Pentacyano(pyridine)chromate(III): Synthesis, Characterization, and Photochemistry

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The $Cr(CN)_5(py)^{2-}$ anion (py = pyridine) has been prepared by acid-promoted methanolysis of $Cr(CN)_6^{3-}$ followed by reaction with pyridine, isolated as the potassium salt, and characterized by absorption spectra (λ_{max}: 403 and 256 nm in H_2O; 411 nm in Me_2SO) and phosphorescence, observed in Me_2SO (λ_{max}, 774 nm; $\tau = 56$ μs at 20 °C) but not in H_2O. In acid aqueous solution the complex decomposes stepwise to $Cr(H_2O)_5(py)^{3+}$; by contrast, the thermal reaction in Me_2SO leads to $Cr(CN)_5(Me_2SO)^{2-}$ with first-order kinetics ($k_{25} = 9.8 \times 10^{-7}$ s^{-1}, $\Delta H^{\ddagger} = 138 \pm 8$ kJ mol^{-1}). Ligand-field (LF) band irradiation results in substitution of py and CN^-. The quantum yields, measured by ligand analysis, spectrophotometry, and HPLC, are as follows: $\Phi_{py} = 0.08$, $\Phi_{CN} = 0.01$ in H_2O (pH 7.2, phosphate buffer) and $\Phi_{py} = 0.04$, $\Phi_{CN} = 0.002$ in Me_2SO. The preference for py release obeys the prediction of the Vanquickenborne−Ceulemans, additive angular overlap model (AOM). A notable feature of this complex is that both types of ligands are π acceptors, and the π effect of py on bond labilization is evidenced by comparison with the photolysis of $Cr(CN)_5(NH_3)^{2-}$. Irradiation of the intense UV absorption due to overlap of charge-transfer (CT) and $\pi \rightarrow \pi^*$, py localized transitions causes the increase of both quantum yields, suggesting the involvement of higher-energy states besides the LF ones. $Co(sep)^{3+}$ (sep = 1,3,6,8,10,-13,16,19-octaazabicyclo[6.6.6]eicosane = sepulchrate) quenches the phosphorescence ($k_q = 1.6 \times 10^9$ M^{-1} s^{-1}) but has no effect on the photoreaction efficiencies: the photochemistry is thus inferred to originate entirely from the lowest quartet excited state(s) in competition with intersystem crossing. The marked solvent effects on the absorption spectrum, on the emission behavior, on the thermal reactivity, on the photolysis quantum yields, and, in particular, on the Φ_{py}/Φ_{CN} ratio, are discussed in terms of the proneness of the cyanide ligand to either protonation or hydrogen bonding and of solvent orientation toward anionic complexes.

Introduction

While cationic chromium(III) complexes of general formula $Cr(NH_3)_5X^{z+}$ have been extensively investigated with regard to their thermal and photochemical ligand substitution reactions, much less analogous information is available for their anionic counterparts, $Cr(CN)_5X^{z-}$. The pentacyanochromates(III) with X = H_2O,[1,2] OH^-,[3,4] Me_2SO,[5] DMF (dimethylformamide),[6] and MeCN[7] have been identified as the products of thermolysis[1,3,4] or photolysis[2,5−7] of $Cr(CN)_6^{3-}$ in the corresponding solvents, and that with X = NCS^- has been separated in solution from mixtures of $Cr(CN)_{6-n}(NCS)_n^{3-}$ anions formed by interaction of CN^- with $Cr(NCS)_6^{3-}$.[8,9] However, obstacles to the study of these compounds have been the difficult isolation of adequate quantities and, sometimes, the instability toward CN^- loss even in moderately acidic media.[1] The only pentacyano complexes thus far obtained as solid salts are $K_3[Cr(CN)_5(OH)]\cdot H_2O$[10] and $K_2[Cr(CN)_5(NH_3)]$,[11] the latter prepared and photochemically characterized in this laboratory.

As part of a program aimed at gaining knowledge of the ground-state and excited-state chemistry of chromium(III) cyano complexes, we have devised the synthesis of the pyridine (py) derivative $Cr(CN)_5(py)^{2-}$, explored its thermal reactivity, and studied its photophysical and photochemical behavior in water and Me_2SO. This work complements our earlier reports on the related species $Cr(CN)_5(NH_3)^{2-}$ [11] and $Cr(NH_3)_5(py)^{3+}$.[12]

As in the case of the pentacyanoammine analogue, the general interest for pentacyano(pyridine)chromate(III) arose from (i) the competition of two photosolvation modes, which appears to be much more solvent sensitive for anionic than for cationic complexes, (ii) the fairly long-lived solution phosphorescence at room temperature, and (iii) the wide energy gap between the photochemically important, lowest ligand-field (LF) excited states of quartet and doublet multiplicity. In addition, worthwhile to be photochemically examined was a property peculiar to the pyridine ligand, such as its π acceptance, expected to have some effect on the bond labilization pattern consequent to LF excitation. Regarding this feature, $Cr(CN)_5(py)^{2-}$ is the first chromium(III) system where *both* types of ligands are π acceptors. The investigation was also prompted by the search of indications on whether there is any particular role of py in a doublet-state reaction, a possibility that was suggested, but was not straightforwardly testable, in our previous investigation of $Cr(NH_3)_5(py)^{3+}$.[12]

Experimental Section

Materials. $K_3[Cr(CN)_6]$,[13] $(Ph_4P)_3[Cr(CN)_6]$,[14] $K_3[Cr(CN)_5(OH)]\cdot 2H_2O$,[15] and $[Co(sep)](PF_6)_3$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]eicosane = sepulchrate)[16] were prepared by literature methods. Pyridine was freed from water by refluxing it over KOH pellets; methanol was similarly treated with CaH_2. Both solvents were then distilled and stored under nitrogen atmosphere. Dimethyl sulfoxide (Me_2SO) was dried with 4−Å molecular sieves. Cation, anion, and gel-filtration chromatography was carried out by means of Sephadex SP C-25, QAE A-25, and G 15 resins, respectively.

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Potassium Pentacyano(pyridine)chromate(III). A 1.22-g portion of $(Ph_4P)_3[Cr(CN)_6]$ (1.0 mmol) was dissolved in 50 mL of anhydrous methanol and mixed with 10 mL of methanolic 0.10 M $(NH_2)SO_3H$. The solution was kept at 25 °C for 30 min in a stoppered flask, preventing contact with air moisture. Formation of $Cr(CN)_5(MeOH)^{2-}$ gradually turned the color from yellow to light orange. A 10-mL volume of pyridine was then added, and the mixture was heated at 50 °C for 60 min. The liquids were removed by rotary evaporation at 30 °C under reduced pressure, leaving an orange-yellow solid consisting of $(Ph_4P)_2[Cr(CN)_5(py)]$ and some unreacted $(Ph_4P)_3[Cr(CN)_6]$.

Chromatographic purification required conversion of the above water-insoluble salts into water-soluble species. A solution of these materials in ethanol (ca. 40 mL) was treated with 3.0 g of CH_3COOK with vigorous stirring. Solubilization of the latter was accompanied by precipitation of the potassium salts of the complexes, which was completed by cooling in a freezer for 1 h. The precipitate was separated by centrifugation and washed with ethanol. Some more product was recovered by evaporation of the alcoholic mother liquor, treatment of the solid with a little water extracting yellow extraneous species, and dissolution of the residue in ethanol followed by reprecipitation as above. A filtered aqueous solution (2−3 mL) of the combined crude products was eluted with water through a 35 × 1.5 cm column of G 15 resin. Two bands were obtained: the faster moving, brownish-yellow fraction carried $Cr(CN)_6^{3-}$ plus minor amounts of unidentified species, while the slower, bright-yellow main fraction consisted of $Cr(CN)_5(py)^{2-}$. When the band separation was incomplete, the overlapping portion was again eluted through the same column, after being reconcentrated. The eluates containing the pure product were rotary-evaporated at 30 °C to a 1−2-mL volume. Addition of 10 mL of 1-propanol precipitated a yellow solid that was collected by centrifugation, washed with ether, and vacuum-dried. All operations were performed in dim light. The overall yield was 120 mg, or 35% of the theoretical.

Anal. Calcd (found) for $K_2[Cr(CN)_5(py)]\cdot 2H_2O$: Cr, 13.85 (13.6); C, 31.99 (32.3); N, 22.39 (22.7); H, 2.42 (2.3); py, 21.07 (20.6).

Analyses and Instrumentation. The complexes were decomposed in aqueous 1 M $HClO_4$ at 80 °C for 10 min, causing acid-catalyzed removal of CN^-, otherwise firmly bound in neutral or basic media. (*Caution!* Me_2SO solutions must be diluted with water to ca. 5:1 before addition of concentrated $HClO_4$, so as to prevent possible explosion). After cooling, the samples were brought to pH ca. 13 with NaOH pellets and boiled for another 10 min to complete decomposition. Cr was determined spectrophotometrically at 374 nm, following oxidation to chromate with alkaline H_2O_2. Calibration with CrO_4^{2-} standards at pH 13 gave $\epsilon = (4.75 \pm 0.02) \times 10^3$ M^{-1} cm^{-1}. Py was determined on the same basic solutions by absorbance measurements at its 257−nm maximum ($\epsilon = 3050$ M^{-1} cm^{-1}), after filtration through 0.4 μm cellulose filters to eliminate the turbidity of $Cr(OH)_3$. C, H, and N were determined by standard organic microanalysis.

The free CN^- content of photolyzed solutions was measured potentiometrically by an Orion 94−06 selective electrode and a Radiometer PHM-84 potentiometer. The pH was adjusted to ca. 12 with NaOH. Dimethyl sulfoxide samples were diluted with water to 5:1 (with cooling) prior to analysis, in order to avoid damage and/or malfunction of the electrode. At this pH, $Cr(CN)_5(py)^{2-}$ is quite stable for a much longer period than that required for analysis, whereas some cyanide is slowly released from the aquo (not from the Me_2SO-solvated) products. Therefore, the amounts of CN^- were extrapolated to the time of alkalinization from several successive measurements. Each run was standardized by a series of fresh KCN solutions: within the 1.0−0.05 mM range, the reproducibility was ±5%.

Determination of photoreleased py required separation from the reaction mixtures by different procedures, depending on the aqueous or nonaqueous nature of the media. Aqueous solutions (1.5 mL) were eluted with water through 3 × 0.5 cm columns of anion exchanger, where all of the (negative) complexes were retained, while py and/or pyH^+ were fully recovered in 5.0-mL flasks containing 0.5 mL of 1.0 M NaOH: the resulting alkaline samples were then analyzed spectrophotometrically as above. In the case of Me_2SO solutions, it was necessary to eliminate the solvent, opaque below ca. 300 nm. Irradiated aliquots (1.5 mL) were diluted to 5.0 mL with aqueous 1.0 mM $HClO_4$, converting free pyridine to pyridinium ion, and loaded onto a 3 × 0.5 cm column of cation exchanger. A 10-mL volume of 1.0 mM $HClO_4$ moved out all Me_2SO together with the complex anions, but left pyH^+ adsorbed. By successive elution with 10 mM NaOH, this was displaced in the py form and completely collected for analysis in a 5.0-mL flask. When $Co(sep)^{3+}$ was employed as a quencher, the same eluant did not remove the adsorbed tripositive complex.

The photoproducts were also determined by HPLC techniques, using a Dionex GP40 chromatograph, an AD20 detector, and a 4600 integrator. For py analysis, the column was a 25 × 0.4 cm Omnipac PCX-500 cation exchanger, eluted by 0.2 M KCl in 2% $MeCN/H_2O$ at pH 3.0 (HCl), at a flow rate of 1.0 mL/min. Before injection, the samples were mixed with an equal volume of 10 mM HCl, turning the free ligand to pyH^+. Me_2SO, as well as the reactant and product complexes, passed with the solvent front; the pyridinium ion was then eluted in ca. 8 min and was measured by its 256-nm absorption maximum $\epsilon = 5500$ M^{-1} cm^{-1}). If present, $Co(sep)^{3+}$ did not interfere, as its elution time was >20 min. The method was standardized each time by pyH^+ solutions of known concentration. The reproducibility of all three types of py determination was better than ±3%.

For fractionation of the complexes, the HPLC column was a 25 × 0.4 cm Ionpac AS-11 anion exchanger, and the detection wavelength was 255 nm. Up to 60 s from injection the eluant was 30 mM/20 mM $NaClO_4$/NaOH; during the successive 180 s its concentration was linearly increased to 270 mM/20 mM 20 $NaClO_4$/NaOH; the flow rate was 1.5 mL min^{-1}. Typical retention times were ca. 120 s for $Cr(CN)_4(OH)(py)^{2-}$, ca. 200 s for $Cr(CN)_5(Me_2SO)^{2-}$, ca. 260 s for $Cr(CN)_5(OH)^{3-}$, and ca. 330 s for $Cr(CN)_5(py)^{2-}$. The free py of aqueous solutions was measurable as a peak eluted at ca. 60 s; in the case of Me_2SO solutions, this was hidden by the strongly absorbing solvent front.

Absorption spectra were measured by either a Cary 17 spectrophotometer or a Hewlett-Packard 8452A diode-array instrument. Phosphorescence spectra were recorded by a Perkin-Elmer 650-10S spectrofluorometer with an R928 photomultiplier. Emission lifetimes were determined 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 phototube, were fed into a Tektronix 468 oscilloscope and then least-squares processed. All samples used for absorption and emission measurements were filtered through 0.4−μm Millipore filters.

Procedures. The solvation reaction of $Cr(CN)_5(py)^{2-}$ in Me_2SO was followed spectrophotometrically at 453, 410, and 320 nm, with reference to the LF maxima of either the reactant or the product, using solutions ∼3 mM in complex. The temperature was controlled to ±0.1 °C, and the reaction was monitored for 3−5 half-lives. Rate constants were determined by nonlinear least-squares fits of 30 or more A_t data points to the expression: $A_t = A_\infty + (A_0 - A_\infty)\exp(-kt)$. In a given run, the results at the different wavelengths agreed to within ±2%. Also, the calculated and experimental (when measured) A_∞ values differed by less than 1% of the total absorption changes occurring during reaction. Activation parameters were obtained from least-squares analysis of $\log(k/T)$ vs $1/T$.

Photoreaction quantum yields were determined by a described apparatus,[17] equipped with a thermopile calibrated by Reineckate[18] and ferrioxalate[19] actinometers. Irradiation bands of 14-nm half-width were selected by a monochromator; incident intensities were around 5 × 10^{-9} einstein s^{-1}. Filtered samples of 2.5-mL volume, ∼3 mM in complex, were photolyzed in 1.0-cm cells at 20.0 ± 0.3 °C under

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stirring. Aqueous solutions were buffered at pH 7.2 (10 mM NaH_2PO_4 + 10 mM Na_2HPO_4). Light absorption was total at 254 nm and partial in the LF region: in the latter situation, the absorbed energy was evaluated as reported earlier.[20] Total photoconversion was generally 15−20%.

Phosphorescence and photolysis quenching in Me_2SO were performed by the use of 0.005−0.5 mM $Co(sep)^{3+}$. As the ∼400-nm LF spectral maximum of the substrate matches the minimum ($\epsilon = 15\ M^{-1}\ cm^{-1}$) of the Co(III) complex, at the most 3% of the radiation was absorbed by the quencher: consequently, correction for mixed absorption was within experimental uncertainty. In all cases, the possible thermal reaction background was taken into account by parallel analyses of photolyzed and dark samples.

Results

Synthesis. The key step in the preparation of pentacyano(pyridine)chromate(III) is the obtainment of substitutionally labile $Cr(CN)_5(MeOH)^{2-}$. A previously devised route to this intermediate was the photolysis of $Cr(CN)_6^{3-}$ in methanol, with the drawback of overly long irradiation periods and small absolute product yields.[11] The alternative procedure developed in this study, is H^+-promoted methanolysis of CN^- (eq 1),

$$Cr(CN)_6^{3-} + H^+ + MeOH \rightarrow Cr(CN)_5(MeOH)^{2-} + HCN \quad (1)$$

accomplished by interaction of equimolar amounts of hexacyanochromate(III) and sulfamic acid. Labilization of a single cyanide ligand by the protons of $(NH_2)SO_3H$ proceeds to at least 90% conversion in a relatively short time (∼30 min) and under very bland conditions (25 °C). The original LF absorption maximum at 382 nm gradually disappears, while a band grows at 435 nm. The red shift is in agreement with replacement of CN^- by a spectrochemically weaker O-coordinated ligand, and the persistence of three crossing points, which are nearly isosbestic (Figure 1, Supporting Information), is consistent with formation of a unique product. If excess sulfamic acid is employed, the process is no longer specific: the larger shifts and the evolution far from isosbestic indicate the loss of more CN^- groups.

The subsequent smooth reaction with pyridine (eq 2) is

$$Cr(CN)_5(MeOH)^{2-} + py \rightarrow Cr(CN)_5(py)^{2-} + MeOH \quad (2)$$

virtually complete in 1 h at 50 °C: thus, only two Cr(III) species of different charge and polarity are involved in the final chromatographic purification. The LF band now shifts back to the blue (403 nm), as expected when N replaces O coordination.

Worthwhile mentioning is the failure of all attempts to synthesize the complex from $Cr(CN)_5(H_2O)^{2-}$ and py in acidic aqueous media, by analogy with the preparation of the cobalt(III) species $Co(CN)_5(py)^{2-}$.[21] Even heterogeneous heating in pure pyridine, in the presence of $(NH_2)SO_3H$ preventing deprotonation of coordinated H_2O, led to mixtures containing insignificant quantities, if any, of the desired product. The use of other anhydrous acids, such as $KHSO_4$ and CCl_3COOH, was unsuccessful.

The crucial point is that the affinity of Cr(III) for N-donors relative to O-donors is lower than that of Co(III). Only weakly O-bonded ligands such as alcohols are readily substituted. Explorative work showed the potentiality of this method in further extending the $Cr(CN)_5X^{z-}$ series.

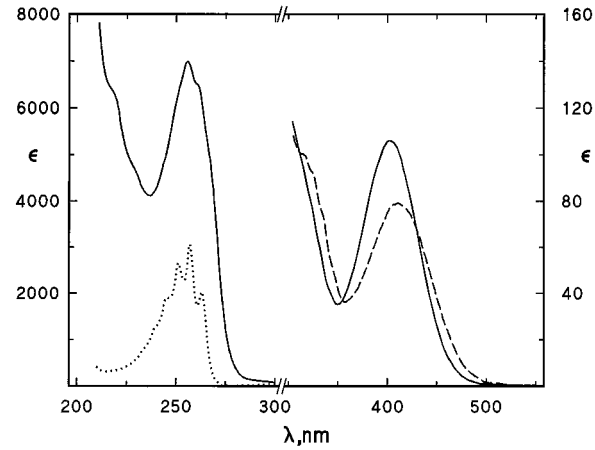

Figure 2. UV (left scale) and vis (right scale) absorption spectra of $Cr(CN)_5(py)^{2-}$ in water (solid line) and dimethyl sulfoxide (dashed line), and absorption band of pyridine (dotted line).

The new complex was characterized by elemental analysis, anion-exchange chromatography, absorption and emission spectra, and solution chemistry. The composition of the potassium salt gives a Cr:py molar ratio of 1.007 ± 0.005 and is congruous with two molecules of H_2O of crystallization. The 2− charge was verified by elution through the anionic resin with 1.5 M NaCl, an ionic strength insufficient to displace $Cr(CN)_6^{3-}$. Additional authentication is provided by the final product of acid-catalyzed CN^- aquation, $Cr(H_2O)_5(py)^{3+}$ (vide infra).

Absorption Spectrum. The UV−vis spectra of $Cr(CN)_5(py)^{2-}$ in aqueous and nonaqueous media are illustrated in Figure 2. The LF maximum at ca. 400 nm pertains to the $^4A_{2g} \rightarrow {}^4T_{2g}$ electronic transition in the O_h approximation. The higher-energy $^4A_{2g} \rightarrow {}^4T_{1g}$ band, normally observed in chromium(III), is, in this case, either totally (in H_2O) or partially (in Me_2SO) hidden by more intense UV absorptions. Table 1 reports the spectral maxima along with the data of related species. As found with other anionic complexes, there are appreciable solvent effects on both the position and the intensity of this LF band. The small bathochromic displacement with respect to $Cr(CN)_5(NH_3)^{2-}$ is congruent with py ($D_q = 1970\ cm^{-1}$) being a slightly weaker-field ligand than NH_3 ($D_q = 2155\ cm^{-1}$).[22,23] Considering the actual C_{4v} microsymmetry of the CrC_5N chromophore, the $^4T_{2g}$ state is postulated to split into its ^4E and $^4B_2$ sublevels. Nevertheless, no splitting of the LF band is apparent because of the small energy separation between the components, as usual for CrA_5X-type complexes.

The strong UV absorption observable in H_2O and obscured in Me_2SO, besides its maximum at 256 nm, presents shoulders at 261 ($\epsilon = 6500\ M^{-1}\ cm^{-1}$), 230 ($\epsilon = 4500\ M^{-1}\ cm^{-1}$), and 218 nm ($\epsilon = 6250\ M^{-1}\ cm^{-1}$). Assignments can be made by analogy with the spectra of $Cr(CN)_5(NH_3)^{2-}$ and $Cr(NH_3)_5(py)^{3+}$. In the pentacyanoammine species, the maximum at 251 nm and the shoulders at 263 and 220 nm have been attributed to charge-transfer (CT) transitions involving cyanide, on the grounds of their close similarity to the features of $Cr(CN)_6^{3-}$ and of their disappearance upon aquation of all CN^- groups.[11] The direction of the charge shift was originally concluded to be metal-to-ligand, i.e., $t_{2g}(\pi,Cr) \rightarrow t_{1u}(\pi^*,CN)$;[24] however, this interpretation was later questioned, and the ligand-to-metal character, namely, $t_{1u}(\sigma,CN) \rightarrow t_{2g}(\pi,Cr)$, was proposed.[14,25] In

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Table 1. Spectral Absorption and Emission Data

species	solvent	absorption: λ, nm (ϵ, M^{-1} cm^{-1})[a]			$^2E_g \rightarrow {}^4A_{2g}$[b] emission		ref
		$^4A_{2g} \rightarrow {}^4T_{2g}$[b]	CT[c]	$\pi\pi^*$(py)	λ, nm	τ_{20}, μs	
$Cr(CN)_5(py)^{2-}$	H_2O	403 (106)	256 (7000)				*d*
	Me_2SO	411 (79)			774	56 ± 1	*d*
$Cr(CN)_5(NH_3)^{2-}$	H_2O	397 (90)	251 (3300)				11
	Me_2SO	406 (77)			777	32	11
$Cr(CN)_5(Me_2SO)^{2-}$	Me_2SO	453 (98)[e]			767		*d*
$Cr(NH_3)_5(py)^{3+}$	H_2O	467 (41)		260 (2900)	668	2	12
	Me_2SO	468 (44)			668		*d*
py	H_2O			257 (3050)			26

[a] ±1%. [b] O_h approximation. [c] Controversially assigned as either $t_{2g}(\pi,Cr) \rightarrow t_{1u}(\pi^*,CN)$ [24] or $t_{1u}(\sigma,CN) \rightarrow t_{2g}(\pi,Cr)$.[14,25] [d] This work. [e] $^4A_{2g} \rightarrow {}^4T_{1g}$ at 339 nm (ϵ = 47 M^{-1} cm^{-1}).

the pentaammine(pyridine) species, the resemblance of the 260-nm peak with that of free pyridine[26] identifies py-localized, fully allowed $\pi \rightarrow \pi^*$ transitions.[12] The two types of absorption are superimposed in our complex, as can be deduced from the magnitude of the molar absorptivity around 260 nm, comparable with the sum of those of the two reference compounds. An additional, confirmatory element is that, after removal of all cyanides to yield $Cr(H_2O)_5(py)^{3+}$, the UV spectrum becomes very similar in shape and intensity to that of $Cr(NH_3)_5(py)^{3+}$: specifically, a less intense, sharper band persists at 260 nm, while the shorter-wavelength shoulders vanish.

Solution Chemistry. Aqueous and nonaqueous solutions of the complex are distinguished by quite different substitutional reactivities.

In water, if the medium is either neutral (phosphate buffer) or alkaline, the constancy of the spectrum for at least 24 h at room temperature denotes high inertness toward ligand loss. By contrast, acidification results in proton-assisted release of all the cyanide groups (eq 3).

$$Cr(CN)_5(py)^{2-} + 5\ H_3O^+ \rightarrow \rightarrow \rightarrow Cr(H_2O)_5(py)^{3+} + 5\ HCN \quad (3)$$

The LF absorption bands progressively move to the red and decrease in intensity. The drift of the spectral crossing points reveals a reaction cascade that ultimately leads to the pentaaqua-(pyridine) complex. This presents maxima at 558 (ϵ = 22 M^{-1} cm^{-1}), 402 (ϵ = 24 M^{-1} cm^{-1}), and 260 nm (ϵ = 3500 M^{-1} cm^{-1}), close to the values given in the literature for $Cr(H_2O)_5(py)^{3+}$ prepared by an independent procedure.[27]

The complexity of the reaction chain precluded any kinetic measurement: however, it was qualitatively observed that cyanide loss becomes slower and slower as more ligands are removed, as in the course of the acid-induced aquation of $Cr(CN)_6^{3-}$.[1] In 0.2 M $HClO_4$, the first two CN^- groups (as judged from the position of the LF band reflecting the average field strength of the six ligands) are replaced in ca. 10 min at 25 °C; complete aquation of all cyanides requires ca. 40 h in 1.0 M acid. The terminal spectrum is then stable for at least 10 days.

In dimethyl sulfoxide solution, the only detectable process is solvation of the py ligand (eq 4). As shown in Figure 3

$$Cr(CN)_5(py)^{2-} + Me_2SO \rightarrow Cr(CN)_5(Me_2SO)^{2-} + py \quad (4)$$

(Supporting Information), three sharp isosbestic points are now maintained at 424, 368, and 351 nm until the displacement of the heterocycle is complete. The nature of the reaction is confirmed by the final analysis of free pyridine, which amounts to 99.5 ± 0.7% of that originally present in the complex. The LF absorption spectrum of the product, with maxima at 453 (ϵ = 98 M^{-1} cm^{-1}) and 339 nm (ϵ = 47 M^{-1} cm^{-1}), then remains unaltered for at least 8 more half-lives.

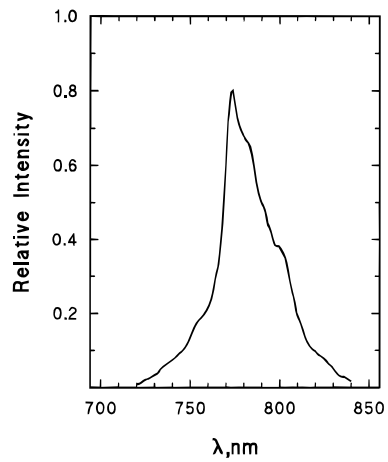

Figure 4. Phosphorescence spectrum of $Cr(CN)_5(py)^{2-}$ in dimethyl sulfoxide solution at room temperature.

The spectral variations obey plain first-order kinetics: solvation rates were measurable at several wavelengths, up to more than 90% conversion. At the temperatures of 45, 60, 75, and 90 °C, the rate constants k, averaged from at least three independent runs, are (3.31 ± 0.15) × 10^{-5}, (4.04 ± 0.06) × 10^{-4}, (3.22 ± 0.10) × 10^{-3}, and (2.52 ± 0.08) × 10^{-2} s^{-1}, respectively, yielding the activation parameters $\Delta H^{\ddagger}$ = 138 ± 8 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 102 ± 24 J mol^{-1} K^{-1}. The activation enthalpy, unusually large for chromium(III), attests to the considerable inertness of this complex, which was advantageous in the photolytic experiments in Me_2SO. Extrapolation at 25 °C gives k = 9.8 × 10^{-7} s^{-1}.

The selectivity of reaction 4 enabled an accurate determination of the LF spectrum of $Cr(CN)_5(Me_2SO)^{2-}$ (Table 1), which had been approximately reported as absorption changes of irradiated Me_2SO solutions of $Cr(CN)_6^{3-}$.[5]

Photophysics. Like the $Cr(CN)_6^{3-}$ and $Cr(CN)_5(NH_3)^{2-}$ anions, $Cr(CN)_5(py)^{2-}$ does not luminesce in aqueous solution at room temperature. On the contrary, in dipolar aprotic media it exhibits a moderately intense, narrow, and structured emission band with maximum at 774 nm in Me_2SO (Figure 4) and 772 nm in DMF, close to the 777-nm (in both solvents) peak of the pentacyanoammine analogue.[11] The emission is clearly attributable to $^2B_1/^2A_1 \rightarrow {}^4B_1$ phosphorescence from the CrC_5N metal center.

The emission decay in Me_2SO is monoexponential, with τ = 56 ± 1 μs at 20 °C, comparable with the value of 32 μs for $Cr(CN)_5(NH_3)^{2-}$ in the same solvent.[11]

(26) *UV Atlas of Organic Compounds*; Verlag Chemie: Weinheim, Germany, 1971.
(27) Bakač, A.; Orhanović, M. *Inorg. Chem.* **1971**, *10*, 2443.

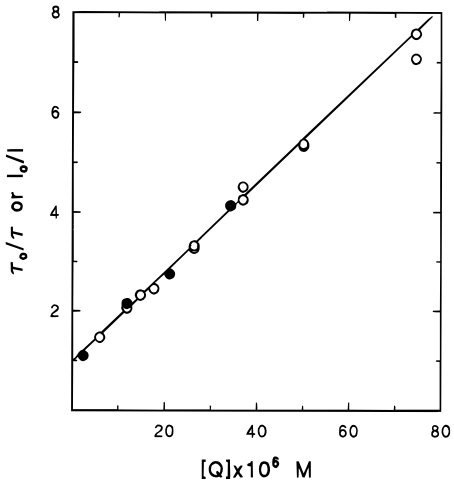

Figure 5. Stern−Volmer type plot for quenching of the emission lifetime (●) and intensity (○) of $Cr(CN)_5(py)^{2-}$ by $Co(sep)^{3+}$ in dimethyl sulfoxide solution at 20 °C.

The phosphorescence is efficiently quenched by $Co(sep)^{3+}$. While other cobalt(III) ammines were found to be good quenchers, the sepulchrate complex was chosen since its cage ligand warrants complete inertness, ruling out undue complications such as reactive quenching or photosensitized reactions. Stern−Volmer plots for both lifetime and intensity quenching are linear and coincident (Figure 5). The agreement excludes significant static quenching through ion pair formation between oppositely charged species. The highest $[Co(sep)^{3+}]$ used (able to quench 90% of the emission) was only 3% of the concentration of the substrate, which sets an upper limit to the degree of ion pairing. The quenching rate constant in Me_2SO is $k_q = 1.6 \times 10^9$ M^{-1} s^{-1} at 20 °C. The interaction is very likely one of energy transfer, on account of the diffusional order of magnitude of the bimolecular parameter and the energy matching of the donor and acceptor levels. The lowest triplets of cobalt(III) amines are, in fact, around 13 000 cm^{-1} or 770 nm.[28]

Photochemistry. Photolyses were performed both in water and in Me_2SO. The pH of 7.2, at which the aqueous samples were buffered, was sufficiently high to inhibit acid-induced thermal loss of CN^-, yet low enough to obtain the photoproducts as aqua complexes, far more inert than the hydroxo forms. The pK_a of $Cr(CN)_5(H_2O)^{2-}$ is, in fact, 9.0,[3,10] and the acidity of $Cr(CN)_4(py)(H_2O)^-$ is presumed to be of the same magnitude. Table 2 is a collection of the photoreaction quantum yields at 20 °C for various experimental conditions.

LF band irradiation causes parallel replacement of pyridine and cyanide by a solvent molecule S (eqs 5 and 6), as revealed

$$Cr(CN)_5(py)^{2-} + S \xrightarrow{h\nu} Cr(CN)_5S^{2-} + py \quad (5)$$

$$Cr(CN)_5(py)^{2-} + S \xrightarrow{h\nu} Cr(CN)_4(py)S^- + CN^- \quad (6)$$

by analysis of the released ligands. Congruent with both processes is the bathochromic shift of the LF maximum. In aqueous solution, well-defined isosbestic points initially persist at 412, 365, and 337 nm. In Me_2SO, the spectral evolution is very similar to that accompanying the thermal loss of py: in particular, above 400 nm it is virtually the same, with a sharp crossing at 424 nm, while at shorter wavelengths the absorption curves decrease slightly in intensity rather than being nearly tangent in the 350−370 nm region (compare Figure 3, Supporting Information).

With regard to photoreaction 5, the Φ_{py} values based on direct determination of pyridine agree, within error limits, with those measured by HPLC analysis of either $Cr(CN)_5(H_2O)^{2-}$ or $Cr(CN)_5(Me_2SO)^{2-}$. Independent preparation of both of these complexes allowed instrumental calibration. In Me_2SO solution, an assessment of Φ_{py} was also made from difference spectra recorded at several photolysis intervals. This mode, which makes up ca. 95% of the photoreactivity in this solvent, is the same as the thermal mode, the product of which has been spectrally characterized in the course of this work (vide supra). The values calculated with the plausible assumption that the variations around 450 nm for the CN^- and py modes are not exceedingly different were compatible with the data of Table 2.

As to photoreaction 6, the large variability of Φ_{CN} arises from the inherent limitations in determining small quantities of cyanide ion, especially in the experiments in Me_2SO. The HPLC chromatograms of photolyzed aqueous samples (where CN^- release is less exiguous) do show the accrual of a peak other than those of $Cr(CN)_5(py)^{2-}$ and $Cr(CN)_5(H_2O)^{2-}$, assigned by exclusion to the tetracyano photoproduct. However, $Cr(CN)_4(py)(H_2O)^-$ is unknown and could not be preparatively isolated for standardization. In any case, an HPLC estimate of Φ_{CN} was attempted, taking as upper and lower extremes for the absorptivity around 260 nm of $Cr(CN)_4(OH)(py)^{2-}$ (the eluant is alkaline) the values of $Cr(CN)_5(py)^{2-}$ ($\epsilon = 7000$ M^{-1} cm^{-1}) and $Cr(CN)_5(OH)^{3-}$ ($\epsilon = 3000$ M^{-1} cm^{-1}, measured in this study). The interval thus established consistently contains the quantum yields obtained from direct CN^- determination.

Irradiations at 254 nm were only carried out in air-equilibrated aqueous solution, as Me_2SO is not transparent in this region. Determination of the free ligands and of the aquated complexes again shows the simultaneous occurrence of processes 5 and 6. While the spectral changes above 380 nm resemble those induced by LF excitation, a very strong absorption develops at shorter wavelengths, with maximum at 365 nm. Such a band grows when pyridine is directly irradiated under identical conditions and is ascribed in the literature to formation of the photohydration product 5-amino-2,4−pentadienal with a quantum yield of 0.03.[29,30] Analysis of the increasing rate of appearance in the course of the photolysis of the complex imputes this species entirely to secondary photochemistry of the free heterocycle. On the basis of the known spectrum of the amino aldehyde ($\epsilon_{365} = 4 \times 10^4$ M^{-1} cm^{-1}),[30] it is concluded that no more than 1−2% of primary pyridine is lost by this process, a fraction that is well within analytical accuracy.

HPLC indicates that in the LF photolysis ca. 95% of the product of reaction 6 consists of one of the two possible $Cr(CN)_4(py)(H_2O)^-$ isomers. The band associated with this product is followed by a minor peak ca. 25 s apart, attributable to the other isomer (that is likely to have a comparable UV absorption). The peak ratio of ca. 20:1 remains constant from the beginning of photolysis up to about 15% conversion, ruling out the possibility that the minor product be due to either secondary photoreactions or thermal processes. The latter occurrence is also excluded by parallel tests on dark samples. A secondary photoprocess does show up as a new band (eluting at ca. 170 s), appearing at longer irradiation times and growing at a faster rate. The 254-nm photolysis gives rise to the same products; the faster moving isomer is still dominant, but the peak ratio is, in this case, only 5.5:1. The lack of authentic

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Table 2. Photolysis Quantum Yields of Pentacyanochromates(III) at 20 °C

complex	medium[a]	λ_{irr}, nm (state)	Φ_N[b,c]	Φ_{CN}[c]	Φ_N/Φ_{CN}
$Cr(CN)_5(py)^{2-}$	H_2O, pH 7.2	400 (LF)	0.078 ± 0.005 (6)	0.011 ± 0.002 (5)	~7
	H_2O, pH 7.2	254 (CT)	0.103 ± 0.006 (6)	0.015 ± 0.003 (3)	~7
	Me_2SO	400 (LF)	0.037 ± 0.005 (11)	0.002 ± 0.001 (4)	~20
	Me_2SO, *Q*	400 (LF)	0.036 ± 0.005 (5)	0.002 ± 0.001 (4)	~20
$Cr(CN)_5(NH_3)^{2-}$	H_2O, pH 7.2	400 (LF)	0.08[d]	0.06[d]	1.3
	Me_2SO	400 (LF)	0.05[d]	0.007[d]	7

[a] *Q* denotes ~5 × 10^{-4} M $Co(sep)^{3+}$ as emission quencher. [b] N denotes either py or NH_3. [c] Number of independent experiments in parentheses; the uncertainties are standard deviations. [d] Reference 11.

samples of *cis*- and *trans*-tetracyano complexes precludes any definitive isomeric assignment.

Several quantum yield measurements in Me_2SO were made in the presence of concentrations of $Co(sep)^{3+}$ able to quench 96−98% of the phosphorescence. The results are given in Table 2. Within the inevitable experimental imprecision, both the py and CN^- photosolvation efficiencies are unaffected by the Co(III) complex. Concerning this point, particularly relevant are the same sequential changes of expanded-scale difference spectra of samples with and without quencher, undergoing identical alternate irradiations.

Discussion

LF Photolysis. In our former studies of the competitive labilization of two different Cr−L bonds, various π bonding situations have been encountered, as classified according to the positive (for π donors), zero (for π noninteracting ligands), or negative (for π acceptors) values of the π_L parameters of the two-dimensional spectrochemical series. Examples are as follows: $Cr(NH_3)_5Cl^{2+}$ ($\pi_{NH_3} = 0$, $\pi_{Cl} > 0$);[31] $Cr(NH_3)_5(py)^{3+}$ ($\pi_{NH_3} = 0$, $\pi_{py} < 0$);[12] *trans*-$Cr(NH_3)_4(NCS)Cl^+$ ($\pi_{NCS} > 0$, $\pi_{Cl} > 0$);[17] *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ ($\pi_{NCS} > 0$, $\pi_{CN} < 0$).[32] From this standpoint, $Cr(CN)_5(py)^{2-}$ ($\pi_{CN} < 0$, $\pi_{py} < 0$) represents a novel case, completing the set of all possible combinations of π interactions.

The π acceptor character of the pyridine ligand has been deduced from IR and Raman data,[33] as well as from low-temperature absorption[33] and emission[34] spectra of various *trans*-$Cr(py)_4XY^{z+}$ complexes. Its magnitude has been quantified by the parameter $\pi_{py} = -580$ cm^{-1}, obtained from analysis of the LF spectra in terms of the additive angular overlap model (AOM).[23] There has been some controversy on the matter.[35,36] Supplementary chemical evidence for Cr−py π back-bonding has been provided by our recent investigation of $Cr(NH_3)_5(py)^{3+}$, the first $Cr(NH_3)_5X^{z+}$-type complex where X photosolvation was found to be more efficient than NH_3 photosolvation.[12]

The overall quantum yields for the LF photolysis of $Cr(CN)_5(py)^{2-}$ are ca. 0.10 in H_2O and ca. 0.04 in Me_2SO: such values, as well as their reduction on passing from water to the aprotic solvent, are in line with those for $Cr(CN)_6^{3-}$ (0.12[2] and 0.03[11]) and $Cr(CN)_5(NH_3)^{2-}$ (0.13 and 0.06).[11] The photosolvation efficiencies of chromium(III) cyano complexes thus definitely appear to be below the 0.3−0.5 range, typical of the acidoam(m)ines.

Pyridine release is largely prevalent upon LF excitation. This result once again confirms the predictive ability of the Vanquickenborne−Ceulemans model,[22,37] already validated by the photolytic behavior of other $Cr(CN)_5X^{z-}$-type anions.[11] The model evaluates the excited-state bond energies, I^*(Cr−L), as a function of the σ_L and π_L AOM parameters, focusing in particular on the lowest excited quartet, acknowledged as the main precursor to the photochemistry of chromium(III).[22,38,39] For $Cr(CN)_5(py)^{2-}$, such a state is anticipated to be ^4E, associated with a high σ^* electron density along the py−CN, *z* axis. According to the I^* values reported in Table 3, the most weakened bond in this state is Cr−py, in agreement with experimental observation.

Table 3. Spectrochemical AOM Parameters and Bond Energies in the Ground (*I*) and Excited States (*I**) of $Cr(CN)_5(py)^{2-}$, Calculated According to the Vanquickenborne−Ceulemans Model[22,37]

quantity,[a] cm^{-1}	L: py	L: CN_{ax}^-	L: CN_{eq}^-
σ_L[b]	5 800	8 480	8 480
π_L[b]	−580	−290	−290
I(Cr−L) in $^4B_1$	10 440	16 380	16 380
I^*(Cr−L) in ^4E	7 060	9 760	14 780
I^*(Cr−L) in $^4B_2$	12 760	17 540	10 890

[a] The LF parameter $B = 550$ cm^{-1} is more suited to cyanochromates(III) than the value of 700 cm^{-1} generally used for chromium(III) am(m)ines (see: Perumareddi, J. R. *Coord. Chem. Rev.* **1969**, *4*, 73); the difference, however, does not modify the relative bond energies. [b] Data from ref 22.

The influence of the π acceptance of pyridine on the photolabilization pattern clearly emerges from a scrutiny of the previous results with $Cr(CN)_5(NH_3)^{2-}$,[11] included in Table 2. In $Cr(CN)_5X^{2-}$ ions, the ^4E state is formed by even depopulation of the d_{xz} and d_{yz} orbitals and accumulation in d_{z^2} of 0.88 and 0.82 electron fractions for X = py and X = NH_3, respectively.[37] This σ-antibonding charge weakens the Cr−N bonds of the two complexes to a similar degree. Since d_{xz} and d_{yz} are π bonding toward py and nonbonding toward NH_3, the depletion of these orbitals removes the extra π stabilization of py but has no effect on NH_3. As a matter of fact, for X = py the Φ_X/Φ_{CN} ratio is ~7 in H_2O and ~20 in Me_2SO, to be compared with the corresponding values of 1.3 and 7 for the X = NH_3 complex.

As py and CN^- are *both* π acceptors, and both lose σ and π stabilization, the preferential mode would be hardly predicted by the earlier σ/π MO qualitative models,[40,41] which only consider the variation of the σ and π bond strengths caused by the electronic transition: the overall effect cannot be established unless the starting bond energies of each ligand are taken into account.[22,37] It may also be noted that the original Adamson's

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rules,[42] which have stimulated much experimental and theoretical development,[22,38,39] would foresee prevalent loss of the strong-field ligand (CN^-) on the weak-field axis (py−CN). The basic reason for these inadequacies resides in the large σ-bond strength of CN^- (expressed by the extreme value of σ_{CN}), which remains a determining component, in spite of its reduction on passing from the ground to the excited state(s). With reference to the calculated[22,37] ground-state quantities of Table 3, it is seen that, even though in the $^4B_1 \rightarrow {}^4E$ transition axial CN^- loses twice as much bonding energy as py, the net outcome is Cr−py bond weakening.

Considering in detail the photorelease of CN^-, the theory (Table 3) anticipates that the most labilized position is the one trans to py. Naturally, this point could not be tested: even if the possible products were known, the customary stereomobility of chromium(III) photosubstitutions[22,38,39] would, in principle, thwart any unequivocal steric conclusion. At the most, it may be recognized that the rather specific (∼95%) formation of one $Cr(CN)_4(py)(H_2O)^-$ isomer is compatible with the stereochemical extension of the AOM model,[22,43] which envisages formation of a single tetracyano isomer as a consequence of axial ligand loss in the ^4E state. The photoselection rules predict a cis configuration for this product; accordingly, the minor product would be trans. The latter would be uniquely attributable to aquation of equatorial CN^- still from the ^4E state:[44] in fact, although the upper $^4B_2$ state, the other possible photochemical precursor, is exclusively antibonding on the equatorial plane (Table 3), it is theoretically expected to lead to cis products only.[43]

UV Photolysis. On passing from 400- to 254-nm irradiation, both Φ_{py} and Φ_{CN} increase by 30%; in addition, the photoaquation of CN^- becomes less stereoselective, in that the abundance of the main $Cr(CN)_4(py)(H_2O)^-$ isomer drops to ca. 85%. This is taken to indicate the participation of higher-energy states besides the LF one(s). The experiments were, of necessity, restricted to aqueous solutions: the absence of emission (a peculiar LF property) in this medium unfortunately prevents any estimate of the efficiency of population of the LF state(s) following 254-nm excitation. Another difficulty arises from the complete overlap of the UV absorptions associated with the py and CN^- ligands.

As far as the photosubstitution of pyridine is concerned, any possible contribution to Φ_{py} by the py-localized π^* state can be attributed to Cr−py bond weakening induced by population of the π^*(py) orbitals acting as acceptors of the metal d_{xz} and d_{yz} electrons.

For the increase of Φ_{CN} in the UV region, it is natural to relate to the CT character of the excitation affecting cyanide, supposed to promote homolytic Cr−CN bond cleavage. The observed substitutional-type products would result from back-transfer of the optically driven electron before the unstable radical fragments separate from the solvent cage. The contrasting literature assignments of the charge shift, either Cr → CN[24] or CN → Cr,[14,25] leave some uncertainty as to the postulated primary formation of either Cr(IV) or Cr(II) species. The second possibility finds support in the reported detection of $Cr(CN)_6^{4-}$ upon UV flashing of alkaline $Cr(CN)_6^{3-}$ in the presence of excess CN^-.[45] This aspect was not further investigated: anyhow, the lower degree of stereospecificity of this photolysis with respect to the LF photolysis is consistent with the nondirectionality of bond labilization expected for that part of CN^- having CT origin.

Role of the LF Excited States. Hints on the reactive or nonreactive function of the lowest doublet state of chromium(III) have often been sought in quenching experiments:[38,39] our observations in Me_2SO solution bear on this issue.

For the widely studied am(m)ine complexes, a portion of the photochemistry is usually quenched on complete quenching of the luminescent doublet. The unquenchable, fast contribution has unanimously been ascribed to reaction from the short-lived quartet excited state(s) in competition with intersystem crossing, whereas there is still some debate about the quenchable, slow contribution mediated by the longer-lived doublet(s). The choice is essentially restricted to two alternatives: (A) doublet state reaction, either direct or via tunneling to a ground-state chemical intermediate, and (B) delayed quartet reaction consequent to back intersystem crossing (bisc). In favor of the second possibility argues much of the evidence gathered thus far, like the detailed data on the solvent, temperature, and pressure dependence of the photophysics and photochemistry of *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ [46] and $Cr(NH_3)_6^{3+}$,[47] and the same proportion of products[32,48,49] (even isomeric products)[50,51] for the quenched and unquenched photolysis components, which suggests a common reactive entity. Obviously, in this class of compounds bisc is allowed on energetic grounds; moreover, it has been proposed that the actual barrier to this process may be lowered, with respect to that inferred from spectroscopy, by strong solvent−complex interactions affecting the quartet and doublet states to different extents.[52]

The situation is different for the pentacyano complexes: the combined top LF strength and large nephelauxetic effect of the CN^- ligands raise the quartet(s) and depress the doublet(s), respectively. The energy separation can be estimated from the doublet emission and the quartet absorption, using for the latter the 5% empirical procedure.[53] The ca. 9000-cm^{-1} gap of $Cr(CN)_5(py)^{2-}$ is much wider than the ca. 4000−cm^{-1} gap of $Cr(NH_3)_5(py)^{3+}$.[12] The value is too large to permit bisc, even allowing for its possible reduction by solvent intervention. Pathway B is thus excluded. The fact that doublet quenching has no effect on both photoreactions also excludes pathway A in our complex; that is, all of the photochemistry is "fast" and has its origin in the quartet state(s) whether during or after vibrational equilibration.

This result adds to previous findings with $Cr(CN)_6^{3-}$ [6] and $Cr(CN)_5(NH_3)^{2-}$:[11] when the excitation energy is "trapped" in the doublet, it is not utilized chemically. The converse, i.e., when bisc is allowed, pathway B is the only possibility, might be fairly common, albeit not absolutely general. Suggestive in this sense is the circumstance that for various simple ammine complexes (having an overall photoreaction efficiency of 0.3−0.4) the unquenchable yields are around 0.1,[32,48,51] just like the total (and unquenchable) yields of the cyano complexes. Other factors being equal, the photochemistry "missing" in the cyanides would be that transpiring when the electronic energy

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can "escape" the doublet via bisc. On the other hand, there are amine-type systems where some or much of the chemistry was concluded to proceed from the doublet, as in $Cr(bpy)_3^{3+}$ [54,55] and *cis*-$Cr(cyclam)(NH_3)_2^{3+}$, the latter demonstrated to react through a seven-coordinate ground-state intermediate.[56]

One purpose of this work was to look for clues on whether pyridine is, for some reason, prone to being photolabilized in the doublet state. This was urged by our apparently anomalous observation that in the LF photolysis of $Cr(NH_3)_5(py)^{3+}$ the quenchable Φ_{py}/Φ_{NH_3} ratio is larger than the unquenchable one.[12] A conceivable alternative was that relaxation of Franck−Condon states and bisc populate ^4E and $^4B_2$ in different proportions. Although indirectly, the nonquenchability of the py mode in the present system supports the second explanation.

Solvent Effects. All properties investigated, namely, thermal solvation, absorption spectrum, emission behavior, and competitive ligand photolabilization, exhibit a pronounced solvent dependence, as was noticed with the congeneric mixed-ligand $Cr(CN)_5(NH_3)^{2-}$ anion.[11] A rationale for these effects is the susceptibility of the basic cyanide ligand to either protonation or hydrogen bonding. Of course, this is likely not to be the sole factor, but its weight is certainly dominating in all cases.

The contrast between the substitution modes of eqs 3 and 4 stems from the availability of protons in H_2O but not in Me_2SO. The high strength of the Cr−CN bond (see the *I*(Cr−L) ground-state energies on Table 3) is markedly reduced by proton uptake: consequently, the leaving ability of the ligands assumes the order CNH ≫ py > CN^-, so that even small equilibrium amounts of protonated complex drive the reactivity toward cyanide release.

The solvatochromism of the absorption spectrum is evident in Table 1 and Figure 2. The LF bands are ordinarily regarded as little solvent sensitive,[57] as tends to be substantiated by occasional reports on chromium(III) cations,[58−60] with the exception of fluoride-containing species, where the LF strength of the F^- ligand is altered by hydrogen bonding with H_2O.[61−64] The available data on negative compounds, such as $Cr(CN)_6^{3-}$,[11,65] $Cr(CN)_5(NH_3)^{2-}$,[11] and *trans*-$Cr(NH_3)_2(NCS)_4^-$,[66] do show more significant variations, like those observed here. The increase of the LF transition energy on passing from nonaqueous to aqueous environments, that is, the intensified ligand perturbation on the metal ion, is ascribed to tightening of the second coordination sphere by hydrogen bond formation between CN^- and H_2O. This points to the importance of solvent orientation. While a cation is surrounded by the oxygen atoms of protic and nonprotic solvents and, therefore, experiences similar interactions in both cases (compare $Cr(NH_3)_5(py)^{3+}$ in Table 1), a negative complex is faced by the positive ends of the solvation molecules: formation or not of hydrogen bonds brings about larger differences. Also noteworthy is the considerable change (35%) of molar absorptivity, which may be justified by different degrees of participation of the two solvents in the vibronic interactions that lessen the Laporte restriction of the LF transitions.

The lack of phosphorescence in aqueous solution is not surprising, given the analogous behavior of the $Cr(CN)_6^{3-}$ [65] and $Cr(CN)_5(NH_3)^{2-}$ anions.[11] Again, hydrogen bonding accounts for an efficient complex−solvent vibrational coupling that enhances the nonradiative relaxation of the emitting doublet state(s).

Table 2 confirms the relevance to photochemistry of solvent orientation and hydrogen bonding. One aspect is the reduction of the total photoreactivity in Me_2SO relative to H_2O, that can be explained by the need for the entering solvent molecule to rotate during the decay of the reacting state, so as to enable attack by the oxygen atom. The nucleophilicity of both solvents is comparable, but the higher viscosity makes ligand photosubstitution less favored in Me_2SO ($\eta = 1.98$ cP at 25 °C) than in H_2O ($\eta = 0.89$ cP). Such an effect, that indeed appears to be peculiar to negatively charged complexes, has been systematically investigated with the *trans*-$Cr(NH_3)_2(NCS)_4^-$ anion.[67,68]

Another aspect of interest is the marked increase of the Φ_{py}/Φ_{CN} ratio on going from H_2O to Me_2SO (Table 2), which results from the fact that Φ_{CN} decreases far more than does Φ_{py}. Two types of explanation may be advanced for the higher value of Φ_{CN} in aqueous medium. The first once more invokes hydrogen bonding, operative in H_2O but not in Me_2SO, which would assist interchange of CN^- only with the protic water molecules. The second, which does not exclude the hydrogen interactions, is based on the capability of the different solvents to stabilize the charge separation in the transition state, as was argued for the medium dependence of Φ_{NH_3}/Φ_{Cl} in the photolysis of $Rh(NH_3)_5Cl^{2+}$.[69] Simple anions, such as CN^- and Cl^-, are more solvated in H_2O than in Me_2SO,[70,71] whereas the neutral py and NH_3 molecules would be less subject to such a discrimination.

The present solvent dependence of the quantum yields also emphasizes the role of chemical factors in photochemistry in addition to that of the electronic factors and further attests to the associative character of the photosubstitution reactions of chromium(III).[22,38,39]

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Supporting Information Available: Figures of spectral changes during reaction, with Figure 1 showing H^+-induced methanolysis of $Cr(CN)_6^{3-}$ and Figure 3 showing solvation of $Cr(CN)_5(py)^{2-}$ in dimethyl sulfoxide (2 pages). Ordering information is given on any current masthead page.

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