tion,[15,19] processes that ultimately yield gaseous hydrogen as a product.

Acknowledgment. We thank Professor Harry B. Gray for originally bringing the properties of $Mo_2(O_2CCF_3)_4$ to our attention and for prepublication communication of results from his laboratory. This work was supported by the National Science Foundation.

Registry No. $Mo_2(O_2CCF_3)_4$, 36608-07-8.

References and Notes

(1) R. H. Fleming, F. L. Geoffroy, H. B. Gray, A. Gupta, G. S. Hammond, D. S. Kliger, and V. M. Miskowski, *J. Am. Chem. Soc.*, **98**, 48 (1976).
(2) G. L. Geoffroy, H. B. Gray, and G. S. Hammond, *J. Am. Chem. Soc.*, **96**, 5565 (1974).
(3) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1978 (1966).
(4) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **6**, 214 (1967).
(5) L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 1571 (1969).
(6) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1972).
(7) W. C. Trogler, E. I. Solomon, I. Trajberg, C. J. Ballhausen, and H. B. Gray, *Inorg. Chem.*, **16**, 828 (1977).
(8) J. G. Norman, Jr., H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977).
(9) We also observed some very short-lived and very broad ("white") emission from the CF_3CO_2H–benzene solutions. This could conceivably indicate some initial photoionization and "solvated electron" emission followed by rapid cage recombination. However, similar emission can be observed from solutions containing small particles,[10] due to surface dielectric breakdown and plasma formation, and we have not eliminated this explanation of the phenomenon.
(10) M. W. Dowley, K. B. Eisenthal, and W. L. Peticolas, *Phys. Rev. Lett.*, **18**, 531 (1967).
(11) G. S. Hammond et al., *J. Am. Chem. Soc.*, **83**, 2396 (1961); **86**, 3197 (1964).
(12) R. E. Kellog, private communication.
(13) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).
(14) W. G. Kerkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).
(15) D. K. Erwin, G. L. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler, and A. A. Zagars, *J. Am. Chem. Soc.*, **99**, 3620 (1977).
(16) F. A. Cotton, B. A. Frenz, E. Pedersen, and T. R. Webb, *Inorg. Chem.*, **14**, 391 (1975).
(17) We have obtained a difference spectrum for solutions in benzene after excitation. There are a λ_{max} at 680 nm for which ϵ_{max} is $\simeq$500, no significant absorption in the interval 400–600 nm, and sharply decreasing absorbance at the region 400–360 nm. The last is due to ground-state depletion. The 680-nm maximum is assigned to a $\delta \rightarrow \delta^*$ transition of the $\sigma^2\pi^4\delta^1\pi^*$ triplet. The shift of the $\delta \rightarrow \delta^*$ transition by about 15 000 cm^{-1} from that of the ground-state molecule (330 nm) is consistent with this analysis.
(18) This conclusion is based upon the variation in absorption spectra of $Mo_2(O_2CCF_3)_4$ in different solvents and on the known structure of a bis(pyridine) adduct (F. A. Cotton and J. G. Norman, Jr., *J. Am. Chem. Soc.*, **94**, 5697 (1972)).
(19) W. C. Trogler and H. B. Gray, unpublished work.

Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506

Photochemistry of Pentacyanoferrate(II) Complexes Containing Aromatic Nitrogen Heterocyclic Ligands

JOSEPH E. FIGARD and JOHN D. PETERSEN*

Received October 10, 1977

Charge-transfer-to-ligand (CTTL) excitation of pentacyanoferrate(II) complexes, $(CN)_5Fe^{II}L^{n-}$ (where L is an aromatic, nitrogen, heterocyclic base), leads to the photosubstitution of L at room temperature in aqueous solution. The nature of the excited state responsible for the photosubstitution reaction is assigned as ligand field (LF) in character. Efficient interconversion between LF and CTTL excited states is observed with the magnitude of the quantum yield dependent on whether the LF ($0.1 < \Phi_L < 1.0$) or CTTL ($\Phi < 0.05$) excited state is lowest in energy. Interconversion between internal ligand excited states and LF or CTTL excited states is apparently not a very efficient process.

Introduction

The photochemical reactivity of transition-metal complexes is dependent, in many cases, on the nature of the excited state generated by photon absorption.[1] The ligand field (LF) excited states of low-spin, d^6 complexes generally undergo ligand labilization, owing to the increase in σ^* orbital population.[2-9] The charge-transfer-to-ligand (CTTL) excited states of d^6 complexes, which may be conceptualized as an oxidized metal/reduced ligand species, are usually unreactive toward photosubstitution reactions and either interconvert to lower energy excited states or deactivate directly back to the ground state.[10,11]

The extreme sensitivity[12] of the wavelength maxima of the CTTL transitions in $(NH_3)_5Ru^{II}L^{2+}$ to substituents on L (where L is a substituted pyridine) enabled Malouf and Ford[10] to vary the magnitude of the photosubstitution reactions markedly by varying the energy of the CTTL excited state with respect to the energy of the LF state. A similar type of tuning of excited states is apparent in metal carbonyl photochemistry. Wrighton and co-workers[11] have studied the photochemistry and emission spectroscopy of $(CO)_5WL$ (where L = substituted pyridine) with the result that changes in the nature of the lowest excited state affect the quantum yield of photochemical substitution and the emission lifetime.

We report herein a study of the photosubstitution reactions of a series of pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles. The major emphasis of this work will center on answering the following two questions. (1) Can the photosubstitutional quantum yield be substantially changed for $(CN)_5Fe^{II}L^{n-}$ complexes by modifying the nature of the lowest excited state? (2) How efficient is the interconversion from an internal ligand (IL) excited state to a LF excited state or from a LF excited state to a CTTL excited state?

Experimental Section

Materials. The recrystallized sodium salts of $(CN)_5Fe^{II}L^{n-}$ (L = pyridine, 4,4′-bipyridine, isonicotinamide, pyrazine, 4-cyanopyridine, 4-acetylpyridine, 4-pyridylpyridinium, *N*-methyl-4,4′-bipyridinium, and *N*-methylpyrazinium) were prepared from $Na_3[(CN)_5Fe(NH_3)]$ by previously described procedures.[13,14] Nonmethylated ligands were commercially available as analytical reagent grade and were used without further purification. Monomethylated ligands were prepared from the reaction of methyl iodide (Fisher AR) with the corresponding heterocycle in chloroform and recrystallized from chloroform prior to complexation. Purity of the ligands was determined by ^1H and ^{13}C NMR spectroscopy. The electronic absorption spectra of the recrystallized $(CN)_5Fe^{II}L^{n-}$ complexes had absorption maxima and molar absorptivities which agreed with previously reported values.[13,14]

Water used as the solvent for synthetic and photolytic reactions was redistilled from alkaline permanganate in an all-glass apparatus and deoxygenated prior to use. Photolysis solutions were maintained at ionic strength 0.2 M using sodium chloride. The trapping agents used in the photolysis reactions (pyridine and 1 M HCl) were introduced to the photolyte solution volumetrically using a Hamilton 50-μL syringe or a 5-mL Fisher hypodermic syringe.

Apparatus. Quantum yields were determined using a continuous beam photolysis apparatus consisting of an Oriel Universal Arc-Source Lamp with a 200-W high-pressure Hg lamp, 1-in. diameter Oriel mercury-line interference filters (365, 436, 546, and 577 nm), an ESCO A-1, 4-in. focal length, fused quartz, collimating lens, and a hollow brass thermostated cell compartment (controlled by a Forma Temp. Jr. constant-temperature circulating bath) all mounted on an Ealing 22-6894 optical bench. Usable intensities of this apparatus, as measured by ferrioxalate[15] ($\lambda_{irr} \leq 436$ nm) or Reineckate[16] ($\lambda_{irr} \geq 436$ nm) actinometry ranged from 1.2×10^{17} to 1.1×10^{19} quanta/min depending on the selection of interference filter.

All absorption spectra and optical density measurements were recorded on a Cary 14 spectrophotometer. The nuclear magnetic resonance spectra, which were used to check the purity of free and methylated ligands and the metal complexes, were recorded on a Varian T-60 (^{1}H) or Varian XL-100-15 (^{13}C) spectrometer.[13] A Corning Model 5 pH meter calibrated against commercially available buffer solutions was used for pH measurements.

Photolysis Procedures. The solutions used for the photolysis studies were generated and transferred into 10-cm absorption cells under argon gas using a previously described apparatus and technique.[17] Samples were irradiated for time periods ranging from 5 to 15 s. Five to seven of these time periods were used for each photolysis run. Spectroscopic changes in the photolysis sample were determined after each time period at the wavelength of irradiation and the wavelength of the CTTL band of the starting complex for use in calculating the quantum yield. All spectroscopic measurements were corrected for thermal substitution reactions (usually found to be 50–100% of the magnitude of the photochemical reaction) by the use of a dark sample which was prepared in manner identical with that for the photolyzed sample.

Pyridine was used as a trapping agent in the photolysis reactions of all complexes in this work except $(CN)_5Fe(py)^{3-}$. When no trapping agent was used, thermal recombination of the $(CN)_5Fe^{II}$ product and the free L generated from the photosubstitution reaction prevented an accurate determination of the initial quantum yield. The amount of pyridine introduced into the photolysis and dark solutions varied with the complex under study and depended on the competition between pyridine and L for the $(CN)_5Fe^{II}$ photolysis product. Optimum results were obtained by adding the minimum amount of pyridine necessary to trap all of the Fe(II) photolysis product and prevent any thermal recombination.

The thermal recombination of pyridine and $(CN)_5Fe^{II}$ generated from the photolysis of $(CN)_5Fe(py)^{3-}$ was prevented by the addition of small amounts of 1 N HCl. Optimum results were obtained when the pH of the solution was maintained between 3 and 4. If the solution was more acidic, protonation of coordinated cyanide ligand altered the nature of the starting complex,[14] while less acidic solutions were not effective in trapping photoaquated pyridine as pyridinium ion (pK_a of pyridine = 5.25[18]). Trapping via protonation of the photoaquated ligands in the other $(CN)_5Fe^{II}L$ complexes was not reasonable since all other pK_a values of L are smaller than 3 and therefore introduce problems with cyano ligand protonation.

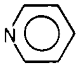
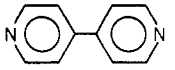
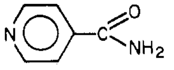
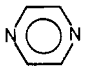
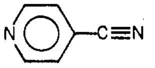
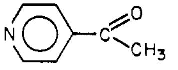
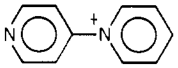
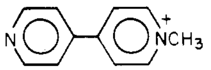
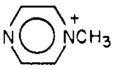
Quantum Yield Calculations. The formula used to calculate quantum yields at the various time periods, Φ_t, is

$$\Phi_t = (\Delta A \cdot V / l \cdot \Delta\epsilon)(I_0{}^{i} \cdot t \cdot F)$$

where ΔA = the change in optical density at the CTTL maximum of the starting complex from time 0 to time t (corrected for dark reaction), $\Delta\epsilon$ = corresponding extinction coefficient difference between the starting complex and the trapped photolysis product at the CTTL maximum of the starting complex (M^{-1} cm^{-1}), V = volume of the photolysis cell (L), l = path length of the photolysis cell (cm), $I_0{}^{i}$ = incident light intensity as determined by ferrioxalate[15] or Reineckate[16] actinometry (einsteins/min), t = irradiation time (min), and F is the average fraction of light absorbed at the irradiation wavelength over the time period t.

The Φ_t value for each time period of the photolysis reaction was plotted vs. percent reaction with initial quantum yields obtained by extrapolation to 0% reaction. These plots proved linear for the first 40% of the reaction; however, most photolysis data were extracted from the first 25% of the reactions. Multiple runs were averaged and reported as mean values with the appropriate average deviation.

Table I. Absorption Spectra of $(CN)_3Fe^{II}L^{n-}$ Complexes[a]

L	λ_{max}, nm (μm^{-1})	ϵ_{max}, M^{-1} cm^{-1}
NH_3	388 (2.58)[b]	
 (1)	362 (2.76)	3.7×10^3 [c]
 (2)	432 (2.32)	5.62×10^3 [c]
 (3)	435 (2.30)	4.57×10^3 [c]
 (4)	452 (2.21)	5.01×10^3 [c]
 (5)	476 (2.10)	5.49×10^3
 (6)	480 (2.08)	3.17×10^3
 (7)	483 (2.07)	3.80×10^3 [c]
 (8)	520 (1.92)	5.62×10^3 [c]
 (9)	660 (1.52)	1.40×10^4

[a] Measured in deoxygenated water at 25 °C. [b] Recorded as a KBr pellet; assigned as $^1E, {}^1A_2({}^1T_1) \leftarrow {}^1A_1$ ligand field transition. [c] Reference 14.

The validity of spectroscopic quantum yield determinations were tested by allowing some of the photolysis reactions to proceed to 100% reaction. In all cases, the final product spectrum agreed with the spectrum calculated on the basis of the trapping agent used.

Results and Discussion

Spectra. The $(CN)_5Fe^{II}L^{n-}$ complexes (where L = substituted pyridine or substituted pyrazine) used in this study all display an intense absorption band (ϵ 10^3–10^5 M^{-1} cm^{-1}) in the visible portion of the spectrum. These absorption bands are extremely dependent on the nature of L and have been assigned as charge transfer to ligand (CTTL) transitions.[14] The maxima of the CTTL bands vary from 362 nm (2.76 μm^{-1}) for L = pyridine to 662 nm (1.51 μm^{-1}) for L = *N*-methylpyrazinium and are listed in Table I in order of descending CTTL energies.

Spectroscopic Quantum Yield Determination. Irradiation of deoxygenated, aqueous solutions (pH 7, μ = 0.02 M, NaCl) of $(CN)_5Fe^{II}L^{n-}$ in the visible spectral region leads initially to photoaquation of the ligand L (eq 1).[19] The identical

$$(CN)_5Fe^{II}L^{n-} \xrightarrow[H_2O]{h\nu} (CN)_5Fe^{II}OH_2{}^{3-} + L \qquad (1)$$

reaction occurs thermally[14] with rate constants of 1.15×10^{-3} and 2.8×10^{-4} s^{-1} when L is 4-methylpyridine and *N*-methylpyrazinium, respectively. However, the thermal recombination reaction (eq 2) is also rapid and complicates the

$$(CN)_5Fe^{II}OH_2{}^{3-} \xrightarrow[\text{rapid}]{+L} (CN)_5Fe^{II}L^{n-} + H_2O \qquad (2)$$

spectroscopic determination of the quantum yield for the

Table II. Photolysis Quantum Yield for the Loss of L from $(CN)_5Fe^{II}L^{n-}$ [a]

L	λ_{max}, CTTL [b]	λ_{irr} [c]	Trapping agent	Φ_L ($\times 10^2$) [d]
1	362	365	H^+ [e]	23 ± 4 (6)
2	432	436	py	34 ± 3 (3)
3	435	436	py	41 ± 3 (4)
4	452	365	py	15 ± 3 (2)
		436	py	39 ± 3 (3)
5	476	436	py	30 ± 1 (2)
6	478	436	py	19 ± 2 (4)
7	483	436	py	4.1 ± 0.7 (4)
8	520	546	py	1.6 ± 0.2 (3)
9	662	365	py	1.0 ± 0.2 (2)
		436	py	2.2 ± 0.3 (3)
		577	py	0.34 ± 0.03 (2)

[a] Aqueous solution (pH 7), $\mu = 0.2$ M (NaCl), and 50 μL-3.0 mL pyridine added unless otherwise noted. [b] Wavelength maximum of CTTL band in nm. [c] Wavelength of irradiation in nm. [d] Initial quantum yield and average deviation in mol/einstein ($\times 10^2$) with the number of independent determinations in parentheses. [e] No pyridine added, pH adjusted to between 3 and 4.5 with 1 N HCl.

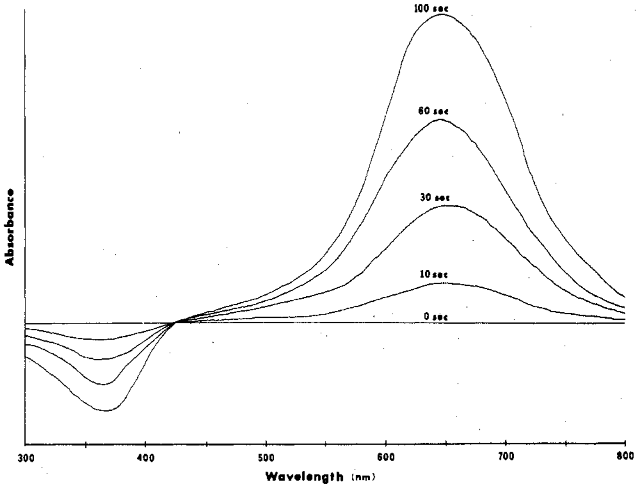
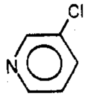
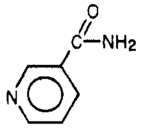
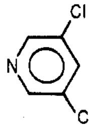
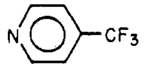
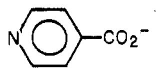


Figure 1. The change in the spectrum of $(CN)_5Fe^{II}(N\text{-Mepyz})^{2-}$ as a function of photolysis time (s) in an aqueous solution containing pyridine (see text).

Table III. Comparisons of the Photochemical Quantum Yields for Loss of L from $(CN)_5Fe^{II}L^{n-}$ and $(NH_3)_5Ru^{II}L^{n-}$

L	$(CN)_5Fe^{II}L^{n+}$ $\Phi_L \times 10^2$, mol/einstein [b]	$(NH_3)_5Ru^{II}L^{n+}$ [a] $\Phi_L \times 10^3$, mol/einstein [c]
1	23 ± 4	45 ± 3
		48 ± 2
		8.5 ± 0.2
		42 ± 2
		22 ± 5
		26 ± 3
2	34 ± 3	
3	41 ± 3	1.07 ± 0.04
4	39 ± 3	1.4 ± 0.1
5	39 ± 1	
6	19 ± 2	0.25 ± 0.06
7	4.1 ± 0.7	
8	1.6 ± 0.2	
9	0.34 ± 0.03	0.04 ± 0.01

[a] Reference 10 and private communication from G. Malouf. [b] Initial quantum yield and average deviation $\times 10^2$ in mol/einstein. [c] Initial quantum yield and average deviation $\times 10^3$ in mol/einstein.

photoaquation of L. The addition of a molar excess of pyridine to the photolysis solution enabled quantum yield determinations for the photosubstitution of L by trapping the Fe(II) as the pyridine complex, $(CN)_5Fe^{II}(py)^{3-}$.

$$(CN)_5Fe^{II}L^{n-} \xrightarrow[\text{py in } H_2O]{h\nu} (CN)_5Fe^{II}(py)^{3-} + L \tag{3}$$

The quantum yields for the reaction in eq 3 are listed in Table II. There is little apparent variation in the quantum yield value as the concentration of pyridine is varied. The stoichiometry of eq 3 (i.e., all of the initial $(CN)_5Fe^{II}L^{n-}$ appears ultimately as $(CN)_5Fe^{II}(py)^{3-}$ in the photolysis product) was confirmed spectrophotometrically. Figure 1 illustrates the confirmation of the overall stoichiometry for the irradiation (λ_{irr} 577 nm) of $(CN)_5Fe^{II}(N\text{-methylpyrazinium})^{2-}$ in aqueous solution containing ~500 ppm of pyridine. The plot is generated by scanning the spectrum with the photolysis sample in the reference beam of the spectrometer and with an identically prepared dark solution in the sample beam. A positive absorbance change is indicative of a decrease in absorbance in the photolysis solution with respect to the dark solution, with a negative absorbance change indicating a corresponding increase in absorbance in the photolysis sample. As the irradiation time increases, the concentration of $(CN)_5Fe^{II}(py)^{3-}$ increases and the concentration of $(CN)_5FeL^{n-}$ decreases in the photolysis solution with respect to the dark solution. The absolute absorbance changes at 362 and 660 nm are consistent with a 1:1 ratio of $(CN)_5Fe^{II}(py)^{3-}$ formed to $(CN)_5Fe^{II}L^{n-}$ decomposed. In addition, isosbestic points were observed for the first 20% reaction for all $(CN)_5Fe^{II}L^{n-}$ species, indicating there are no complicating secondary thermal or photochemical reactions.

For irradiation of $(CN)_5Fe^{II}(py)^{3-}$, protons were used as a trapping agent (eq 4). Over the pH range of 3.0–4.5 (where

$$(CN)_5Fe^{II}(py)^{3-} \xrightarrow[H_3O^+]{h\nu,\ \text{CTTL}} (CN)_5Fe^{II}OH_2{}^{3-} + pyH^+ \tag{4}$$

photoaquated pyridine is substantially protonated and not much protonation of coordinated cyano ligand has occurred[14]), the photoaquation quantum yield is invariant within the experimental uncertainty.

Quantum Yield Dependence on CTTL Energy. The quantum yield for the photosubstitution of L from $(CN)_5Fe^{II}L^{n-}$ is extremely sensitive to the nature of L. There is a severe drop in quantum yield when the CTTL maximum occurs at wavelengths greater than 480 nm (Tables II and III). Similar behavior has been observed by Malouf and Ford[10] for the analogous $(NH_3)_5Ru^{II}L^{n+}$ complexes and by Wrighton et al.[11] for $(CO)_5WL$ complexes. Our results will be compared to the results of the $(NH_3)_5Ru^{II}L^{n+}$ complexes[10] since Toma and Malin[14] have shown an approximate linear correlation between the CTTL energy maxima of $(NH_3)_5Ru^{II}L^{n+}$ and $(CN)_5Fe^{II}L^{n-}$ pairs as a function of L.

Malouf and Ford[10] have interpreted their dramatic drop in Φ_L (for $(NH_3)_5Ru^{II}L^{n+}$) when λ_{max}(CTTL) >460–470 nm as

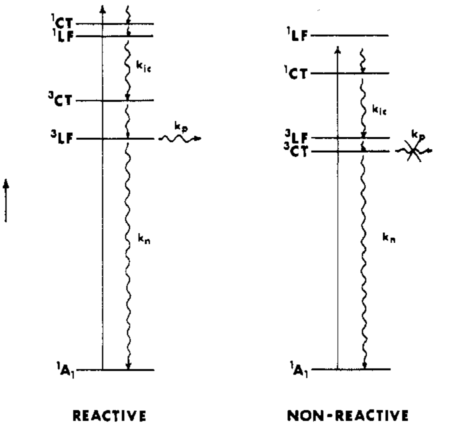


Figure 2. Proposed energy level diagrams for $(CN)_5Fe^{II}L^{n-}$ which are photochemically reactive ($\Phi_L > 0.1$) and nonreactive ($\Phi_L < 0.05$).

a reversal in the order of the triplet excited states. We make the same claim for the $(CN)_5Fe^{II}L^{n-}$ with the two limiting cases illustrated in Figure 2. The model assumes that the substituent groups on the pyridine ring do not alter substantially the energy of the ligand field excited states. This assumption is strengthened by the fact that the isoelectronic $(CN)_5Co^{III}L^{n-}$ complex ions, where there is no CTTL band in the visible region to mask the lowest ligand field transition, have $^1E,^1A_2 \leftarrow {}^1A_1$ transitions that are insensitive to the substituent on the pyridine ligand. The $(CN)_5Co^{III}L^{n-}$ complexes all have LF band maxima at ~354 nm.[20] When the energy of the CTTL excited state is higher than the LF excited state, reactions characteristic of LF excited states (i.e., ligand substitution reactions) occur, and the complexes are reactive ($0.1 < \Phi_L < 1.0$). When the CTTL is moved to lower energy than the LF excited state (by the use of appropriate electron-withdrawing substituents on L), the complexes become nonreactive ($\Phi < 0.05$) owing to the slow thermal substitution of an excited state which may be conceptualized as an oxidized metal/reduced ligand species ($(CN)_5Fe^{III}L\cdot^{n-}$).

There are a number of fruitful comparisons which can be made between the $(CN)_5Fe^{II}L^{n-}$ and $(NH_3)_5Ru^{II}L^{n+}$ systems. When L = NH_3 (i.e., $(CN)_3Fe^{II}NH_3{}^{3-}$ and $Ru^{II}(NH_3)_6{}^{2+}$), the maxima of the lowest energy spin allowed ligand field transition ($^1T_1 \leftarrow {}^1A_1$) are 388[21] and 385 nm,[22] respectively. The maxima of the nonobserved LF band when L is a substituted pyridine should also occur in the same region.[23] Assuming similar Stokes shifts for the Ru^{II} and Fe^{II} complexes, we might expect the wavelength of the break-off points in Φ_L to be similar. In fact, the sharply defined break-off point in the $(CN)_5Fe^{II}L^{n-}$ complexes occurs when λ_{max}(CTTL) >480 nm (~0.5 μm^{-1} lower than the Franck–Condon state in $(CN)_5Fe^{II}NH_3{}^{3-}$) while the $(NH_3)_5Ru^{II}L^{n+}$ complexes[10] show a larger reduction (although the break-off point is not as well defined) in quantum yield as λ_{max}(CTTL) becomes longer than 460–470 nm (~0.43–0.48 μm^{-1} lower than the Franck–Condon state in $Ru^{II}(NH_3)_6{}^{2+}$). This similarity in the energy of the ^{1}LF band (L = NH_3) and the similarity of the crossover point (λ_{max}(CTTL) 460–480 nm) suggest that the photochemical reactivity of the two metal systems is originating from the same type of excited state.

Ford et al.[2] have argued that the substitution reactive state for the photosubstitution of L and NH_3 from $(NH_3)_5Ru^{II}L^{n+}$ is ligand field in character and probably the $^3E,^3A_2(^3T_1)$ LF state. This state also appears to be the best choice for photochemical reactivity in the $(CN)_5Fe^{II}L^{n-}$ complexes, on the basis of both the similarity in the crossover energies and the emission studies[24] on the $(CN)_5Fe^{II}L^{n-}$ complexes.

Although the absorption spectra in the ligand field region of $(CN)_5Fe^{II}NH_3{}^{3-}$ and $Ru(NH_3)_6{}^{2+}$ are similar and the crossover energy between the reaction and nonreactive complexes are about the same, the CTTL maxima for a specific L are different for the Fe(II) and Ru(II) analogues. This difference is due to energy match and overlap integral differences between the Fe(II) and Ru(II) d_π atomic orbitals and the π^* orbital on L. The result of this difference in interaction is that the CTTL maximum for a specific L in $(CN)_5Fe^{II}L^{n-}$ is at a higher energy than the CTTL energy maximum for the corresponding $(NH_3)_5Ru^{II}L^{n+}$ species. This requires that the substituent on L in the Fe(II) complexes must be more electron withdrawing than the substituent on L in the Ru(II) complex in order to place the CTTL state below the LF state. *The fact that the crossover occurs at a different place in the ligand series (Table III) for the two metal centers rules out anomalous behavior of the ligand as a source of the drastic change in quantum yield.*

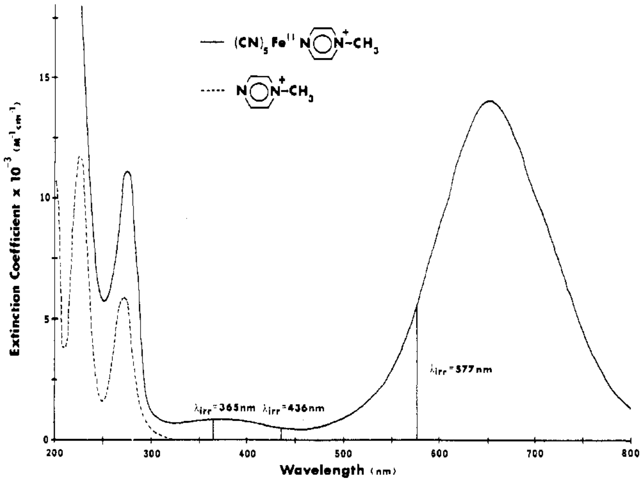


Figure 3. Electronic absorption spectra of $(CN)_5Fe^{II}(N\text{-Mepyz})^{2-}$ and *N*-Mepyz$^+$.

The observations that the $(CN)_5Fe^{II}L^{n-}$ complexes have larger quantum yields than the corresponding $(NH_3)_5Ru^{II}L^{n+}$ complexes[10] when the LF state is lower in energy than the CTTL state and the diminished photochemical reactivities of both metal centers when the CTTL state is lower than the LF state arise from the following considerations: (1) The $(CN)_5Fe^{II}L^{n-}$ species are more labile in the ground-state electronic configuration than the corresponding $(NH_3)_5Ru^{II}L^{n+}$ species and this is also probably true in the ligand field excited state. (2) The photochemistry of the $(CN)_5Fe^{II}L^{n-}$ complexes proceeds by a one-channel process with only the loss of L detected. The $(NH_3)_5Ru^{II}L^{n+}$ photolysis reactions occur by more than one channel with L, cis NH_3, and trans NH_3 all being photosubstituted.[2] (The lack of a multichannel process in the photochemistry of $(CN)_5Fe^{II}L^{n-}$ can possibly be attributed to the relatively large differences in the CN^- and L ligands. For the $(NH_3)_5Ru^{II}L$ species, both the LF and CTTL excited states have reduced π bonding with respect to the ground state. The decreased π bonding in the excited state makes it more difficult for the metal center to differentiate between ammine ligand and a substituted pyridine ligand.) (3) The amine complexes of pentacyanoferrate(III) are d^5 low spin[25] as are the amine complexes of pentaammineruthenium(III).[26] If we conceptualize the CTTL excited state as an oxidized metal/reduced ligand configuration, neither of the metal centers would be expected to be very labile. (For the reaction $(CN)_5Fe^{III}NH_3 + SCN^- + H^+ \rightarrow (CN)_5Fe^{III}SCN + NH_4{}^+$, $k \leq 3 \times 10^{-8}$ M^{-1} s^{-1}.[25] Estimates for the reaction $(NH_3)_5Ru^{III}(NH_3) + H_3O^+ \rightarrow (NH_3)_5Ru^{III}OH_2 + NH_4{}^+$ are that $k << 10^{-5}$ s^{-1}.[26])

Wavelength-Dependent Quantum Yields. The electronic spectra of *N*-methylpyrazinium (*N*-Mepyz$^+$) and

$(CN)_5Fe^{II}(N\text{-Mepyz})^{2-}$ are illustrated in Figure 3. The spectrum of N-Mepyz$^+$ consists solely of $\pi \rightarrow \pi^*$ bands at λ <300 nm. The complex ion $(CN)_5Fe^{II}(N\text{-Mepyz})^{2-}$ has three absorption regions, the highly absorbing CTTL band ($Fe^{II} \rightarrow N\text{-Mepyz}^+$) centered at 662 nm, internal ligand ($\pi \rightarrow \pi^*$) and CTTL ($Fe^{II} \rightarrow CN$) at λ <300 nm, and a small band centered at ~380 nm (ϵ ~800 M^{-1} cm^{-1}) which corresponds to the $^1E,^1A_2 \leftarrow {}^1A_1$ ligand field transition.[27]

Irradiation of $(CN)_5Fe^{II}(N\text{-Mepyz})^{2-}$ in the $Fe^{II} \rightarrow N$-Mepyz$^+$ CTTL region (λ_{irr} 577 nm) or the ligand field region (λ_{irr} 436 or 365 nm) leads to loss of N-Mepyz$^+$. The quantum yields (Table II) for this process are 3.4×10^{-3}, 2.2×10^{-2}, and 1.0×10^{-2} mol/einstein, respectively. The low quantum yields (~10^{-2}) obtained from ligand field irradiation indicate that the large decrease in Φ when λ_{max}(CTTL) >480 nm is not due to using lower energy irradiation but is a property of the excited-state ordering in the complex ion. In addition, the small increases in quantum yield obtained when the LF rather than the CTTL state is populated initially indicate that internal conversion from LF to CTTL is the predominant process occurring with reaction out of the LF only mildly competitive. An approximate calculation of the internal conversion efficiency (assuming Φ(LF) ~ 0.38 and Φ(CTTL) ~ 3.4×10^{-3}) in going from the LF state to the CTTL state indicates that close to 95% of the excited ions are internally converting to the CTTL state.

The pyrazine complex, $(CN)_5Fe^{II}(pyz)^{3-}$, shows a wavelength dependence for the photosubstitution of pyz when irradiated at 436 and 365 nm (Table II). Irradiation at 436 nm (λ_{max}(CTTL) 452 nm) results in a quantum yield of 0.39 for the loss of pyrazine. This value is similar to the values obtained when L is isonicotinamide (λ_{max}(CTTL) 435 nm, $\Phi_L = 0.41$) and when L is 4-cyanopyridine (λ_{max}(CTTL) 476 nm, $\Phi_L = 0.39$). However, irradiation of $(CN)_5Fe^{II}(pyz)^{3-}$ at 365 nm leads to a reduction in the quantum yield for pyrazine loss to 0.15. Spectroscopically, 365 nm corresponds to the high-energy side of the $Fe^{II} \rightarrow$ pyz CTTL band and includes the low-energy tail of the π–π^* band of coordinated pyrazine. Also, the lowest LF singlet absorption band, although not observed, should appear in this region of the spectrum. The smaller quantum yield for loss of pyridine at λ_{irr} 365 nm with respect to λ_{irr} 436 nm suggests that at least one of the absorbing states at 365 nm (^{1}CTTL, ^{1}IL, or ^{1}LF) has a deactivation pathway independent of the lower energy, reactive LF state. Irradiation of $(CN)_5Fe^{II}(pyz)^{3-}$ at 313 nm (predominantly IL) results in spectroscopic changes that are not consistent with the sole reaction being simple ligand substitution processes.[28]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

Registry No. $(CN)_5Fe^{II}L^{3-}$(L = **1**), 37475-75-5; $(CN)_5Fe^{II}L^{3-}$(L = **2**), 37475-72-2; $(CN)_5Fe^{II}L^{3-}$(L = **3**), 40299-77-2; $(CN)_5Fe^{II}L^{3-}$(L = **4**), 40299-78-3; $(CN)_5Fe^{II}L^{3-}$(L = **5**), 62704-26-1; $(CN)_5Fe^{II}L^{3-}$(L = **6**), 65293-58-5; $(CN)_5Fe^{II}L^{2-}$(L = **7**), 65293-57-4; $(CN)_5Fe^{II}L^{2-}$(L = **8**), 37475-67-5; $(CN)_5Fe^{II}L^{2-}$(L = **9**), 40299-79-4; N-mepyz$^+$, 17066-96-5.

References and Notes

(1) See A. W. Adamson and P. D. Fleischauer, Ed., "Concepts of Inorganic Photochemistry", Wiley, New York, N.Y., 1975.
(2) D. A. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Petersen, D. P. McDonald, and P. C. Ford, *J. Am. Chem. Soc.*, **94**, 6665 (1972).
(3) R. E. Hintze and P. C. Ford, *J. Am. Chem. Soc.*, **97**, 2664 (1975).
(4) J. D. Petersen and P. C. Ford, *J. Phys. Chem.*, **78**, 1144 (1974).
(5) P. C. Ford and J. D. Petersen, *Inorg. Chem.*, **14**, 1404 (1975).
(6) J. D. Petersen, R. J. Watts, and P. C. Ford, *J. Am. Chem. Soc.*, **98**, 3188 (1976).
(7) T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **92**, 5733 (1970); *J. Phys. Chem.*, **76**, 1937 (1972).
(8) A. W. Zanella, M. Talebinasab-Sarvari, and P. C. Ford, *Inorg. Chem.*, **15**, 1980 (1976).
(9) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 3027 (1974).
(10) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 7213 (1977).
(11) M. S. Wrighton, H. B. Abrahamson, and D. L. Morse, *J. Am. Chem. Soc.*, **98**, 4105 (1976).
(12) P. Ford, De F.P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).
(13) J. E. Figard, J. V. Paukstelis, E. F. Byrne, and J. D. Petersen, **99**, 8417 (1977).
(14) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).
(15) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(16) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
(17) P. C. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, **7**, 1976 (1968).
(18) "Handbook of Chemistry and Physics", 53rd ed, The Chemical Rubber Co., Cleveland, Ohio, 1972.
(19) Although no specific analysis was performed to determine the amount of photosubstituted CN^-, the spectral properties of the photolysis product indicate that this pathway is either minor or nonexistent at the irradiation wavelengths used in this study.
(20) H. D. Wohlers and J. D. Petersen, unpublished observations.
(21) Recorded as KBr pellet since in aqueous solution the half-life for aquation of NH_3 from $(CN)_5Fe^{II}NH_3{}^{3-}$ is less than 40 s (H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 2080 (1973)).
(22) H.-H. Schmidtke and D. Garthoff, *Helv. Chim. Acta*, **49**, 2039 (1966).
(23) There are only small differences in the spectrochemical series between NH_3 and py-X for d^6 metal systems of this type. For $(NH_3)_5Rh^{III}L^{n+}$, the difference in maxima for the $^1E,^1A_2(^1T_1) \leftarrow {}^1A_1$ band is only 3 nm.[6]
(24) Preliminary experiments on the emission spectroscopy of $(CN)_5Fe^{II}$-(isonicotinamide)$^{3-}$ (KBr pellet, 77 K) indicate that the Gaussian emission band results from the $^3A_2,^3E(^3T_1) \rightarrow {}^1A_1$ transition. The 0–0 energy of this transition has been approximated at 1.419 μm^{-1} (705 nm). (J. E. Figard, R. J. Watts, and J. D. Petersen, work in progress.)
(25) A. D. James, R. S. Murray, and W. C. E. Higginson, *J. Chem. Soc., Dalton Trans.*, 1273 (1974).
(26) J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Am. Chem. Soc.*, **90**, 5928 (1968).
(27) The assignment of the band at ~380 nm as a LF band of $(CN)_5Fe^{II}(N\text{-Mepyz})^{2-}$ arises from the similarity in maxima with the corresponding $(CN)_5Fe^{II}NH_3{}^{3-}$ complex (388 nm). The band at ~380 nm cannot be due to contamination of the compound with $(CN)_5Fe^{II}NH_3{}^{3-}$, since the latter does not exist in aqueous solution (see ref 21).
(28) Irradiation in the internal ligand region (313 nm) results in large spectroscopic changes. These changes could be attributed to efficient photosubstitutional processes (in which case $\Phi_L \approx 1.0$) or photochemical degradation of free or coordinated ligand.