**Table V.** Exchange Interaction Parameters ($\mathcal{H} = -J\hat{S_i}\cdot\hat{S_j}$) for the Compounds with the Bridging Ligands $(C_6O_4X_2)^{2-}$, with X = H, Cl[a]

| ion | compd | S | $J/cm^{-1}$ | ref |
|---|---|---|---|---|
| | *Binuclear Complexes* | | | |
| Cu(II) | $Cu_2(C_6O_4H_2)(Me_5dien)_2(BPh_4)_2$ | $1/2$ | ±0.2 | 18 |
| | $Cu_2(C_6O_4H_2)(dpt)_2(BPh_4)_2$ | $1/2$ | −9.2 | 18 |
| | $Cu_2(C_6O_4Cl_2)(Me_5dien)_2(BPh_4)_2$ | $1/2$ | ±0.2 | 18 |
| | $Cu_2(C_6O_4Cl_2)(dpt)_2(BPh_4)_2$ | $1/2$ | −4.0 | 18 |
| Ni(II) | $Ni_2(C_6O_4H_2)(tren)_2(BPh_4)_2$ | 1 | −2.2 | 18 |
| | $Ni_2(C_6O_4Cl_2)(tren)_2(BPh_4)_2$ | 1 | −3.6 | 18 |
| Fe(II) | $Fe_2(C_6O_4H_2)_3(H_2O)_4$ | $5/2$ | −4.0 | 29 |
| | $Fe_2(C_6O_4Cl_2)_3(H_2O)_4\cdot 4H_2O$ | $5/2$ | −2.0 | 29 |
| | *Chains* | | | |
| Cu(II) | $Cu(C_6O_4H_2)$ | $1/2$ | −19.5 | 9 |
| | $Cu(C_6O_4Cl_2)$ and $Cu(C_6O_4Cl_2)L_2$ | b | b | this work |
| Fe(II) | $Fe(C_6O_4H_2)(H_2O)_2$ | 2 | −2.8 | 29 |
| | $Fe(C_6O_4Cl_2)(H_2O)_2$ | 2 | −0.2 | 29 |

[a] Abbreviations: $Me_5dien$ = 1,1,4,7,7-pentamethyldiethylenetriamine; dpt = dipropylenetriamine; tren = 2,2',2''-triaminotriethylamine; $BPh_4$ = tetraphenylborate.   [b] See Table IV.

the apparently weak accuracy on the exchange parameter determination should lead to some prudence in the interpretation of the magnetic properties. Nevertheless the magnitude of the antiferromagnetic coupling could be related to the efficiency of the $d_{yz}$ and $d_{zx}$ π-exchange pathways in addition to the $d_{x^2-y^2}$ σ-exchange pathway. (iii) Finally the inadequacy of the Heisenberg Hamiltonian to describe the exchange in-

teraction between orbitally degenerate ions prohibits any discussion on the results concerning the Fe(II) compounds.

**Registry No.** $Cu(C_6O_4Cl_2)$, 29504-40-3; $Cu(C_6O_4Br_2)$, 27882-04-8; $Cu(C_6O_4Cl_2)(NH_3)_2$, 74482-51-2; $Cu(C_6O_4Cl_2)(py)_2$, 74482-53-4; $Cu(C_6O_4Cl_2)(anil)_2$, 74482-55-6; $Cu(C_6O_4Cl_2)(2\text{-Meim})_2$, 74482-57-8; $Cu(C_6O_4Cl_2)(bzim)_2$, 74482-59-0; $Cu(C_6O_4Cl_2)(im)_2$, 74482-61-4; $Cu(C_6O_4Br_2)(NH_3)_2$, 74482-63-6.

**Supplementary Material Available:** Some experimental EXAFS spectra in *k* and *R* space, *k* and *R* filtered spectra and fittings, and *R*-space simulated spectra (15 pages).[30] Ordering information is given on any current masthead page.

(30) *k*- and *R*-space spectra of $Cu(C_6O_4Cl_2)(NH_3)_2$, $CuC_2O_4\cdot{}^1/_3H_2O$, and $CuC_2O_4(NH_3)_2\cdot 2H_2O$, *R*-space filtered spectra for the bromine shells in $Cu(C_6O_4Br_2)$, and *R*-space simulated spectra of $Cu(C_6O_4Br_2)$ are given as supplementary material.

(31) A tetrahedral environment of copper in $CuX_4$ is known when X is a halogen. This is very rare in $CuO_4$. We found only one well-documented case: $CuCr_2O_4$, a spinel structure where copper(II) lies in a distorted tetrahedral environment (see ref 19, p 493). Moreover, a copper(II) chain with a 90° twisted bromanilato bridging ligand would lead to orthogonal magnetic orbitals and consequently to an intrachain ferromagnetic coupling. See, for instance, O. Kahn, J. Galy, P. Tola, and H. Coudanne, *J. Am. Chem. Soc.*, **100**, 3931 (1978).

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# Photochemistry of the Cyanopentaamminechromium(III) Ion

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Ligand field (LF) irradiation of the $Cr(NH_3)_5(CN)^{2+}$ ion in acidic aqueous solution leads to exclusive aquation of $NH_3$, while only $CN^-$ is released thermally. The quantum yields ($\Phi = 0.33$ mol einstein$^{-1}$) are wavelength independent throughout the LF region. Unlike the other acidopentaammines of chromium(III), the lowest quartet excited state of this complex is $^4B_2$, with equatorial antibonding character. Photolabilization of $NH_3$ can be accounted for by Adamson's rules and by various theoretical models. The possible involvement of the upper $^4E$ state is discussed. The photoproduct $Cr(NH_3)_4(H_2O)(CN)^{2+}$ consists of a mixture of cis and trans isomers in a ca. 2:1 ratio. Equatorial photoaquation is suggested to occur with partial stereochemical change. $NH_3$ loss is the only photoreaction also upon charge-transfer (CT) excitation. The quantum yields and the product distribution are virtually the same as in the LF photolysis, indicating efficient conversion of CT (metal-to-ligand) states to LF ones.

## Introduction

The photolytic behavior of $Cr(NH_3)_5X^{2+}$-type ions upon ligand field (LF) excitation continues to be the subject of thorough investigation.[1] Thus far, relevant results have been gathered for X = Cl,[2-4] NCS,[5,6] Br,[7] $N_3$,[8] OCOR,[9] and F.[10,11] These have significantly contributed to the development of

semiempirical[12] and theoretical[13-18] models that account for ligand labilization in terms of the antibonding properties of the lowest quartet excited state. In all the above systems (including the controversial case of X = F)[19,20] such a state is $^4E$ and is associated with a predominant $d_{z^2}$ antibonding character, i.e., with preferential bond weakening along the $NH_3-X$ direction.

In order to explore the photochemistry of an uncommon member of this family, we have recently synthesized and

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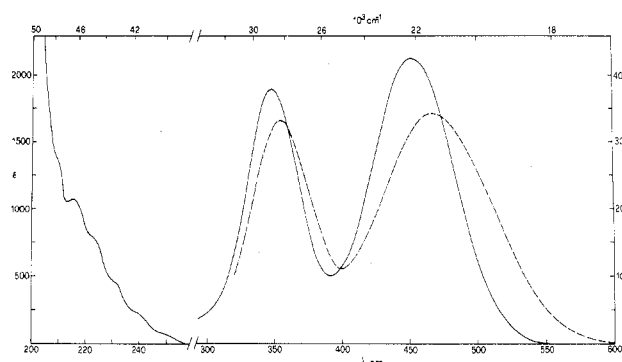(20) Kirk, A. D. *Inorg. Chem.* **1979**, *18*, 2326.
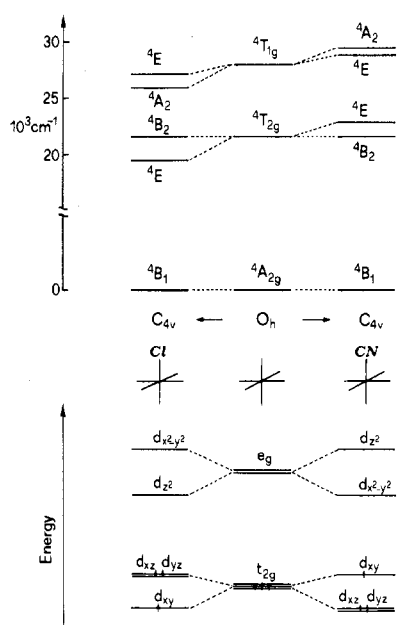
**Figure 1.** Schematic state and orbital energy level diagram for Cr-(NH$_3$)$_5$X$^{2+}$-type complexes, having axial ligand field strengths lower (left; for example, X = Cl) and higher (right; X = CN), respectively, than on the equatorial plane. Data (upper part) are from ref 22.



**Figure 2.** Ligand field ($\epsilon$ on the right) and charge-transfer ($\epsilon$ on the left) absorption spectra in 10$^{-3}$ M HClO$_4$: solid line, Cr(NH$_3$)$_5$(CN)$^{2+}$; broken line, photoproduced Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$.

characterized Cr(NH$_3$)$_5$(CN)$^{2+}$.[21] A number of properties distinguish the complex with X = CN from all other acido-pentaammines studied to date. (1) The largest basicity of the acido group, lending considerable stability to the Cr–N bond in the ground state,[21] may somehow affect the excited-state behavior. (2) The spectrochemical position of X$^-$ is higher than that of NH$_3$. Therefore, the average LF strength along the z axis is larger (rather than smaller), with respect to the xy plane. LF theory[22] predicts a different succession of the excited states which arise on passing from cubic to tetragonal field, as indicated in Figure 1. The lowest spin-allowed excited state is expected to be $^4B_2$, $\sigma$ antibonding exclusively in d$_{x^2-y^2}$, i.e., on the equatorial (NH$_3$)$_4$ plane only. (3) The $\pi$-bonding system of CN$^-$ is such that the charge-transfer (CT) absorption band is related to a metal-to-ligand excitation,[21] rather than to the more usual ligand-to-metal transition.

The present study was undertaken to provide a test for bond destabilization theories,[12-18] with regard to a photoactive excited state of unusual nature for a chromium(III) $C_{4v}$ complex. In addition, the results may allow some insight into the stereochemistry of in-plane photolabilization, which is now drawing increasing interest.[11,20,23,24] At the moment, the photochemical literature on chromium(III) cyanides appears to be confined to Cr(CN)$_6$$^{3-}$ [25-29] and Cr(H$_2$O)$_5$(CN)$^{2+}$.[30]

## Experimental Section

**Materials. Cyanopentaamminechromium(III) perchlorate** was obtained by cyanide anation of [Cr(NH$_3$)$_5$(Me$_2$SO)](ClO$_4$)$_3$ in dimethyl sulfoxide (Me$_2$SO), as already described,[21] and was recrystallized twice. The maxima of the LF absorption spectrum in aqueous

solution (Figure 2) occur at 451 ($\epsilon$ 42.6) and 347 nm (37.7). In addition, a sequence of shoulders is observed in the CT absorption region at 251 ($\epsilon$ 60), 241 (200), 232 (440), 224 (760), 217 (1060), and 210 nm (1330).[21]

*cis-* and *trans-***Diaquotetraamminechromium(III) perchlorate** salts were prepared, and recrystallized, by standard methods.[31] The LF absorption spectra in 1 M HClO$_4$ solution are reported in Table II. All other chemicals employed were of reagent grade.

**Analytical Procedures.** Cyanide determination was performed potentiometrically, with use of an Amel Model 201-CN Sens-Ion electrode coupled with a Radiometer Model PHM 84 research pH meter. Samples were buffered at pH 12, and calibration plots were run in parallel with each set of measurements, with use of KCN. Blank experiments showed that the presence of cyano complexes in solution did not bring about any inconvenience, as thermal release of cyanide at these pH levels is quite negligible.[21]

Photoreleased ammonia was analyzed as proton uptake, according to an earlier published method.[7] Since free CN$^-$ ion produced by the thermal reaction (vide infra) contributes to H$_3$O$^+$ neutralization, uncoordinated NH$_3$ was determined from the differences between the moles of acid consumed in the irradiated and in the dark samples. Both these amounts were measured as pH changes relative to the pure solvent, by a glass microelectrode, connected to the above-mentioned pH meter. The ionic strength was kept constant at 0.5 M by means of sodium perchlorate. By this procedure, only photoaquated cyanide, if any, is expected to affect the $\Delta$pH values, and the photolytic H$^+$ uptake may be corrected, in principle, for the CN$^-$ contribution.

Independent determinations of ammonia were accomplished by means of an Orion Model 95-10, NH$_3$-sensing electrode. Solutions were brought to pH ca. 13 by adding NaOH prior to measurement. Calibration was done each time, using freshly prepared ammonia (NH$_4$Cl + NaOH) standards. The sensitivities of the two methods for NH$_3$ analysis were comparable in the 5 $\times$ 10$^{-5}$–5 $\times$ 10$^{-4}$ M range, and the results agreed within experimental error.

Ion-exchange separations of the photoproducts were carried out with 4 $\times$ 1 cm columns of Sephadex SP-C25 cationic resin, in the sodium form. Elution was with sodium perchlorate of the desired concentration and pH (vide infra). Electronic absorption spectra were recorded with either a Shimadzu UV 200S or a Cary 17 spectrophotometer, while optical densities at given wavelengths were read with a Beckman DU instrument.

**Photolysis Procedures.** The general apparatus has been described previously.[32] Isolation of irradiating wavelengths was by means of either interference filters or a Bausch & Lomb high-intensity grating monochromator. Incident intensities were usually around 5 $\times$ 10$^{-9}$ einstein s$^{-1}$ and were monitored either with instruments[32] or by using the Reineckate[33] and ferrioxalate[34] actinometers. Samples of 3-mL volume were photolyzed in 1 cm path length spectrophotometer cells, placed in a thermostated holder at 20.0 $\pm$ 0.5 °C. Solutions were ca. 10$^{-2}$ M in Cr(NH$_3$)$_5$(CN)$^{2+}$ and 10$^{-3}$ M in HClO$_4$, and the ionic strength was adjusted to 0.5 M with NaClO$_4$. Under these conditions,

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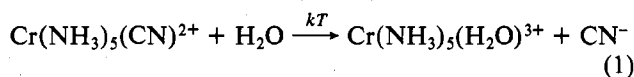(33) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.
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a fraction of the light was transmitted, and the absorbed energy was evaluated as reported elsewhere.[35] Less than 3% conversion was enough to generate analytically suitable amount of products, so inner filter effects and secondary photolysis could be completely ignored. Irradiation periods ranged between 10 and 20 min. At this pH, the dark reaction is sufficiently slow so that no more than 0.5% $CN^-$ is released thermally, during photolysis. In any case blank solutions were analyzed simultaneously with the irradiated ones, in order to take into account the thermal process.

When the photoproduct was to be obtained in larger amounts for preparative purposes, photolyses were performed to about 15% reaction. A broad band-pass filter was used, which allowed light absorption by the whole low-energy LF band of the complex at a much higher intensity, without protracting the irradiation time. No ionic strength was added in this case, in order to avoid interference during the subsequent chromatographic experiments.

## Results

**Photoaquation Reaction.** The thermal behavior of cyanopentaamminechromium(III) has been examined in detail over a wide range of acidities and ionic strengths, as part of the characterization of the new complex.[21] As for most of the acidopentaammines,[36] the sole dark process is aquation of the acido group (eq 1). In acidic media, cyanide is readily re-

$$Cr(NH_3)_5(CN)^{2+} + H_2O \xrightarrow{kT} Cr(NH_3)_5(H_2O)^{3+} + CN^-$$
(1)

placed by solvent, mainly through an acid-catalyzed pathway. The high basicity of $CN^-$ is responsible for efficient protonation of the leaving ligand. On the contrary, the complex ion is quite stable in neutral or alkaline solution at room temperature.

The photolysis conditions resulted from a compromise, such as to simultaneously satisfy the following requirements: (i) sufficiently slow dark reactivity ($k_{obsd} = 1.6 \times 10^{-6}$ s$^{-1}$ at 20 °C, pH 3, and $\mu = 0.5$ M), (ii) an acid concentration suitable for determination of photoreleased base by hydrogen ion consumption, and (iii) complete protonation of the possible photoaquation products ($pK_a$ values of chromium(III) monoaquo complexes are around 5),[32,36] in order to avoid postirradiation effects, due to the usually fast decomposition of hydroxo compounds. Also, since coordinated cyanide may undergo partial $H^+$ uptake, the available data[21] allowed an estimate of less than 0.004% for the protonated form in $10^{-3}$ M HClO$_4$ ($\mu = 0.5$ M), so that $Cr(NH_3)_5(CN)^{2+}$ was indeed the only species to be photolyzed.

The spectrum of aqueous $Cr(NH_3)_5(CN)^{2+}$ is displayed in Figure 2. The two LF absorptions are associated with the $^4B_1 \rightarrow {}^4B_2, {}^4E$ and $^4B_1 \rightarrow {}^4E, {}^4A_2$ excitations, in order of increasing energy. No splittings of the octahedral parent states ($^4T_{2g}$ and $^4T_{1g}$, respectively) are observable, because of the small energy differences (1200 and 600 cm$^{-1}$) between the sublevels in quadrate symmetry.[22]

Under irradiation at any wavelength in the LF region, both bands are appreciably shifted to the red, consistently with entry of the lower field $H_2O$ ligand in the coordination sphere. Expanded-scale differential spectrophotometry shows the permanence of three well-defined isosbestic points at 473 ($\epsilon$ 34), 398 (11), and 360 nm (32), which indicate that either a single product or a constant ratio of products is involved. Progressive acid consumption accompanies these changes and the coincidence between proton uptake and direct $NH_3$ determination demonstrates that no photoprocess, other than generation of ammonia, is taking place. Moreover, the contents of uncoordinated cyanide were found to be the same in the dark and irradiated solutions. To further check this important point, we carried out some $CN^-$ measurements at 5

**Table I.** Quantum Yields for Ammonia Photoaquation of $Cr(NH_3)_5(CN)^{2+}$ in $1 \times 10^{-3}$ M HClO$_4$ at 20 °C

| irradiation wavelength, nm | transition[a] | $\Phi_{NH_3}$,[b] mol einstein$^{-1}$ |
|---|---|---|
| 495 ± 7 | $^4B_1 \rightarrow {}^4B_2$ | 0.33 ± 0.01 |
| 455 ± 7 | $^4B_1 \rightarrow {}^4B_2, {}^4E\ ({}^4T_{2g})$ | 0.33 ± 0.01 |
| 420 ± 7 | $^4B_1 \rightarrow {}^4E\ ({}^4T_{2g})$ | 0.33 ± 0.01 |
| 350 ± 7 | $^4B_1 \rightarrow {}^4E\ ({}^4T_{1g}), {}^4A_2$ | 0.33 ± 0.01 |
| 250 ± 4 | $t_{2g} \rightarrow t_{1u}\ (\pi^*, CN)$ | 0.31 ± 0.02 |
| 235 ± 4 | | 0.34 ± 0.02 |

[a] The tetragonal LF absorption components overlap; the prevalent excitation is indicated. Octahedral parents in parentheses. [b] Average of at least four independent runs.

°C, in order to gain precision by minimizing possible thermal reaction effects of the products. Even under these conditions, no difference was ever detected between photolyzed and blank aliquots. The spectral variations, as well as $NH_3$ appearance, depend linearly on the absorbed photon energy throughout photolysis (usually 3–5%). The quantum yield values for ammonia photoaquation at several LF wavelengths are collected in Table I. On the basis of the analytical sensitivity, an upper limit of $5 \times 10^{-4}$ mol einstein$^{-1}$ could be established at all wavelengths for the quantum yield of possibly photoinduced cyanide release.

Irradiation of the CT absorption band gives rise to essentially the same spectral evolution as observed in the LF photolysis. Also in this case, only $NH_3$ is photoproduced, practically with the same efficiency as upon excitation in the visible region. Again, the quantum yields (included in Table I) appear to be wavelength independent within error limits.

**Product Characterization.** The LF spectrum of the photoaquated species $Cr(NH_3)_4(H_2O)(CN)^{2+}$ was first evaluated by relating the optical density changes to the concentrations of free $NH_3$. On the assumption of photorelease of one $NH_3$ group/complex ion, the absorption curve shown in Figure 2 was obtained, with maxima at 468 ($\epsilon$ 34) and 355 nm (33).

The photoproduct was then actually isolated by cation-exchange chromatography. After irradiation to about 15% reaction (see the Experimental Section), samples were made ca. $5 \times 10^{-3}$ M in NaOH and ca. 0.1 M in NaClO$_4$. At this pH the aquation product is completely converted into the monopositive $Cr(NH_3)_4(OH)(CN)^+$ ion. Elution through the cationic resin with $5 \times 10^{-3}$ M NaOH + 0.1 M NaClO$_4$ solution permitted full separation of the hydroxo compound from the 2+ charged, unreacted complex. The red color of the first fraction (the LF absorption maxima are at 490 and 385 nm) is in agreement with the low spectrochemical position of $OH^-$. The other (yellow) band, moving more slowly, consists of pure $Cr(NH_3)_5(CN)^{2+}$. Upon acidification (to pH ca. 3.3, to avoid acid-catalyzed $CN^-$ loss) the color of the first eluate turns to yellow-orange, and the maxima shift to 468 and 355 nm. Analysis of chromium in solution led to a quantitative determination of the spectrum, confirming the extinction coefficients independently measured, as mentioned above. The LF band positions are consistent with coordination of one $H_2O$ ligand. In addition, the intense CT absorption remains unchanged with respect to the starting complex. The typical vibrational sequence indicates cyanide to be still bound to chromium.

A further step was to pursue the isomeric characterization of the $Cr(NH_3)_4(H_2O)(CN)^{2+}$ species. The cis- and trans-$Cr(NH_3)_4(CN)_2^+$ cations have been recently prepared in this laboratory, as well as the respective products of thermal aquation.[37] The spectral features of the photolysis product(s) were intermediate between those of cis- and trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$. The data are summarized in Table II.

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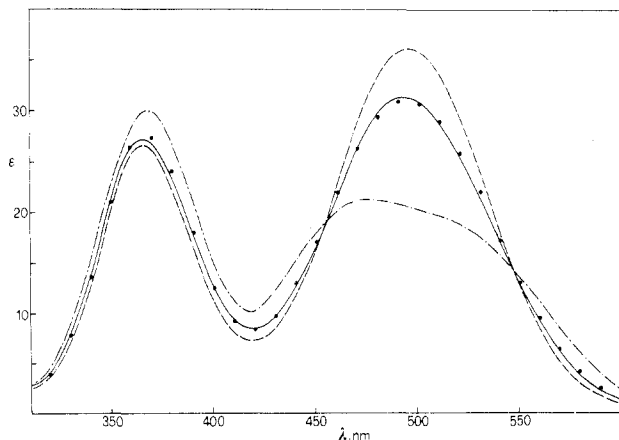
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**Table II.** Ligand Field Absorption Data for Some Chromium(III)–Tetraammine Complex Ions in Aqueous Solution

| | | wavelength, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$) | | | |
|---|---|---|---|---|---|
| | | max | min | max | ref |
| $Cr(NH_3)_4(H_2O)(CN)^{2+}$ [a] | photoproduct[c] | 468 (34.0 ± 0.5) | 400 (11.2 ± 0.3) | 355 (33.2 ± 0.5) | d |
| | cis isomer | 468 (31 ± 2) | 400 (11 ± 1) | 355 (33 ± 2) | 37 |
| | trans isomer | 468 (47.7) | 400 (10.4) | 354 (32.1) | 37 |
| $Cr(NH_3)_4(H_2O)_2{}^{3+}$ [b] | aquated photoproduct | 492 (31.5 ± 0.5) | 418 (8.5 ± 0.3) | 366 (28.0 ± 0.5) | d |
| | cis isomer | 495 (36.2) | 418 (7.4) | 366 (26.6) | d, 31 |
| | trans isomer | 475 (21.4) | 418 (10.2) | 368 (30.2) | d, 31 |

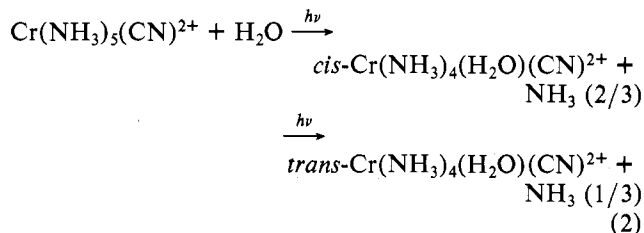[a] In 10$^{-3}$ M HClO$_4$. [b] In 1 M HClO$_4$. [c] Upon ligand field irradiation. [d] Present work.



**Figure 3.** Ligand field absorption spectra of $Cr(NH_3)_4(H_2O)_2{}^{3+}$ ions in 1 M HClO$_4$: - - -, cis isomer; · · ·, trans isomer; —, species obtained by thermal aquation of photoproducts. The circles indicate the calculated absorption for a mixture of 67% *cis*- and 33% *trans*-diaquotetraammine complexes.

While there is little doubt that a mixture of isomers is formed, the spectra of the two aquocyano complexes are not sufficiently differentiated to provide a precise stereochemical determination. An additional inaccuracy factor is introduced by some uncertainty about the extinction coefficients of the pure cis isomer, due to experimental complications during its isolation.[37]

A more satisfactory result was then sought, through spectral analysis of the species obtained by subsequent thermal aquation of the photoproduct(s). The test appeared feasible on the grounds that stereorigidity is a general property of substitutions of chromium(III) complexes in the ground state.[36,38] Present experience with cyanoammines[37] shows that both Cr-(NH₃)₄(CN)₂⁺ isomers undergo acid-catalyzed aquation of the cyanide groups in two successive steps and, in fact, eventually yield the corresponding *cis*- and *trans*-Cr(NH₃)₄-(H₂O)₂³⁺ ions with complete retention of configuration.

Acidification to pH ca. 0 of the solution of photoproduced $Cr(NH_3)_4(H_2O)(CN)^{2+}$ causes release of all the cyanide (within 1 h at room temperature) to give a mixture of Cr-(NH₃)₄(H₂O)₂³⁺ species, the spectrum of which is depicted in Figure 3. Such a spectrum then remains virtually unchanged for 24 h. Also the spectra of authentic samples of *cis*- and *trans*-Cr(NH₃)₄(H₂O)₂³⁺ do not change under identical conditions, for the same period of time. Both these ions are known to be relatively inert.[31,36] As indicated in Table II and in Figure 3, unlike the absorption features of the parent aquocyano compounds, the LF bands of the diaquo isomers are significantly different, both in shape and in intensity. The spectrum of the Cr(NH₃)₄(H₂O)₂³⁺ mixture (again, quantitatively characterized by chromium analysis in solution) can be nicely fitted by a linear combination of the absorption curves of the individual diaquotetraamminechromium(III) complexes. Five independent experiments gave 66 ± 3% *cis*- and 34 ± 3%

*trans*-Cr(NH₃)₄(H₂O)₂³⁺. This finding provides definite evidence that the LF photolysis of cyanopentaamminechromium(III) produces both the *cis*- and the *trans*-aquocyanotetraammine species in ca. 2:1 ratio (see eq 2).

$$Cr(NH_3)_5(CN)^{2+} + H_2O \xrightarrow{h\nu}$$

$$cis\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + NH_3 \ (2/3)$$

$$\xrightarrow{h\nu}$$

$$trans\text{-}Cr(NH_3)_4(H_2O)(CN)^{2+} + NH_3 \ (1/3) \tag{2}$$

An identical procedure for isomer identification was applied to CT photolysis. Also in this case a mixture of products was obtained, the distribution of which (60 ± 5% cis and 40 ± 5% trans) appears not to be substantially different with respect to LF excitation.

## Discussion

**Quantum Yields.** The excited-state chemistry of Cr-(NH₃)₅(CN)²⁺ (eq 2) is totally different from the thermal reactivity, which involves exclusive loss of coordinated CN⁻ (eq 1). The "antithermal" behavior is quite extreme, relative to all the Cr(NH₃)₅X²⁺ systems examined so far, where, besides NH₃, the X⁻ groups are photoreleased with small, but finite, quantum yields.

The efficiencies for NH₃ photoaquation (Table I) are constant throughout the LF region, down to the low-energy tail of the first absorption band. This implies that most, if not all, of the Cr–NH₃ bonds are cleaved in the lowest excited state of a given spin multiplicity. The reactivity of the lowest quartet is widely recognized,[1] although evidence has recently been obtained for simultaneous definite chemistry of the lowest doublet.[39,40]

Figure 1 illustrates the electronic situation of cyanopentaamminechromium(III) as predicted by LF calculations.[22] The pattern is atypical among all other acidopentaammines, since the splittings of the $O_h$ energy levels result to be opposite to the usual occurrence, with ⁴B₂ as the lowest excited quartet, having the $(d_{xz}, d_{yz}, d_{x^2-y^2})$ configuration.[22] The change of electron distribution in ⁴B₂ with respect to the ground state corresponds to an angular motion of 45° around the $z$ (CN–NH₃) axis of the charge lying on the $xy$ plane, without affecting any other direction. As the σ-antibonding $d_{x^2-y^2}$ orbital points toward the four equatorial NH₃ ligands, selective destabilization of the latter should follow. Within this general picture, the results may be viewed more in detail in the light of the current photolysis models, which are all concordant in justifying photoinduced detachment of in-plane NH₃.

(1) Adamson's rules[12] account for bond rupture along the $x$ and $y$ (NH₃–NH₃) axes on the basis of the lower average

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(39) Maestri, M.; Bolletta, F.; Moggi, L.; Balzani, V.; Henry, M. S.; Hoffman, M. Z. *J. Chem. Soc., Chem. Commun.* **1977**, 491; *J. Am. Chem. Soc.* **1978**, *100*, 2694.

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field strength in these directions.

(2) According to the MO–LF, $\sigma/\pi$ bonding theories,[13–16] the $^4B_1 \rightarrow {}^4B_2$ transition reduces $\sigma$ donation on the $xy$ plane, while it would strengthen the $\pi$ bonds on the same plane. As $NH_3$ is a $\sigma$ donor only, in-plane $\pi$ bonding is nonexistent, and the net result is labilization of equatorial ammonia. The axial electron density (including $\pi$ back-donation from the $d_{xz}$ and $d_{yz}$ orbitals to $CN^-$) should not be altered with respect to the ground state.

(3) With use of the additive angular overlap model of Vanquickenborne and Ceulemans,[18] the equatorial (eq) and axial (ax) bond energies associated with the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation (the $\pi$ parameter for $CN^-$ is negative) are evaluated as $I^*(Cr-NH_3)_{eq} = {}^5/_4 \sigma(NH_3) = 8980 \text{ cm}^{-1}$, $I^*(Cr-NH_3)_{ax} = 2\sigma(NH_3) = 14\,370 \text{ cm}^{-1}$, and $I^*(Cr-CN^-) = 2\sigma(CN^-) - 2\pi(CN^-) = 17\,550 \text{ cm}^{-1}$. Again, the equatorial bonds result to be the most weakened ones.

It should be pointed out that, even though the lowest excited quartet is $^4B_2$, some chemistry may occur in the upper $^4E$ state as well. In view of the relatively small energy gap, thermal equilibrium between the two states cannot be ruled out, in principle. In addition, the considerable distortion away from the ground-state geometry may bring the two vibrationally equilibrated states even closer than inferred spectroscopically.[1] It follows that a fraction (supposedly small) of $NH_3$ may be photoreleased from the axial position, since $^4E$ is antibonding mainly in $d_{z^2}$. The Vanquickenborne analysis[18] would indeed predict loss of apical $NH_3$, but not of $CN^-$, for this state. Therefore, even with the assumption of two reactive levels, $NH_3$ is the only ligand expected (and found) to be photoaquated.

The CT absorption spectrum (Figure 2) exhibits a series of shoulders. The constancy and the magnitude (ca. 1600 $\text{cm}^{-1}$) of the energy differences between these features are consistent with a vibrational progression, related to the C–N stretch in the $t_{2g} \rightarrow t_{1u}$ ($\pi^*$, CN) excited state.[21] The CT transition is a metal-to-ligand one; i.e., its direction is opposite to that characteristic of acidoammines with $\pi$-donor acido groups. As the $t_{2g}$ ($d_{xz}$, $d_{yz}$) orbitals are $\pi$ bonding, CT excitation should remove $\pi$ stabilization between Cr and $CN^-$. Nevertheless, the bonds that are broken upon UV irradiation are again the Cr–$NH_3$ ones, with essentially the same quantum yield as in the LF photolyses. Both the photoreaction efficiencies and the isomer composition of the photoproduct, very similar in the two types of photolysis, would suggest efficient conversion of CT states to the LF manifold.

**Stereochemistry.** The configuration of the ammonia photoaquation products of acidopentaammines cannot, alone, provide unequivocal information as to the stereochemical course of photoreaction.[1] The possibility of $NH_3$ release from

both axial and equatorial positions, coupled with the stereomobility of chromium(III) photosubstitutions,[1,32] precludes any definite stereochemical conclusion, unless the original site of the labilized ligand is identified. Despite this limitation, an important feature does immediately appear: the LF photolysis of $Cr(NH_3)_5(CN)^{2+}$ generates a mixture of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ in a ca. 2:1 ratio, rather than a single isomer.

For the other $Cr(NH_3)_5X^{2+}$ ions, *cis*-$Cr(NH_3)_4(H_2O)X^{2+}$ is the sole species arising from $NH_3$ photosolvation following irradiation of the long-wavelength LF band, when X = $Cl$,[3] NCS,[6] Br,[7] or OCOR.[9] $NH_3$ labeling tests[4] and studies of *trans*-$Cr(en)_2(NH_3)X^{2+}$ systems[11,41] have demonstrated that release of apical $NH_3$ leads exclusively to *cis*-aquoacido products. Furthermore, trans $\rightarrow$ cis isomerization appears to be a general requirement when axial bond weakening is involved.[1] For X = F axial photoaquation is accompanied by equatorial $NH_3$ displacement, and, besides the cis product, some trans isomer is formed.[11]

On the above grounds, it may be reasonably inferred that all the *trans*-$Cr(NH_3)_4(H_2O)(CN)_2^+$ product (corresponding to 34% of $NH_3$ loss) arises from photolabilization of in-plane $NH_3$. In this context, at least one-fourth of the *cis*-aquocyano isomer (corresponding to 16% of free $NH_3$) would be also related to equatorial bond rupture, as no more than 50% of uncoordinated ammonia may be attributed to axial detachment. This extreme would correspond to the limiting case in which the $^4B_2$ and $^4E$ energy levels were degenerate, so that $d_{x^2-y^2}$ and $d_{z^2}$ were equally populated, with assumption of similar equatorial and axial quantum yields. Given the equatorial antibonding character of the lowest excited quartet, even a small departure from octahedral symmetry is likely to considerably increase the amount of cis product connected with in-plane labilization.

In conclusion, although this system is intrinsically not unambiguous, the product distribution confirms that the photoactive state is unusual and strongly suggests equatorial photoaquation to occur with partial stereochemical change. A current study[37] of the more diagnostic *trans*-$Cr(NH_3)_4$-$(CN)_2^+$ complex, where in-plane labilization is univocally established, does corroborate this indication.

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