(Pyridine)pentaamminechromium(III). Synthesis, Characterization, and Photochemistry

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Received July 14, 1995[⊗]

The $Cr(NH_3)_5(py)^{3+}$ ion has been obtained by metathesis of $Cr(NH_3)_5(Me_2SO)^{3+}$ in pyridine, isolated as the perchlorate salt, and characterized by absorption (λ_{max} at 467, 352, and 260 nm) and emission spectra (λ_{max} at 668 nm, $\tau = 2.0$ μs at 20 °C in water) and by the py aquation rate ($k = 5 \times 10^{-4}$ s^{-1} at 80 °C). Ligand-field (LF) band irradiation in acid aqueous solution (10^{-2} M $HClO_4$) induces photoaquation of py ($\Phi = 0.26$) and NH_3 ($\Phi = 0.16$). HPLC indicates that the latter reaction gives rise to both *cis*- and *trans*-$Cr(NH_3)_4(py)(H_2O)^{3+}$, with the predominance of the cis isomer. This is the first $Cr(NH_3)_5X^{z+}$ species where $\Phi_x > \Phi_{NH_3}$: the result is compared with the predictions of various photolysis models and is taken as chemical evidence for π-acceptance by the py ligand. The photostereochemistry is also discussed. The phosphorescence is totally quenched by $Cr(C_2O_4)_3^{3-}$ ($k_q = 2.7 \times 10^9$ M^{-1} s^{-1}), while the photoreactions are only in part. On 470-nm excitation, the Φ_{py}/Φ_{NH_3} ratio is ∼1 and ∼2 for the unquenchable and the quenchable contributions, respectively. Such a difference, suggesting at least two reactive precursors, can be interpreted in terms of the photochemistry proceeding from either the lowest doublet and quartet excited states or, alternatively, from the ^4E and $^4B_2$ states. Irradiation of the very distinct absorption of coordinated pyridine results in both doublet-state emission and loss of py and NH_3. Comparison of this photobehavior with the LF results gives an efficiency of 0.7 for conversion of the py−localized $\pi\pi^*$ states into the Cr−localized LF states, confirmed by the wavelength dependence of the relative emission yields. Some py release ($\Phi = 0.03$) is concluded to originate in the $\pi\pi^*$ states.

Introduction

A number of pyridine complexes of chromium(III) have been known since the early times of coordination chemistry.[1,2] Although some have received spectroscopic[3−7] and photophysical[8−10] attention, no photochemistry has been reported to date for any of these compounds.

Various features of the pyridine ligand (py) warrant an examination in a photochemical context. One is the fair degree of π acceptance, as inferred from IR[4] and electronic[4,5] spectroscopy and expressed by a comparatively large negative value of the π_{py} parameter in the two-dimensional spectrochemical series.[5,11] This is expected to bear significantly on the selectivity of ligand loss caused by ligand-field (LF) excitation. Thus far, the only monodentate π-acceptor group dealt with in photochemical studies of chromium(III) has been cyanide. However, the Cr−CN σ bonding, exceedingly strong even in the excited states, overpowers any possible π contribution to preferential bond cleavage, so that π effects cannot be evidenced for this ligand.[11,12] On the contrary, as the Cr−py σ-bond strength is not extreme, the π-bonding component of pyridine is postulated to be a discriminating factor in photolabilization, a prediction never before tested for π-accepting ligands in relation to the current photolysis models.[11]

An additional point of interest is that, upon coordination to the metal ion, the N-heterocycle retains its typical, intense UV spectral band associated with $\pi-\pi^*$ transitions. Such a ligand-localized (LL) absorption is often clearly distinct from both the LF and the charge-transfer (CT) absorptions which occur at lower and higher energies, respectively. These species are, therefore, suited to an investigation of the possible migration of the excitation energy from LL, or ligand-centered, to LF, or metal-centered, states.

As an approach to the exploration of the excited-state chemical behavior of the Cr−py moiety, we have chosen the $Cr(NH_3)_5(py)^{3+}$ prototype. Pentaammine complexes have, in fact, played an important role in the experimental[13,14] and theoretical[11] development of chromium(III) photochemistry: more than a dozen $Cr(NH_3)_5X^{z+}$ species have been investigated, with anionic and neutral X ligands spanning a variety of electronic and bonding properties. Since the complex in question had not previously been described, a synthetic challenge was added to the photochemical study.

Experimental Section

Materials. $[Cr(NH_3)_6](ClO_4)_3$,[15] $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$,[16] and $K_3[Cr(CN)_6]$[17] were prepared by standard methods. $[Cr(NH_3)_5(Me_2SO)](ClO_4)_3$ was obtained by heating $[Cr(NH_3)_5(H_2O)](ClO_4)_3$ in anhydrous dimethyl sulfoxide, as reported elsewhere.[18] Reagent grade pyridine was dried by refluxing it over KOH pellets and was then distilled and stored under nitrogen atmosphere. Sephadex SP C-25 and QAE A-25 resins were used as cation and anion exchangers, respectively.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

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0020-1669/96/1335-0974$12.00/0

Caution! Even though no inconvenience was incurred in the present preparations, perchlorate salts of complexes with organic ligands should be regarded as potentially explosive if heated or shocked.

(Pyridine)pentaamminechromium(III) Perchlorate. A 600-mg amount of $[Cr(NH_3)_5(Me_2SO)](ClO_4)_3$ (1.2 mmol) was dissolved in 100 mL of anhydrous pyridine at room temperature, and the solution was heated at 60 °C for 30 min under magnetic stirring. The reaction flask was stoppered to prevent contact with air moisture. The original purple-red color gradually turned orange, but some red, unreacted starting material reprecipitated. The solid redissolved on cooling; the solution was then kept at room temperature in the dark for 24 h to complete the reaction. Dilution with an equal volume of ether resulted in the appearance of a yellow salt that was recovered on a sintered glass filter, repeatedly washed with at least three 20-mL portions of absolute ethanol, and vacuum dried over P_2O_5. The crude product (360 mg) was dissolved in a minimum quantity (ca. 10 mL) of water, and the residual turbidity was removed by centrifugation. Dropwise addition of 10 mL of 70% w/w $HClO_4$ precipitated yellow crystals; after standing in a refrigerator for several hours, these were collected by filtration and washed and dried as above. The overall yield was 240 mg or 40%. Anal. Calcd (found) for $[Cr(NH_3)_5(py)](ClO_4)_3 \cdot H_2O$: Cr, 9.76 (9.8); C, 11.27 (10.3); H, 4.16 (4.1); N, 15.78 (15.6).

Analyses and Instrumentation. Cr was determined spectrophotometrically at 374 nm, following decomposition of the complex salt with 1 M NaOH and oxidation to chromate by alkaline hydrogen peroxide. Calibration plots were obtained by use of CrO_4^{2-} standards at pH 12, with ϵ values around 4.7×10^3 M^{-1} cm^{-1}. C, H, and N were determined by standard organic microanalysis.

Analysis of free py and NH_3 in photolyzed solutions involved separation of the released ligands from the reaction mixtures. This was accomplished by elution through 4 × 0.6 cm columns of cation exchanger with 0.10 M $NaClO_4$ at pH 2.0 ($HClO_4$). While all the (tripositive) complexes were retained by the resin, the pyH^+ and NH_4^+ ions were completely recovered in a 10-mL volume of eluate. When $Cr(C_2O_4)_3^{3-}$ was employed as a quencher, ca. 1 cm of anion exchanger was layered on top of the cationic resin so as to adsorb this complex also. Pyridine was measured spectrophotometrically at 256 nm (ϵ 5500 M^{-1} cm^{-1}) with reference to the absorption maximum of the pyridinium ion; alternatively, and often as an internal check, the samples were alkalinized and the absorbance of the organic base (ϵ 3050 M^{-1} cm^{-1}) was read at 257 nm. Ammonia was determined by an Orion 95-12 selective electrode and a Radiometer PHM-84 potentiometer: the sample pH was adjusted to ca. 13 with NaOH, and standardization was performed during each run by means of a series of fresh NH_4Cl + NaOH solutions.

Analysis of the photoreaction products was also carried out by an HPLC technique, using a Dionex GP40 chromatograph, an AD20 detector, and a 4600 integrator. A 25-cm PCX 500 cation-exchange column was employed, and the eluant was 1.5 M KCl in 2% acetonitrile/water at pH 2.0 (HCl). Cr–py complexes and pyH^+ were determined by their absorption maxima at 260 and 256 nm, respectively. Typical elution times were 4.4 min for pyH^+, ca. 12 min for $Cr(NH_3)_4(H_2O)(py)^{3+}$, and ca. 17 min for $Cr(NH_3)_5(py)^{3+}$. The method was standardized in the course of each determination using pyH^+ and $Cr(NH_3)_5(py)^{3+}$ solutions of known concentration: the reproducibility was always higher than 97%.

UV–vis absorption spectra were obtained with either a Cary 17 instrument or a Hewlett-Packard 8452A diode-array spectrophotometer. Emission spectra were recorded by a Perkin-Elmer 650-10S spectrofluorometer with an R928 photomultiplier. Phosphorescence lifetimes were measured by a J & K System 2000 frequency-doubled ruby laser, delivering 20-ns pulses of 200-mJ energy at 347 nm. The decays, monitored by an R928 tube, were fed into a Tektronix 468 oscilloscope and then least-squares-processed. All samples used for absorption and emission measurements were filtered through 0.45-μm Millipore filters.

Procedures. Relative phosphorescence yields were obtained as ratios of the intensities, I_λ, emitted at 668 nm upon excitation at various λ's. The method employed saturated solutions of the complex (7.5×10^{-2} M in 1×10^{-3} M $HClO_4$), the absorbances of which were sufficiently high (∼3 in the vis region; >20 in the UV region) that virtually all the emission occurred from the front window of the cell. The fluorometer sample holder was modified so that part of the emission was reflected into the detector by a mirror not interfering with the excitation beam. Correction was applied for the different incident intensities at the various wavelengths: such intensities were measured both by actinometry and by a thermopile, with a better than 95% agreement.

The setup for determination of photoreaction quantum yields was that already described,[19] equipped with a thermopile calibrated by ferrioxalate[20] and Reineckate[21] actinometry. The half-width of the irradiation bands, selected by a monochromator, was 14 nm; the light intensities were ca. 5×10^{-9} einstein s^{-1}. Stirred samples of 2.5-mL volume, $\sim 5 \times 10^{-3}$ M in complex and 1.0×10^{-2} M in $HClO_4$, were photolyzed at 20.0 ± 0.3 °C in 1.0-cm cells. Absorption of radiation was complete at 254 nm and only partial in the vis region: in the latter case, the absorbed energy was evaluated by a reported procedure.[22] Total photolysis was usually 10–15%. Emission and photoreaction quenching were studied in the presence of 1.5×10^{-4}–1.5×10^{-3} M $Cr(C_2O_4)_3^{3-}$ at the same pH of 2.0. In all experiments, parallel analyses of photolyzed and dark samples allowed for any possible thermal reaction background.

Results

Preparation. Even though (pyridine)pentaamminecobalt(III) and several substituted-pyridine analogues have been described in the literature,[23,24] no chromium(III) complexes of this type have been reported to date. In the case of cobalt(III), the customary synthetic procedure was replacement of coordinated dimethylformamide (dmf) by the N-heterocycle in dmf solution. Similar attempts with both $Cr(NH_3)_5(dmf)^{3+}$ and $Cr(NH_3)_5(Me_2SO)^{3+}$ in the respective dipolar aprotic solvents, and also in methanol suspensions, either resulted in no reaction or led to complex decomposition on prolonged heating. The failure is evidently due to the fact that the preference for N-donor ligands relative to O-donor ligands is, in general, lower for Cr(III) than for Co(III).[2]

The new $Cr(NH_3)_5(py)^{3+}$ species can only be obtained if the metathesis of $Cr(NH_3)_5(Me_2SO)^{3+}$ is carried out in pure, anhydrous pyridine. Since the solubility of the reactant in this liquid is modest (ca. 10^{-2} M), relatively large amounts of the heterocycle are required. Some complication arises from the unusual decrease of the solubility in pyridine of the parent complex with increasing temperature and from the absence of any reaction under heterogeneous conditions even at 60 °C. If the reaction is protracted at room temperature after the residual substrate has redissolved, the yield is improved and, more importantly, contamination of the product by the starting material is prevented. The two (equally charged) species are, in fact, hardly separable by selective reprecipitation with various anions and by either cation-exchange or gel-filtration chromatography.

Absorption Spectrum. Figure 1 displays the UV–vis features of (pyridine)pentaamminechromium(III) in aqueous solution. The two LF maxima at 467 and 352 nm, associated with the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions in the O_h approximation, are compared in Table 1 with literature data for the closely related imidazole (im) complex[25] and for $Cr(NH_3)_6^{3+}$.[26] These are consistent with the occurrence of the CrN_6 chromophore in the novel compound. The small red shift of the spectrum of $Cr(NH_3)_5(py)^{3+}$ relative to the hexaammine

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Table 1. Spectral Absorption and Emission Features in Aqueous Solution

	absorption: λ, nm (ϵ, M^{-1} cm^{-1})			$^2E_g \rightarrow {}^4A_{2g}{}^a$ emission		
species	$^4A_{2g} \rightarrow {}^4T_{2g}{}^a$	$^4A_{2g} \rightarrow {}^4T_{1g}{}^a$	$\pi \rightarrow \pi^*$	λ, nm	τ_{20}, μs	ref
$Cr(NH_3)_5(py)^{3+}$	467 (40.6)[b]	352 (34.1)[b]	260 (2900)	668	2.0	*c*
$Cr(NH_3)_5(im)^{3+}$ [d]	466 (41)	353 (35)				25
$Cr(NH_3)_6{}^{3+}$	465 (40)[e]	351 (33)[e]		666	2.2	26,[e] 28[f]
py			257 (3050)			27
pyH^+			256 (5500)			27

[a] O_h approximation. [b] ±0.5 M^{-1} cm^{-1}. [c] This work. [d] im = imidazole. [e] Other literature absorption data in ref 26. [f] Emission data.

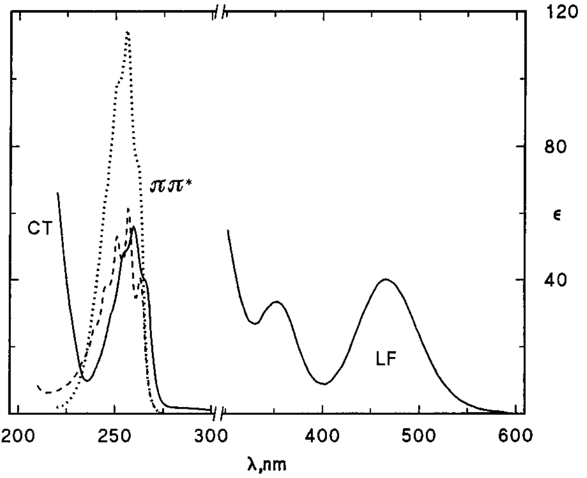

Figure 1. UV (left scale) and vis (right scale) absorption spectra in aqueous solution: solid line, $Cr(NH_3)_5(py)^{3+}$; dashed line, pyridine; dotted line, pyridinium ion.

is in agreement with the spectrochemical position of py (Dq = 1970 cm^{-1}) slightly lower than that of NH_3 (Dq = 2155 cm^{-1}).[11]

The very distinct, intense band at higher energies is readily attributed to py–localized, or LL, fully allowed $\pi-\pi^*$ transitions, on the basis of its correspondence with the spectra of pyridine and pyridinium,[27] reported for comparison in Table 1 and Figure 1. The virtually unperturbed absorptions of the py and CrN_6 moieties suggest little coupling between the pyridine π system and the chromium(III) d electrons.

The even stronger absorption deeper in the UV is typical of a CT transition, the direction of which (ligand-to-metal or vice versa) remains undetermined.

Thermal Solution Behavior. The $Cr(NH_3)_5(py)^{3+}$ ion is quite inert in acid aqueous media at room temperature. In both 0.01 and 2.0 M $HClO_4$, its absorption spectrum does not change appreciably for 24 h: this circumstance was beneficial to the photochemical study. Pyridine aquation (eq 1) becomes effective at higher temperatures, as evidenced by the accrual of pyridinium ion in solution, the red displacement of the LF bands, and, particularly, the drop of optical density in the 280–330 nm interval, where free py and pyH^+ absorb less than coordinated py (Figure 1). The movement of the crossing points during the spectral evolution denotes subsequent, stepwise loss of NH_3, as expected from the reaction cascade to which $Cr(NH_3)_5(H_2O)^{3+}$ is subject.[26] In order to reduce the error caused by the disappearance of the primary product, the rate of reaction 1 can be estimated from the initial decrease in absorption at 482 nm, corresponding to an isosbestic point between $Cr(NH_3)_5(H_2O)^{3+}$ and its successive aquation product, *cis*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$. The pseudo-first-order rate constant determined in 0.2 M $HClO_4$ at 80 °C is $k = 5 \times 10^{-4}$ s^{-1}; that is, py aquation is about 3 times faster than NH_3 aquation of both $Cr(NH_3)_6{}^{3+}$ and $Cr(NH_3)_5(H_2O)^{3+}$ ($k = 1.5 \times 10^{-4}$ s^{-1}) under the same conditions.[26]

$$Cr(NH_3)_5(py)^{3+} + H_3O^+ \rightarrow Cr(NH_3)_5(H_2O)^{3+} + pyH^+ \quad (1)$$

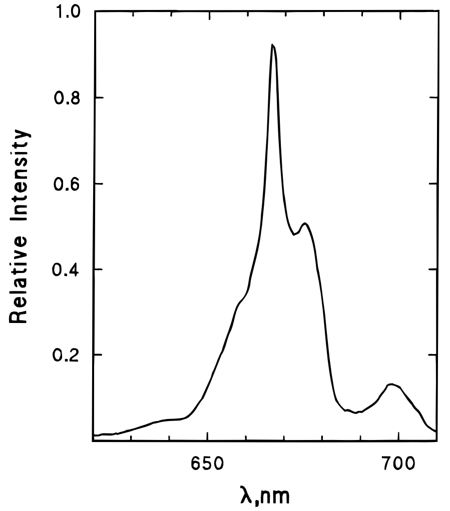

Figure 2. Emission spectrum of $Cr(NH_3)_5(py)^{3+}$ in acid aqueous solution (10^{-3} M $HClO_4$) at room temperature.

Photophysics. The complex luminesces in acidic aqueous solution at room temperature. Figure 2 shows the moderately intense and structured emission band, assigned to $^2E_g \rightarrow {}^4A_{2g}$ (O_h) phosphorescence. The emission decay is monoexponential with $\tau = 2.0 \pm 0.1$ μs at 20 °C. Both the maximum and the lifetime are very close to the values reported for the $Cr(NH_3)_6{}^{3+}$ model compound (Table 1).[28]

The relative emission yields as a function of the excitation energy, are $I_{352}/I_{467} = 1.03 \pm 0.05$ and $I_{260}/I_{467} = 0.73 \pm 0.07$ (three determinations), where the subscripts denote the wavelengths (nm) of irradiation.

The phosphorescence is quenched by the $Cr(C_2O_4)_3{}^{3-}$ and $Cr(CN)_6{}^{3-}$ ions. Stern–Volmer plots for aqueous solutions are linear, with bimolecular k_q parameters at 20 °C of 2.7×10^9 and 0.40×10^9 M^{-1} s^{-1}, respectively. The higher quenching efficiency of the tris(oxalato) complex is in agreement with energy-matching expectations. The doublet state energies E_D are, in fact, 14 300 cm^{-1} for $Cr(C_2O_4)_3{}^{3-}$ [29] and 12 500 cm^{-1} for $Cr(CN)_6{}^{3-}$,[30] as compared with E_D = 15 000 cm^{-1} for $Cr(NH_3)_5(py)^{3+}$. That, at least in the latter case, the quenching is indeed one of excitation energy transfer is shown by experiments in Me_2SO, where induced 800-nm emission, typical of $Cr(CN)_6{}^{3-}$, is observed. Such emission would not be expected to be observable in water because of the short ^2E_g lifetime of $Cr(CN)_6{}^{3-}$ in this solvent.[31] Also the OH^- ion behaves as a

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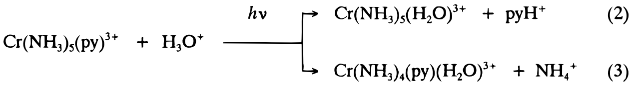
Table 2. Photoaquation Quantum Yields of $Cr(NH_3)_5(py)^{3+}$ at pH 2.0 and 20 °C

λ_{irrn}, nm	$\Phi_{py}{}^{b}$	$\Phi_{NH_3}{}^{b}$
470	0.258 ± 0.014 (6)	0.156 ± 0.013 (5)
470, Q[a]	0.044 ± 0.003 (4)	0.042 ± 0.007 (5)
254	0.229 ± 0.011 (5)	0.111 ± 0.011 (5)
254, Q[a]	0.066 ± 0.007 (4)	0.031 ± 0.005 (5)

[a] Q denotes photolyses in the presence of $Cr(C_2O_4)_3{}^{3-}$ as quencher; the quantum yield values are extrapolated to infinite quencher concentration. [b] The uncertainties are given as standard deviations; the numbers of independent determinations are given in parentheses.

good quencher, as it usually does toward a variety of chromium(III) emitters: at pH 12 (NaOH) the phosphorescence is totally extinguished.

Photochemistry. Irradiation of either the LF or the $\pi\pi^*$(py) bands of aqueous $Cr(NH_3)_5(py)^{3+}$ brings about a red shift of the vis spectral maxima. Three isosbestic points (the positions of which change slightly with the type of excitation) persist in all cases up to at least 15% total conversion. Analysis of free ligands reveals that both pyridine and ammonia are photolyzed in parallel and to comparable extents:



$$Cr(NH_3)_5(py)^{3+} + H_3O^+ \xrightarrow{h\nu} Cr(NH_3)_5(H_2O)^{3+} + pyH^+ \qquad (2)$$

$$Cr(NH_3)_5(py)^{3+} + H_3O^+ \xrightarrow{h\nu} Cr(NH_3)_4(py)(H_2O)^{3+} + NH_4{}^+ \qquad (3)$$

The quantum yields for py and NH_3 photoaquation at 20 °C and pH 2.0 ($HClO_4$) upon LF and $\pi\pi^*$ excitation are collected in Table 2: each entry is the average of four or more runs. The values obtained by direct analysis of py and NH_3 agree, within experimental error, with those independently measured by HPLC analysis of pyH^+ and $Cr(NH_3)_4(py)(H_2O)^{3+}$.

As the latter complex could not be preparatively isolated for a UV spectral measurement, its HPLC determination was based on the reasonable assumption that the molar absorptivity at 260 nm is the same for $Cr(NH_3)_5(py)^{3+}$ and $Cr(NH_3)_4(py)(H_2O)^{3+}$: both these species, in fact, contain one py ligand responsible for absorption at this wavelength, where either $Cr(NH_3)_6{}^{3+}$ or $Cr(NH_3)_5(H_2O)^{3+}$ is quite transparent ($\epsilon < 5$ M^{-1} cm^{-1}). The assumption was validated by the concordance of the results for the two products of reaction 3.

HPLC also provides evidence that both *cis*- and *trans*-$Cr(NH_3)_4(py)(H_2O)^{3+}$ are photogenerated: the band of the aqua pyridine product is split into two peaks that are not fully separated, their maxima being only ca. 1 min apart in the chromatogram. The peak with the larger area has a longer retention time. It was not possible to establish with absolute certainty whether this corresponds to the cis or the trans isomer; however, experience with cation-exchange resins suggests a cis geometry for the major product, since the more polar cis complexes usually undergo slower elution than their trans counterparts. The peak areas allow an estimate of 20−30% trans isomer. Any possible difference between the isomer proportions on 470- and 254-nm excitation is hidden by the large variability arising from incomplete band resolution.

The two photoreactions are partially quenched by the above-mentioned emission quenchers. The results for $Cr(C_2O_4)_3{}^{3-}$ quenching are included in Table 2. For solubility reasons, these experiments were performed under conditions where only ca. 92% of the phosphorescence was quenched; given in the table are the quantum yields extrapolated to infinite quencher concentration as previously described.[32] The use of the tris(oxalato) ion proved advantageous in both the 470- and the 254-nm photolyses, because its spectral minima, occurring just in these regions, minimized the corrections for mixed absorption. In addition, the intrinsic photoreactivity of this complex, consisting of racemization only ($\Phi = 0.09$),[33] did not cause any analytical interference. The percentages of the two $Cr(NH_3)_4(py)(H_2O)^{3+}$ isomers under quenching conditions are within the range observed in the absence of quencher.

Table 3. Excited-State Bond Energies (cm^{-1}) of $Cr(NH_3)_5(py)^{3+}$ Calculated by Use of the Parameters[a] and Procedures of Refs 11 and 37

state (σ^* pop.)	$I^*(Cr{-}py)^{b}$	$I^*(Cr{-}NH_3)_{ax}$	$I^*(Cr{-}NH_3)_{eq}$
^4E (81% d_{z^2})	7 490	8 560	11 880
$^4B_2$ (100% $d_{x^2-y^2}$)	12 760	14 370	8 980

[a] $\sigma_{py} = 5800$ cm^{-1}; $\pi_{py} = -580$ cm^{-1}; $\sigma_{NH_3} = 7180$ cm^{-1}; $\pi_{NH_3} = 0$ cm^{-1}; $B = 700$ cm^{-1}. [b] Average values for the nonlinearly ligating pyridine ligand (see text).

The $Cr(NH_3)_6{}^{3+}$−py System. The spectrum of an equimolar aqueous solution of $Cr(NH_3)_6{}^{3+}$ and pyridinium is quite similar to that of $Cr(NH_3)_5(py)^{3+}$ (see Table 1) since the hexaammine ion absorbs very little in the 230−270 nm range where the absorption of the organic molecule occurs. Irradiation of this mixture at pH 2.0 into the py−localized band does not produce any observable effect on $Cr(NH_3)_6{}^{3+}$: neither phosphorescence nor NH_3 aquation is photosensitized by the uncoordinated heterocycle.

Discussion

LF Photolysis: Comparison with Theory. As a general remark, (pyridine)pentaamminechromium(III) is the first example of a $Cr(NH_3)_5X^{z+}$ complex where the LF photoaquation efficiency is larger for X than for NH_3. In fact, in all the pentaammines studied earlier, the quantum yields for photosolvation of the heteroligands were found to be lower, sometimes by orders of magnitude, than those for photosolvation of NH_3.[13,14] From another standpoint, the preferentially photosubstituted ligand is here the one lost in the thermal reaction, in contrast with the previous typically “antithermal” photolabilizations.

More specifically, the present unusual result can be primarily ascribed to the π-acceptor character of pyridine, as opposed to the π donation of all other common monodentate ligands, excluding CN^-. Significant π acceptance by the py ligands has been inferred from low-temperature, single-crystal electronic absorption and emission spectra, as well as from IR and Raman spectroscopy of *trans*-$Cr(py)_4F_2{}^+$.[4] Additional support has been found in the phosphorescent behavior of a group of *trans*-$Cr(py)_4AB^{z+}$ complexes (A, B = halogenides or H_2O) in various 77 K glasses.[9] The extent of π bonding has also been expressed quantitatively by LF spectral analysis of these complexes using the additive angular overlap model (AOM). The π_{py} parameter of the two-dimensional spectrochemical series for the Cr−py bond has been found to be negative (−580 cm^{-1}), denoting a considerable degree of π back-donation.[5] This conclusion has been the subject of some dispute:[34−36] our study then provides a test for this matter from a photochemical point of view and, in general, a test of the photolabilization theories for mixed-ligand complexes in a yet unexplored situation.

Not unexpectedly, the LF spectrum of $Cr(NH_3)_5(py)^{3+}$ is O_h-like, although in the actual C_{4v} symmetry the $^4T_{2g}$ state is anticipated to split into its $^4B_2$ and ^4E components. By using the σ_L and π_L AOM parameters of py and NH_3 given in Table

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3 (or the corresponding Dq_L values), the splitting is estimated as ca. 450 cm^{-1}.[11] The lowest quartet excited state, on the electron distribution of which all the models are focused, is determined to be ^{4}E, with most of its σ-antibonding charge (81% d_{z^2})[37] on the py$-$NH$_3$ z axis.

Both the early σ/π MO models[38,39] elaborated around the original notion of photolabilized axis[40] and the subsequent AOM development[37] correctly predict the observed photoreactivity (Table 2). The former qualitative approaches explain the preference for py release in terms of a general σ-bond weakening along the z direction, combined with the loss of π stabilization for py but not for NH$_3$: the d_{xz} and d_{yz} orbitals depleted by the $^4B_1 \rightarrow {}^4E$ transition are, in fact, π bonding toward π-acceptor ligands such as pyridine and nonbonding toward NH$_3$. These changes are quantified by the Vanquickenborne$-$Ceulemans methodology, whereby the excited-state bond energies I^*(Cr$-$L) are evaluated as a function of the σ_L and π_L AOM ligand parameters:[11,37] the I^* values are reported in Table 3. The finding that $\Phi_{py} > \Phi_{NH_3}$ is accounted for by the lowest strength of the Cr$-$py bond in the ^{4}E state.

While for our complex the expectations of the two types of models coincide, as has been pointed out,[11,37] this is not always the case. As mentioned earlier, a π-acceptor ligand that behaves in a different way is CN$^-$. The extremely strong ground-state σ component of the Cr$-$CN bond (described by the top value of σ_{CN}) is still dominant in the excited state(s) despite the decrease of its absolute magnitude: any possible competition between cyanide and other ligands due to π effects (π stabilization for π donors and π destabilization for CN$^-$) is thus completely obscured by the σ effects.[32,41] By contrast, since σ_{py} is in the central range of the σ_L parameters, the π_{py} contribution can play its role in competitive bond cleavage. The present results may therefore be taken as independent *chemical evidence* for Cr$-$py π back-bonding as deduced from spectroscopy.

Concerning the π_{py} value employed to calculate the I^* quantities of Table 3, it is worthwhile to recall that pyridine has been established to be a nonlinear π acceptor; i.e., in *trans*-Cr(py)$_4$AB^{z+} species, each py molecular plane forms an angle with the equatorial plane of the complex defined by the four Cr$-$N bonds.[5] The AOM parametrization then requires two terms related to π bonding,[5] and in principle, two different I^* values would be needed. The use of the average parameter $\pi_{py} = -580$ cm^{-1} given in the literature[5,11] appears the most reasonable approach, also in view of possible fast rotation of the py ligand in the pentaammine complex.

A last note is that preferential aquation of the formally weak-field ligand (py) on the formally weak-field axis (py$-$NH$_3$) does not comply with the historical photolysis rules of Adamson,[40] which would predict mainly NH$_3$ aquation. The rules were generally found to hold for systems with π-donor ligands (with the well-known exception of F$^-$),[11,13,14] the LF (and σ bonding) strengths of which tend to decrease as the extent of π donation increases.

Stereochemistry of NH$_3$ Photoaquation. HPLC definitely indicates formation of *both* Cr(NH$_3$)$_4$(py)(H$_2$O)$^{3+}$ isomers upon NH$_3$ photorelease, even though the uncertainty in their proportion is relatively large; furthermore, it suggests the cis configuration for the predominant isomer.

According to theory (Table 3), in the mainly axially antibonding ^{4}E state most of NH$_3$ would be lost from the coordination site trans to py.[11,37] The related stereochemical model[11,42] predicts *cis*-Cr(NH$_3$)$_4$(py)(H$_2$O)$^{3+}$ as the exclusive product of this photoaquation mode. Indeed, the likely cis configuration of the major product is congruent with the expectations, but the finding that also the other isomer is photogenerated is somewhat unexpected.

In the framework of this model, such a finding requires a more elaborate explanation. An alternative possibility for NH$_3$ loss is equatorial bond labilization, the obvious candidate of which is the upper $^4B_2$ state, σ antibonding entirely in the xy plane (Table 3). The proximity ($\sim 2RT$) of $^4B_2$ and ^{4}E would enable some population of $^4B_2$, whether in thermal equilibrium or in nonequilibrium proportion, the latter consequent to branching during relaxation from Franck$-$Condon states. The photoselection rules, however, anticipate a cis product for this mode also.[11,42]

The trans product would only arise from aquation of in-plane NH$_3$ in the lower ^{4}E state (where a 19% fraction of the σ^*-electron density is in the xy plane).[37] The reaction would take place through a trigonal bipyramid (tbp) with py in an equatorial position, obtained by bending of the py$-$Cr$-$NH$_3$ axis after departure of NH$_3$: the tbp would be generated in its $^4A_1$ excited state in which solvent attack would be allowed trans to the weaker-field py ligand. A sequence of this type was first proposed[11,43] when the unusual finding of 15% *trans*-Cr(NH$_3$)$_4$(H$_2$O)F^{2+} product in the photolysis of Cr(NH$_3$)$_5$F^{2+} [44,45] led to the recognition of the need for electronically excited tbp intermediates.

It should be kept in mind that, although there is now sufficient evidence for associative or concerted photolysis pathways in cationic Cr(III) complexes,[11−14] the predictions of the foregoing dissociative model have usually been found to hold. It has been argued[46] that these two aspects are not necessarily in contrast: the photoreaction intermediates may well be asymmetric heptacoordinated species where the departing and entering ligands are loosely bound, their motions being controlled by the same electronic driving forces that operate in the limiting dissociative picture.

The likelihood of a ^{4}E path leading to the trans isomer is corroborated by the fact that the calculated axial and equatorial Cr$-$NH$_3$ bond energies of Cr(NH$_3$)$_5$(py)$^{3+}$ in ^{4}E (Table 3) are not very different from those of Cr(NH$_3$)$_5$F^{2+} (9120 and 11 600 cm^{-1})[11] and are virtually identical to those of Cr(NH$_3$)$_5$(H$_2$O)$^{3+}$ (8590 and 11 860 cm^{-1}),[11] another complex for which formation of 10% trans photoproduct has been reported.[47]

It is quite possible that also in other Cr(NH$_3$)$_5$X^{z+} systems minor amounts (<10%) of trans products have previously gone undetected because of analytical inadequacy, as stereochemical analysis was generally based on LF absorption spectra, not always sufficiently different for the two Cr(NH$_3$)$_4$(H$_2$O)X^{z+} isomers. A further, and perhaps more important, limiting factor in this regard is the frequent, unavoidable formation of stereoretentive thermal products from either the reactant or the major photoproducts.

Finally, it should be noted that if there is any equatorial component of NH$_3$ loss, whatever the precursor state, then the

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preference for py labilization relative to axial NH_3 is even higher than inferred from the overall Φ values.

LF State Reactivity. The partial quenching of the photoreactivity of $Cr(NH_3)_5(py)^{3+}$ upon total doublet-state quenching conforms to the behavior of several chromium(III) am(m)ines.[13,14] While there is agreement in assigning the unquenchable (or fast) component to reaction from the lowest quartet excited state(s) in competition with intersystem crossing, the actual origin of the quenchable (or slow) component is still at issue. Customary hypotheses for the latter, doublet-mediated photochemistry have been (i) direct doublet reaction, (ii) crossing to the transition state of a ground-state reaction, and (iii) delayed reaction through the quartet state(s) following back intersystem crossing (bisc). Recent detailed studies of solvent, temperature, and pressure effects on the emission lifetime of *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ do support bisc as the main route of doublet-state depletion.[48] In relation to this point, the barrier to bisc that the slow photochemistry would have to overcome has been proposed[46] to be lowered by strong solvent−complex interactions, with respect to the value obtained spectroscopically, sometimes judged too high to be compatible with such a process. Bisc would lead to a sort of solvent-perturbed excited quartet species from which reaction would proceed.[46] The matter may be further complexed by the possible occurrence of long-lived seven-coordinate chemical intermediates deriving from the decay of the doublet (via bisc?),[49] which could be confused with the above excited species.

Returning to the quenching of the photochemical reactions, the patterns of various complexes giving rise to two[50−52] or even three[32] photoproducts have been recognized as good evidence in favor of bisc:[12,14,32] the same product distribution—including the stereochemistry—for the fast and slow pathways points to a common reactive entity, which can be only the quartet state(s).

At variance with these patterns stands our observation that in the LF photochemistry of $Cr(NH_3)_5(py)^{3+}$ the mode ratios are quite different for the unquenchable ($\Phi_{py}/\Phi_{NH_3} \sim 1$) and the quenchable ($\Phi_{py}/\Phi_{NH_3} = 0.21/0.11 \sim 2$) contributions. This clearly implies more than one reactive state, to say the least.

The simpler interpretation of this result envisages a doublet-state reaction, either direct or indirect via tunneling to a ground-state intermediate, in addition to a quartet-state reaction: the doublet is attributed a higher preference for py release (which is the more quenchable mode) compared with that of the quartet. The preference of the doublet (or an intermediate derived from it) for py aquation, which is also the thermal mode, is consistent with the electronic and structural similarities of the doublet and the ground state. Doublet reactivity would not be totally novel, as it has been demonstrated in the case of $Cr(bpy)_3^{3+}$.[53,54]

In light of current thinking, an alternative explanation is conceivable, however, based on an exclusive quartet-state reaction. In this view, the multiple states involved are, naturally, ^4E and $^4B_2$, which theory suggests are inclined to loss of py and NH_3, respectively (Table 3). Our findings can be accommodated by assuming that the partitioning of the excitation energy between these states consequent to bisc is different from the outcome of direct relaxation of Franck−Condon states. Such a relaxation, hence the fast photochemistry, may involve dissipation of excess vibrational energy along different reaction channels, as described by the DOSENCO theory.[55]

Either hypothesis is affected by some difficulty, however. In the first case, the genuine quartet chemistry would be characterized by $\Phi_{py} \sim \Phi_{NH_3}$, not in full agreement with the theoretical predictions discussed earlier. The second possibility is somewhat inconsistent with the aforementioned model for solvent-assisted bisc, which postulates population of the two quartet states via the two different routes “in the same or very similar non-Boltzmann proportions” because the solvation environments of the Franck−Condon quartet (believed to react mainly during relaxation) and the doublet states are thought to be very similar, both being similar to that of the ground state.[46] This picture would also rule out thermal equilibrium between $^4B_2$ and ^4E, notwithstanding the very small separation of these states in the present system.

In summary, the available data do not allow a definitive choice between the two alternatives, although the first appears more appealing; in order to gain further insight into the problem, a detailed investigation is planned on the wavelength and temperature dependence of the two LF reactive contributions.

UV Photolysis and Communication between LL and LF States. The 668-nm emission induced by irradiation of the py moiety of the complex, shows that the ligand-centered $\pi\pi^*$ states are partially converted to the Cr-centered LF states. The I_{260}/I_{467} ratio gives an efficiency $\eta_{IC} = 0.7$ for such an internal conversion, while the I_{352}/I_{467} value close to unity indicates that, as usual, within the LF manifold there is a virtually complete cascade of the excitation energy to the lowest excited state(s).

Independent information on η_{IC} can be obtained from the 254-nm photolyses. Table 2 shows that, on passing from LF to LL excitation, there is a change in both the absolute and the relative efficiencies of the two aquation modes, as well as in their quenchable fractions. Given that the quenchability, like the phosphorescence, is a peculiar LF property, the quantum yield for each photoreaction in the absence (Φ_{254}) and in the presence of quencher ($\Phi_{254}{}^Q$) can be expressed by

$$\Phi_{254} = \Phi_{LL} + \eta_{IC}\Phi_{LF} \qquad (4)$$

$$\Phi_{254}{}^Q = \Phi_{LL} + \eta_{IC}\Phi_{LF}{}^Q \qquad (5)$$

where Φ_{LL} refers to the photochemistry proceeding via the $\pi\pi^*$ states and Φ_{LF} and $\Phi_{LF}{}^Q$ are the data for 470-nm irradiation. Combination of eqs 4 and 5 yields $\eta_{IC} = 0.76 \pm 0.05$ for the py mode and $\eta_{IC} = 0.71 \pm 0.10$ for the NH_3 mode, both in good agreement with the emission results.

LL → LF internal conversion physically corresponds to energy migration from the peripheral pyridine molecule to the central chromium(III) ion. There is no evidence for such a transfer when the two species are not linked together; $Cr(NH_3)_5(py)^{3+}$ may then be regarded as a simple supramolecular system[56] where the highly absorbing py unit, per se nonemissive and only slightly photoreactive,[57,58] acts as an antenna and conveys a considerable fraction of its excitation energy to the Cr center which utilizes it in emission and chemical reactions.

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The Φ_{LL} quantities obtained from eqs 4 and 5 are 0.03 ± 0.01 for py and $<$0.01 for NH_3. In spite of the large uncertainty, some pyridine aquation can be concluded to originate from the LL state(s) or, at least, from states (e.g., CT) other than LF and to be accompanied by little or no NH_3 aquation, which would be entirely attributable to LF reaction. The labilization of pyridine in the LL state(s) can be accounted for by Cr−py bond weakening consequent to population of the π*(py) orbitals involved in the π acceptance of the d_{xz} and d_{yz} electrons of chromium(III).

Acknowledgment. This investigation was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica.

IC950904Z