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Ligand Field Photochemistry of *trans*-Tetraamminechromium(III) Complexes with One Strong-Field and One Weak-Field Axial Ligand

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The ligand field photolysis of three *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} ions, with X = H$_2$O, NCS$^-$, and F$^-$, has been studied in acidic aqueous solution (10^{-3} M HClO$_4$). These complexes are electronically unusual, in that the CN$^-$ and X axial groups act in opposition on the splittings of the octahedral states and, moreover, are respectively π-acceptors and π-donors. In each case photoaquation of all three types of ligands is observed. For X = H$_2$O, trans $\rightarrow$ cis photoisomerization is taken as a measure of water photoexchange. The total quantum yields are in the 0.2–0.4 range, virtually wavelength independent. Equatorial and axial reactivities are of comparable magnitude, their ratios being 0.32, 2.5, and 3.0 for X = H$_2$O, NCS$^-$, and F$^-$, respectively, upon irradiation of the long-wavelength maximum. This is consistent with the small energy separation between the lowest excited quartet states, ^{4}E and ^{4}B$_2$. The results are compared with the predictions of various photolysis models and are analyzed particularly in terms of excited-state σ- and π-bonding changes. All three complexes phosphoresce from the lowest doublet state under photochemical conditions, with 20 °C lifetimes of 1.1, 30, and 0.2 μs, respectively. Luminescence and photoreaction quenching by Cr(C$_2$O$_4$)$_3$$^{3-}$ have been investigated in the case of *trans*-Cr(NH$_3$)$_4$(CN)(NCS)$^+$. The quantum yields for the three photoaquation modes decrease in parallel with emission and, upon complete doublet quenching, one-fourth of the photoreactivity remains unquenched. The proportion in ligand labilization is the same for both the unquenchable and the quenchable photochemistry. This suggests a common precursor (^{4}E/^{4}B$_2$) for all photoreactions, hence, doublet deactivation mainly via back intersystem crossing to the lowest excited quartet state(s).

Introduction

Studies of the ligand field (LF) photochemistry of *trans*-CrN$_4$XY^{z+}-type ions, where N = ammonia and amines and X, Y = acido groups, have been numerous.[1,2] Among the available chromium(III) species, the tetraamines of D_{4h} or C_{4v} symmetry are, in fact, the most suited to provide unequivocal information on two main points: the selectivity of photolabilization and the stereochemistry of photosubstitution. The above geometries are, of course, privileged in relation to the basic idea of "photoactivated axis", first introduced by Adamson's rules[3] and successively elaborated by various models.[4-10]

The majority of the complexes investigated to date have been those with axial ligands of lower spectrochemical strength than the equatorial amines. More recently, attention has been devoted to systems with spectrochemically higher axial groups, namely, the *trans*-CrN$_4$(CN)$_2$$^+$ ions with N$_4$ = (NH$_3$)$_4$,[11] (en)$_2$,[12] cyclam,[13] and tet a.[14] The photochemically relevant feature distinguishing between the two families is the different energy ordering of the LF states,[15] hence, the different antibonding characters of the lowest excited quartet: mainly axial (^{4}E state) for the former and equatorial (^{4}B$_2$ state) for the latter.

Given these contrasting properties, we thought it worthwhile to explore new situations arising from the presence on the tetragonal axis of both a strong-field and a weak-field ligand. We report here on the LF photolysis in acidic aqueous medium of the newly synthesized *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} complexes,[16,17] where

X = H$_2$O, NCS$^-$, and F$^-$. The CN$^-$ and X groups exert opposing effects on the splittings of the LF states on descending from O_h to C_{4v} symmetry. Moreover, the π-acceptor and π-donor characters of the heteroligands introduce unusual π-bonding conditions along the z axis. These peculiarities and the possibility of studying three simultaneous photosubstitution modes make the above compounds particularly adapted to test the degree of detail the current photolysis theories[8-10] are able to handle.

Additional interest in these species resides in their solution phosphorescence under photochemical conditions. In particular, the fairly intense and long-lived doublet-state emission of the X = NCS$^-$ complex provides an opportunity of studying its quenching in parallel with that of three distinct and sufficiently efficient photoreactions. Some clues are thus sought as to the long-debated question about the actual origin of the quenchable part of photochemistry.[1,2]

Experimental Section

Materials. ***trans*-[Cr(NH$_3$)$_4$(H$_2$O)(CN)] (ClO$_4$)$_2$.** A suspension of 1.0 g of *trans*-[Cr(NH$_3$)$_4$(CN)$_2$](ClO$_4$)[16] in 38 mL of 0.10 M HCl was stirred for 30 min at 25 °C. Acid-catalyzed aquation occurs with full stereoretention.[16] To the final solution was added a 10-mL portion of aqueous 16 M LiCl, and after ice cooling, the precipitate was collected by filtration, washed with ethanol and then with ether, and vacuum-dried. The chloride salt was converted into the perchlorate by reprecipitation from aqueous solution at pH 3.5 (ca. 20 mL) with 25 mL of 3.0 M LiClO$_4$ in methanol. The product was recrystallized from water by addition of aqueous concentrated NaClO$_4$ and washed and dried as above. Anal. Calcd for [Cr(NH$_3$)$_4$(H$_2$O)(CN)](ClO$_4$)$_2$: Cr, 14.32; NH$_3$, 18.76; CN, 7.17. Found: Cr, 14.1; NH$_3$, 18.6; CN, 7.0. The maxima of the LF absorption spectrum in acidic aqueous solution (10^{-3} M HClO$_4$) occur at 468 (ϵ (M^{-1} cm^{-1}) 48.0) and 354 nm (ϵ 32.2),[16] as illustrated in Figure 1.

***trans*-[Cr(NH$_3$)$_4$(CN)(NCS)](ClO$_4$)** and ***trans*-[Cr(NH$_3$)$_4$(CN)F]-(ClO$_4$)** were obtained by stirring a suspension of 0.50 g of *trans*-[Cr-(NH$_3$)$_4$(H$_2$O)(CN)]Cl$_2$ in 25 mL of methanol, in the presence of either NH$_4$NCS (6.5 g) or NH$_4$F (0.65 g). After 24 h at 40 °C, the thiocyanate and fluoride salts of the products were separated by filtration, repeatedly washed with ethanol and then with ether, and vacuum-dried. Conversion into the respective perchlorates and recrystallization were accomplished by procedures similar to those employed for the cyano aquo complex. Anal. Calcd for [Cr(NH$_3$)$_4$(CN)(NCS)](ClO$_4$): Cr, 17.12; NH$_3$, 22.43; NCS, 19.12. Found: Cr, 16.9; NH$_3$, 22.0; NCS, 19.3. Calcd for [Cr(NH$_3$)$_4$(CN)F](ClO$_4$): Cr, 19.65; NH$_3$, 25.74; F, 7.18. Found: Cr, 19.2; NH$_3$, 25.1; F, 7.3. The LF spectra (Figure 1) exhibit maxima at 466 (ϵ 80.0) and 355 nm (ϵ 51, shoulder) for the X = NCS$^-$

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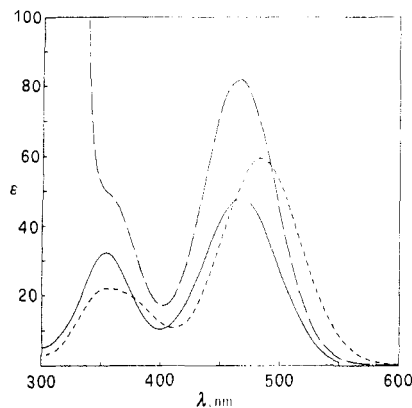
Figure 1. Ligand field absorption spectra of *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} complexes in 1 × 10^{-3} M HClO$_4$ solution: (—) X = H$_2$O; (–·–) X = NCS$^-$; (---) X = F$^-$.

complex and at 483 (ϵ 59.5) and 355 nm (ϵ 21.8) for the X = F$^-$ species.

A detailed account on the preparation, characterization, and solution behavior of the present complexes, as well as of other *trans*-Cr(NH$_3$)$_4$-(CN)X^{z+}-type complexes, is given elsewhere.[17] Definite evidence for the trans configuration of these three species is found in the known spectra[16,18,19] of the terminal aquation products, exclusively *trans*-Cr-(NH$_3$)$_4$(H$_2$O)X$^{(z+1)+}$.[17]

K$_3$[Cr(C$_2$O$_4$)$_3$]·3H$_2$O was prepared by a standard procedure.[20]

Analyses. Released cyanide was determined potentiometrically by an Amel 201-CN Sens-Ion electrode. Samples were brought to pH ca. 12 with NaOH prior to measurement. Free fluoride was analyzed likewise, by means of an Amel 201-F electrode, after adjusting the pH to 5.5 by the addition of acetate buffer. A Radiometer PHM 84 potentiometer was employed. Calibration plots were obtained in parallel with each set of determinations, by use of fresh KCN or NaF standards. In the range of concentrations encountered, the reproducibility was ±3% for CN$^-$ and ±2% for F$^-$. Both reactant and product complexes were found not to interfere with analyses, as thermal release of CN$^-$ and F$^-$ is quite negligible at the above pH values.

Thiocyanate ion was determined spectrophotometrically at 450 nm (ϵ 4300) as the iron(III) complex. Because of the low concentrations, 5 cm pathlength cells were employed, and all complexes were removed by adsorption on 3 × 1 cm columns of Sephadex SP-C25 cationic (Na$^+$) resin, followed by elution with 1 × 10^{-3} M HClO$_4$. The sensitivity was further increased with respect to the standard procedure,[21] by a fivefold increase of the reagent concentration (0.5 M Fe^{3+} + 2.5 M HClO$_4$) and a reduction of its volume. Separation was necessary because chromium(III) species absorb substantially at the wavelength of analysis; in addition, the different CN$^-$ aquation rates of the reactant and the photoproduct are considerably enhanced by the acidity of the reagent.

Uncoordinated ammonia was measured by two independent methods. One procedure consisted of monitoring proton uptake by NH$_3$ in a ca. 10^{-3} M HClO$_4$ solution, the ionic strength of which was kept constant at 0.10 M by addition of NaClO$_4$.[22] A glass microelectrode was immersed in the reaction cell during photolysis. The acid consumed in both the irradiated and the dark samples was calculated from the pH differences with the pure solvent (rather than from the ΔpH between the two solutions). Since thermal and photochemical CN$^-$ contribute to acid neutralization, NH$_3$ was obtained by subtracting the amounts of cyanide, independently determined, from the overall consumption of H$_3$O$^+$. The buffering action of the photoproducts was considered in principle, as acid dissociation of coordinated H$_2$O tends to reduce the above pH differences. This interference was unimportant for the monoaquo complexes, which around pH 3 are more than 99% protonated, their pK_a values being above 5.0.[16,23] In the photolysis of *trans*-Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ the effect was not negligible, due to the higher acidity of the diaquo products (e.g., pK_a = 4.9 for *cis*-Cr(NH$_3$)$_4$(H$_2$O)$_2$$^{3+}$),[24] although often the correction was still within experimental error. Direct ammonia measurements were carried out by an Orion 95-10 NH$_3$ sensing electrode, following alkalinization of the samples to pH ca. 13 with NaOH. Standardization was

performed during each group of analyses, by use of fresh ammonia (NH$_4$Cl + NaOH) solutions. The sensitivities of the two methods were comparable in the 5 × 10^{-5}–5 × 10^{-4} M range, and the results agreed within instrumental uncertainty.

The chromium content of solution samples was measured spectrophotometrically at 374 nm (ϵ 4760), after oxidation to chromate by means of alkaline hydrogen peroxide.

Chromatographic separation of the Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ species from samples of photolyzed *trans*-Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ was accomplished by use of Sephadex SP-C25 cationic exchanger, in the sodium form. Elution was with NaClO$_4$ of the desired concentration (see Results), at a pH of either 3.5 or 10.0, depending on the need of having the aquo complexes in their protonated or deprotonated forms, respectively. If the pH was to be changed by addition of acid or base, the samples were cooled and the changes were followed potentiometrically. All operations were performed in dim light.

In order to determine the isomeric composition of mixtures of Cr-(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ complexes, or of their thermally aquated products, Cr(NH$_3$)$_4$(H$_2$O)$_2$$^{3+}$, the LF spectra were fitted with linear combinations of those for the pure trans and cis isomers. A computerized least-squares minimization method was adopted, extending over 120 wavelengths, as already reported for analogous cases.[25] The quality of the result was checked by comparing the chromium concentration given by the fitting with that independently determined by chemical analysis. The agreement was generally within ±2%.

Equipment and Procedures. Emission spectra were obtained by use of a Perkin-Elmer 650-10S spectrofluorimeter. Phosphorescence decays were measured by means of a J.K. System 2000 frequency-doubled ruby laser. Excitation was at 347 nm, with 25-ns pulses of ca. 200-mJ energy. Emissions were monitored at their maxima by a Hamamatsu R928 photomultiplier, with wavelength selection by means of an Applied Photophysics high-intensity grating monochromator. The signals were fed into a Tektronix 468 digital oscilloscope, the output of which was processed by a Cromemco computer through a IEE 488 interface. Lifetime values were obtained from least-squares fittings of the first-order decay plots. The samples were essentially the same as those employed for the photolyses (vide infra) and were placed in thermostated, 1.0-cm^2 fluorimeter cells.

Optical densities were determined with a Beckman DU spectrophotometer, while complete absorption spectra were recorded by a Cary 17 instrument. All solutions employed for either absorption or emission measurements were filtered through 0.45-μm Millipore cellulose filters just before use.

The photolysis apparatus has been described previously.[26] Light intensities were (2–5) × 10^{-9} einstein s^{-1}, as monitored by a thermopile, calibrated vs. the Reineckate actinometer.[21] Aliquots of 2.5-mL volume were irradiated in 1.0 cm pathlength cells, kept at 20.0 ± 0.5 °C, and stirred. For measurement of quantum yields of ligand release, solutions were (3–6) × 10^{-3} M in complex and 1 × 10^{-3} M in HClO$_4$, at an ionic strength of 0.10 M, adjusted with NaClO$_4$. Photolysis times were 10–30 min, depending on the irradiation wavelength and on the extent of decomposition, generally 5–15%.

Emission and photoreaction quenching of *trans*-Cr(NH$_3$)$_4$(CN)-(NCS)$^+$ were studied in the presence of 1 × 10^{-5}–3 × 10^{-3} M Cr-(C$_2$O$_4$)$_3$$^{3-}$, under the above conditions of temperature, acidity, and ionic strength. Irradiation was protracted so as to obtain product concentrations comparable to those observed in the absence of quencher.

Determination of the efficiency of photoisomerization of *trans*-Cr-(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ required ca. 1.5 × 10^{-2} M solutions of complex in ca. 5 × 10^{-3} M HClO$_4$, and ca. 30% total photolysis. No ionic strength was added in this case, so as not to hinder the chromatographic separations. All samples were Millipore-filtered prior to photolysis. Light absorption was usually partial, and the absorbed energy was determined as already reported.[27] Inner filter effects of the photoproducts were taken into account;[27] however, below 15% conversion the corrections were within analytical error. In the quenching experiments the irradiation wavelength of 480 nm was chosen in correspondence to a minimum of the LF spectrum of Cr(C$_2$O$_4$)$_3$$^{3-}$. Correction for mixed absorption was significant only for quencher concentrations above 5 × 10^{-4} M, with a maximum extent of ca. 15%. After photolysis, analyses were performed in parallel on identical irradiated and dark aliquots, so as to allow for thermal aquation of CN$^-$.

Results

For all three *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} ions the dark reactivity is one of cyanide aquation. As observed in other aqueous chro-

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Table I. Quantum Yields for the Ligand Field Photolysis of *trans*-Cr(NH₃)₄(CN)X^{z+} Complexes in 1 × 10⁻³ M HClO₄ at 20 °C

X	λ$_{irrn}$, nm^a (state)^b	Φ$_{CN}$-^{c}	Φ$_X$^{c}	Φ$_{NH_3}$^{c}	Φ$_{eq}$/Φ$_{ax}$
H₂O	465 ($^4T_{2g}$)	0.061 ± 0.010 (5)	0.117 ± 0.006^d (2)	0.058 ± 0.012 (4)	0.32
	355 ($^4T_{1g}$)	0.071 ± 0.011 (2)	0.096 ± 0.006^d (3)	0.059 ± 0.013 (4)	0.35
NCS⁻	505 ($^4T_{2g}$)	0.062 ± 0.009 (3)	0.0196 ± 0.0008 (2)	0.247 ± 0.006 (3)	3.0
	465 ($^4T_{2g}$)	0.082 ± 0.005 (4)	0.0183 ± 0.0005 (3)	0.254 ± 0.007 (4)	2.5
	360 ($^4T_{1g}$)	0.064 ± 0.004 (2)	0.0200 ± 0.0006 (2)	0.253 ± 0.005 (2)	3.0
F⁻	485 ($^4T_{2g}$)	0.095 ± 0.005 (5)	0.011 ± 0.001 (4)	0.315 ± 0.010 (4)	3.0
	360 ($^4T_{1g}$)	0.074 ± 0.005 (3)	0.009 ± 0.001 (2)	0.330 ± 0.005 (3)	4.0

^{a} Irradiation bands of 14 nm half-width. ^{b} O_h approximation. ^{c} Number of independent determinations in parentheses. ^{d} Quantum yield for trans → cis photoisomerization.

mium(III) tetraammines,[16,28,29] the process is completely stereo-retentive, leading to *trans*-Cr(NH₃)₄(H₂O)X$^{(z+1)+}$ products only.[17] Acid catalysis is extensive, and kinetic studies in progress indicate that the reactive species are largely, if not solely, the protonated forms, *trans*-Cr(NH₃)₄(CNH)X$^{(z+1)+}$.[17] At low acidities, the pseudo-first-order rate constants for CN⁻ loss, k_{obsd}, depend linearly on [H₃O⁺]. Photolyses were carried out at pH ca. 3, so as to comply with the following conditions. (i) Thermal aquation was relatively slow at 20 °C: k_{obsd} = ca. 2 × 10⁻⁶ s⁻¹ for X = H₂O,[30] ca. 6 × 10⁻⁶ s⁻¹ for X = NCS⁻, and ca. 3 × 10⁻⁵ s⁻¹ for X = F⁻. (ii) Proton uptake by coordinated CN⁻ was less than 0.5%, so that the actually photolyzed species were the unprotonated complexes. (iii) The sensitivity of the ΔpH measurements for NH₃ and CN⁻ analysis was satisfactory. (iv) The acidic H₂O ligands were virtually undissociated (vide supra), and even small amounts of unstable hydroxo complexes were avoided.

The general pattern of reactivity upon excitation in the LF region is analogous for the three compounds. Both LF absorption maxima undergo red shifts, suggesting that H₂O replaces one or more ligands, which, with the exception of F⁻, are spectrochemically stronger than the entering solvent. In each case three sharp isosbestic points, well evident in difference spectra throughout photolysis, denote constant ratios of products. The pH increases, and hydrogen ion consumption follows clean zero-order kinetics. The spectral and pH stability of photolyzed solutions excludes postirradiation reactions. Also, up to 2 h after photolysis, the differences in CN⁻ concentration between irradiated and dark samples remain constant within error limits. This shows that, under the present pH conditions, the rates of thermal CN⁻ aquation of the photoproducts are sufficiently low and, moreover, are in the same range as those of the reactants.

Table I collects the quantum yields for the various photo-reactions of each system. The excitation wavelengths correspond to the LF absorption maxima and, in the case of X = NCS⁻, also to the low-energy side of the first band.

***trans*-Cr(NH₃)₄(H₂O)(CN)²⁺.** The spectral crossing points are located at 495, 415, and 368 nm. NH₃ and CN⁻ photoaquate in parallel at comparable rates and account for the whole proton uptake. The sum of the quantum yields for release of these ligands (ca. 0.1) appeared rather small, however, compared with the total efficiencies (0.3–0.4) for photosubstitution in chromium(III) acido ammines,[1,2] and suggested the occurrence of a third photoreaction. Trans → cis rearrangement was the most likely process, in light of the well-known behavior of other trans acido aquo tetra-ammines.[1,2,26]

Determination of photoisomerization yields involved separation of the starting trans cyano aquo complex (A²⁺) and of the possible cis isomer (B²⁺) from all other chromium(III) species. This was accomplished by combining cation-exchange chromatography with deprotonation and reprotonation of the H₂O ligands. Besides A²⁺ and B²⁺, photolyzed mixtures contained Cr(NH₃)₃(H₂O)₂(CN)²⁺ (C²⁺) and Cr(NH₃)₄(H₂O)₂³⁺ (D³⁺), due respectively to NH₃ and CN⁻ aquation (thermal plus photochemical for the latter). Additionally, at the 30% conversion level required by this procedure, secondary photoproducts, such as Cr(NH₃)₂(H₂O)₃(CN)²⁺ (E²⁺) and Cr(NH₃)₃(H₂O)₃³⁺ (F³⁺), could not be ignored.

Photolyzed solutions were alkalinized at pH ca. 10, at which the complex charges were as follows: A⁺, B⁺, C⁰, D⁺, E⁻, F⁰. Elution through the cationic resin by 1 × 10⁻⁴ M NaOH moved off C⁰, E⁻ and F⁰, while A⁺, B⁺ and D⁺ were retained. These were successively displaced by 5 × 10⁻³ M NaClO₄ at pH 10, and reacidification to pH 3.5 restored A²⁺, B²⁺, and D³⁺. Further elution through another column by 0.07 M NaClO₄ at pH 3.5 yielded an orange solution containing A²⁺ and B²⁺, whereas the pink band of D³⁺ remained adsorbed.

The LF spectra of the eluates (quantified by subsequent chromium analysis) were fitted by linear combinations of those for *trans*- and *cis*-Cr(NH₃)₄(H₂O)(CN)²⁺.[16] As in previous work,[31] the sensitivity of isomeric determination was considerably improved by performing such a fitting on the corresponding Cr(NH₃)₄(H₂O)₂³⁺ ions, as the absorption differences are substantially larger for the diaquo than for the cyano aquo isomers. The mixture of diaquo complexes was obtained by thermal aquation of CN⁻, which is totally stereorigid[16] and goes to completion within 1–2 h in the dark, at pH ca. 0 and at room temperature. The above treatment showed that trans → cis rearrangement is indeed the predominant photoreaction mode (Table I). Photoisomerization was taken as a measure of H₂O photoexchange, by analogy with other well-characterized systems, where axial photolysis is prevalent and the quantum yields for formation of cis products equal those for axial ligand loss.[26,32]

Similar analyses were applied to D³⁺, after recovering it with 0.5 M NaClO₄ at pH 3.5. Due to the low concentration and to the likely presence of thermally aquated products in this fraction, only semiquantitative estimates were possible, which indicated that at least three-fourths of the CN⁻ photoaquation product, Cr(NH₃)₄(H₂O)₂³⁺, was in the cis configuration. The complexity of the system hindered any attempt to gather isomeric information on the NH₃ photoaquation product(s).

***trans*-Cr(NH₃)₄(CN)(NCS)⁺ and *trans*-Cr(NH₃)₄(CN)F⁺.** The behavior of these two complexes is quite similar. The absorption changes induced by LF irradiation show isosbestic points at 496, 411, and 369 nm for the former and at 507, 430, and 402 nm for the latter, independent of the excitation wavelength. All three types of ligands are simultaneously photoreleased but, in contrast with the cyano aquo system, NH₃ loss now predominates over the two other photosubstitution modes. Again, the quantum yields for acid consumption independently determined match the sum of those for NH₃ and CN⁻ photoaquation. In both cases X⁻ substitution is the minor photoprocess.

When photolyzed solutions of the thiocyanato complex were made alkaline for either ammonia or cyanide determination, they became unstable with respect to loss of NCS⁻ but not of NH₃ and CN⁻. Thus, the apparent quantum yields for NH₃ and CN⁻ aquation were independent of the time elapsed after alkalinization, whereas NCS⁻ could be reliably determined only after separation from the irradiated samples. The instability of thiocyanato aquo complexes of chromium(III) in basic medium has been noticed in other instances.[21,33]

Even though the NH₃ aquation products could be isolated in fair amounts by an ion-exchange technique, stereochemical

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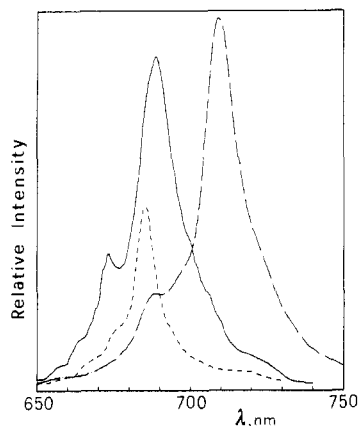
Figure 2. Emission spectra of *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} complexes in 1 × 10^{-3} M HClO$_4$ solution at room temperature: (—) X = H$_2$O; (−·−) X = NCS$^-$; (---) X = F$^-$.

Table II. Emission Behavior of *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} Complexes in Aqueous 1 × 10^{-3} M HClO$_4$

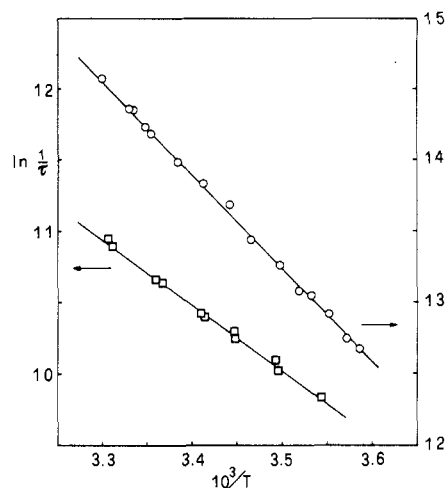| X	λ_{max}, nm	$\tau^0{}_{20°C}$, μs	E^*, kcal mol^{-1}	ln A
H$_2$O[a]	688	1.10 ± 0.02	13.1 ± 0.2	36.3 ± 0.3
NCS$^-$	709	30.0 ± 0.5	9.1 ± 0.3	26.1 ± 0.8
F$^-$	685	0.23 ± 0.02		

[a] Data from ref 36.

analyses were precluded by the lack of knowledge on all of the four possible Cr(NH$_3$)$_3$(H$_2$O)(CN)X$^+$ isomers. In contrast, while both forms of the Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ and Cr(NH$_3$)$_4$-(H$_2$O)X^{2+} products were known,[16,18,19,34] their small proportion and the interference by thermal products made isomeric characterization impossible. The stereochemistry, however, was beyond the scope of this work.
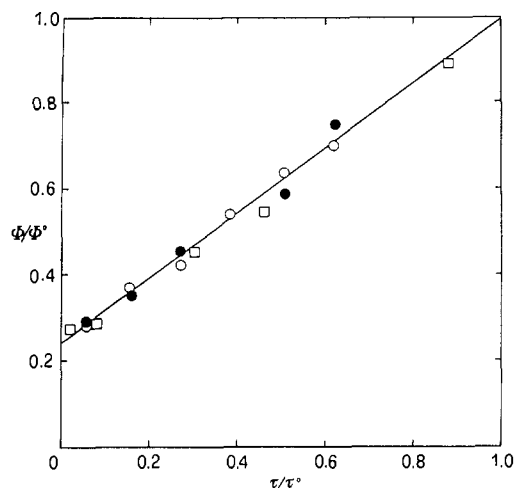
Quenching of Emission and Photochemistry of *trans*-Cr-(NH$_3$)$_4$(CN)(NCS)$^+$. Acidic aqueous solutions of all three *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} complexes luminesce at room temperature in the 650–750-nm region. The emission spectra, shown in Figure 2, are narrow and structured, like those of other chromium(III) cyano ammines,[35,36] and are likewise assigned to phosphorescence from the lowest doublet state(s). The luminescence decays exponentially in all cases, with correlation coefficients larger than 0.998 in the least-squares fittings of the decay signals. Table II reports the emission maxima and lifetimes at 20 °C, τ^0, and for X = H$_2$O and X = NCS$^-$ also the apparent activation energies, E^*, and frequency factors, A, in the equation 1/τ^0 = A exp($-E^*/RT$). The temperature dependence, determined over a range of ca. 25 °C, is illustrated in Figure 3. Arrhenius parameters were not obtained for the X = F$^-$ complex, as its emission is weaker and shorter lived than that of the other compounds.

The phosphorescence is quenched by the hydroxide ion. For X = NCS$^-$ a Stern–Volmer plot is linear with a bimolecular quenching rate constant k_q = 1.9 × 10^8 M^{-1} s^{-1} at 20 °C. Quantification of OH$^-$ quenching was not possible for X = H$_2$O and X = F$^-$. In the former case the basic medium deprotonates coordinated water, generating a nonemitting hydroxo species, while in the latter it brings about cloudiness, due to fast thermal decomposition.

The tris(oxalato)chromate(III) ion was found to be an efficient doublet quencher for our complexes. The relatively long emission decay of *trans*-Cr(NH$_3$)$_4$(CN)(NCS)$^+$ enabled a detailed investigation using reasonably low amounts of Cr(C$_2$O$_4$)$_3$$^{3-}$. At 20 °C, the k_q values for lifetime quenching are 3.3 × 10^8 M^{-1} s^{-1}

(34) Poyung-Hsien Chung, N. H.; Davis, S. R. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2849.

(35) Zinato, E.; Adamson, A. W.; Reed, J. L.; Puaux, J. P.; Riccieri, P. *Inorg. Chem.* **1984**, *23*, 1138.

(36) Zinato, E.; Adamson, A. W.; Riccieri, P. *J. Phys. Chem.* **1985**, *89*, 839.

Figure 3. Temperature dependence of the emission lifetimes of *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} complexes in 1 × 10^{-3} M HClO$_4$ solution: (O) X = H$_2$O (right scale); (□) X = NCS$^-$ (left scale).

Figure 4. Quenching of the three photoaquation reactions of *trans*-Cr-(NH$_3$)$_4$(CN)(NCS)$^+$ by Cr(C$_2$O$_4$)$_3$$^{3-}$ vs. emission quenching under the same conditions: (O) CN$^-$; (□) NCS$^-$; (●) NH$_3$.

Table III. Quenching of the Photoreactions of *trans*-Cr(NH$_3$)$_4$(CN)(NCS)$^+$ by Cr(C$_2$O$_4$)$_3$$^{3-}$ in Aqueous Solution at 20 °C[a]

10^4[Cr(C$_2$O$_4$)$_3$$^{3-}$], M	Φ_{CN^-}[b,c]	Φ_{NCS^-}[c]	Φ_{NH_3}[b,c]
0.076		0.0163	
0.676		0.0100	
0.987	0.057		0.189
1.36		0.0083	
1.58	0.052		0.150
2.58	0.044		
4.29	0.034		0.117
6.78		0.0052	
8.78	0.030		0.088
26.6	0.023	0.0050	0.073

[a] Irradiation at 480 nm in 1 × 10^{-3} M HClO$_4$ solution. [b] μ = 0.10 M (NaClO$_4$). [c] Average uncertainties estimated from duplication of experiments: CN$^-$, ±10%; NCS$^-$, ±3%; NH$_3$, ±5%.

at μ = 0.10 M (NaClO$_4$) and 2 × 10^9 M^{-1} s^{-1} in the absence of NaClO$_4$.

Also, the photoreactivity decreases in the presence of Cr-(C$_2$O$_4$)$_3$$^{3-}$. An experimental advantage with this quencher is that its LF spectral minimum matches the maxima of the tetraammines, thus reducing mixed absorption. Additionally, its own substitutional photochemistry consists of racemization only, with a quantum yield of 0.09,[37] and does not cause analytical inter-

(37) Spees, S. T.; Adamson, A. W. *Inorg. Chem.* **1962**, *1*, 531.

Table IV. Relevant Spectrochemical Data (cm^{-1}) for *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} Complexes, Evaluated by Use of the Parameters and Procedures of Ref 8[a]

X	σ_X	π_X	$\bar{\sigma}_{ax}$	$\bar{\pi}_{ax}$	$E(^4E) - E(^4B_2)$	$E(d_{xz}, d_{yz}) - E(d_{xy})$	$E(d_{x^2-y^2}) - E(d_{z^2})$
H$_2$O	5940	500	7210	105	−165	210	−60
NCS$^-$	6410	380	7450	45	310	90	−530
F$^-$	7630	1700	8060	705	−100	1410	−1750

[a] σ_{CN^-} = 8480 cm^{-1}; π_{CN^-} = −290 cm^{-1}; $\bar{\sigma}_{eq}$ = σ_{NH_3} = 7180 cm^{-1}; $\bar{\pi}_{eq}$ = π_{NH_3} = 0.

ference. Direct photolyses at 570 nm (LF maximum), under our experimental conditions, gave an upper limit of 10^{-3} for the quantum yield of oxalate photoaquation, as determined by proton uptake. Quenching of the three photoaquation reactions of *trans*-Cr(NH$_3$)$_4$(CN)(NCS)$^+$ was studied on 480-nm excitation, and the results for 10 different Cr(C$_2$O$_4$)$_3$$^{3-}$ concentrations are summarized in Table III. While the ionic strength modifies the k_q values, it has no appreciable effect on either the emission lifetimes, τ°, or the photoreaction yields, Φ°.

The linearity of a plot of Φ/Φ° vs. τ/τ°, shown in Figure 4, indicates that photochemistry and emission are quenched in parallel. Moreover, the quantum yields for the three photosubstitution modes are reduced in the same proportion, within experimental uncertainty. Extrapolation to infinite quencher concentration gives the following fractions of unquenchable reaction upon complete phosphorescence quenching: CN$^-$, 24 ± 2%; NCS$^-$, 26 ± 1%; NH$_3$, 25 ± 2%.

Discussion

Quantum Yields: Comparison with Models for Quartet Photoreactivity. The LF absorption bands (Figure 1) of the three complexes examined are assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions, in the O_h approximation and in order of increasing energy. Although the actual complex symmetries are C_{4v}, in no case are such bands (particularly the long-wavelength one) split. The splittings of the $^4T_{2g}$ and $^4T_{1g}$ states into the respective $^4B_2$ + ^4E and ^4E + $^4A_2$ sublevels depend on the difference between axial and equatorial LF strengths[15] and can be evaluated by means of the σ and π parameters of the two-dimensional spectrochemical series.[8,10] For example, eq 1 gives the energy gap between the
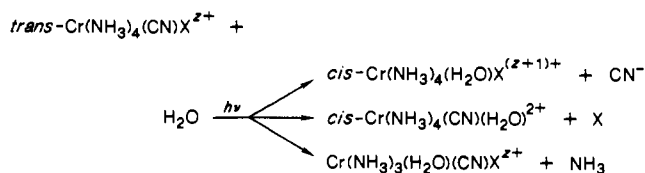
$$E(^4E) - E(^4B_2) = \frac{3}{2}(\bar{\sigma}_{ax} - \bar{\sigma}_{eq}) - 2(\bar{\pi}_{ax} - \bar{\pi}_{eq}) \qquad (1)$$

two components of $^4T_{2g}$. As expected, the balancing of the CN$^-$ and X spectrochemical strengths, respectively higher and lower than that of NH$_3$, results in an average axial field not markedly different from the equatorial one. Thus, the calculated ^4E–$^4B_2$ separations (Table IV) are by far the least among all trans tetraamines thus far dealt with, the usual splittings being larger than 2000 cm^{-1}.[38] While these species are geometrically tetragonal, they can be regarded as electronically quasi-octahedral.

For *trans*-Cr(NH$_3$)$_4$X$_2$$^+$ ions, the ratio between equatorial and axial photoreactivity upon LF excitation varies over a range of 10^4. The available data show that Φ_{eq}/Φ_{ax} tends to increase with increasing (1) spectrochemical position of X, hence, $\Delta E(^4E$–$^4B_2)$, (2) σ-donor strength of X, and (3) $d_{x^2-y^2}$ population in the lowest excited quartet. The most relevant quantities appear to be (1) and (2).[38] The fine tuning of the axial field, made possible by the simultaneous effects of CN$^-$ and X, places the mixed-ligand complexes in the transition region between predominantly axial and predominantly equatorial photoactivation, associated with the lowest excited quartet being either ^4E or $^4B_2$. The photolysis models,[3-10] all related to the antibonding charge distribution of these states, can thus be tested under conditions where $^4B_2/^4E$ discrimination is expected to be small, and the factors subject to testing should be essentially the σ- and π-bonding properties of the ligands.

The observed photochemistry is, in general, congruent with the above picture, as labilization involves all coordinated groups (Scheme I). The cis configuration for the products of axial photolysis is demonstrated for X = H$_2$O and, by analogy, is assumed for X = NCS$^-$ and F$^-$. The quantum yields of Table I do not exhibit significant wavelength dependence, and for X =

Scheme I

trans-Cr(NH$_3$)$_4$(CN)X^{z+} +

H$_2$O $\xrightarrow{h\nu}$

   cis-Cr(NH$_3$)$_4$(H$_2$O)X$^{(z+1)+}$ + CN$^-$
   cis-Cr(NH$_3$)$_4$(CN)(H$_2$O)$^{2+}$ + X
   Cr(NH$_3$)$_3$(H$_2$O)(CN)X^{z+} + NH$_3$

Table V. Excited-State Bond Energies for *trans*-Cr(NH$_3$)$_4$(CN)X^{z+} Complexes, Calculated according to Ref 8–10

X	state	I^*(Cr–CN$^-$), cm^{-1}	I^*(Cr–X), cm^{-1}	I^*(Cr–NH$_3$), cm^{-1}
H$_2$O	^4E	10 920	8 950	11 660
	$^4B_2$	17 550	12 890	8 980
	$^4T_{2g}$	13 130	10 260	10 770
NCS$^-$	^4E	11 100	9 310	11 590
	$^4B_2$	17 550	13 590	8 980
	$^4T_{2g}$	13 250	10 740	10 720
F$^-$	^4E	11 590	15 260	11 380
	$^4B_2$	17 550	18 670	8 980
	$^4T_{2g}$	13 570	16 400	10 580

NCS$^-$ the constancy is verified to extend to the low-energy side of the first LF band. The indication is that the photoreactions proceed from either a unique state or more states essentially in thermal equilibrium.

Postponing the matter of "fast" and "slow" reactivity (vide infra), we first compare the results with the photolabilization theories, with primary reference to the additive angular overlap model,[8-10] regarded as the most quantitative among the available treatments. Table V reports the bond energies for the various ligands, calculated for the ^4E and $^4B_2$ states by use of the σ and π parameters. Also, the $^4T_{2g}$ state is considered, in order to preliminarily check the extent to which a perfectly octahedral behavior is approached. The data for $^4T_{2g}$ are evaluated by eq 2, assuming complete state degeneracy.[9]

$$I^*(^4T_{2g}) = \frac{1}{3}I^*(^4B_2) + \frac{2}{3}I^*(^4E) \qquad (2)$$

It is seen that for the two systems with the smaller state splittings, the $^4T_{2g}$ approximation does predict which ligand is preferentially displaced: H$_2$O for *trans*-Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ and NH$_3$ for *trans*-Cr(NH$_3$)$_4$(CN)F$^+$. Even for *trans*-Cr(NH$_3$)$_4$(CN)(NCS)$^+$, which loses mainly NH$_3$, such an approximation is not far from being fully correct. However, closer comparison of Tables I and V shows that, especially for the cyano aquo and cyano thiocyanato ions, a more adequate interpretation is in terms of predominant reaction of one of the split states.

The photoreactivity of *trans*-Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ is by three-fourths axial, consistent with the dominant d_{z^2} character of ^4E, designated by eq 1 as the lowest excited quartet. The bond strengths predicted for this state are in fair agreement with the observed order of labilization: $\Phi_{H_2O} > \Phi_{CN} > \Phi_{NH_3}$. As a further refinement, the similar CN$^-$ and NH$_3$ quantum yields may be justified by some intervention of the upper $^4B_2$ component, which, unlike ^4E, is more prone to NH$_3$ than to CN$^-$ loss. Thermal equilibrium between ^4E and $^4B_2$ is certainly compatible with a separation of only $0.8RT$.

Opposite to the previous case, ca. two-thirds of the photochemistry of *trans*-Cr(NH$_3$)$_4$(CN)(NCS)$^+$ consists of NH$_3$ aquation, in conformity with the equatorial ($d_{x^2-y^2}$) antibonding distribution of the $^4B_2$ state, that calculations now place slightly below ^4E (by ca. $1.5RT$). Of course, some reaction from ^4E, presumably CN$^-$ and NCS$^-$ release, is quite possible in this case

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(38) See Table III of ref 11.

also. It should be noticed that the model under consideration would predict a stronger bond for CN^- than for NCS^- in both excited states, in contrast with the observation that $\Phi_{CN^-} > \Phi_{NCS^-}$.

The photobehavior of *trans*-$Cr(NH_3)_4(CN)F^+$ is of particular interest, as it is dominated by loss of NH_3, although the antibonding charge is anticipated to be either more dense on the z axis (in the ^4E limiting case) or, at the most, uniformly distributed along the three axes (in the $^4T_{2g}$ approximation). Due to the proximity of the two sublevels (ca. $0.5RT$), the real situation is probably between the 67% d_{z^2} population calculated for the former case[8] and the 50% associated with the latter. It is noteworthy that the findings ($\Phi_{NH_3} > \Phi_{CN^-} > \Phi_{F^-}$) are reproduced by the theory for any of the excited states of Table V. Equatorial labilization, even upon preferential axial activation, is evidently favored by the strong ground-state bonding of both CN^- and F^-, which retains importance in the excited states. This complex is reminiscent of the previously studied *trans*-$Cr(en)_2F_2^+$ and *trans*-$Cr(NH_3)_4F_2^+$ ions;[4,39,40] a difference, however, is that the lowest excited quartet of the last two compounds is definitely ^4E. Judging from the relative magnitude of the quantum yields, here the $^4T_{2g}$ description seems more appropriate and, furthermore, is in line with the $^4E-^4B_2$ spacing being the smallest.

σ and π Effects on Photolabilization. The role of the various types of ligands may be better understood by analyzing their σ and π contributions to the excited-state behavior. Table IV shows that, within the angular overlap framework, all three complexes are characterized by average axial properties such that $\bar{\sigma}_{ax} > \bar{\sigma}_{eq}$ and $\bar{\pi}_{ax} > \bar{\pi}_{eq}$, hence, by the orbital ordering of eq 3. This

$$d_{xy} < d_{xz}, d_{yz} \ll d_{x^2-y^2} < d_{z^2} \qquad (3)$$

sequence is rather uncommon among the trans tetraamines and so far has been encountered only in the difluoro ones.[9] The splitting of the t_{2g} set is relatively large for $X = F^-$ and small for $X = NCS^-$, being proportional to the π-donor ability of X. The gap between the e_g orbitals, reflecting the extent of σ donation from X, is again the greatest for $X = F^-$, while it is minimal for $X = H_2O$. The most familiar condition, determined by any other pair of weak-field axial groups, is $\bar{\sigma}_{ax} < \bar{\sigma}_{eq}$ and $\bar{\pi}_{ax} > \bar{\pi}_{eq}$,[8] whereas the $\bar{\sigma}_{ax} > \bar{\sigma}_{eq}$ and $\bar{\pi}_{ax} < \bar{\pi}_{eq}$ combination is found only in trans dicyano complexes.[11-14] By the way, the ordering of eq 3 does not imply that the lowest excited quartet should correspond to the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ excitation.[9]

trans-$Cr(NH_3)_4(CN)F^+$ is most unusual, in that it presents the least state splitting, despite the largest orbital splittings, owing to mutual compensation of σ and π effects. Thus, differently from authentic octahedral species, where orbital and state degeneracies are interdependent, here the d_{z^2} and $d_{x^2-y^2}$ orbitals need not be degenerate in order to be populated to comparable extents. Another difference from O_h ions is that, even if accidental state degeneracy enables uniform population of d_{z^2} and $d_{x^2-y^2}$, the excitation energy is not equally distributed among the various bonds, as each bond absorbs an amount proportional to the spectrochemical strength ($3\sigma-4\pi$) of the ligand.[8]

Regarding the equatorial photosolvation of the present complexes, as well as that of all other *trans*-CrN_4XY^{z+} ions, the only significant factor responsible for NH_3 labilization is the gain of σ-antibonding character in the equatorial plane, both in $^4B_2$ ($d_{x^2-y^2}$) and in ^4E (ca. $^3/_4$ d_{z^2}, $^1/_4$ $d_{x^2-y^2}$). No π interactions need be considered for ammonia.

More interesting is the axial photoreactivity, as it involves competition between the two heteroligands. Preferential CN^- or X release is substantially related to the $d_{xz}, d_{yz} \rightarrow d_{z^2}$ transition, associated with ^4E. Regardless of the state ordering, of the relative orbital and state population, and of the prevalence of axial or equatorial aquation, only such an excitation can destabilize the σ bonds along the z direction within the $^4B_2/^4E$ context. At the same time, depletion of d_{xz} and d_{yz} weakens the $Cr-CN^-$ π bonds and strengthens the $Cr-X$ ones, because the t_{2g} orbitals are π

bonding for CN^- and π antibonding for X.

In the case of *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ the predominance of $Cr-H_2O$ over $Cr-CN^-$ bond cleavage is not unexpected. Even though the latter bond absorbs more excitation energy and loses π stabilization, the strong ground-state σ bonding of cyanide continues to be a decisive factor in the excited state.

On the basis of similar literature parameters for H_2O and NCS^-,[10] one would expect analogous conclusions for *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ (see Table V). As discussed above, the predictions are in disagreement with the observed order of labilization ($CN^- > NCS^-$), and no simple explanation can be offered, unless different σ and π values are employed for NCS^-.

Finally, *trans*-$Cr(NH_3)_4(CN)F^+$ allows direct comparison between the two monodentate ligands with the top bonding strengths. No information in this regard could be previously obtained from the individual trans dicyano[11] and trans difluoro[40] complexes, as both largely, or exclusively, undergo NH_3 aquation, moreover, from different photoactive states ($^4B_2$ and ^4E, respectively). The observed preference for CN^- loss clearly arises from π interactions. Although the σ bond in the ground state is stronger for CN^- than for F^-, fluoride acquires a great amount of excited-state π stabilization, while cyanide is π destabilized.

Comparative application of previous σ/π qualitative models[5,6] to axial reactivity leads to prediction of a larger degree of labilization for CN^- than for X in all three cases. The wrong prediction for $X = H_2O$ is essentially due to the fact that, while these models are still based on the general excited-state σ weakening, combined with the π-donor stabilization and π-acceptor destabilization, they do not take into account differences in the ground-state energies, which are large when the $Cr-CN^-$ and $Cr-H_2O$ bonds are compared.

For completeness, some comparison is made with the early rules by Adamson.[3] The first rule (the weakest field axis is mainly labilized) is obeyed by the aquo and thiocyanato complexes but not by the fluoro complex. The reason is that the formally weaker field axis of the latter contains two strongly bound ligands, and bonding aspects are not considered by the rules. The second rule, applied to axial competition (the strong-field ligand preferentially aquates), holds for $X = NCS^-$ and $X = F^-$. Its inadequacy in the $X = H_2O$ case is again explained by the bonding differences between water and cyanide. Interestingly, for *trans*-$Cr(NH_3)_4$-$(CN)F^+$ the same factors that cause the first rule to fail make the second rule work, as the ligand field discrimination can emerge owing to the similar bonding strengths of CN^- and F^-.

Quenchable vs. Unquenchable Photochemistry. Among the three *trans*-$Cr(NH_3)_4(CN)X^{z+}$ ions investigated, the $X = NCS^-$ one appeared the most suitable for an accurate quenching study, thanks to its unusually long-lived emission. To our knowledge, this represents the first chromium(III) system in which *three* significant photosubstitution reactions are coupled with a relatively slow doublet decay under photolytic conditions. The quenching experiments were also prompted by the above-discussed discrepancy between the Φ_{NCS^-} results and the predictions of the Vanquickenborne–Ceulemans theory. A possibility to be checked was that some specific doublet chemistry was superimposing on quartet reactivity, on which the model is solely based.

The mechanism of quenching by $Cr(C_2O_4)_3^{3-}$ is very likely one of energy transfer. Although tris(oxalato)chromate(III) does not emit in room-temperature solution, its lowest doublet, seen in absorption at 698 nm,[41] lies energetically close to the emitting states of the cyano ammines (Table II). Also, the quenching rate constants are of the order observed for other donor–acceptor complex pairs participating in collisional processes.[42] The above make improbable "noninnocent" or reactive quenching, as that sometime induced by the OH^- ion,[43,44] which may introduce am-

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(40) Kirk, A. D.; Frederick, L. A. *Inorg. Chem.* **1981**, *20*, 60.

(41) Adamson, A. W. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1955.

(42) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F. *Coord. Chem. Rev.* **1975**, *15*, 321.

(43) Sandrini, D.; Gandolfi, M. T.; Juris, A.; Balzani, V. *J. Am. Chem. Soc.* **1977**, *99*, 4325.

(44) Frink, M. E.; Magde, D.; Sexton, D.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 1238.

biguity.

Our results may be thus summarized: (1) on complete quenching of the lowest doublet state(s), one-fourth of the photoreactivity remains unquenched; (2) there is no detectable difference in the Φ_{CN^-}:Φ_{NCS^-}:Φ_{NH_3} proportion (4:1:13) between the quenchable and the unquenchable photochemistry. The discussion refers to a conventional d^3 excited-state scheme, as that of ref 45, where Q_1^0 and D_1^0 are the general notations for the lowest thermally equilibrated excited quartet and doublet state(s), respectively.

The unquenchable part of each reaction mode pertains to complex molecules that never pass through D_1^0. Partial unquenchability is well-known for chromium(III),[1,2] and there is agreement in assigning these reaction components to the short-lived Q_1^0 state, formed in competition with prompt intersystem crossing to D_1^0, during vibrational relaxation of the Franck–Condon Q_1 state.

The quenchable portions are then assigned to excited molecules traversing the longer-lived D_1^0 state. By optical[45,46] and conductivity[47] monitoring of products, it was demonstrated that the unquenchable photochemistry is "fast", or in the subnanosecond range, whereas the quenchable one is "slow", its rate being indeed equal to that of D_1^0 disappearance. For the latter, three possibilities are currently at issue: (1) direct D_1^0 reaction;[45,48–50] (2) back intersystem crossing, followed by Q_1^0 reaction;[51–53] (3) crossing from D_1^0 to a reactive ground-state intermediate.[54]

All three pathways are expected to be activated. As discussed earlier[35] for both associative and dissociative D_1^0 reaction, either polarization of the uniform orbital population of the doublet by an entering group or dissociation of a ligand should require some activation. Back intersystem crossing obviously involves an energy barrier related (not equal) to the Q_1^0–D_1^0 separation and to possible changes in geometry, as well as solvent reorganization accompanying such changes. Also the vibrationally promoted surface crossing to a ground-state intermediate (which may either react or relax) is envisaged as a temperature-activated process.[54]

The temperature dependence observed for the decay of D_1^0 (ca. 9 kcal mol^{-1}) is certainly compatible with each of the above possibilities. The quenching results instead argue in favor of pathway 2. Labilization of three different ligands in the same proportion for both the unquenchable and quenchable contributions indicates a single source for all photochemistry, which must then be Q_1^0. It is highly improbable that two states such as Q_1^0 and D_1^0, of different electronic configurations ($t_{2g}^2e_g$ and t_{2g}^3), and conceivably different equilibrium structures, be characterized by identical chemical behavior, although numerous reactive combinations are available in principle. Analogous considerations apply to comparison between Q_1^0 and a possible ground-state intermediate originating from D_1^0 and branching into various substitutional channels, plus vibrational relaxation.[54] This conclusion is in line with the fact that the photoreactivity is entirely explainable by the models based on the antibonding properties of the quartet states.

A more restrictive interpretation of the data would merely point to a single reactive entity, which, in theory, may be either an excited state or a ground-state intermediate (gsi). For the latter occurrence, one need only assume that both the fast and slow

stages eventually proceed through the same gsi. However, the congruence of the labilization pattern with the $^4E/^4B_2$ electron distribution suggests that such a gsi should, at least in part, retain some features (e.g., distortions and bond elongations) of the excited quartets. In this picture, the respective routes to the gsi would be $Q_1 \rightarrow Q_1^0 \rightarrow$ gsi and $Q_1 \rightarrow D_1^0 \rightarrow Q_1^0 \rightarrow$ gsi (rather than $Q_1 \rightarrow D_1^0 \rightarrow$ gsi for the latter) and the conclusions about D_1^0 deactivation would not be modified.

Equal product ratios for fast and doublet-mediated photochemistry have already been observed and taken as evidence for back intersystem crossing, in systems that either undergo two reactions, such as en/NCS$^-$ aquation of *trans*-Cr(en)$_2$(NCS)$_2^+$[55] and aquation/anation of Cr(NH$_3$)$_6^{3+}$,[56] or give rise to isomeric mixtures, such as Λ-Cr(en)$_3^{3+}$[53] and Cr(NH$_3$)$_5$(CN)$^{2+}$.[35] There is, however, a remote chance that the constancy of ratios of two photosubstitutions arising from two different transition states be fortuitous or that a constant isomeric proportion be the consequence of chemical events subsequent to the photochemical ones. This chance should tend to zero when the constancy of ratios is verified for the cleavage of three different metal–ligand bonds.

It should be kept in mind that in the present complexes, as in the ones mentioned above, the sublevels of $^4T_{2g}$ are either degenerate or close enough in energy to allow establishment of thermal equilibrium between them: therefore, they would be populated in the same proportion by either relaxation from upper Franck–Condon states or back intersystem crossing. The wavelength independence of the product ratios is consistent with this picture. The same interpretation accommodates the different patterns for the unquenchable and quenchable contributions, as well as the wavelength dependence of the mode ratio, when the $^4B_2$–^4E separation is larger, as in *trans*-Cr(en)$_2$(NCS)F$^+$.[57] In such cases, partitioning between the two states upon direct Q_1 relaxation may be different from that following back intersystem crossing.

Returning to the unquenchable component, an alternative proposal is prompt reaction during relaxation to Q_1^0, as described by the DOSENCO model.[58] Evidence for such a mechanism is sought in the wavelength dependence of quantum yields along the envelope of the lowest-energy LF band. Although the total Φ values do not appear to change significantly on passing from the maximum to the tail of such a band, small variations in the unquenchable fractions (representing only one-fourth of the overall photochemistry) may well go undetected within our limits of accuracy, so that little can be concluded about this possible reactive route. A related point is that, in the DOSENCO hypothesis, the equality of ratios for the fast and slow reaction stages would require that the Q_1 state be initially populated by back intersystem crossing in the same range of vibrational levels from which prompt reaction is thought to take place.

Conclusions. (1) Quartet reactivity, whether fast or delayed, appears to be dominant in these tetraammines, which prove particularly diagnostic toward the various photolysis theories. Our results further confirm the superiority of the additive angular overlap approach[8,9] over the previous models. This model not only predicts which ligand is preferentially lost in all cases but, for two complexes, also anticipates the order of leaving ability of the other groups. A literature survey shows that the theory in question accounts for the relative importance of three photosubstitution modes in several other *trans*-CrN$_4$XY^{2+} ions, reacting mainly from ^4E, and having the following X and Y groups, respectively: NCS$^-$, Cl$^-$;[26,59] H$_2$O, NCS$^-$;[26] F$^-$, Cl$^-$;[60] NCS$^-$, F$^-$;[61] DMF, Cl$^-$.[32] Another minor exception is the H$_2$O, Cl$^-$ term (predicted, NH$_3$ < Cl$^-$ <

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H$_2$O; found, Cl$^-$ < NH$_3$ < H$_2$O).[26]

(2) If the average axial and equatorial parameters (that is, the average bonding strengths) are not very different, as for X = H$_2$O and NCS$^-$, even small state splittings appear sufficient to favor either $^4B_2$ or ^4E reaction. It should be noticed, however, that especially when small separations are involved, the spectral differences may not properly reflect the differences between the states from which chemistry proceeds, because of presumably different distortions from octahedral geometry during vibrational equilibration.

(3) The combined ratios of axial quantum yields establish the following propensity to photolabilization: F$^-$ < NCS$^-$ < CN$^-$ < H$_2$O, suggesting a stronger Cr–NCS$^-$ bonding than inferred spectroscopically. As was originally pointed out,[8] some of the σ and π values may bear uncertainties, which could become crucial at the present level of detail. Especially for thiocyanato complexes, the obtainment of correct parameters may be hampered by the lack of splitting (or asymmetry) in the LF bands,[21,23,33,34,62] due to the close spectrochemical positions of NCS$^-$ and amines. In addition, a charge-transfer band partially obscures one of the LF maxima[33] (see Figure 1). Separation of σ from π contributions in eq 1 and in analogous relations by help of Gaussian analysis of the spectra may be sometimes too approximate. Values of σ_{NCS^-} and π_{NCS^-} somewhat higher than in ref 10, but such that $10Dq_{NCS^-}$ remains unaffected, would justify $\Phi_{CN^-} > \Phi_{NCS^-}$. Also, the latter parameter has been recently reported[63] to be 370 cm^{-1} larger than

that in the literature.[10] Our general preparative experience with thiocyanate[17] and literature aquation and anation data[23,33,64,65] indicate that NCS$^-$ is a very good nucleophile (comparable to F$^-$) toward chromium(III). Photochemistry may thus be helpful in assessing more correct parameter values.

(4) The constancy of product ratios for the prompt and slow photochemistry suggests a unique reactive precursor. In a conventional description, this can be accounted for by back intersystem crossing as the main pathway of doublet deactivation. An equivalent, but perhaps more adequate, interpretation is that in terms of a single potential surface, with intercommunicating minima of quartet and doublet character, resulting from spin–orbit coupling under reduced symmetry.[43,66] The transition state for reaction should then either correspond to the quartet minimum or at least retain some memory of its antibonding distribution.

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Dihydrogen vs. Dihydride. Correlations between Electrochemical or UV PES Data and Force Constants for Carbonyl or Dinitrogen Ligands in Octahedral, d^6 Complexes and Their Use in Explaining the Behavior of the Dihydrogen Ligand

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For d^6, octahedral carbonyl complexes there is a linear correlation between $E_{1/2}$(ox) values for reversible d^5 ↔ d^6 couples at room temperature and carbonyl force constants k(CO) for values reported in the literature and measured here: $E_{1/2}$(ox) = 0.567(k(CO) + Δk_L) − 8.02. The correlation coefficient, r, is 0.97, and σ = 0.17 V when the force constant is corrected for the effect of the ligand trans to the CO by the ligand parameter Δk_L. The first ionization energies, IP, of such complexes as determined by UV PES show a poorer correlation: IP = 0.873(k(CO) + Δk_L) − 6.34, r = 0.92, σ = 0.28 eV. The correlation $E_{1/2}$(ox) = 0.688 IP − 4.22, r = 0.94, is obtained from data for 12 complexes where both $E_{1/2}$(ox) and IP values have been measured; this equation is close enough to the one derived from combining the first two equations to verify the internal consistency of the correlations. Octahedral, d^6 dinitrogen complexes also show a fair correlation: $E_{1/2}$(cor) = 0.434(k(N$_2$) + 2Δk_L) − 7.74, where $E_{1/2}$(cor) = $E_{1/2}$(ox) for 4d metals and $E_{1/2}$(cor) = $E_{1/2}$(ox) − 0.26 for 5d metals, σ = 0.18 V, and r = 0.91. Here the trans ligand appears to have twice the effect on k(N$_2$) as on k(CO) and equivalent complexes of 5d metals have lower k(N$_2$) values than those of 4d metals with the same $E_{1/2}$(ox) value. The Δk_L parameters can be related to both Timney's and Bursten's parameters. The correlations can be used to estimate the $E_{1/2}$(ox) (or IP) values of matrix-isolated species like Cr(N$_2$)(CO)$_5$. They can also be used to postulate that stable molecular hydrogen complexes, M(η^2-H$_2$)L$_5$, where all L groups are not usually the same in the complex, are obtained for complexes that have η^2-H$_2$ trans to CO and that form derivatives M(N$_2$)L$_5$ or M(CO)L$_5$ with $E_{1/2}$(ox) ≈ 0.0 V or for those that have η^2-H$_2$ trans to a good σ-donor like H$^-$ and that have $E_{1/2}$(ox) ≈ 1.0 V for dinitrogen or carbonyl derivatives. This translates into a range, ν(N$_2$) = 2060–2150 cm^{-1}, for the dinitrogen derivatives where the corresponding H$_2$ complex will be stable to homolytic cleavage or irreversible H$_2$ loss at 25 °C.

A well-known phenomenon of transition-metal carbonyl coordination chemistry is that as complexes become more reducing because of a change of ligand or a reduction in the oxidation state of the metal, then the C–O stretching frequencies of carbonyl ligands in the complexes decrease. The same trend is observed for other ligands like thiocarbonyl, dinitrogen, isocyanides, and nitrosyl, whose bonding involves dπ(metal) → pπ*(ligand) back-donation. Thus, infrared and Raman spectroscopy are useful tools for indirectly probing the energetics of metal complexes. We present here useful equations that are determined for octahedral carbonyl or dinitrogen complexes with the metal in the d^6 oxidation

state that roughly express these trends. The equations are best linear fits to an extensive set of force constant, electrochemical, and photoelectron data. They are applied here to understand the bonding and reactivity of related molecular hydrogen complexes, which are of current interest.[1–14]

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