_3–Cr–CN bending. As this motion does not conserve symmetry elements, the intermediate is obtained in its first excited state, which is $^4B_2$, due to the strong field of the equatorial heteroligand.[34] Depending on whether solvent entry occurs in the excited state of the bipyramid (cis attack to equatorial CN^-) or in its $^4A_1$ ground state (trans attack to equatorial CN^-), the cis-*fac* and cis-*mer* products would be respectively obtained.[36]

In the upper, $^4B_2$ state (equatorially antibonding) the allowed NH_3–Cr–CN bending would give rise to a five-coordinate intermediate with two equatorial cyanides, again in an excited state ($^4A_1$, since the equatorial heteroligand is in this case a weak-field one).[34] Water coordination either in the excited-state or in the ground-state bipyramid ($^4B_2$) would now lead to trans-*mer* (trans attack to equatorial NH_3) and cis-*mer* species (cis attack to equatorial NH_3), respectively.

The observed photoproduct configurations are those expected for the ^4E state, and the ca. 1:2 ratio of cis-*mer* to cis-*fac* at lower excitation energies would indicate prevalent excited-state reaction of the trigonal bipyramid. The increase of the cis-*mer* percentage at shorter wavelengths may be ascribed to $^4B_2$ reactivity, consistent with the quantum yield trends. The absence of experimentally detectable (less than 5%) quantities of trans-*mer* product is not incompatible with this interpretation, thanks to the lack of knowledge of the proportion of excited-state to ground-state reaction of the intermediate. The stereochemistry is thus adequately explained by the Vanquickenborne–Ceulemans approach, on the basis of a dominant ^4E participation. It should be noticed, however, that in the present case this theory becomes less specific than usual, since the possibility of excited-state and ground-state

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(34) For a generalization of the stereochemical predictions see: Vanquickenborne, L. G.; Ceulemans, A. *Coord. Chem. Rev.* **1983**, *48*, 157.

(35) See Figure 2 of ref 4 for a representation of the Vanquickenborne–Ceulemans model, applied to a *cis*-$Cr(NH_3)_4X_2^+$ complex in D_{4h} approximation. It should be kept in mind that for X = F and X = CN the state orderings are different, both in the original hexacoordinated complex and in the trigonal bipyramid intermediates.

(36) See Figure 8 of ref 34.

reactions for both the ^4E and $^4B_2$ intermediates (the latter required by the wavelength dependence) would, in principle, justify any amount of the cis-*fac* and cis-*mer* isomers, and even the possible presence of trans-*mer* product.

The associative model assumes formation of a seven-coordinate intermediate, by solvent approach trans to the labilized ligand,[2-4] and the expectations are substantially those of a concerted, edge-displacement mechanism. On a statistical basis, axial labilization (^4E) should produce a 1:1 ratio of cis-*mer* (H_2O entry on the NH_3–NH_3 edges) and cis-*fac* isomers (attack on the NH_3–CN edges). For release of equatorial NH_3 ($^4B_2$), statistical trans coordination would result in a 1:2:1 distribution of cis-*mer*, cis-*fac*, and trans-*mer* species, respectively.

This mechanism also accounts for the stereochemical findings in terms of predominant ^4E photoreactivity. The percentage of cis-*fac* product, higher than statistical, may be attributed to preferential migration of the negatively charged cyanide ligands away from the incoming solvent molecule. The lack of trans-*mer* product (related to $^4B_2$) may be also explained by electrostatic repulsion, hindering access of water between the CN^- groups. A possible incongruence of this description is that at higher excitation energies (assumed to enhance the involvement of $^4B_2$, as suggested by the wavelength dependence) the proportion of cis-*fac* isomer should increase, in contrast with observation.

To sum up, the stereochemistry of the photoproducts and, roughly, their distribution are consistent with both mechanisms, if chemical deactivation is thought to take place mainly in the lowest excited quartet. Neither model satisfactorily accounts for the wavelength dependence and for the missing trans-*mer* product. A more detailed analysis is virtually impossible since (i) there are too many unknown parameters and (ii) the adopted D_{4h} symmetry may well be an oversimplification.

A survey of the available data on the photostereochemistry of NH_3 aquation in other chromium(III) tetraammines shows that a definitive choice between the two models cannot be made yet. The behavior of *cis*-$Cr(NH_3)_4F_2^+$ is more compatible with the Vanquickenborne–Ceulemans theory;[4] that of *trans*-$Cr(NH_3)_4F_2^+$ is consistent with both mechanisms,[4] while for *trans*-$Cr(NH_3)_4(CN)_2^+$ the results are best rationalized by the edge-displacement approach.[3,37] Several aspects of the stereochemistry are therefore still elusive, specially in systems of the present complexity. Regardless of the mechanistic details, independent studies of solvent[38] and high-pressure[39] effects indicate that, at least for cationic chromium(III) complexes, associative, or concerted, photoreaction paths are preferred.

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Registry No. *cis*-$Cr(NH_3)_4(CN)_2^+$, 77981-98-7; $Cr(NH_3)_3(H_2O)(CN)_2^+$ (1,2-CN-3-H_2O isomer), 86023-23-6; $Cr(NH_3)_3(H_2O)(CN)_2^+$ (1,2-CN-6-H_2O isomer), 76333-25-0; $Cr(NH_3)_3(H_2O)_3^{3+}$, 85404-37-1.

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(37) Application of the dissociative model to the higher excited quartet of *trans*-$Cr(NH_3)_4(CN)_2^+$, ^4E_g, incorrectly considered reaction through both an excited-state and a ground-state bipyramid, leading to cis-*mer* and trans-*mer* dicyanoaquo products, respectively. Such an intermediate is instead expected to react in its ground state ($^4B_2$) and to yield cis-*mer* product only.[34] This difference, however, does not modify the conclusions drawn in ref 3.

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Contribution from the Department of Chemistry and Department of Mathematics,
St. Patrick's College, Maynooth, Co. Kildare, Ireland

Mollweide Projections: Molecular Orbital Symmetries on the Spherical Shell, Tetrahedral and Other Symmetries, and δ Orbitals in Metal Clusters

C. M. QUINN,* J. G. McKIERNAN, and D. B. REDMOND

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The pictorial approach to the generation of group orbitals based on the representation of basic symmetry requirements with Mollweide projections is further developed. General rules are given for the application of this technique to the major classes of structures commonly found for molecules. The utility of the technique for the analysis and discussion of σ-, π-, and δ-type interactions of atomic orbitals is illustrated.

Recently[1] we have proposed the use of a cartographic device, the Mollweide projection, for the construction and presentation of symmetry-adapted functions for molecular point-group structures within the generator orbital approach to the LCAO approximation. In this paper we demonstrate the utility of the method for the other commonly occurring molecular symmetries than $\hat{O}_h$ and illustrate the simple manner in which σ-, π-, and δ-type interactions can be analyzed and discussed within the same framework.

The essential philosophy of the generator orbital approach[2,3] is the reproduction, with the use of local functions (the atomic orbitals) sited at atomic positions about a chosen origin determined by the molecular point group, of the nodal structures of actual or imagined orbitals sited at that chosen origin. The role of these generator orbitals is the detailing of the possible basis function symmetries as nodal patterns for the point group irreducible representations. This is so because the set of atomic orbitals of any atom sited at the origin (basis functions, in the orbital spherical harmonic components, of the irreducible representations of the spherical group $\hat{R}_3$) provide an overcomplete set of functions from which can be chosen compo-

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* To whom correspondence should be addressed at the Department of Chemistry.

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