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Photochemistry of Pentacyanocobaltate(III) Complexes Containing Aromatic Nitrogen Heterocyclic Ligands

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The photochemical reactivity of d^6 transition-metal complexes containing aromatic nitrogen heterocyclic ligands (L) has been reported for pentacyanoferrate(II),[2] pentaammineruthenium(II)[3] and -rhodium(III),[4] and pentacarbonyltungsten(0)[5] complexes. The electronic absorption spectra of the low valent Fe(II), Ru(II), and W(0) compounds are dominated by intense metal-to-ligand charge-transfer (MLCT) bands in the visible and near-ultraviolet spectral regions. The MLCT band maxima are sensitive to the nature of L and substituent groups on L. In addition, the quantum yield for photosubstitution of L is dependent on the wavelength maximum of the MLCT band.[2,3,5] As electron-withdrawing substituents shift the MLCT maximum to longer wavelength, a discontinuity in quantum yield is observed. The severe drop-off in quantum yield, as the MLCT maxima is red shifted, has been attributed to a crossover of a reactive ligand field (LF) and nonreactive MLCT excited states.[2,3,5]

In this work, we report the results of LF photolysis of the pentacyanocobaltate(III) complexes, $(CN)_5Co^{III}L^{n-}$. These Co(III) complexes are isoelectronic to the $(CN)_5Fe^{II}L^{(n+1)-}$ complexes previously studied[2] but do not display any low-energy MLCT bands or exhibit substantial π back-bonding in the ground state.[6] The choices of L for this study correspond to the ligands which result in both photochemically reactive and nonreactive $(CN)_5Fe^{II}L^{(n+1)-}$ complexes.[2]

Experimental Section

Materials. The $K_x[Co(CN)_5L]$ complexes used in this study were prepared by using analytic reagent grade ligands (L = pyridine, 3,5-dichloropyridine, isonicotinamide, pyrazine, 4-cyanopyridine) and $Co(CN)_5H_2O^{2-}$, prepared by the previously described procedure.[7] For L = *N*-methylpyrazinium, the iodide salt of the ligand was prepared by the reaction of pyrazine and methyl iodide.[6] The water used for synthetic and photolytic purposes was redistilled from an alkaline permanganate solution in an all-glass apparatus.

Spectroscopy. All absorption spectra and the optical density measurements used for quantum yield determinations were recorded on a Cary Model 14 UV–vis–near-IR spectrophotometer. The atomic absorption data were taken with the use of a Perkin-Elmer 460 atomic absorption spectrometer with a Jarrell-Ash 45-456 cobalt cathode, neon gas, 20-µA lamp. Calibration of the AA spectrometer utilized 10.75–32.25 ppm solutions of $CoCl_2$, which were generated by dissolution of cobalt metal in concentrated hydrochloric acid, followed by serial dilution.

Syntheses. The $K_x[Co(CN)_5L]\cdot nH_2O$ complexes were prepared by heating ~100 mL of 0.2 M $Co(CN)_5H_2O^{2-}$ solution[7] with a 2–12-fold excess of L at 50 °C for 17 h. After the mixture was heated, the volume of the solution was reduced to 5–10 mL, the excess free ligand which precipitated was filtered off, and the crude product was precipitated by addition of ethanol. Recrystallization from hot water was sufficient to purify all complexes except for the case where L = *N*-methylpyrazinium. The purified complexes were collected, washed with ethanol and then ether, and dried under vacuum. The product yields approximated 40%, with spectral properties listed in Table I.

The crude *N*-methylpyrazinium complex contained a substantial free-ligand impurity. The free ligand was removed by first washing with copious amounts of ethanol and then passing an aqueous solution of the crude complex through a 10-cm column of Dowex 50W-X4 cation-exchange resin in the K^+ form. The ion-exchange column

Table I. Electronic and Atomic Absorption Data of $(CN)_5CoL^{n-}$ Complexes[a]

complex	ν_{max}[b]	ϵ_{max}[c]	% Co_{AA}[d]	% Co_{EA}[e]
$K_2[(CN)_5CoN\bigcirc]$	2.84	267[f]	100	93
$K_2[(CN)_5CoN\bigcirc]$ (Cl, Cl)	2.87	263	98	100.5
$K_2[(CN)_5CoN\bigcirc-CONH_2]\cdot H_2O$	2.83	276	97	102
$K_2[(CN)_5CoN\bigcirc N]$	2.87	264	102	103
$K_2[(CN)_5CoN\bigcirc-CN]\cdot 0.75 H_2O$	2.82	269	100	96
$K[(CN)_5CoN\bigcirc NCH_3]$	2.92	500	99	98

[a] Measured in H_2O at 25 °C. [b] Lowest ligand field maximum, $^1E^a, ^1A_2 \leftarrow ^1A_1$, in μm^{-1}. [c] In $M^{-1} cm^{-1}$. [d] Percentage of theoretical yield from column 1 as determined by atomic absorption spectroscopy. [e] Percentage of theoretical yield from column 1 as determined by electronic absorption spectroscopy from extensive photolysis of $(CN)_5CoL^{n-}$. [f] Reference 10.

separated the complex (reddish band) from the free ligand (yellow band). The product was isolated by evaporation and recrystallized from hot water. The hygroscopic product was collected, washed with ethanol and then ether, and dried in an oven at 75 °C. The overall yield was only ~5%.

Confirmation of compound purity was established by using a variety of methods. Attempts at C, H, and N analyses by two companies failed to yield accurate C and N values for the compounds prepared here as well as for $K_3[Co(CN)_6]$ (Alfa Inorganics). The low values obtained for C and N are presumably due to incomplete CN^- breakdown which has been observed for iron cyanophenanthroline compounds.[8] Qualitative confirmation that L had been incorporated into the $Co(CN)_5H_2O^{2-}$ complex ion was obtained by electronic absorption and ^{13}C NMR[6] spectroscopies. Quantitative data for complex purity were obtained by cobalt atomic absorption spectroscopy and by photolysis of $Co(CN)_5L^{n-}$ to completion and back-calculating the concentration from the $Co(CN)_5H_2O^{2-}$ complex which formed. The results of these latter methods appear in Table I along with the electronic absorption data for the $Co(CN)_5L^{n-}$ complexes.

Photochemistry. Quantum yields were determined at 25 °C with the use of apparatus and calculative procedures described previously.[2] The wavelength of irradiation in this work was 2.74 μm^{-1} with light intensities, as measured by ferrioxalate actinometry,[9] ranging from 4.5×10^{17} to 1.2×10^{18} quanta/min.

Results and Discussion

Spectra. The $(CN)_5Co^{III}L^{n-}$ complexes (where L = pyridine, pyrazine, or their substituted derivatives) used in this study all display $^1E^a, ^1A_2 \leftarrow ^1A_1$ absorption bands with maxima around 2.85 μm^{-1} (351 nm) with extinction coefficients on the order of 270 $M^{-1} cm^{-1}$. (The compound where L = *N*-methylpyrazinium has $\epsilon \simeq 500$ $M^{-1} cm^{-1}$ with a maximum at

(1) NSF-URP Summer Fellow, 1976.
(2) Figard, J. E.; Petersen, J. D. *Inorg. Chem.* **1978**, *17*, 1059.
(3) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213.
(4) Petersen, J. D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 3188.
(5) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.
(6) Figard, J. E.; Paukstelis, J. V.; Byrne, E. F.; Petersen, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417.
(7) Adamson, A. W.; Chiang, A.; Zinato, E. *J. Am. Chem. Soc.* **1969**, *91*, 5467.
(8) Purcell, K. F.; Yeh, S. M.; Eck, J. S. *Inorg. Chem.* **1977**, *16*, 1708. Shriver, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 1405. Shriver, D. F.; Posner, J. *Ibid.* **1966**, *88*, 1672.
(9) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.
(10) Barca, R.; Ellis, J.; Tsao, M.-S.; Wilmarth, W. K. *Inorg. Chem.* **1967**, *6*, 243.

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Table II. Comparisons of the Photochemical Quantum Yields for Loss of L from $(CN)_5ML^{n-}$

	Φ_L, mol/einstein	
L	M = Co(III)[a]	M = Fe(II)[b]
pyridine	0.17 ± 0.02 (3)	0.23
3,5-dichloropyridine	0.40 ± 0.02 (5)	
isonicotinamide	0.12 ± 0.01 (4)	0.41
pyrazine	0.24 ± 0.02 (6)	0.39
4-cyanopyridine	0.14 ± 0.01 (5)	0.30
N-methylpyrazinium	0.22 ± 0.02 (4)	0.022[c]

[a] Initial quantum yield and average deviation with number of determinations in parentheses ($\bar{\nu}_{irr}$ = 2.74 μm^{-1}). [b] Initial quantum yield from ref 2. [c] For irradiation of 2.29 μm^{-1}.

2.92 μm^{-1} (342 nm), but absorption in this region is intensified by the low-energy tailing of an internal ligand band.) The insensitivity of the maximum of the lowest energy, spin-allowed, absorption band to changes in L is characteristic of the LF nature of this transition (see also rhodium(III) ammine homologues[3]) but differs from the isoelectronic $(CN)_5Fe^{II}L^{(n+1)-2}$ and analogous $(NH_3)_5RuL^{n+3}$ and $(CO)_5WL^5$ systems where this absorption band is MLCT in nature and extremely sensitive to changes in L. For discussion purposes, the cobalt compounds are listed in Table II by descending order of the MLCT maxima energies for the isoelectronic $(CN)_5Fe^{II}L^{(n+1)-}$ complexes.[2]

Quantum Yield Determinations. Irradiation of air-saturated or deoxygenated, aqueous solutions (pH 7, $[(CN)_5Co^{III}L]$ = (2 ± 1) × 10^{-3} M) leads to the photoaquation of L with initial quantum yields as reported in Table II. Thermal control studies show that over the time span of the photolysis experiment, generally 0.5–2 h, no degradation of the dark solution is observed. The photolyzed sample undergoes a continuous spectral change from $(CN)_5Co^{III}L^{n-}$ to $(CN)_5Co^{III}OH_2^{2-}$ with isosbestic points maintained throughout the entire photodecomposition. The final absorption spectrum of extensively irradiated solutions corresponds exactly to a spectrum of authentic $(CN)_5Co^{III}OH_2^{2-}$ with the calculated concentration of Co(III) showing excellent agreement with the gravimetric concentration of the starting compound, $(CN)_5Co^{III}L^{n-}$. These results coupled with the atomic absorption studies on K_x-$[(CN)_5Co^{III}L]\cdot xH_2O$ indicate that the initial complexes are pure and that extensive photolysis of $(CN)_5Co^{III}L^{n-}$ leads solely to $(CN)_5Co^{III}OH_2^{2-}$.

Comparison to the Isoelectronic Fe(II) System. Quantum yields for the photoaquation of L from $(CN)_5Co^{III}L^{n-}$ in this work and the previously reported[2] $(CN)_5Fe^{II}L^{(n+1)-}$ complexes are reported in Table II. The choice of various ligands in the study encompasses isoelectronic Fe(II) compounds which are photochemically reactive[2] (i.e., ^{3}LF state presumed lower in energy than MLCT; L = pyridine, isonicotinamide, pyrazine, and 4-cyanopyridine) and photochemically nonreactive[2] (i.e., MLCT state presumed lower in energy than ^{3}LF; L = N-methylpyrazinium). We observe substantial substitutional reactivity (Φ_L > 0.1) for all of the Co(III) compounds in this study. This suggests that the drop-off in quantum yield in the Fe(II) sequence when L = N-methylpyrazinium is not anomalous ligand behavior but is due to a crossover of LF and MLCT states as previously postulated.[2]

A comparison of the quantum yields for the isoelectronic $(CN)_5Fe^{II}$ and $(CN)_5Co^{III}$ systems for L in which LF reactivity is observed for both metal centers (i.e., L ≠ N-methylpyrazinum) shows one interesting correlation. In all such choices of L, the Co(III) quantum yield is smaller than the analogous Fe(II) quantum yield. This may reflect a greater difficulty in breaking the M–L bond in the excited state of the 2– charged $(CN)_5Co^{III}$ metal center than in the 3– charged $(CN)_5Fe^{II}$. This explanation is consistent with electrostatic considerations of removing a nitrogen base from the metal

center and parallels, but is less dramatic than, the relative ground-state substitutional reactivity (from ref 2 and this work). However, any direct comparison of Fe(II) and Co(III) quantum yields relies on the unlikely assumption that the lifetimes of the Co(III) and Fe(II) excited states (and thus the nonradiative decay rates) are similar for the two compounds.

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Electrochemical and Spectroscopic Studies of Uranium(IV), -(V), and -(VI) in Carbonate–Bicarbonate Buffers[1]

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Disproportionation of uranium(V) produced electrochemically by reduction of uranyl ion in bicarbonate solutions was reported by Brancia and Pravdic.[2] Stabilization of U(V) in carbonate solutions with pH >11 was observed by these and other workers.[3-5] In each case the U(V)–carbonate solution was observed to be colorless. Spectroscopic studies[6,7] of uranyl ion in carbonate and bicarbonate media indicate that the $UO_2(CO_3)_3^{4-}$ ion is formed in both solutions. Recently a need for more detailed knowledge of the chemistry of actinide ions in basic media has arisen in connection with deducing their chemistry in the environment. In this work we report the results of polarographic, cyclic voltammetric, and spectroscopic studies of U(IV), -(V), and -(VI) in carbonate and bicarbonate media. Polarographic studies were in excellent agreement with those reported previously.[2] Cyclic voltammetric scans confirmed the irreversible reduction to U(V) in both solutions, but disproportionation of the U(V) was observed only in the bicarbonate solutions. The oxidation of U(V) in carbonate was followed spectroscopically for the first time. Reduction in bicarbonate produced U(IV), the spectrum of which is now reported and the oxidation of which was also followed spectroscopically for the first time.

Experimental Section

Anhydrous powdered Na_2CO_3 (analytical reagent, Mallinckrodt, St. Louis, MO, and ultrapure, Alfa Products, Danvers, MA), certified $NaHCO_3$ (Fisher Scientific Co., Fair Lawn, NJ), and $UO_2(ClO_4)_2$ (Research Organic/Inorganic Chemical Corp., Sun Valley, CA) were used as received. Solutions were prepared by using triply distilled

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(2) M. Branica and V. Pravdic, "Polarography 1964", Vol. 1, G. J. Hills, Ed., Macmillan, London, 1966, p 435.
(3) D. Cohen, *J. Inorg. Nucl. Chem.*, **32**, 3525 (1970).
(4) L. A. McClaine, E. P. Bullwinkel, and J. C. Huggins, *Proc. Int. Conf. Peaceful Uses At. Energy, 1st*, **8**, 26–37 (1955).
(5) S. Casadio and F. Orlandini, *J. Electroanal. Chem.*, **26**, 91 (1970).
(6) S. O. Cinneide, J. P. Scanlan, and M. J. Hynes, *J. Inorg. Nucl. Chem.*, **37**, 1013 (1975).
(7) J. P. Scanlan, *J. Inorg. Nucl. Chem.*, **39**, 635 (1971).