density toward the carbonyl π^* orbitals as a major stabilizing factor,[27] for inductive effects should make NCS^- a stronger π-donor than the very tightly held NCO^-.

Only equilibria containing the fluoro ligand are highly sensitive to the presence of water or other polar molecules. Values of $K_{X/F}$ (X = Cl, Br, I) obtained carefully in benchtop experiments were higher by factors of 3–5 than those measured under rigorously anhydrous (glovebox) conditions.[5a] Addition of methanol (ca. 200-fold molar excess relative to Rh) to the 1/1 $Rh(PPh_3)_2(CO)NCO/(PPN)Cl$ mixture afforded a weak new carbonyl band at 2026 cm^{-1} (where a band was observed upon treating $RhL_2(CO)OClO_3$ in CH_2Cl_2 with 500-fold excess of methanol, characteristic of $RhL_2(CO)S^+$ species[28]); however, only the slightest decrease in absorbance of the coordinated isocyanate C–N stretching band was noted, and the shape and wavenumber maximum of the carbonyl band of the original mixture remained essentially unchanged. Similar results were noted for the 1/1 $Rh(PPh_3)_2(CO)O_2CMe/(PPN)Cl$ and $Rh(PPh_3)_2(CO)O_2CPh/(PPN)Cl$ mixtures. All experiments other than those containing the fluoro ligand afforded no differences within experimental error for those values of $K_{Z/Y}$ determined anhydrously and those determined aerobically.

Studies by Songstad and co-workers[16] have shown that PPN^+ salts are strongly associated in CH_2Cl_2 as ion pairs, with association constants of 1.5 (±0.3) × 10^3 independent of anion nature. Their results suggest little thermodynamic preference in formation of PPN^+Y^- relative to PPN^+Z^-; if so, then our $K_{Z/Y}$ values (where we were able to measure them using our limited range of $[(PPN)Z]_0/[RhY]_0$ ratios) and limits may be taken as estimates of relative stabilities of RhZ and RhY in solution.

Solution mixtures of $Rh(PCy_3)_2(CO)Cl$ and $Rh(PCy_3)_2(CO)Y$ for Y = NCS, NCSe, and O_2CMe afforded IR spectra from 2300 to 1900 cm^{-1} inconsistent with the presence of only the two Rh(I) Vaska species. Pertinent spectra for the Y = NCS case are displayed in Figure 2; a very similar pattern was observed for the Y = NCSe case. In the former set of spectra, the intensities of the anionic ligand C–N stretching band were observed to be much lower than expected for simply (unchanged) more dilute Rh–NCS, and the carbonyl band patterns were strongly dependent upon the [Rh–NCS]/[Rh–Cl] ratio. For Y = O_2CMe, a similar terminal carbonyl band pattern shift was noted. A possible rationalization for such a phenomenon is ligand bridge formation;[29] that it occurs for the very bulky PCy_3 complexes but not the somewhat less hindered PPh_3 and $AsPh_3$ analogues suggests loss of one or more ligands before bridge formation occurs. $[Rh(CO)_2Cl]_2$ reacts with 2 equiv of the very bulky ligand $P(Bu^t)_3$ followed by metathesis of a bridging chloride with an organothiolate ligand to form the mixed-bridge dimer *cis*-$RhL(CO)(\mu\text{-}SR)(\mu\text{-}Cl)RhL(CO)$.[30] Work is in progress to further define the nature of interaction between the respective Vaska species. No such interactions (i.e., no deviations from Beer's law behavior noted) were seen for Y = NCO, O_2CPh, ONO_2, OTf, and F. As for the analogous PPh_3 and $AsPh_3$ systems, the infrared spectra of the $Rh(PCy_3)_2(CO)NCO/(PPN)Cl$ mixtures showed no measurable quantities of $Rh(PCy_3)_2(CO)Cl$.

Our results show a very wide range of anion affinities for the $RhL_2(CO)^+$ species; particularly striking is preference of the rhodium(I) carbonyl cations for the isocyanate anion. We are currently studying the generality of such bonding patterns in low-valent transition-metal complexes, especially to learn whether the marked preference for the isocyanate anion is general or limited to cases in which the anionic ligand is trans to CO or other strongly π-back-bonding ligands. We are also expanding our technique to include UV–visible spectroscopy to be able to measure equilibrium constants for some Z/Y pairs whose IR spectra do not present sufficient resolution of respective analytical bands.[31]

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., and the University of South Alabama Research Committee. We also thank Prof. Russ Drago of the University of Florida for helpful discussions.

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Photochemistry of Aqueous *trans*-Cyanochlorotetraamminechromium(III). Evidence for an Excited-State Trans Effect

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The *trans*-$Cr(NH_3)_4(CN)Cl^+$ complex has been prepared and photolyzed in acidic aqueous solution (10^{-3} M $HClO_4$). Ligand-field (LF) irradiation causes release of CN^- ($\Phi = 0.31$) and NH_3 ($\Phi = 0.09$), with essentially wavelength-independent quantum yields. The main photoreaction, CN^- aquation, and its stereochemistry (>90% cis product) contrast with stereoretentive loss of Cl^- in the ground state. The photobehavior is in disagreement with the LF additive angular overlap model, predicting preferential photolabilization of Cl^-. The proposed explanation is a kind of excited-state trans effect, arising from mutual interaction of CN^- and Cl^-, respectively π-acceptor and π-donor ligands. Charge-transfer (CT) excitation leads to photoaquation of CN^- ($\Phi = 0.14$), Cl^- ($\Phi = 0.06$), and NH_3 ($\Phi = 0.16$). The results suggest a photoactive CT($Cl \rightarrow Cr$) state and a photoinert CT($Cr \rightarrow CN$) one. Comparison between the LF and CT photochemistries allows evaluation of the intrinsic CT reactivity ($\Phi \sim 0.2$) and of the efficiency ($\eta \sim 0.4$) of conversion of CT to LF states. The latter is confirmed by the relative phosphorescence yields as a function of the excitation wavelength.

Introduction

By now, some 20 *trans*-$Cr(NH_3)_4XY^{z+}$ and *trans*-$Cr(en)_2XY^{z+}$ ions have been studied photochemically,[1-4] playing a major role in the development and testing of the models for the preferential photosolvation[4-9] and the photostereochemistry[10] of chromium(III).

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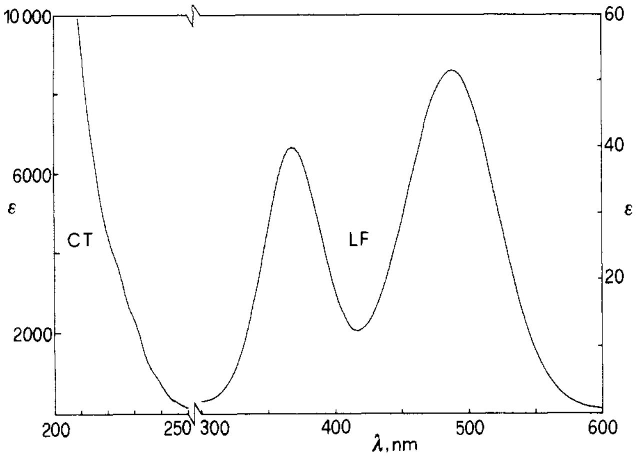

Figure 1. Ligand-field (right scale) and charge-transfer (left scale) absorption spectrum of *trans*-$Cr(NH_3)_4(CN)Cl^+$ in 1 × 10^{-3} M $HClO_4$ solution.

Of the *trans*-tetraammines, those with X and/or Y = CN^- have drawn our attention because of several interesting features. (i) Unlike all other X and Y acido groups, cyanide has a higher field strength than equatorial amines, which determines atypical excited-state sequences[11] and, hence, atypical photolabilization patterns. (ii) CN^- is a π acceptor, in contrast with the π-donor character of the common monodentate ligands. Metal-to-ligand (rather than the usual ligand-to-metal) charge-transfer transitions are then possible. (iii) Phosphorescence is usually emitted by these complexes in room-temperature solution.[12]

Thus, the photolysis of *trans*-$Cr(NH_3)_4(CN)_2^+$ has yielded stereochemical information on the photoaquation of the in-plane NH_3 ligands,[13] which, for most of the other systems, represents only a minor photoreaction mode.[1-4] Also, a recent investigation of the *trans*-$Cr(NH_3)_4(CN)X^{z+}$ ions with X = H_2O, NCS^-, and F^-,[14] has proven particularly diagnostic toward the current photolysis theories,[4-9] in terms of σ and π contributions to labilization in the excited states.

As an extension of the above studies, we have examined the ligand-field (LF) and charge-transfer (CT) photochemistry in acidic aqueous solution of the *trans*-$Cr(NH_3)_4(CN)Cl^+$ ion, newly obtained in this laboratory.[15] This complex affords one more opportunity for model testing when three concurrent photosubstitutions are possible and an uncommon ligand combination is involved. The electronic and σ/π-bonding differences between the two axial groups are here the largest among the available species of this type, and interestingly, the LF photobehavior does not conform to the predictions of the Vanquickenborne–Ceulemans angular overlap model,[4,9] presently regarded as the most reliable approach. An explanation for the disagreement can be indeed found in the contrasting properties of CN^- and Cl^-.

Experimental Section

Materials. *trans*-Cyanochlorotetraamminechromium(III) Perchlorate. A suspension of *trans*-$[Cr(NH_3)_4(Me_2SO)Cl](ClO_4)_2$[16] (1.6 g) and NaCN (2.2 g) in methanol (25 mL) was stirred for 4 h 30 min at 45 °C. After ice-cooling, the orange-red cyanide salt of the product was separated by centrifugation, repeatedly washed with methanol, and vacuum-dried. The perchlorate salt was obtained by reprecipitation from aqueous solution with 10 M $NaClO_4$, washed with ethanol and then with ether, and dried. Further recrystallization was accomplished in the same manner. Yield: 10–15%. The LF absorption spectrum in acidic aqueous solution (10^{-3} M $HClO_4$) presents maxima at 488 nm (ϵ 51.5 M^{-1} cm^{-1}) and 368 nm (ϵ 40.0 M^{-1} cm^{-1}), as illustrated in Figure 1. A detailed description of the preparation, characterization, and solution behavior of this complex is given elsewhere.[15] The trans configuration is unambiguously proven by the known spectral features of the stepwise aquation products: exclusively *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ and then *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$.[15]

$[Co(NH_3)_5F](NO_3)_2$ was prepared by a standard procedure[17] and converted to the perchlorate salt by reprecipitation from water.

Analyses. Chromium was determined spectrophotometrically at 374 nm (ϵ 4760 M^{-1} cm^{-1}), following oxidation to chromate by boiling alkaline hydrogen peroxide.

Free CN^- ion was measured potentiometrically by an Amel 201-CN electrode and a Radiometer PHM 84 potentiometer. Likewise, photoreleased NH_3 was analyzed by an Orion 95-12 ammonia-sensing electrode. In both cases the sample pH was brought to ca. 12 and the ionic strength was adjusted to 0.10 M by the addition of NaOH and $NaClO_4$. Calibration was performed during each run, using a series of fresh KCN or NH_3 (NH_4Cl + NaOH) standards. At the above pH both the reactant and the product complexes were found to undergo some decomposition, slowly liberating CN^- and NH_3. In order to minimize this interference, each type of measurement was done on an individual aliquot, just after alkalinization. It was verified that over a period of 5 min, possible extra amounts of CN^- and NH_3 thermally released in basic medium, were unappreciable within the analytical reproducibility of ±3% for both ligands.

Co^{2+} ion was determined spectrophotometrically at 625 nm (ϵ 1650 M^{-1} cm^{-1}), after addition of the thiocyanate–acetone reagent.[18]

Uncoordinated Cl^- was analyzed either potentiometrically by an Amel 201-Cl electrode or spectrophotometrically by the mercuric thiocyanate method.[19] In the latter case, to a 2.5-mL sample were added 0.2 mL of a saturated solution of $Hg(SCN)_2$ in ethanol and then 0.3 mL of aqueous 0.8 M $Fe(NO_3)_3$ in 4 M $HClO_4$. The NCS^- ion displaced by Cl^- was determined at 450 nm as the iron(III) complex. Standardization curves were obtained by use of KCl. Separation of free Cl^- from reaction mixtures was necessary for the following reasons. (a) Under our conditions, the rates of thermal Cl^- aquation of the reactant and the photoproducts are nonnegligible; (b) CN^- aquation is enhanced by the high acidity of the reagent; (c) Hg^{2+} catalyzes the release of both Cl^- and CN^-. Solutions were eluted by 10^{-3} M $HClO_4$ through a 15 × 7 mm column of Sephadex SP C-25 cation exchanger. All complexes, as well as NH_4^+, were retained, while Cl^- and HCN were displaced. The latter was then eliminated by elution with 10^{-3} M $HClO_4$ through a 15 × 7 mm column of Sephadex QAE A-25 anionic resin. Successive treatment with 0.2 M $NaClO_4$ in 10^{-3} M $HClO_4$ led to recovery of Cl^-. The cationic column was ice-cooled, so as to slow down any thermal reaction. The precision allowed by the complexity of this procedure was ±10%.

The above cationic column, again kept at 0 °C, was employed for photoproduct isolation. The eluent was 0.02 M $NaClO_4$ for the 1+ charged complexes and 0.2 M $NaClO_4$ for the 2+ ones, both at pH 3.

Equipment and Procedures. Luminescence spectra were measured by use of a Perkin-Elmer 650-10S spectrofluorometer. Relative phosphorescence quantum yields were determined by comparing the intensities, I_λ, emitted by a given sample upon excitation at different wavelengths. These were chosen so that the optical densities and, hence, the correction factors for fractional light absorption were similar. Since the excitation bands were 10 nm wide, the overall transmittance was determined by integration of the spectral distribution of the exciting source and the absorption curve of the complex, as previously reported.[20] The ratios of incident intensities were measured both by actinometry[21,22] and by use of Rhodamine B as a quantum counter,[23] with a better than 95% agreement. The uncertainties were ±6% for I_{370}/I_{490} and ±17% for I_{255}/I_{490}. The large value of the latter stems essentially from the difficulty in evaluating the transmittance in the 250–260-nm interval, due to the

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Table I. Photoaquation Quantum Yields of *trans*-$Cr(NH_3)_4(CN)Cl^+$ in 1×10^{-3} M $HClO_4$ at 10 °C

λ_{irr}, nm[a]	transition	Φ_{CN^-}[d]	Φ_{Cl^-}[d]	Φ_{NH_3}[d]
540	$^4B_1 \rightarrow {}^4E, {}^4B_2({}^4T_{2g})$[b]	0.319 ± 0.010 (2)	<0.02 (2)	0.080 ± 0.016 (3)
490	$^4B_1 \rightarrow {}^4E, {}^4B_2({}^4T_{2g})$[b]	0.310 ± 0.017 (8)	<0.02 (4)	0.087 ± 0.013 (7)
365	$^4B_1 \rightarrow {}^4A_2, {}^4E({}^4T_{1g})$[b]	0.314 ± 0.016 (6)	<0.02 (3)	0.085 ± 0.009 (6)
245	$\pi(Cl) \rightarrow e_g^*(Cr)$[c] $t_{2g}(Cr) \rightarrow \pi^*(CN)$[c]	0.138 ± 0.007 (4)	0.06 ± 0.01 (4)	0.159 ± 0.014 (3)

[a] Irradiation bands of 14-nm half-width. [b] O_h parent states. [c] O_h approximation. [d] Numbers of independent experiments in parentheses.

steep profile of the CT band. Phosphorescence lifetimes were obtained by the apparatus described previously.[14]

Optical densities were read by means of a Beckman DU spectrophotometer, while absorption spectra were recorded by a Cary 17 instrument. Fitting of absorption spectra by those of known species was performed by a computerized least-squares minimization method, as reported earlier.[14] The results were validated by comparison of the chromium concentration given by the fitting with that chemically determined. All solutions to be used for either absorption or emission spectral measurements were filtered through 0.45-μm Millipore cellulose filters.

The irradiation setup was that already described,[24] equipped with a thermopile periodically calibrated vs. the Reineckate[21] and ferrioxalate[22] actinometers. Incident intensities were between 10^{-9} and 10^{-8} einstein s^{-1}. For quantum yield determination, solutions were (4–5) × 10^{-3} M in complex and 1×10^{-3} M in $HClO_4$ and were photolyzed in either 1.0- or 3.0-cm cells, maintained at 10.0 ± 0.5 °C, and stirred. All samples were Millipore-filtered as above. In the LF photolyses, solutions were partially transmitting, and the absorbed energy was evaluated by a reported procedure.[20] Irradiation times were 15–30 min, and total conversion never exceeded 10%. In order to obtain amounts of the main photoproduct suitable for isomeric identification, 8×10^{-3} M samples at pH 3 were photodecomposed to about 25%. A 500-W xenon lamp was employed, in combination with broad band-pass filters, enabling absorption by the whole LF region. Parallel formation of thermal products was thus restrained by reducing the irradiation time to 4 min and, especially, by keeping the temperature at 0 °C. For the same reason, it was important to handle all solutions and glassware at 0–5 °C before and after photolysis. All analyses were performed in parallel on identical irradiated and dark aliquots, so that any thermal reaction was always taken into account.

Results

In moderately acidic solution and in the dark, *trans*-$Cr(NH_3)_4(CN)Cl^+$ undergoes efficient chloride aquation, with full stereoretention.[15] The latter is substantiated by the known LF spectrum of the only product, *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$,[25] and conforms to the usual behavior of chromium(III) complexes in aqueous media.[26,27] The rate of Cl^- loss is acid-independent between pH 2.5 and 4.0. At low pH values (<ca. 2) CN^- is also released through an H_3O^+-assisted pathway. While a kinetic account of these competitive reactions will be reported separately,[15] the thermal reactivity was preliminarily explored, since it was expected to impose some limitation on the photochemical studies. Photolyses were carried out in 1×10^{-3} M $HClO_4$ at 10 °C, so as to reasonably contain thermal aquation: under these conditions, the pseudo-first-order rate constant for Cl^- release is $k_{obsd} = 2.7 \times 10^{-5}$ s^{-1}.

Irradiation of the LF bands causes a red displacement of the visible absorption maxima. Difference spectra with dark solutions exhibit isosbestic points at 506, 425, and 376 nm, which indicate constant product ratios. Free ligand analysis reveals parallel photoproduction of cyanide and ammonia. Up to 10% conversion, this follows zero-order kinetics, as do the spectral changes. Within experimental precision, no differences are observable between the concentrations of uncoordinated Cl^- of dark and photolyzed samples. The spectral shift is consistent with the higher field CN^- and NH_3 ligands being replaced by the spectrochemically weaker H_2O molecule.

The quantum yields for photoaquation of the three ligands at various excitation wavelengths are reported in Table I. Each entry is the average of two to eight independent experiments. More restrictive upper limits for Φ_{Cl^-} could not be established because of the thermal lability of chloride and the elaborate analytical procedure.

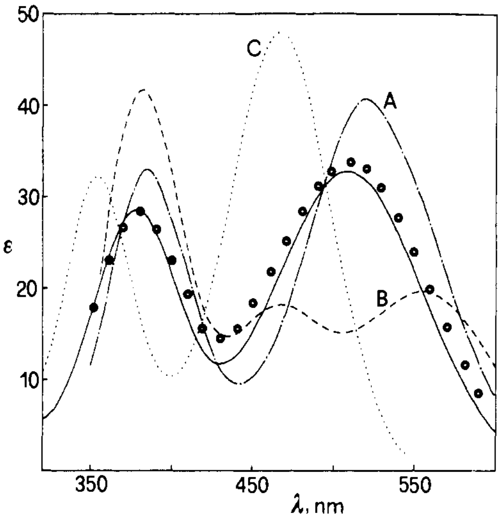

Figure 2. Ligand-field absorption spectra of chromium(III) aquo tetraammine complexes in acidic aqueous solution: –·–, *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ (A); ---, *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ (B); ···, *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ (C); —, mixture of the products of CN^- photoaquation and Cl^- thermal aquation. Circles: best fit corresponding to 77% A, 0% B, 23% C.

The principal photoproduct, arising from CN^- release, was isolated by ion-exchange chromatography. The dipositive charge of $Cr(NH_3)_4(H_2O)Cl^{2+}$ allowed its separation from the reactant, as well as from the NH_3 photoaquation product, both monopositive. Despite the precautions adopted for holding back the thermal reaction (within 4–5% of total decomposition), the presence of *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ (20–25%) in the fraction containing the 2+ species was unavoidable. The LF spectra of these eluates were made quantitative by chromium analysis and fitted by linear combinations of the absorption curves for *cis*- and *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ [24] and *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$,[25] as illustrated in Figure 2. The photoproduct appeared to consist largely (>90%), if not solely, of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. The marked spectral differences between the two aquochloro isomers[24,28] warrant confidence in such a three-component fit.

The complex was also irradiated in the CT band, which is quite distinct from the LF ones, as evident in Figure 1. In addition to NH_3 and CN^-, Cl^- was also photoreleased in this case, with relatively small, but definite, yields. The results are included in Table I.

Some 245-nm photolyses were carried out with oxygen-free (argon-saturated) solutions in the presence of $Co(NH_3)_5F^{2+}$ as a potential scavenger for Cr^{2+}.[29] Cobaltous ion was actually observed. However, since at this wavelength the cobalt(III) complex itself undergoes photoredox decomposition ($\Phi_{Co^{2+}} = 0.17$), the unfavorable conditions of mixed light absorption obscured beyond error limits possible small Co^{2+} yields due to Cr^{2+} sca-

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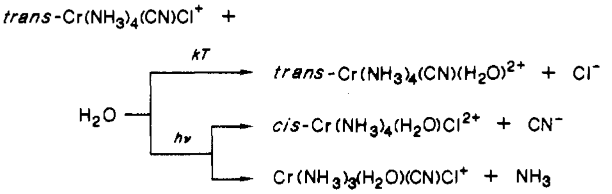
venging, expectedly in the 10^{-2}–10^{-3} M range, as found in similar situations.[30,31]

Under photolysis conditions, *trans*-$Cr(NH_3)_4(CN)Cl^+$ luminesces moderately in the 660–730-nm region, with a maximum at 697 nm. The emission is assigned to phosphorescence from the $^2A_1/^2B_1$ lowest doublet state(s), as is that of other chromium(III) cyano ammines.[12,14,32] The luminescence decay of fresh solutions is monoexponential, with a lifetime of 0.31 ± 0.02 μs at 20 °C. When the samples are allowed to stand, a biphasic decay develops, the slow component corresponding to the lifetime of *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ (1.1 μs at 20 °C),[12] consistent with the observed thermal reaction mode. The relative emission efficiencies, as a function of the irradiation energy, are $\Phi_{370}/\Phi_{490} = 0.98 \pm 0.06$ and $\Phi_{255}/\Phi_{490} = 0.41 \pm 0.07$ (four determinations), where the subscripts refer to the wavelengths (nm) of excitation.

As is true for several other transition-metal systems,[14,31,32] hydroxide ion quenches the phosphorescence. However, emission and photoreaction quenching by OH^- could not be studied, owing to fast thermal decomposition in basic medium. On the other hand, the rather short doublet lifetime renders inefficient any quenching by other chromium(III) species in concentrations as high as 10^{-2} M. This is congruent with the observation that τ is independent of the presence of aquation products.

Discussion

LF Photochemistry. This complex offers a further, significant example of antithermal LF excited-state chemistry of Cr(III). As summarized in eq 1, both the photoaquation modes and the



(1)

photostereochemistry contrast sharply with the stereoretentive loss of Cl^- in the ground state. The latter can be accounted for by the large kinetic trans effect of CN^-[29,33] and is discussed elsewhere.[15] Within the experimental scatter caused by the thermal lability of the complex, the quantum yields of Table I do not exhibit significant wavelength dependence throughout the LF region, down to the low-energy side. This suggests the involvement of either one state or more states in thermal equilibrium.

The results are analyzed primarily in terms of the Vanquickenborne–Ceulemans model,[9] currently accepted as the standard reference. From O_h to C_{4v} symmetry, the photochemically relevant $^4T_{2g}$ excited state splits into the $^4B_2$ and ^4E components.[11] By means of the σ and π LF parameters available for NH_3, CN^-, and Cl^-,[4,9] the ^4E level is estimated to lie 835 cm^{-1} below $^4B_2$. As for other *trans*-$Cr(NH_3)_4(CN)X^{z+}$ ions, this energy spacing is relatively small, compared with that (>2000 cm^{-1}) of the typical *trans*-tetraamines.[34] Mutual compensation of the LF strengths of CN^- and Cl^-, respectively higher and lower than that of NH_3, brings about an average axial field not very different from the equatorial one. The LF absorption bands of Figure 1 appear indeed octahedral-like.

From another point of view, the $^4B_2$–^4E separation is sufficiently larger than in the previously studied species with X = H_2O, NCS^-, and F^- (100–300 cm^{-1})[14] that one may anticipate prevalence of axial over equatorial antibonding photobehavior, on the basis of the dominant d_{z^2} character of ^4E. A related feature is that the relationships of the average axial and equatorial parameters are $\sigma_{ax} < \sigma_{eq}$ and $\pi_{ax} > \pi_{eq}$, different from those of the other members of this family, where $\sigma_{ax} > \sigma_{eq}$ and $\pi_{ax} > \pi_{eq}$; i.e., here the low σ value of Cl^- determines the same orbital sequence encountered in the *trans*-$Cr(NH_3)_4XY^{z+}$ complexes with two weak-field axial ligands.[9]

Table II. Spectrochemical Parameters for Each L Ligand and Excited-State Bond Energies for *trans*-$Cr(NH_3)_4(CN)Cl^+$, Calculated According to the Vanquickenborne–Ceulemans Model[4,9] (cm^{-1})

	L		
	CN^-	Cl^-	NH_3
σ_L[a]	8 480	5 580	7 180
π_L[a]	−290	900	0
I^*(Cr–L) in ^4E	10 780	9 600	11 720
I^*(Cr–L) in $^4B_2$	17 550	12 970	8 980

[a] Data from ref 9.

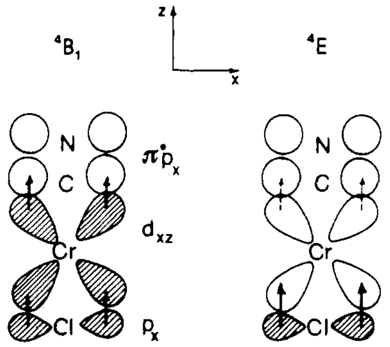


Figure 3. Schematic representation of the metal and ligand orbitals of π symmetry in the *xz* plane for the $^4B_1$ ground state (left) and ^4E lowest excited quartet state (right) of *trans*-$Cr(NH_3)_4(CN)Cl^+$: blank, unoccupied orbitals; shaded, occupied or semioccupied orbitals. For clarity, only the axial ligands are shown, as the equatorial NH_3 groups are not involved in π bonding. Because of the degeneracy of the ^4E state, the same description applies to the *yz* plane.

The essential finding is that $\Phi_{CN^-} \gg \Phi_{Cl^-}$, far beyond the uncertainty introduced by the nuisance of the dark reactions. The quantum yields for cyanide aquation are the highest observed thus far in chromium(III)–cyano complexes,[3,13,35-37] including $Cr(CN)_6^{3-}$.[38,39] Table II reports the bond energies, I^*(Cr–L), for each L type of ligand in the ^4E and $^4B_2$ states, evaluated by the additive angular overlap procedure.[9] Comparison with Table I shows that, while the prevalence of axial labilization ($\Phi_{ax}/\Phi_{eq} \sim 4$) is congruent with the nature of the predicted lowest excited quartet, the major photoprocess, CN^- aquation, is in marked contrast with the theoretical expectation that $\Phi_{CN^-} < \Phi_{Cl^-}$. It should be noted that a weaker bonding for Cl^- than for CN^- is anticipated not only for ^4E but also (and to a larger extent) for the upper, $^4B_2$, state. The d_{xz}, $d_{yz} \rightarrow d_{z^2}$ transition, associated with ^4E, indeed destabilizes the Cr–CN^- π bond and stabilizes the Cr–Cl^- one, since the t_{2g} orbitals are π bonding for CN^- and π antibonding for Cl^-. However, according to the model, these changes are not sufficient to labilize CN^-, as the strong ground-state σ bonding of this ligand would remain a determining factor in the excited state. It is therefore surprising that the remarkable ground-state lability of chloride has no counterpart in the excited state, the axial reactivity of which is just reversed.

The explanation we propose for such a notable disagreement is a kind of excited-state trans effect. The point is that, in *trans*-$Cr(NH_3)_4XY^{z+}$ complexes, the excited-state bonding changes of X and Y should not be regarded as independent of each other when the properties of the axial groups are so diverse and contrasting as in the present case. The good π-donor and π-acceptor abilities of Cl^- and CN^- may give rise to a combined

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push–pull action, providing an extra stabilization for Cl^-. This mutual interaction, resulting in an increased charge shift from Cl^- to Cr^{3+}, would be enhanced by depletion of the d_{xz} and d_{yz} orbitals in the excited state, as schematized in Figure 3. The unusually high value of Φ_{CN^-} may also imply a labilizing action of Cl^- toward CN^-. This effect is opposite to the ground-state trans effect, whereby CN^- destabilizes Cl^- principally through a strong σ donation along the z axis. The latter is certainly attenuated in the ^4E excited state by the insertion of σ^* charge in the d_{z^2} orbital between CN^- and Cl^-.

The above explanation may also account for our earlier observation that, for the analogous *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ ion, $\Phi_{CN^-} > \Phi_{NCS^-}$,[14] again in contrast with the theory.[4,9] For the latter complex, however, CN^- and NCS^- releases are lesser photoreaction modes. The discrepancy appeared not so critical and was attributed to inadequacy of the available σ_{NCS^-} and π_{NCS^-} spectroscopic parameters[4,9] in describing the strong ground-state $Cr-NCS^-$ bond. In the present case this second possibility is ruled out, as there is little doubt about the relatively weak bonding of Cl^-.

NH_3 photoaquation represents a minor chemical deactivation path for this complex. As in numerous other instances,[2,4,9,14,24,31] it can be assigned either to the equatorial σ^* component of ^4E (23.7% $d_{x^2-y^2}$)[9] or to partial intervention of $^4B_2$ (100% $d_{x^2-y^2}$), made accessible by an energy gap of ca. $4RT$ between these states.[9]

Our results are consistent with Adamson's semiempirical rules.[5] It is interesting that the second rule (the strong-field ligand on the weak-field axis is preferentially photoaquated) would not be obeyed if the complex behaved "normally", according to the current standard.[9] It may be noticed that in the original paper by Adamson[5] "a type of trans effect" is mentioned in rule 2 and that subsequently this point has never been taken up.

Since the (direct or indirect) involvement of the lowest doublet in the photoreactivity continues to be of major interest,[1-3,14] some information in this regard would have been desirable. While the emission properties were satisfactorily characterized, the impossibility of performing quantitative luminescence and photoreaction quenching experiments precluded any indication of this aspect.

As to the stereochemistry of CN^- photoaquation, our findings are not unexpected. The dominant, if not exclusive, cis configuration of the product of axial bond cleavage is in agreement with both the symmetry-restricted mechanism of dissociative type[4,10] and the associative, or concerted, edge-displacement mechanism.[2,13] It may be remarked that, had Cl^- been labilized instead of CN^-, this system would have been more discriminating. According to the first model, a $Cr(NH_3)_4(CN)^{2+}$ fragment nascent in the ^4E state should lead to a mixture of *cis*– and *trans*–cyanoaquo products, respectively related to the $^4B_2$ excited state and to the $^4A_1$ ground state of the trigonal-bipyramidal intermediate.[4,10] On the contrary, the second approach would still predict one isomer only.

CT Photochemistry. Ligand labilization is less selective than in the LF region. Specifically, Φ_{CN^-} drops to about half of its original value, and Φ_{NH_3} almost doubles. Moreover, although small, Φ_{Cl^-} is now definitely measurable. There is a considerable change in the $\Phi_{CN^-}:\Phi_{Cl^-}:\Phi_{NH_3}$ proportion from ca. 4:0:1 to ca. 2:1:2. Similar losses of specificity have already been observed in other chromium(III) systems on passing from LF to CT excitation.[24,31,40-42]

The nonzero value of Φ_{Cl^-} and the increase of Φ_{NH_3} imply an inherent CT reactivity. The CT band of *trans*-$Cr(NH_3)_4(CN)Cl^+$ (Figure 1) is associated with both the $\pi(Cl^-) \rightarrow e_g^*(Cr)$ and $t_{2g}(Cr) \rightarrow \pi^*(CN^-)$ transitions, occurring in opposite directions. By comparison with the spectra of $Cr(NH_3)_5Cl^{2+}$[40] and $Cr(NH_3)_5(CN)^{2+}$,[43] the onset of both types of absorptions is expected at about 260–270 nm. Irradiation at 245 nm should therefore populate the two CT states to comparable extents. A simple, yet reasonable, interpretation of the fact that Φ_{Cl^-} increases, while Φ_{CN^-} decreases with respect to LF photolysis, is that the former state is chemically active, while the latter is not. This is corroborated by the observation that CT excitation of other chromium(III)–chloro complexes enhances Φ_{Cl^-} by as much as 2 orders of magnitude,[24,40,42] whereas $Cr(NH_3)_5(CN)^{2+}$ exhibits the same reactivity ($\Phi_{NH_3} = 0.33$ and $\Phi_{CN^-} < 5 \times 10^{-4}$) upon LF and CT irradiation.[36] A further, supporting consideration is that a Cr(II) species is certainly less unstable than a Cr(IV) one.

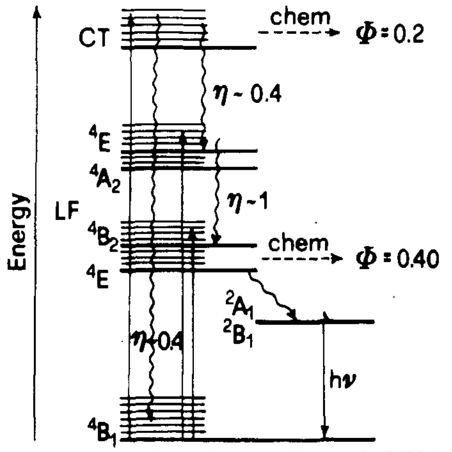

Figure 4. Schematic energy-level diagram of *trans*-$Cr(NH_3)_4(CN)Cl^+$, with the efficiencies of some excited-state processes.

Even though the nature of the transition suggests primary homolytic bond fission for the CT reactions, the ultimate products are substitutional like the LF ones, because of the strong reducing power of Cr(II); that is, the unpaired electron would have essentially unit probability of being recaptured by the radical ligand before this leaves the solvent cage and a water molecule coordinates. While, in some chromium(III) systems with less oxidizable ligands, photoredox activity could be actually demonstrated by either flash photolysis[30,44-46] or scavenging techniques,[30,31,45,46] the present conditions were too unfavorable for obtaining such a direct evidence.

Connected with this matter is communication between CT and LF states. The photoaquation quantum yield of an L ligand on 245-nm irradiation can be expressed by eq 2, where the CT and

$$\Phi_L = \Phi_L^{CT} + \eta_{IC}\Phi_L^{LF} \qquad (2)$$

LF superscripts denote the intrinsic photochemistries of the two types of states and η_{IC} is the efficiency of internal conversion between them. Since the constancy of the quantum yields and of the relative emission intensities upon 370- and 490-nm irradiation indicates virtually 100% relaxation to the lowest level(s) within the LF manifold, the following analysis is possible. If Φ_{CN^-} is assigned entirely to LF reaction consequent to CT excitation ($\Phi_{CN^-}^{CT} = 0$), then $\eta_{IC} = 0.44 \pm 0.04$. Accordingly, on the basis of the LF reactivity ratio one can evaluate $\Phi_{NH_3}^{CT} = 0.12 \pm 0.02$. As $\Phi_{Cl^-}^{CT} = 0.06 \pm 0.01$, the total CT chemical deactivation yield amounts to ca. 0.2. The excited-state processes and their relative importance are schematized in Figure 4.

Should some CN^- aquation take place in the CT state, the above η_{IC} value would represent an upper limit. However, that η_{IC} is actually close to 0.4 is confirmed by the doublet emission behavior, which is an independent observable, peculiar to the LF states. A $I_{255}/I_{490} = 0.41 \pm 0.07$ ratio indicates that CT → LF interconversion cannot be less efficient than 34%. To our knowledge, only one estimate of this kind ($\eta_{IC} \sim 0.7$) has been previously reported for a chromium(III) complex.[31]

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Finally, by difference, 40% of the CT excitation energy is dissipated directly to the ground state, without passing through the LF energy levels.

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Registry No. *trans*-$[Cr(NH_3)_4(CN)Cl]ClO_4$, 116301-75-8; *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, 19544-03-7; NH_3, 7664-41-7; CN^-, 57-12-5; Cl^-, 16887-00-6.

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Protolytic Properties of Perxenic Acid

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Spectra and protolytic properties of aqueous perxenic acid in the pH range –0.2 to 13 were studied by conventional and stopped-flow spectrophotometry. The following p*K* values and limits were found (25.0 °C): $pK_{H_4XeO_6} < 0$, $pK_{H_3XeO_6^-} = 4.29 \pm 0.03$; $pK_{H_2XeO_6^{2-}} = 10.81 \pm 0.04$. The enthalpy of dissociation (25.0 °C) of $H_3XeO_6^-$ is 0 ± 5 kJ mol^{-1}; that of $H_2XeO_6^{2-}$ is 3 ± 2 kJ mol^{-1}.

Introduction

Because of the rapid decomposition of perxenates by acids[1,2]

$$HXeO_6^{3-} + 3H^+ \rightarrow XeO_3 + 2H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

little is known of the equilibrium properties of perxenic acid in acid aqueous solution. It has been pointed out, however, that perxenic acid may possess unusual protolytic properties.[3] Raman spectra of aqueous alkaline perxenate solutions show that the Xe(VIII) species present in these solutions are octahedrally coordinated,[4] which implies the formula H_4XeO_6 for the perxenic acid itself. This accords with the crystal structure of alkali-metal perxenates.[5]

Protonation of perxenate to $H_3XeO_6^-$ and H_4XeO_6 has not heretofore been observed because of the rapidity of reaction 1. A p*K* value of 10.5 has been measured for the acid dissociation of $H_2XeO_6^{2-}$,[3] and a lower p*K* limit of 14 has been set for the dissociation of $HXeO_6^{3-}$.[4] Assumption of a 4–5 unit difference between successive pK's suggests $pK_1 \sim 2$ for the acid dissociation of H_4XeO_6, in disagreement with Pauling's empirical rules,[6] which predict a value between –2 and –3 for pK_1 of such an acid. In the present investigation we have determined the protolytic equilibria of perxenic acid in the pH range –0.2 to 13 by time-resolved spectrophotometric measurements.

Experimental Section

Time-resolved absorbance measurements of perxenate solutions were made at pH <7 with an Aminco-Marrow stopped-flow apparatus[7] and at pH >7 with a Cary 219 spectrophotometer. A cell length of 1 cm was used with both instruments. The temperature was kept constant to within 0.1 °C. A few experiments were made with a nonthermostated SF-51 High-Tech stopped-flow spectrophotometer with an optical path of 0.2 cm. The temperature in these experiments was ambient (23 ± 2 °C). Absorbance readings on the Aminco-Marrow instrument were calibrated against readings on the Cary instrument in the wavelength range $200 < \lambda < 300$ nm, using a 10^{-4} mol dm^{-3} periodate solution at pH 11, which has a spectrum similar to that of perxenate solutions (vide infra). The error of absorbance readings on the stopped-flow instruments was typically 1–2%. A source of error in the present stopped-flow measurements was a slow decomposition of the perxenate stock solution when kept in the storage syringe of the Aminco-Marrow instrument. Correction for the decomposition was obtained by repeating the measurements in the opposite order with fresh solutions.

The solution studied resulted from mixing a perxenate stock solution, which contained 10^{-2} mol dm^{-3} NaOH and 10^{-4} to 3×10^{-3} mol dm^{-3} Na_4XeO_6, with an equal volume of a solution containing a buffer or an acid. Perxenate stock solutions were prepared by dissolving an appropriate quantity of sodium perxenate, weighed on a Cahn Electrobalance, in 5 or 10 mL of 10^{-2} mol dm^{-3} NaOH solution. Ionic strength was adjusted with sodium perchlorate. The pH of the mixed solution at zero time after the mixing was set equal to the pH of a solution that resulted from mixing with the buffer or acid a solution of the same composition as the stock solution but in which sodium perxenate was replaced by an appropriate quantity of sodium hydroxide. The pH was measured with a Radiometer pH M 64 Research pH meter using a Radiometer G 202 C glass electrode and a Radiometer K 701 calomel electrode. The pH calibration was made with Radiometer type S 1316 and S 1326 standard buffers.

Scheme I

$$H_4XeO_6 = H_3XeO_6^- + H^+ \qquad (2)$$
$pK_1 < 0^a$
$$H_3XeO_6^- = H_2XeO_6^{2-} + H^+ \qquad (3)$$
$pK_2 = 4.29 \pm 0.03;^a\ \Delta H_2° = 0 \pm 5\ \text{kJ mol}^{-1\ a,d}$
$$H_2XeO_6^{2-} = HXeO_6^{3-} + H^+ \qquad (4)$$
$pK_3 = 10.75 \pm 0.02,^b\ 10.8,^b\ 10.81 \pm 0.04;^{a,d}\ \Delta H_3°, = 3 \pm 2\ \text{kJ mol}^{-1\ a,d}$
$$HXeO_6^{3-} = XeO_6^{4-} + H^+ \qquad (5)$$
$pK_4 > 14^c$

[a] This work. [b] Data from ref 3 extrapolated to zero ionic strength. [c] Reference 4. [d] Error estimated.

Acids were titrated with sodium hydroxide solutions standardized against potassium hydrogen phthalate. Sodium perxenate was prepared as described previously.[3] The molar weight was 380. Perchloric acid and sulfuric acid were Merck Suprapur. Water was triply distilled. All other chemicals were Merck p.a.

Results and Discussion

Protolytic Properties. Scheme I shows protolytic equilibria among perxenate species at 25.0 °C. (Unless stated otherwise, the errors given are standard deviations obtained by least-squares treatment).

The spectra of perxenate solutions in the pH regions –0.2 to 2, 6 to 8, and 12 to 13, which we assign to $H_3XeO_6^-$, $H_2XeO_6^{2-}$, and $HXeO_6^{3-}$, respectively, are shown in Figure 1.

The spectra of $HXeO_6^{3-}$, $H_2XeO_6^{2-}$, and XeO_3 agree with spectra measured previously.[3] Molar absorption coefficients determined here of $HXeO_6^{3-}$ at 239 nm (max), of $H_2XeO_6^{2-}$ at

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