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Preparation, Reactivity, and Stability of Mixed-Metal Bimetallic Complexes Containing the Pentacyanoferrate(II) Moiety

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A series of mixed-metal bimetallic complexes of the type $(CN)_5Fe^{II}LM^{III}L'_5$, where L = 4-cyanopyridine, pyrazine, or 4,4'-bipyridine and $M^{III}L'_5 = Rh^{III}(NH_3)_5$ or $Co^{III}(CN)_5$, have been prepared and characterized. These complexes are formed by the reaction $(CN)_5Fe^{II}OH_2 + LM^{III}L'_5 \rightleftharpoons (CN)_5Fe^{II}LM^{III}L'_5$. The rate constant for dimer formation, k_2, is a factor of 10^3 smaller for $M^{III} = Co(III)$ ($\sim 1\ M^{-1}\ s^{-1}$) than for Rh(III) ($\sim 10^3\ M^{-1}\ s^{-1}$). This is due to a charge effect in the formation of an outer-sphere encounter complex. The rate constants for bimetallic dissociation, k_{-2}, are relatively insensitive ($\sim 10^{-3}\ s^{-1}$) to the nature of the remote metal and indicate a dissociative decomposition. The formation constant of the bimetallic complex, K_2, parallels k_2 and is larger for the $LRh^{III}(NH_3)_5$ complexes than for $LCo^{III}(CN)_5$ complexes bound to the $(CN)_5Fe^{II\ 3-}$ fragment.

Introduction

There have been numerous studies on the thermal[1–8] and photochemical[9–11] reactions of unsaturated nitrogen heterocyclic ligands (L) bound to pentacyanoferrate(II) and pentaammineruthenium(II) metal centers. The near ultraviolet and visible spectra of these complexes are dominated by an intense metal-to-ligand charge transfer (MLCT) band assigned as $p\pi^*$ (L) $\leftarrow$ $d\pi$ (M) in character.[1,12] The energy of the MLCT band maximum is very sensitive to substituent changes on L (i.e., the energy of the π^* orbitals of free L), with more electron-withdrawing substituents causing red shifts in the MLCT maximum as well as greater ground-state delocalization of electron density into L (π back-bonding).[1]

For the pentacyanoferrate(II) complexes, kinetic and equilibrium studies have suggested that the formation reaction (k_1 in eq 1) occurs by a D or possibly I_d mechanism[2,13] while

$$(CN)_5Fe^{II}OH_2 + L' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CN)_5Fe^{II}L'$$
$$K_1 = k_1/k_{-1} \tag{1}$$
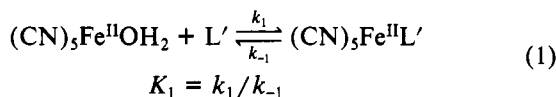
the dissociation reaction (k_{-1} in eq 1) is most probably D in character.[1,3] The comparison of k_1 to a variation in charge on a variety of entering ligands L' (where L' is N-heterocycle,[1] CN^-,[13] SO_3^{2-},[13] imidazole,[4,5] glycinate,[4] histidine,[4] and aliphatic amine and ammonium ions[14]) has led to the suggestion that k_1 depends on the diffusion-controlled approach of L' followed by Fe(II)–L' bond formation. In addition, the stability of the $(CN)_5Fe^{II}L'$ complexes, as a consequence of π back-bonding, is evidenced by the large formation constants found for eq 1 ($k_1 \gg k_{-1}$).[2]

The parallelism observed in the thermal chemistry of (C-N)$_5$Fe^{II}L and (NH$_3$)$_5$Ru^{II}L is observed in the photochemistry as well. Both Fe(II)[9] and Ru(II)[10] centers show photosubstitution reactions for loss of L and have quantum yields which depend on the energy of the MLCT maximum. That is, when the energy of the MLCT maximum is greater than $\sim 2.1\ \mu m^{-1}$ for Fe(II) and Ru(II) complexes, photosubstitution quantum yields are large and relatively invariant but these quantum yields drop off dramatically as the MLCT maximum is red shifted from 2.1 μm^{-1}. The interpretation for the Fe(II)[9] and Ru(II)[10] systems, as well as the similar behavior observed for $(CO)_5WL$ complexes,[15] is that the dropoff point coincides to a crossover of the ligand-substituent-sensitive, but unreactive, MLCT excited state and a ligand-substituent-insensitive, but reactive, ligand field (LF) excited state.

Previously,[16] we took advantage of the ability to turn on and off the photosubstitution reactions at $(NH_3)_5Ru^{II}L$ centers and prepared and studied the photochemistry of the mixed-metal bimetallic complexes $(NH_3)_5Ru^{II}LRh^{III}(NH_3)_5^{5+}$ (L = 4-cyanopyridine and pyrazine). One of these, L = 4-CNpy, upon absorption of light into the MLCT band, associated predominantly with $p\pi^*$ (L) $\leftarrow$ $d\pi$ (Ru), resulted in a reaction characteristic of a ligand field (LF) excited state of Rh(III). Our interpretation[16] is that this system is undergoing an intramolecular energy transfer process. In extending this work to the $(CN)_5Fe^{II}L$ system, the thermal stabilities of complexes of the type $(CN)_5Fe^{II}LRh^{III}(NH_3)_5$ and $(CN)_5Fe^{II}L\ Co^{III}\text{-}(CN)_5^{5-}$, as well as the formation and dissociation kinetics of such differently charged species, needed to be determined before attempting the photochemistry. The results of these thermal studies are reported herein.
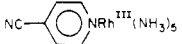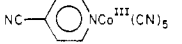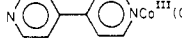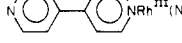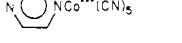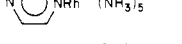
Experimental Section

Materials. Analytical reagent grade compounds were used for all preparations described in this work. Water used for syntheses, equilibrium constant measurements, and kinetic measurements was redistilled from alkaline permanganate in an all glass apparatus. The $LiClO_4$ used to adjust ionic strength was prepared from Li_2CO_3 and $HClO_4$. Sodium pentacyanoaminoferrate(II) was prepared by published methods[17] as was the N-methylpyrazinium iodide[18] used in trapping experiments.

Spectroscopy. All absorption spectra and absorbance measurements used in kinetic and stability measurements were recorded on a Cary 14 UV–visible–near-IR spectrophotometer. The atomic absorption data used for iron and cobalt analysis were obtained on a Perkin-Elmer

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Table I. Electronic Spectra of $(CN)_5Fe^{II}L$ Mixed-Metal Bimetallic Complexes

L	E_{max}, μm^{-1}	$10^{-3}\epsilon_{max}$,[a] M^{-1} cm^{-1}
NC—〈ring〉—NRh^{III}(NH$_3$)$_5$	2.50	~4.5[c]
NC—〈ring〉—NCo^{III}(CN)$_5$	2.33	~3
N〈ring〉—〈ring〉NCo^{III}(CN)$_5$	2.18	3.2
N〈ring〉—〈ring〉NRh^{III}(NH$_3$)$_5$	2.08, 1.94[b]	5.4[c]
N〈ring〉NCo^{III}(CN)$_5$	1.90	4.0
N〈ring〉NRh^{III}(NH$_3$)$_5$	1.75	9.3, 8.2,[c] 8.0[d]

[a] Assigned as N-heterocycle $\leftarrow$ Fe^{II} ($p\pi^* \leftarrow d\pi$) MLCT transition, 25 °C, with H$_2$O as solvent unless otherwise noted. [b] Solid-state (KBr pellet) electronic spectrum; see ref 6. [c] $\mu = 0.5$ (LiClO$_4$). [d] $\mu = 1.0$ (LiClO$_4$).

Model 403 atomic absorption spectrometer calibrated with commercial standards. Carbon, hydrogen, and nitrogen analysis for the iron–rhodium complexes were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses. Pentaamminerhodium(III) Complexes, [Rh(NH$_3$)$_5$-L](ClO$_4$)$_3$. The complexes [Rh(NH$_3$)$_5$L](ClO$_4$)$_3$ (L = pyrazine (pz), 4-cyanopyridine (4-CNpy), and 4,4'-bipyridine (4,4'-bpy)) were prepared by one of two previously reported procedures.[19,20] The pyrazine complex was prepared as previously reported,[20] whereas the other two complexes resulted from the following modifications of the literature procedure.[19] A mixture of 0.455 g (0.9 mmol) of [Rh(N-H$_3$)$_5$O](ClO$_4$)$_3$,[21] 22 mmol of the corresponding ligand, L, and 8 mL of N,N-dimethylacetamide was heated at 100–110 °C for 5 h. The solution was filtered hot and then added to 200 mL of isobutyl alcohol. The suspension was cooled overnight at 5 °C. The white crystals which formed were collected, washed with ethanol and then ether, and dried under vacuum: L = pz, yield 0.48 g (89%); L = 4-CNpy, yield 0.49 g, (93%); L = 4,4'-bpy, yield 0.54 g (93%). When necessary, recrystallization from hot water reduced the yields by 15–25%.

Pentacyanocobaltate Complexes, K$_2$[Co(CN)$_5$L]·xH$_2$O. The preparation of K$_2$[Co(CN)$_5$L]·xH$_2$O complexes (L = pz, 4-CNpy, and 4,4'-bpy) from Co(CN)$_5$H$_2$O^{2-} has been previously reported.[22] The Co(CN)$_5$H$_2$O^{2-} used to prepare the above compounds was prepared by a modification of the photolytic procedure of Adamson et al.[23] A 0.04 M solution of K$_3$[Co(CN)$_6$] (6.55 g in 500 mL of H$_2$O) was placed in an Ace Pyrex immersion apparatus and irradiated with a Hanovia 450-W medium-pressure mercury lamp. During the 5-h irradiation, nitrogen gas was continuously bubbled through the system and the solution pH was adjusted to 7 every hour with dilute perchloric acid. The resulting Co(CN)$_5$H$_2$O^{2-} solution was used directly in preparation of K$_2$[Co(CN)$_5$L]·xH$_2$O complexes.

Pentacyano(pentaamminerhodium(III))iron(II) Complexes, [(C-N)$_5$FeLRh(NH$_3$)$_5$]·xH$_2$O. The bimetallic compounds of pentaamminerhodium(III) and pentacyanoferrate(II) bridged by pz, 4-CNpy, and 4,4'-bpy were prepared by the same method. A pressure-equalizing separatory funnel, containing 2 mL of water, was placed on a round-bottom flask containing 49 mg (0.18 mmol) of Na$_3$[Fe(CN)$_5$NH$_3$]·3H$_2$O and 0.18 mmol of [Rh(NH$_3$)$_5$L](ClO$_4$)$_3$. After the entire system was deoxygenated for 15 min with chromous-scrubbed nitrogen in the dark, the water was added to the solid Fe(II) and Rh(III) compounds. The red or purple product which

formed and precipitated immediately was collected in a sintered glass filter, washed twice with ice water, ethanol, and then ether, and dried under vacuum: L = pz, yield 72 mg (74%); L = 4-CNpy, yield 81 mg (77%); L = 4,4'-bpy, yield 111 mg (92%). Electronic absorption spectroscopy data are reported in Table I.

Anal. Calcd for C$_9$H$_{19}$N$_{12}$FeRh·5H$_2$O (L = pyrazine): C, 19.9; H, 5.4; N, 30.9; Fe, 10.3. Found: C, 19.8; H, 4.7; N, 30.7; Fe, 9.8. **Anal.** Calcd for C$_{15}$H$_{23}$N$_{12}$FeRh·7.9H$_2$O (L = 4,4'-bipyridine): C, 26.8; H, 5.8; N, 25.0; Fe, 8.3. Found: C, 26.8; H, 5.8; N, 24.1; Fe, 8.2. **Anal.** Calcd for C$_{11}$H$_{19}$N$_{12}$FeRh·6H$_2$O (L = 4-cyanopyridine): C, 22.5; H, 5.3; N, 28.7; Fe, 9.5. Found: C, 22.9; H, 5.1; N, 27.4; Fe, 9.2.

Decacyanocobaltate(III)ferrate(II) Complexes, Na$_3$K$_2$[(CN)$_5$FeL-Co(CN)$_5$]. Equal molar amounts of recrystallized Na$_3$[Fe(CN)$_5$N-H$_3$]·3H$_2$O (0.400 g, 1.23 mmol) and recrystallized K$_2$[Co(CN)$_5$L] (1.23 mmol) (L = pz, 4-CNpy, 4,4'-bpy) were dissolved in 15 mL of deoxygenated water. After 15 min of stirring in the dark, the solution was frozen in isopropyl alcohol/dry ice and the solvent was removed with a Virtis Model 10-135 freeze dryer: L = pz, 0.42 g (100%); L = 4-CNpy, 0.46 g (100%); L = 4,4'-bpy, 0.52 g (100%).

Analysis. The Fe–Co bimetallic compounds were very sensitive to air oxidation, are hygroscopic, and decompose in the solid state. Thus, C, H, and N analysis were not consistent with the stoichiometric addition of the well-characterized monometallic fragments used in preparation. However, we were able to obtain iron and cobalt analysis by atomic absorption spectroscopy within hours of compound preparation. It was assumed that there were no waters of hydration. **Anal.** Calcd for L = pz: Fe, 9.7; Co, 9.8. Found: Fe, 8.9; Co, 9.8. **Anal.** Calcd for L = 4,4'-bpy: Fe, 8.6; Co, 8.7. Found: Fe, 8.6; Co, 8.9. **Anal.** Calcd for L = 4-CNpy: Fe, 9.4; Co, 9.4. Found: Fe, 9.6; Co, 9.7.

The electronic spectra and extinction coefficients reported for these bimetallic compounds in Table I were obtained by recording the spectrum of a known amount of Fe monomer in a 20–100-fold excess of Co monomer. The absorption maximum obtained in this fashion is identical with the maximum of the freshly prepared and isolated solid bimetallic complexes dissolved in water.

Extinction Coefficient Measurements. Due to the differing degrees of dissociation of the bimetallic compounds into the monometallic components in aqueous solutions, molar extinction coefficients were determined with an excess of monomeric unit LCo(CN)$_5^{2-}$ for Fe–Co and LRh(NH$_3$)$_5^{3+}$ for Fe–Rh complexes. The amount of excess monometallic components added were governed by the magnitude of the equilibrium constant (CN)$_5$FeOH$_2^{3-}$ + LML'$_5$ $\rightleftharpoons$ (CN)$_5$FeLML'$_5$ such that less than 1% of Fe was left in the monometallic form.

Equilibrium Constants. Stability constants for the bimetallic complexes in 0.5 M LiClO$_4$ (Fe–Rh) and H$_2$O (Fe–Co) were measured at 25 °C by one of two methods. For bimetallic complexes which show a substantial dissociation in the measuring solution, direct measurement of K was made by preparing solutions of various concentrations of the bimetallic complex or unequal concentrations of the monometallic units and monitoring the absorbance of the MLCT band in the bimetallic complex. For bimetallic complexes which did not show substantial dissociation into monometallic units (Fe–Rh), an alternate method was used. The bimetallic complex was placed in 0.5 M LiClO$_4$ with a variable amount of pyridine. The solution was allowed to proceed to equilibrium and analyzed for amounts of (CN)$_5$Fe(py)$^{3-}$ and Fe–Rh bimetallic complex by the absorbance values at the respective MLCT bands. Equilibrium was reached from both directions by allowing one cuvette to proceed from a bimetallic/Fe(py) mixture to equilibrium while another sample in an identical cuvette was irradiated to complete formation of (CN)$_5$Fe-(py)$^{3-}$ + LRh(NH$_3$)$_5$ and thermal return to equilibrium was permitted.

Kinetic Experiments. The kinetics were carried out with freshly prepared solutions, mixed in the dark at 25 °C, according to conventional procedures. For systems involving measurement of bimetallic formation rates, initial Fe monomer concentrations were kept below 3×10^{-5} M to avoid formation of the Fe$_2$(CN)$_{10}^{6-}$ dimer.[24] The treatment of data is described in the results. The formation constants, K_2 for the Co(III) reactions, and the dissociation constants, k_{-2} for the Rh(III) reactions, show average deviations of ~10%. Correlation coefficients for all kinetic studies were 0.995 or better. The equilibrium

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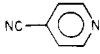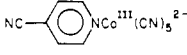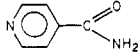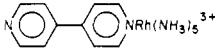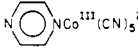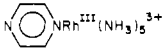(20) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
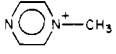(21) Bushnell, G. W.; Lalor, G. C.; Moelwyn-Hughes, E. A. *J. Chem. Soc. A* **1966**, 719.
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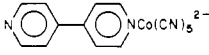
Table II. Kinetics and Equilibrium Parameters for $(CN)_5Fe^{II}L^a$

L	E_{max}, μm^{-1} [b]	k_2,[c] M^{-1} s^{-1}	k_{-2},[d] s^{-1}	K_2,[e] M^{-1}	ref
(pyridine)	2.76	3.65×10^2	1.10×10^{-3}	3.3×10^5	1, 2
NC—(py)	2.47	2.35×10^2	9.7×10^{-2}	2.42×10^3	3, f
NC—⟨⟩NCo^{III}(CN)$_5^{2-}$	2.33	1.6	6.7×10^{-4}	2.4×10^3	g, h
(isonicotinamide, —C(=O)NH$_2$)	2.30	2.96×10^2	7.3×10^{-4}	4.0×10^5	1, 2
(pyrazine)	2.22	3.80×10^2	4.2×10^{-4}	9.0×10^5	1, 2
N⟨⟩—⟨⟩NCo(CN)$_5^{2-}$	2.20	3.0	1.2×10^{-4}	2.6×10^4	g, h
N⟨⟩—CN	2.10	3.83×10^2	1.02×10^{-3}	3.75×10^5	3
N⟨⟩—⟨⟩NRh(NH$_3$)$_5^{3+}$	2.08	1.4×10^3	7.0×10^{-4}	2×10^6	h
N⟨⟩NCo^{III}(CN)$_5^{2-}$	1.90	0.5	1.2×10^{-4}	4×10^3	g, h
N⟨⟩NRh^{III}(NH$_3$)$_5^{3+}$	1.75	2.6×10^3	7.4×10^{-4}	3.5×10^6	h
		1.1×10^3	7.4×10^{-4}	1.5×10^6	h, i
N⟨⟩N$^+$—CH$_3$	1.52	5.50×10^2	2.8×10^{-4}	2.0×10^6	1, 2, i

^{a} $\mu = 0.50$ M (LiClO$_4$); $T = 25$ °C unless otherwise noted. ^{b} For MLCT absorption band. ^{c} Rate constant for formation of $(CN)_5Fe^{II}L$. ^{d} Rate constant for dissociation of $(CN)_5Fe^{II}L$. ^{e} Formation constant, k_2/k_{-2}. ^{f} $\mu = 0.10$ M (LiClO$_4$). ^{g} H$_2$O solvent. ^{h} This work. ^{i} $\mu = 1.0$ M (LiClO$_4$).
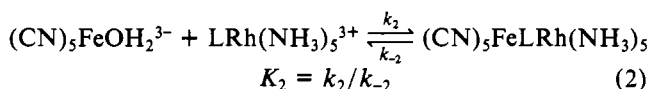
constants, K_2 for the Co(III) systems, gave average deviations from 10 to 20%, while the corresponding Rh(III) systems showed deviations of <10%. A minimum of three runs was used for each rate constant and equilibrium constant listed in Table II.

Results

Electronic Spectra. The electronic spectra of the mixed-metal bimetallic complexes of pentacyanoferrate(II) are given in Table I. All of the complexes have intense bands in the near-UV–visible spectral region with molar extinction coefficients ranging from 3×10^3 to 10^4. This intense transition has been assigned as a metal-to-ligand charge-transfer (MLCT) transition which is presumed to be a $p\pi^* \leftarrow d\pi$ excitation localized mainly on the Fe(II) center and the bridging, nitrogen, heterocyclic ligand. This type of assignment has previously been made by Creutz and Taube[20] for the similar compound $(NH_3)_5Ru^{II}pzRh^{III}(NH_3)_5^{5+}$.

In every case except L = 4-CNpy, the maximum of the Fe(II)–Rh(III) compound is red-shifted with respect to the Fe(II)–Co(III) bimetallic complex. In addition, with the exception of the 4-CNpy-bridged Fe(II)–Rh(III) compound, all bimetallic complexes have their MLCT band red-shifted with respect to the monometallic Fe(II)–L compounds. The extinction coefficients for the Rh(III) bimetallic complexes are larger than the Co(III) counterparts. In contrast to the monometallic $(CN)_5Fe^{II}L^1$ or $(NH_3)_5Ru^{II}L^{12}$ units, the MLCT band of these bimetallic complexes are reasonably symmetric, especially for those compounds which have long-wavelength maxima (i.e., pz-bridged complexes) that are greatly separated from internal ligand or other prominent spectral features.

Rate and Equilibrium Studies. The Fe(II)–Rh(III) bimetallic complexes exist in equilibrium with the monometallic fragments as shown in eq 2. Since the equilibrium constant,

$$(CN)_5FeOH_2^{3-} + LRh(NH_3)_5^{3+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (CN)_5FeLRh(NH_3)_5$$

$$K_2 = k_2/k_{-2} \qquad (2)$$

K_2, largely favors the bimetallic complexes, competition studies with an N-heterocycle (L') such as pyridine (py), isonicotin-
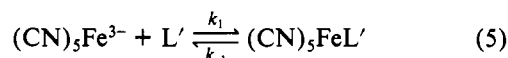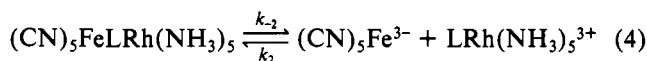
amide (isn), and N-methylpyrazinium (N-Mepz$^+$) (with use of eq 1) were necessary to measure the equilibrium constants. From eq 1 and 2, we get eq 3. (For simplicity, cyano groups

$$K' = K_2/K_1 = [FeLRh][L']/[LRh][Fe^{II}L'] \qquad (3)$$

will be left off of Fe(II) and Co(III) metal centers and ammine ligands left off Rh(III).)

By measuring K' under a variety of L' concentrations, approaching the equilibrium from both sides (see Experimental Section), and using Toma and Malin's[2] values for K_1, we calculate the K_2 values given in Table II.

The dissociation rates, k_{-2}, for the Fe(II)–Rh(III) bimetallic complexes were measured in an excess of [LRh] with kinetic data consistent with the mechanism described by eq 4 and 5.

$$(CN)_5FeLRh(NH_3)_5 \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} (CN)_5Fe^{3-} + LRh(NH_3)_5^{3+} \qquad (4)$$

$$(CN)_5Fe^{3-} + L' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CN)_5FeL' \qquad (5)$$

The rate law for the mechanism, when $LRh(NH_3)_5^{3+}$ is kept in excess, is eq 6. At large [L'], k_{obsd} reduces to k_{-2} (Table
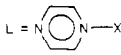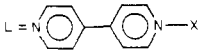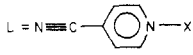
$$\frac{-d[FeLRh]}{dt} = k_{obsd}([FeLRh] - [FeLRh]_\infty)$$

$$k_{obsd} = \frac{k_1 k_{-2}[L'] + k_{-1}k_2[LRh]}{k_2[LRh] + k_1[L']} \qquad (6)$$

II). The limit of k_{obsd} as [L'] approaches 0 is k_{-1}. With literature values for k_{-1} and k_1,[2] eq 6 indicates that k_{obsd} should reach a limiting value (k_{-2}) at [L'] > 0.005 M (which is observed for all L' ligands studied). In addition, at [L'] < 0.005 M, k_{obsd} has a value between k_{-1} and k_{-2} for all trapping agents used as expected from eq 6.

The formation rate constants, k_2, for the Fe(II)–Rh(III) bimetallic complexes were calculated from the equilibrium constants, K_2, and the dissociation rate constants, k_{-2}. The values for k_2 were confirmed not to be smaller than reported by directly measuring lower limits of k_2 with dilute solutions

Table III. Comparison of the MLCT Maxima of Monomeric and Dimeric Pentacyanoferrate(II) Complexes, $(CN)_5Fe^{II}L$

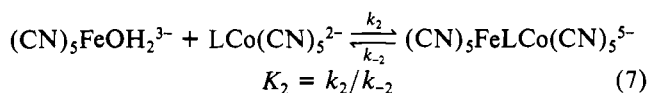| $L = N\!\!-\!\!\bigcirc\!\!-\!\!X$		$L = N\!\!-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-\!\!X$		$L = N\!\!\equiv\!\!C\!\!-\!\!\bigcirc\!\!-\!\!X$	
X	$E_{max},^a$ μm^{-1}	X	$E_{max},^a$ μm^{-1}	X	$E_{max},^a$ μm^{-1}
	2.22		2.32	$Rh(NH_3)_5^{3+}$	2.50
$Fe(CN)_5^{3-}$	1.98^b	$Fe(CN)_5^{3-}$	2.25^b		2.47^c
$Co(CN)_5^{2-}$	1.90	$Co(CN)_5^{2-}$	2.20	$Co(CN)_5^{2-}$	2.33
$Rh(NH_3)_5^{3+}$	1.75	$Rh(NH_3)_5^{3+}$	2.08	CH_3^+	1.80^b
CH_3^+	1.52^b	CH_3^+	1.94^b		

^{a} MLCT band associated mainly with $p\pi^*$ (L) $\leftarrow d\pi$ (Fe(II)). ^{b} Reference 18. ^{c} Reference 13.

of $(CN)_5FeOH_2^{3-}$ and $LRh(NH_3)_5^{3+}$ on the Cary 14 spectrophotometer.

The equilibrium constant, K_2, and the rate of formation, k_2, for the Fe(II)–Co(III) bimetallic complexes were measured simultaneously (eq 7). The reaction proved to be first order

$$(CN)_5FeOH_2^{3-} + LCo(CN)_5^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (CN)_5FeLCo(CN)_5^{5-}$$

$$K_2 = k_2/k_{-2} \tag{7}$$

in Fe(II) monomer and first order in Co(III) monomer. Since the equilibrium constants are not as large for Fe(II)–Co(III) as for Fe(II)–Rh(III) bimetallic complexes, it was not practical to run the reaction in a large enough excess of $LCo(CN)_5^{2-}$ to drive the reaction completely to the bimetallic complex. The rate law for eq 7 thus becomes[25]

$$d[FeLCo]/dt = k_2[([FeOH_2]_{in} - [FeLCo])([LCo]_{in} - [FeLCo])] - k_{-2}[FeLCo]$$

where $[FeOH_2]_{in}$ is initial concentration of $(CN)_5FeOH_2^{3-}$ and $[LCo]_{in}$ is initial concentration of $LCo(CN)_5^{2-}$. From the integrated form of the rate law,[25] linear plots were expected and obtained for $\ln[([FeOH_2]_{in}[LCo]_{in} - [FeLCo]_\infty[FeLCo])/([FeLCo] - [FeLCo]_\infty)]$ vs. t with the slope of the line corresponding to k_2. The k_2 values in Table II were generated from the above plots, while equilibrium constants were calculated from the same data with the equilibrium concentration of the bimetallic complex, $[FeLCo]_\infty$.

The dissociation rate constants, k_{-2}, were calculated from K_2 and k_2 and appear in Table II as well. Even though the rate of bimetallic decomposition is about the same for both sets of bimetallic complexes, direct measurement of k_{-2} for the Fe(II)–Co(III) species was complicated by small K_2 values which, when compared to the Fe(II)–Rh(III) species, led to smaller equilibrium concentrations of bimetallic complex and larger equilibrium concentrations of $(CN)_5FeOH_2^{3-}$. Small bimetallic concentrations led to an insensitivity in the bimetallic dissociation trapping experiments, while large iron aquo concentrations led to complications due to iron oxidation and/or formation of $Fe_2(CN)_{10}^{6-}$.[24]

Discussion

The energy maximum of the MLCT band associated with the pentacyanoferrate(II) and unsaturated, nitrogen heterocyclic ligand (L) is susceptible to changes at the remote sites of L. Table III summarizes the change in MLCT energy maximum for a variety of species (X) bound to remote sites of the L ligands pz, 4,4'-bpy, and 4-CNpy. In all cases except L = 4-CNpy, remote coordination to L of a metal complex or other Lewis acid, shifts the MLCT band associated with $(CN)_5Fe^{II}L$ to lower energy. For L = 4-CNpy, X = Rh($NH_3)_5^{3+}$, the MLCT band is actually blue-shifted from X = lone pair. Since this ligand is unique in that nitrile is bound

to $(CN)_5Fe^{II}$, our original thought was that π-electron communication between the pyridine ring and the nitrile functionality in the bridging ligand may be poor. Another possibility was that the remote $Rh(NH_3)_5^{3+}$ was variably involved in the π system of the different metal bimetallic complexes as well as participating as a Lewis acid. However, the large variability in the MLCT maximum for NCR, NCpyX and NCPhX compounds for $(CN)_5Fe^{II}$ [3] and $(NH_3)_5Ru^{II}$ [26] complexes appear to rule out the former explanation, while Mössbauer and electrochemical results from this laboratory[27] suggest, at this time, that there is little or no remote metal π interaction with Rh(III) or Co(III) in the iron bimetallic systems.

For L = pz or 4,4'-bpy, the position of the MLCT maximum in Table III directly parallels the σ acceptor or Lewis acid strength of the substituent X. The strongest Lewis acid is CH_3^+,[28] which corresponds to the largest red-shift from free ligand. In comparing the magnitude of the shifts for L = pz and 4,4'-bpy, the larger shifts are observed for L = pz.

σ acceptor	CH_3^+	Rh(III)	Co(III)	Fe(II)	free space
L = pz shift (μm^{-1})	0.70	0.47	0.32	0.24	0
L = 4,4'-bpy shift (μm^{-1})	0.38	0.24	0.12	0.07	0

This is not surprising since the distance between metal centers is much larger in the 4,4'-bpy complex and since there is NMR evidence[18] that the carbon–carbon single bond connecting the pyridine rings attenuates the electron communication between the rings.

Toma and Malin[1] were the first to report linearity of the plot of MLCT energy maxima for $(CN)_5Fe^{II}L$ vs. $(NH_3)_5Ru^{II}L$. Including data for substituted pyridines,[1,12] nitriles,[3,26b] and the bimetallic complexes[29] (Figure 1), only L = N-Mepz$^+$ and the Rh(III) bimetallic complexes diverge from the line. Of the Rh(III) bimetallic complexes, the 4,4'-bpy-bridged system actually lies very close to the line while L = 4-CNpyRh($NH_3)_5^{3+}$ and pzRh($NH_3)_5^{3+}$ lie well above and below the line, respectively. Even though MLCT energy maxima seem to correlate well with reduction potentials[27] for both Fe(II)–Rh(III) and Ru(II)–Rh(III) bimetallic complexes, the linearity of the plot in Figure 1 breaks down for these species. The source of this discrepancy may lie in the fact that water solvation of the electrically neutral Fe(II)–Rh(III) species must be substantially different than the solvation of the 5+ Ru(II)–Rh(III) complexes. Large charge separation of $(CN)_5Fe^{3-}$ and $Rh(NH_3)_5^{3+}$ by the lengthy bridge 4,4'-bpy may allow independent solvation at each end of this complex and, thus, a system that will interact with a polar solvent in a manner similar to that of the ruthenium(II) counterpart.

We find (Table II) that there is a reasonably small range of values of the dissociation rate constant (k_{-2}) of $(CN)_5Fe^{II}L$. The ligand L varies from neutral and monocationic ligands to metal-containing polycationic or polyanionic ligands while k_{-2} varies from 1.2×10^{-4} to 9.7×10^{-2} s^{-1}. In fact, if the upper value (L = 4-CNpy) is removed,[30] the values span only 1 order of magnitude (10^{-4}–10^{-3} s^{-1}). There does appear to be a tendency for slower dissociation in complexes exhibiting greater π back-bonding (π back-bonding assumed to be larger

(25) Laidler, K. J. "Chemical Kinetics"; McGraw-Hill: New York, 1965; p 21.

(26) (a) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227; (b) *Ibid.* 495.
(27) Pfenning, K. J.; Lee, L.; Petersen, J. D., work in progress. The Mössbauer isomer shift and quadrupolar splitting and the $E^{o\prime}$ values obtained from cyclic voltammetry studies parallel the positions of the MLCT maxima and do not suggest anything other than remote metal σ-withdrawing effects.
(28) It is not surprising that $Rh(NH_3)_5^{3+}$ is a stronger Lewis acid than $Co(CN)^{2-}$ since the pK_a values of the aquo complexes, $Rh(NH_3)_5H_2O^{3+}$ and $Co(CN)_5H_2O^{2-}$, are 5.9 and 9.7, respectively.
(29) Reference 16, this work, and work in progress.
(30) Nitrile bound ligands typically have k_{-2} values $\sim$2 orders of magnitude faster than pyridine bound ligands.[3]

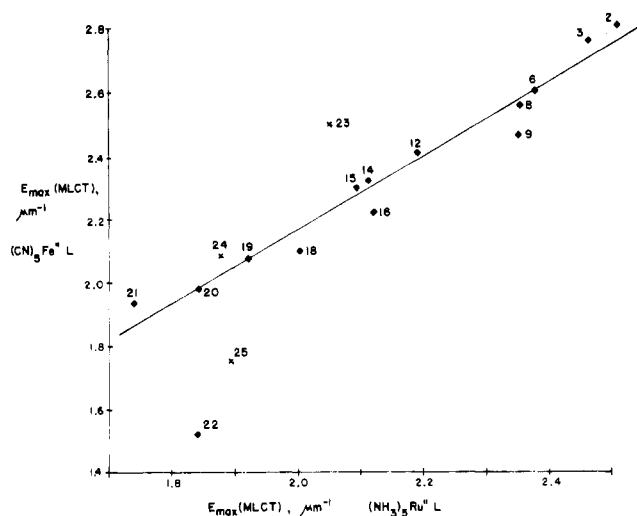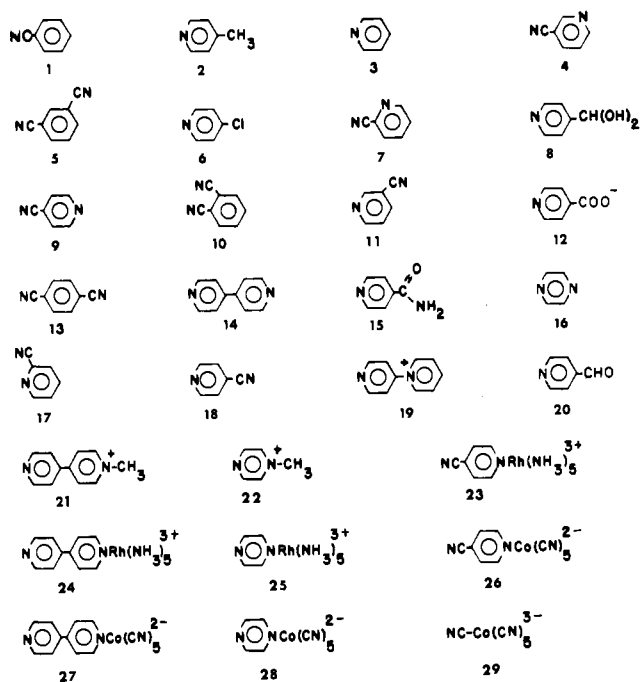**Figure 1.** Energy maxima of metal-to-ligand charge-transfer bands in $(CN)_5Fe^{II}L$ complexes vs. that in the corresponding $(NH_3)_5Ru^{II}L$ complexes. The line represents all Fe and Ru monomers except L = N-Me(pz)$^+$; slope = 1.16, intercept = -0.17, R = 0.946 (♦ represents Fe and Ru monomers, × represents Fe-Rh and Ru-Rh complexes).

Key to Ligands in Figures 1 & 2

for lower energy MLCT maxima). There are a number of reports[1,13,14] favoring a dissociative (D) mechanism for loss of L from $(CN)_5Fe^{II}L$. In fact, in studies on complexes such as $(CN)_5Fe(3,5-Me_2py)^{3-}$ in mixed solvents, Blandamer et al.[31] have suggested that it is the solvation of the metal center, and not that of the leaving group, that most greatly affects the substitution reaction rate. Thus, it is not surprising that, in the series of monometallic and bimetallic Fe(II) complexes, heterocycles having about the same Fe(II)–L bond energy have about the same k_{-2} value.

Another indication of a dissociative mechanism for k_{-2} is the linear free energy relation observed in Figure 2. Figure 2, adapted from ref 3 and 32, but including points for the bimetallic complexes, also includes a least-squares fit[3] of log
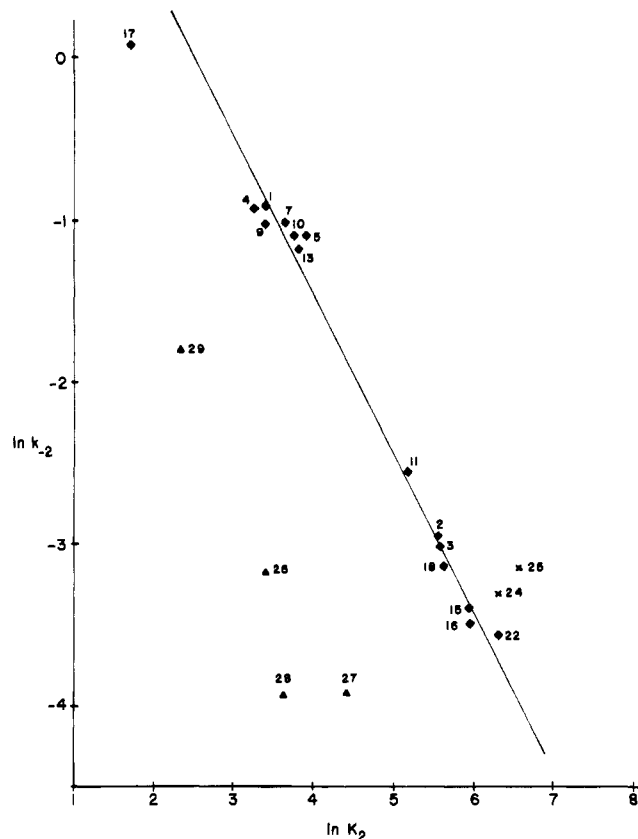

Figure 2. Linear free energy relationships (log k_{-2} vs. log K_2) for $(CN)_5Fe^{II}$ complexes of ligands with a variety of charges. The terms k_{-2} and K_2 refer to the rate constant for $(CN)_5Fe^{II}L$ dissociation and the formation constant for $(CN)_5Fe^{II}L$, respectively. The line represents the least-squares fit from ref 3 (♦ represents Fe monomers, × represents Fe-Rh complexes, ▲ represents Fe-Co complexes).

k_{-2} = 2.45–0.98 log K_2. The near-linear fit and slope approximating -1.0 have been interpreted[33,34] as involving a D mechanism.

The position of the bimetallic complexes on Figure 2 is such that the incoming Rh(III)-containing ligands lie slightly above the line, while the Co(III)-containing ligands (including $(NC)Co(CN)_5^{3- 35}$) lie well below the line. These deviations from the line drawn in Figure 2 can be attributed to a charge effect of incoming ligand on the formation reaction (k_2). Since k_2 must be constant in order to have a linear log k_{-2} vs. log K_2 plot with a slope of -1.0, the deviation can be easily seen by looking at the k_2 values in Table II. This behavior can be explained by considering a two-step process for k_2.[4,34] In the first process contributing to k_2, diffusion-controlled approach of ligand L (highly dependent on the charge of L) forms an encounter complex, which is followed by metal–ligand bond formation in the inner sphere of the reactant. If, for a given charge of ligand L, the rate of Fe(II)–L bond formation is constant for the encounter complex, then each set of incoming ligands with a specific charge should lie along a line with slope -1.0 and offset to the left or right of the line formed by neutral ligands in Figure 2, depending on whether L is negative or positive, respectively.

We can approximate the difference in energy (and thus the contribution to the rate constant) of forming an encounter complex between the Fe–Co and Fe–Rh bimetallic complexes by using simple electrostatic arguments.[36] The rate constant,

(31) Blandamer, M. J.; Burgess, J.; Haines, R. I. *J. Chem. Soc., Dalton Trans.* **1976**, 1293.

(32) James, A. D.; Murray, R. S. *J. Chem. Soc., Dalton Trans.* **1975**, 1530.

(33) Langford, C. H. *Inorg. Chem.* **1965**, *4*, 265.

(34) Haim, A. *Inorg. Chem.* **1970**, *9*, 426.

(35) James, A. D.; Murray, R. S.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1273.

k_2, should be proportional to the probability (P_r) of finding the incoming Co or Rh ion at a distance, r, of the Fe center and is given in eq 8. For the eq 9, Z_A and Z_B are the charges

$$k \propto P_r = 4\pi r^2 (dr)(N/V)e^{-U/kt} \tag{8}$$

$$U = Z_A Z_B e_0^2 / \epsilon r(1 + \kappa r) \tag{9}$$

$$\kappa^2 = 8\pi N e_0^2 \mu \rho / 1000 e kT \tag{10}$$

on the Fe and Co or Rh metal centers, e_0 is the electronic charge in esu, ϵ is the dielectric constant (~ 75). From eq 10, N is Avogadro's number, μ is the ionic strength, ρ is the density of the solvent, k is the Boltzmann constant in erg/K, and T is the temperature (298 K). The value of κ in dilute, aqueous solution at 25 °C is 0.329 $\mu^{1/2}$ in Å^{-1}, thus the κr term is much smaller than 1 in low ionic strength systems. With the assumption that the Fe(II)–L bond-formation activation energy term is constant for incoming LCo^{III}(CN)$_5$ and LRh^{III}(NH$_3$)$_5$ (i.e., the change in rate constant in going from Co to Rh with identical L reflects only the change in electrostatic term), r can be calculated from eq 8–11 for the bridging ligands

$$\ln (k_2(Rh)/k_2(Co)) = (U_{Co} - U_{Rh})/kT \tag{11}$$

4,4'-bpy and pz. The value obtained in this simple calculation for r are 13.4 Å for L = pz and 18.7 Å for L = 4.4'-bpy. These values are consistent with the difference in bridge length and are about twice the expected metal–metal bond distance in the bimetallic complexes. This seems to be reasonable in that the metal–metal distances in the transition state leading to bimetallic complex formation are not known (presumably, they are larger than the metal–metal distance in the bimetallic complex), and the assumptions made that the bond-formation contributions are the same for LCo^{III}(CN)$_5$ and LRh^{III}(NH$_3$)$_5$. Thus, the quantitative results seem reasonable, but more important, the qualitative results that longer bridges (4,4'-bpy > 4-CNpy > pz) insulate the charges of the two metal centers leading to larger k_2 values for the longer bridges in Co(III), and the reverse for Rh(III) are borne out by the data in Table II.

A last point emerging from the rate data in Table II is the ionic strength dependence on the rates of reaction and stability of (CN)$_5$Fe^{II}pzRh^{III}(NH$_3$)$_5$. An increase in the ionic strength from 0.5 to 1.0 does not change k_{-2}, but a decrease in k_2 and

thus K_2 arises, as expected, from a more efficient solvation of the charge-separated species with respect to the neutral bimetallic complexes.

The bimetallic formation constant, K_2, although dependent on both k_2 and k_{-2}, parallels k_2 because of the small variations in k_{-2}. Thus the most important contribution to complex stability is the charge of L. Even though π back-bonding stabilization may be greater for L = N-Mepz$^+$, the larger positive charge for pzRh(NH$_3$)$_5^{3+}$ makes the Fe(II) complex of the latter more stable.

Conclusion

Complexes of the type (CN)$_5$Fe^{II}L, where L in this work consists of an unsaturated, nitrogen heterocyclic ligand and either Rh(NH$_3$)$_5^{3+}$ or Co(CN)$_5^{2-}$ as a remote substituent, exhibit MLCT bands characteristic of the non-remote-metal complexes with the remote metal center acting as an electron-withdrawing substituent. The rate of formation (k_2) of bimetallic complexes depends on the charge of the incoming ligand, LRh^{III}(NH$_3$)$_5^{3+}$ or L Co(CN)$_5^{2-}$, which is attacking the (CN)$_5$Fe^{II} center. The Rh(III)-containing ligands form bimetallic complexes 10^3 times more rapidly than the Co-(III)-containing ligands. This is interpreted as a difference in the diffusion-controlled approach of the two metal centers and not in the metal–ligand bond formation in the subsequent inner-sphere complex. The bimetallic dissociation rate constants, k_{-2}, are less sensitive to nonmetallic complex charges, and the process is shown to be dissociative by trapping experiments. The equilibrium constant, K_2, parallels k_2 and is much larger for the Rh(III) than Co(III) complexes. In terms of the thermal chemistry, the most stable dimers are those in which the monomeric units are oppositely charged.

(36) Davidson, N. "Statistical Mechanics"; McGraw-Hill: New York, 1962; Chapter 21.