function to the more polarizable carbonyl group.

We note finally that reduction of the oxamato derivative of $(NH_3)_5Co^{III}$ is complicated by formation of a strongly absorbing yellow species (λ_{max} = 410 nm), which can be prepared also by adding oxamic acid to Ti(III) solutions. Absorbance data at a number of acidities (of which the entries in Table VIII are representative) conform to eq 15, where l is the optical

$$\text{Abs} = \frac{l\epsilon[\text{Ti}^{\text{III}}]_{\text{T}}}{1 + \frac{K_{\text{dis}}}{K_{\text{A}}^2}\left(\frac{[\text{H}^+]}{[\text{HOx}]}\right)^2} \qquad (15)$$

path length, ϵ the molal extinction coefficient of the absorbing species, $[Ti^{III}]_T$ the total concentration of added Ti^{III}, K_{dis} the dissociation constant of the absorbing species, K_A the acidity constant of oxamic acid (determined independently as 1.8×10^{-2} M in this medium), and [HOx] the concentration of added oxamic acid. Expression 15 corresponds to that applying to a system in which the principal absorbing species is a dioxamato complex of Ti^{III}, $(H_2NCOCOO)_2Ti^+$, a complex which, to our knowledge, has not yet been reported. A nonlinear least-squares refinement of the absorbance data (unweighted) leads to a value of 350 ± 40 M^{-1} cm^{-1} for the molal extinction coefficient and $(3.7 \pm 0.7) \times 10^{-7}$ M^2 for the dissociation constant ($TiOx_2^+ \rightleftharpoons Ti^{3+} + 2Ox^-$).

The extinction coefficient of the dioxamato complex lies close to that reported[36] for the analogous dioxalato complex (490 M^{-1} cm^{-1}) and suggests that both are chelates. However the oxalato complex ($K_{dis} = 3 \times 10^{-13}$ M^2 at 10 °C) is by far the more stable, a difference that is attributable to the additional unit of negative charge on the oxalato anion.

Registry No. I, 84731-51-1; II, 19306-89-9; III, 49861-86-1; IV, 84731-52-2; V, 19306-91-3; VI, 84731-53-3; $R(NH_3)_5Co^{III}$ (R = 2-formylbenzoato), 42532-71-8; $R(NH_3)_5Co^{III}$ (R = 4-formylbenzoato), 19743-65-8; $R(NH_3)_5Co^{III}$ (R = acetato), 16632-78-3; $R(NH_3)_5Co^{III}$ (R = formato), 19173-64-9; $R(NH_3)_5Co^{III}$ (R = glycolato), 31279-86-4; Ti, 7440-32-6.

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Electrochemistry of Mixed-Metal Bimetallic Complexes Containing the Pentacyanoferrate(II) or Pentaammineruthenium(II) Metal Center

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The electrochemistry of a series of mixed-metal bimetallic complexes of the type $B_5MLM'B'_5$, where $B_5M = (CN)_5Fe^{II}$ or $(NH_3)_5Ru^{II}$, L = pyrazine, 4,4'-bipyridine, or 4-cyanopyridine, $M'B'_5 = Rh^{III}(NH_3)_5$ or $Co^{III}(CN)_5$, is reported. The bimetallic complexes all have metal-to-ligand charge-transfer (MLCT) bands associated with the M–B unit ($d_\pi M \rightarrow p_\pi{}^*L$). The effect of the remote metal center, $M'B'_5$, is to function as a Lewis acid, shifting the MLCT maximum to lower energy and shifting the $M^{III/II}$ reduction potential more positive with respect to free B_5ML. The remote metal influence is attenuated by longer bridging ligands and by reduced π-overlap. A comparison of the electrochemical data of the mixed-valence Fe(II)/Fe(III) and Ru(II)/Ru(III) complexes to the mixed-metal Fe(II)/Co(III) and Ru(II)/Rh(III) complexes has enabled a quantitative measure of the stabilization due to electron delocalization in the mixed-valence complexes. The results show that electron delocalization is greater for the ruthenium complexes than for the iron complexes, is a small contributor to the total stabilization of the mixed-valence state, and even in ruthenium drops off rapidly as the length of the bridge increases.

Introduction

There have been numerous studies on the thermal[1-9] and photochemical[10-12] 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 $d_\pi M \rightarrow p_\pi{}^*L$ in character.[2,13] 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 d_π-electron density into L (π-back-bonding).[2]

Numerous types of instrumental methods have been used, in addition to electronic spectroscopy, to probe the extent of π-back-bonding from Fe(II) or Ru(II) into various L ligands. Electrochemical measurements are one such method that has been used for $Fe(CN)_5L$[2,14,15] and $Ru(NH_3)_5L$[16-18] complexes. In these previous studies, a positive increase in the reduction

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potential, $E^\circ(M^{III/II})$, has been interpreted, in general, as an increase in π-back-bonding in the M(II) complex.

There has been a large interest in bimetallic systems, especially mixed-valence complexes and the insight they can provide in the area of metal–metal interactions.[19,20] Numerous studies on mixed-valence systems[21–28] have focused on the stability of the mixed-valence complex over the isovalent complexes and the contributing factors to this increased stability.

Recently, we reported[1] the preparation and thermal stability of a number of mixed-metal bimetallic complexes containing the pentacyanoferrate(II) metal center. Spectroscopically, attaching the second metal center to a remote site of the ligand pyrazine (pz), 4-cyanopyridine (4-CNpy), or 4,4′-bipyridine (4,4′-bpy) gave rise to a red shift of the MLCT band just as would be expected for a Lewis acid substituent. However, the photochemistry of these bimetallic complexes[29,30] does not follow the trends observed for the monometallic systems. Both monometallic Fe(II)[10] and Ru(II)[11] centers show photosubstitution reactions for loss of L and have quantum yields that depend on the energy of the MLCT maximum. That is, when the energy of the MLCT maximum is greater than ~2.1 μm^{-1} for Fe(II) and Ru(II) complexes, photosubstitution quantum yields are large and relatively invariant but drop off dramatically as the MLCT maximum is red shifted from 2.1 μm^{-1}. The interpretation for the Fe(II)[10] and Ru(II)[11] systems, as well as the similar behavior observed for $(CO)_5WL$ complexes,[31] is that the drop-off 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.

The lack of correlation of the photochemistry of the monometallic Fe(II) and Ru(II) systems to their bimetallic counterparts (large photosubstitution quantum yields are observed for complexes with the MLCT maximum >2.1 μm^{-1}[30]) has led to the studies reported in this work. In addition, the study of the electrochemistry of the mixed-metal bimetallic complexes also will allow us to comment on the σ-donor strengths of various nitrogen heterocyclic ligands and assess the various contributions to the stability of ruthenium and iron mixed-valence complexes.

Experimental Section

Materials. Analytical reagent grade compounds were used for all preparations described in this work. Water used for synthesis and electrochemistry was redistilled from alkaline permanganate in an all-glass apparatus.

Syntheses. The complexes $[Rh(NH_3)_5L](ClO_4)_3$, $K_2[Co(CN)_5L]$, $[(CN)_5FeLRh(NH_3)_5]$, and $Na_3K_2[(CN)_5FeLCo(CN)_5]$ were prepared as previously reported.[1] The procedures of Malouf and Ford[11] and Ford et al.[13] were used to prepare the $Ru(NH_3)_5L^{2+}$ complex ions in situ for use in the cyclic voltammetry studies. The monometallic Fe(II) complexes, $Na_x[Fe(CN)_5L]$, and the bimetallic $Na_6[[Fe(CN)_5]_2L]$ complexes were prepared by the procedure of Toma and Malin[2] and Figard et al.[32] The Ru(II)/Rh(III) bimetallic complexes, $[(NH_3)_5RuLRh(NH_3)_5](ClO_4)_5$, were prepared by the procedure of Creutz and Taube[21] for the L = pyrazine complex.

Table I. Electronic Absorption Spectroscopy and Electrochemistry of Monometallic and Bimetallic Complexes of Pentacyanoferrate(II), $Fe(CN)_5L$

L	ν_{max}(MLCT), μm$^{-1\ a}$	$E^{\circ\prime}$ (ΔE), V (mV)^b	ref
H_2O		0.375 (80)	*c*
		0.39^d	18
4-Mepy	2.81	0.45^d	2
py	2.76	0.438 (65)	*c*
		0.47^d	2
4-CNpyRh$(NH_3)_5^{3+}$	2.50	0.603 (60)	*c*
4-CNpyCo$(CN)_5^{2-}$	2.33	0.59 (80)	*c*
4,4′-bpy	2.32	0.507 (62)	*c*
isn	2.30	0.494 (67)	*c*
		0.50^d	2
4,4′-bpyFe$(CN)_5^{3-}$	2.25	0.406 (76)^e	*c*
		0.538 (80)^f	
pz	2.22	0.633 (60)	*c*
		0.55^d	
4,4′-bpyCo$(CN)_5^{2-}$	2.20	0.53 (120)	*c*
4-CNpy	2.10	0.573 (66)	*c*
4-acetylpyridine	2.08	0.538 (60)	*c*
N-pyridylpyridinium	2.08	0.55^d	2
4,4′-bpyRh$(NH_3)_5^{3+}$	2.08	0.518 (80)	*c*
pzFe$(CN)_5^{3-}$	1.98	0.508 (60)^e	*c*
		0.618 (60)^f	
N-methyl-4,4′-bipyridinium	1.92	0.538 (65)	*c*
pzCo$(CN)_5^{2-}$	1.90	0.62 (116)	*c*
pzRh$(NH_3)_5^{3+}$	1.75	0.713 (61)	*c*
N-Mepz	1.51	0.78^d	2

^{a} ν_{max} of the metal-to-ligand charge-transfer ($d_\pi(Fe) \rightarrow \pi^*(L)$) band. ^{b} Average of oxidation and reduction peaks in cyclic voltammogram (unless noted) in 1 M KCl, reported vs. NHE and uncorrected for junction potential. ^{c} This work. ^{d} Determined potentiometrically. ^{e} For the 6–/5– couple. ^{f} For the 5–/4– couple.

Table II. Electronic Absorption Spectroscopy and Electrochemistry of Monometallic and Bimetallic Complexes of Pentaammineruthenium(II), $Ru(NH_3)_5L$

L	ν_{max}(MLCT), μm$^{-1\ a}$	$E^{\circ\prime}$ (ΔE), V (mV)^b	ref
H_2O		+0.066 (58)	16
py	2.46	+0.305 (58)	16
		+0.35^c	*d*
4-CNpy	2.35	+0.573 (60)	*e*
pz	2.12	+0.490 (58)	16
4,4′-bpy	2.06	+0.327 (63)	*e*
4-CNpyRh$(NH_3)_5^{3+}$	2.05	+0.682 (68)	*e*
4,4′-bpyRu$(NH_3)_5^{2+}$	1.92	+0.331 (-)	25
4,4′-bpyRu$(NH_3)_5^{3+}$	1.90	+0.407 (-)	25
pzRh$(NH_3)_5^{3+}$	1.89	+0.683 (68)	*e*
		+0.710^c	21
pyrazinium	1.89	+0.685 (calcd)	16
4-cyanopyridinium	1.88	+0.676 (55)	*e*
4,4′-bpyRh$(NH_3)_5^{3+}$	1.87	+0.388 (65)	*e*
N-Mepz	1.86	+0.87 (PT)	21
pzRu$(NH_3)_5^{2+}$	1.83	+0.350 (58)	16
pzRu$(NH_3)_5^{3+}$	1.77	+0.740 (58)	16

^{a} ν_{max} of the metal-to-ligand charge-transfer ($d_\pi(Ru) \rightarrow \pi^*(L)$) band. ^{b} Average of oxidation and reduction peaks in cyclic voltammogram (unless noted) in 1 M KCl, reported vs. NHE and uncorrected for junction potential. ^{c} Determined potentiometrically. ^{d} Shepherd, R. E. Ph.D. Dissertation, Stanford University, 1971. ^{e} This work.

The purity of all complexes was determined by comparison of the electronic spectra with the previously reported values. Electronic

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Table III. Electronic Spectra, Formal Potentials, and Association Constants for Pentacyanoferrate(II) and -(III) Complexes, $(CN)_5FeL$, at 25 °C

L	ν_{max}, μm^{-1} [a]	$E°'_{III/II}$, V[b]	K_{II}, M^{-1} [c]	K_{III}, M^{-1} [d]	K_{II}/K_{III}
H_2O		0.375			
py	2.76	0.438	3.3×10^5	2.8×10^4	1.2×10
$4\text{-CNpyCo}^{III}(CN)_5$	2.33	0.59	2.4×10^3	0.6	4×10^3
pz	2.21	0.64	9.0×10^5	3×10	3×10^4
$4,4'\text{-bpyCo}^{III}(CN)_5$	2.18	0.53	2.6×10^4	7×10	4×10^2
$4,4'\text{-bpyRh}^{III}(NH_3)_5$	2.08	0.518	2×10^6	8×10^3	2.6×10^2
$\text{pzCo}^{III}(CN)_5$	1.90	0.62	4×10^3	0.3	1×10^4
$\text{pzRh}^{III}(NH_3)_5$	1.75	0.713	3.5×10^6	6.7	5.2×10^5
N-Mepz	1.52	0.78	2.0×10^6	0.3	7×10^6

[a] MLCT absorption maximum, Fe(II) → N heterocycle. [b] Standard reduction potential, uncorrected for junction potential, and reported vs. NHE. [c] Reference 1 and references therein; $\mu = 0.5$ M ($LiClO_4$), unless otherwise noted. [d] Calculated by using eq 1.

spectra were recorded on a Cary 14 or a Bausch & Lomb Spectronic 2000 spectrophotometer.

Electrochemistry. Cyclic voltammograms were obtained with a Bioanalytical Systems instrument (Model CV1B). The platinum-disk working electrode (1.5-mm diameter) was polished with 1-μm alumina powder prior to each series of scans. A silver chloride coated silver wire in 0.10 M KCl served as a reference electrode (nominally +0.288 V vs. NHE) and was separated from the working solution by an agar bridge filled with KCl. A short piece of 14-gauge platinum wire was used as an auxiliary electrode. The cell was constructed from a 60° glass funnel sealed at the stem. This arrangement permitted recording of voltammograms with as little as 1 mL of solution. All scans were recorded in deoxygenated 0.10 M KCl solution with N_2 blowing over the top during the scan. Scan rates ranging from 30 to 150 mV/s were used. The potentials reported for the redox couples are estimates obtained by averaging the anodic and cathodic peak potentials, are referenced to the normal hydrogen electrode, and are uncorrected for junction potential.

Results

The complexes listed in Tables I–III are organized according to descending frequency of the maximum of the Fe(II) → L or Ru(II) → L metal-to-ligand charge-transfer (MLCT) transition. (The ligand abbreviations used in all Tables and throughout the text are py = pyridine, 4-CNpy = 4-cyanopyridine, 4,4′-bpy = 4,4′-bipyridine, 4-Mepy =4-methylpyridine, isn = isonicotinamide, and *N*-Mepz = *N*-methylpyrazinium.) The MLCT band is the dominant spectral feature in the near-UV-vis spectral region with molar extinction coefficients ranging from 3×10^3 to 10^4 M^{-1} cm^{-1}. The assumption that the MLCT band is localized mainly on the Fe(II) (or Ru(II)) center and the bridging ligand is consistent with assignments made previously by Creutz and Taube[21] for $(NH_3)_5Ru^{II}pzRh^{III}(NH_3)_5^{5+}$.

Tables I and II contain the results of cyclic voltammetry studies on the series of pentacyanoferrate(II) and pentaammineruthenium(II) complexes, $Fe^{II}(CN)_5L$ and $Ru^{II}(NH_3)_5L$, respectively. The $E°'$ values reported in these tables represent the average of the potentials for the anodic and cathodic peaks. The potentials are measured vs. a Ag/AgCl electrode but reported vs. NHE. The peak-to-peak separation is listed in millivolts in parentheses and is normally around 60–70 mV with the exception of the Fe/Co bimetallic complexes listed in Table I. Within experimental uncertainty, we will treat all $E°'$ values, with the exception of the Fe/Co bimetallic systems,[33] as reversible, one-electron processes. On the assumption that diffusion and activity coefficients of the oxidized and reduced forms are comparable,[34] the $E°'$ values approximate $E_{1/2}$. For the bimetallic Fe/Fe or Ru/Ru systems reported in Tables I and II, respectively, two couples are listed representing the (III,II/II,II) and (III,III/III,II) one-electron processes. In all the multiredox complexes reported in this study, the peak separation was sufficient to identify each redox couple in the multistep electron-transfer process. In both Tables I and II, there is a general trend for the reduction potential to increase as the maximum of the MLCT band is shifted to longer wavelength.

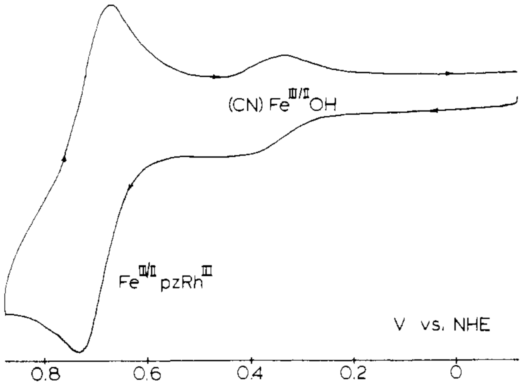

Figure 1. Cyclic voltammogram of 1 mM $(CN)Fe(pz)Rh(NH_3)_5$ in 0.01 M KCl at a scan rate of 50 mV/s. The two sets of reversible waves are due to the $(CN)_5Fe^{III/II}OH_2$ and $(CN)_5Fe^{III/II}(pz)Rh(NH_3)_5$ couples arising from the K_{II} equilibrium in Scheme I.

Scheme I

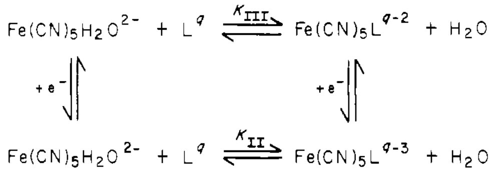

Table III reports the reduction potential of some monometallic and bimetallic complexes of pentacyanoferrate(II), the previously reported formation constants for these complexes (K_{II}),[1,3] and the calculated formation constant of the Fe(III) analogue (K_{III}). The value for K_{III} is calculated by using eq 1 and Scheme I. The cyclic voltammogram of $(CN)_5Fe(pz)Rh(NH_3)_5$ is shown in Figure 1. There are two reversible one-electron processes shown for the two electroactive species involved in the K_{II} equilibrium ($FeOH_2$ and Fe(pz)Rh). These calculated values for K_{III} vary from 0.3 to 2.8×10^4 M^{-1} and reflect the σ-donor ability of L for the $Fe(CN)_5^{2-}$ metal center.[15] The last column in Table III, K_{II}/K_{III}, is a measure of the relative π-acceptor ability of L and this value directly parallels $E°'$.

$$E°'(Fe(CN)_5L^{q-2/q-3}) = E°'(Fe(CN)_5H_2O^{2-/3-}) + \frac{RT}{F} \ln \frac{K_{II}}{K_{III}} \quad (1)$$

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(33) Although the peak separation for the Fe/Co is much greater than 60 mV (80–120 mV), the anodic and cathodic peak heights are approximately equal, the peak separation is not a function of scan speed (30–200 mV/s), and so the average potential will be used as a very approximate value for $E_{1/2}$.

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Table IV. Substituent Effects on the Reduction Potential of Pentacyanoferrate(II) and Pentaammineruthenium(II) Complexes

	$E^{\circ\prime}(\mathrm{Fe^{III/II}})$, V			$E^{\circ\prime}(\mathrm{Ru^{III/II}})$, V	
X	$(CN)_5Fe$-4,4'-bpy-X	$(CN)_5Fe(pz)$-X	X	$(NH_3)_5Ru$-4,4'-bpy-X	$(NH_3)_5Ru(pz)$-X
$Fe(CN)_5{}^{3-}$	+0.406	+0.508	$Ru(NH_3)_5{}^{2+}$	+0.331	+0.350
$Co(CN)_5{}^{2-}$	+0.53	+0.62	free	+0.327	+0.490
$Fe(CN)_5{}^{2-}$	+0.538	+0.618	$Rh(NH_3)_5{}^{3+}$	+0.388	+0.683
free	+0.507	+0.633	H^+		+0.685
$Rh(NH_3)_5{}^{3+}$	+0.518	+0.713	$Ru(NH_3)_5{}^{3+}$	+0.407	+0.740
$CH_3{}^+$		+0.78	$CH_3{}^+$		+0.87

Table V. Cyclic Voltammetry of Mixed-Valence Ruthenium(II, III) and Iron(II, III) Complexes and Their Mixed-Metal Analogues

	$E^{\circ\prime}((NH_3)_5Ru^{III/II}LM^{III}(NH_3)_5)$[a]			$E^{\circ\prime}((CN)_5Fe^{III/II}LM^{III}(CN)_5)$[b]		
L	$M^{III} = Ru^{III}$	$M^{III} = Rh^{III}$	$\Delta E^{\circ\prime}$[c]	$M^{III} = Fe^{III}$	$M^{III} = Co^{III}$	$\Delta E^{\circ\prime}$[c]
pz	+0.740	+0.683	57[d]	+0.618	+0.62[e]	~-2
4,4'-bpy	+0.407[f]	+0.388	19	+0.538	+0.53[e]	~8

[a] Reduction potential for the Ru(III/II) couple (vs. NHE) in the diruthenium complex and the mixed-metal ruthenium/rhodium complex in volts. [b] Reduction potential for the Fe(III/II) couple (vs. NHE) in the diiron complex and the mixed-metal iron/cobalt complex in volts. [c] Difference in millivolts in the reduction potential of the homometallic and heterometallic systems. [d] A similar value is obtained by using the results found in ref 21. [e] Accuracy is questionable since peak-to-peak separation of ~100 mV was observed. [f] Reference 25.

Discussion

Electronic Spectroscopy and Reduction Potential. Upon comparison of the ν_{max}(MLCT) values and $E^{\circ\prime}$ values reported in Table I for the pentacyanoferrate(II) complexes, a general trend emerges. There is a tendency for the reduction potential to increase as the MLCT band is shifted to lower frequency. This is only a general tendency, and its source has been discussed previously.[2,14,15] The nonexact nature of the correlation is due to a number of variables. Such things as the changes in σ-donor/π-acceptor ability of the ligand, differences in M–L orbital overlap and energy match, and variations of excited-state nuclear distortions from ground state will have different effects on ν_{max} and $E^{\circ\prime}$. However, the general rule that the lower ν_{max} involves greater ground-state π-back-bonding and thus a larger reduction potential does seem qualitatively correct.

The similar results and interpretations can be used to discuss the ν_{max}(MLCT) and $E^{\circ\prime}$ values for pentaammineruthenium(II) complexes in Table II. However, here we see an even greater deviation from the general trend of larger $E^{\circ\prime}$ values for smaller ν_{max}(MLCT) values. In the case of the 4,4'-bipyridine series of complexes, all $E^{\circ\prime}$ values, regardless of whether a remote metal center is present or not, are smaller than what would be expected on the basis of ν_{max}. One possible explanation for this behavior is that the source of the small ν_{max} value is a low-energy π^* level on 4,4'-bpy but that a poor metal–ligand orbital overlap is minimizing ground-state π-back-bonding and thus leading to lower reduction potentials than expected.

Remote Metal Center Substituent Effects. The various energy match/orbital overlap variations make it difficult to assess the σ-donor/π-acceptor contributions for various ligand/ligand–remote metal center systems. In order to directly compare the effects of various remote metal centers, we have tabulated various complexes containing the same bridging ligand in Table IV. The upper portion of Table IV deals with the pentacyanoferrate(II) complexes bridged by 4,4'-bpy or pz. The trend observed for pz, and somewhat for 4,4'-bpy, is that $E^{\circ\prime}$ is affected by the charge on the remote end of the ligand bridge. Attachment of a negatively charged remote metal center (i.e., $Fe(CN)_5{}^{3-,2-}$ or $Co(CN)_5{}^{2-}$) lowers the reduction potential while a positive center (i.e., $Rh(NH_3)_5{}^{3+}$ or $CH_3{}^+$) raises the reduction potential with respect to pz. This charge effect indicates that an electrostatic repulsion makes it easier to remove an electron from the highly negative charged complexes such as $[Fe(CN)_5]_2pz^{6-}$ than it is from $Fe(CN)_5pzRh(NH_3)_5$ or $Fe(CN)_5(N\text{-Mepz})^{2-}$. This variation of $E^{\circ\prime}$ is more pronounced for the shorter pz system than for the 4,4'-bpy system, which agrees with this assessment and with the interpretation that communication between metal centers is greatly attenuated by increased bridge length in these complexes.[1] In fact, when the metal centers are well separated, as is the case for 4,4'-bpy, there is very little deviation in the value of $E^{\circ\prime}$ at all, when the remote center is varied.

The lower half of Table IV contains the substituent-effect data for the pentaammineruthenium(II) complexes of 4,4'-bpy and pz. As was the case for the $Fe(CN)_5L$ systems described above, charge on the remote metal center affects $E^{\circ\prime}$ for L = pz, such that the larger metal center charges make oxidation more difficult. As before, this behavior is attenuated for L = 4,4'-bpy, which shows much less variation in $E^{\circ\prime}$ values.

Association Constants. In Table III, the $E^{\circ\prime}$ values for mono- and bimetallic pentacyanoferrate(II) complexes are listed for complexes in which the formation constant, K_{II}, is known[1,3] (Scheme I). The values for K_{III} and the ratio K_{II}/K_{III} are calculated by using Scheme I and eq 1. Toma and Creutz[15] have used the calculated K_{III} values as a measure of σ-donor ability of L in monometallic pentacyanoferrate(II) complexes with the result that larger K_{III} values are observed for the ligands with the higher Brønsted basicity. (The reason K_{III} is used, in this case, is that π-back-bonding between Fe(III) and L in $Fe(CN)_5L^{2-}$ is considered minimal.[15]) In our study, the K_{III} values for all of the bimetallic complexes fall between the py (2.8×10^4 M^{-1}) and the N-Mepz$^+$ values (0.3 M^{-1}), which have ligand pK_a values of 5.3 and −5.8, respectively. Intuitively, we would expect that attaching a non-π-back-bonding metal center to the remote end of a ligand L would reduce the basicity of the free base site on L. This has been observed for the Ru(III) system[13] $Ru(NH_3)_5pz^{3+}$ and also seems to be the case when $Co(CN)_5{}^{2-}$ or $Rh(NH_3)_5{}^{3+}$ is bound to the remote end of pz. The reduction in K_{III} (or ligand basicity) does not appear to be as significant when the remote metal center is a larger distance from the free base site as in 4,4'-bpy. The K_{III} values for 4,4'-bpy$Rh(NH_3)_5{}^{3+}$ and 4,4'-bpy$Co(CN)_5{}^{2-}$ are 8×10^3 and 7×10 M^{-1}, respectively. These equilibrium constants are larger than the other bimetallic equilibrium constants by at least 1–2 orders of magnitude. The 2 orders of magnitude difference in the Rh^{III}- and Co^{III}-4,4'-bpy K_{III} values has been previously explained[1] for K_{II} by the difference in charge of the remote metal center. This variation in charge of the remote center/bridging ligand complex has been shown[1] to have an effect of up to 3 orders of magnitude on the rate of formation of the bimetallic complex with $Fe(CN)_5H_2O^{3-}$. This same trend in K_{II} and K_{III} is observed as well for the pz-bridged bimetallic complexes, $(CN)_5Fe(pz)Rh(NH_3)_5$ and $(CN)_5Fe(pz)Co(CN)_5^{5-}$. Thus in all systems where the remote metal is in close proximity to the $Fe(CN)_5^{3-}$ center (i.e., pz-bridged species) or in systems where the remote site is not very basic to begin with (i.e., 4-CNpyCo$(CN)_5^{2-}$), values for K_{III} are ≤ 7 M^{-1}. For free ligands such as pz, py, and longer bridges like 4,4′-bpy, K_{III} is ≥ 30 M^{-1}.

The final column in Table III corresponds to the K_{II}/K_{III} ratio. This number has been used previously[15] to equate π-acceptor ability by dividing out σ-donor ability with K_{III}. Arithmetically, eq 1 shows that K_{II}/K_{III} directly parallels $E°'$ for $Fe(CN)_5L$. As indicated earlier in the Discussion, the parallelism between ν_{max} and $E°'$ does approximate a π-back-bonding sequence where the 4,4′-bpy bimetallic complexes are a little weaker π-acceptors (from $E°'$ or K_{II}/K_{III}) than expected on the basis of ν_{max}.

Electronic Delocalization in Mixed-Valence Complexes. The stability of the mixed-valence state [2,3] in complexes such as the Creutz–Taube ion,[21] $(NH_3)_5Ru(pz)Ru(NH_3)_5^{5+}$, as well as other ligand-bridged Ru(II)–Ru(III) systems[35–40] has been expressed in terms of instability of the isovalent [2,2] state, the inductive effect of the 3+ remote charge in the mixed-valence state, and a minor contribution due to electron delocalization. The comparison of Ru(II)/Ru(III) to Ru(II)/Rh(III) reduction potentials, as well as the corresponding Fe(II)/Fe(III) to Fe(II)/Co(III) reduction potentials, allows assessment of the electron delocalization contribution to mixed-valence-state stability.[23,25] This comparison of data appears in Table V. On the left side of Table V, the reduction potentials are listed for the couple $Ru(NH_3)_5^{3+/2+}$ when $Ru(NH_3)_5^{3+}$ or $Rh(NH_3)_5^{3+}$ is remotely bound to the electroactive center through a pz or 4,4′-bpy bridge. The results for the pz bridge system are virtually identical with those of Creutz and Taube.[21] With the assumption that the inductive effects of remote Ru(III) and Rh(III) on the Ru(III)/Ru(II) reduction potential are approximately the same, the difference in reduction potential should reflect the mixed-valence-state delocalization that occurs in the remote bound Ru(III) system and not the remote bound Rh(III) system. For the difference of 57 mV in the reduction potential of the pz bridge complexes, a stabilization by electron delocalization of 1.3 kcal can be calculated. In the 4,4′-bpy-bridged system, the difference in reduction potentials is only 19 mV. This corresponds to 0.4-kcal stabilization by electron delocalization and agrees with the classification of the 4,4′-bpy mixed-valence ion as a weakly interacting system.[23,25]

The right-hand side of Table V compares the Fe(III)/Fe(II) reduction potentials using the pz and 4,4′-bpy bridging ligands and either $Fe(CN)_5^{2-}$ or $Co(CN)_5^{2-}$ as the remote metal center. As was the case for the Ru(III) vs. Rh(III) comparison, the inductive effects of the Fe(III) and Co(III) remote centers should be about the same. Unfortunately, the large peak-to-peak separation observed in the cyclic voltammogram of the Fe/Co systems makes the accuracy of the values in the $M^{III} = Co^{III}$ column questionable, as well as an interpretation difficult. However, it does appear that the difference in reduction potential, $\Delta E°'$, is smaller for the iron system than the ruthenium system. This would indicate that the stabilization by electron delocalization of the mixed-valence state is smaller for iron than for ruthenium. This point agrees with previous conclusions[1–3] that π-back-bonding into L is smaller for $Fe(CN)_5L^{3-}$ complexes than for the corresponding $Ru(NH_3)_5L^{2+}$ complexes.

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Registry No. $Na_3[Fe(CN)_5(H_2O)]$, 14100-31-3; $Na_3[Fe(CN)_5(4\text{-Mepy})]$, 61502-03-2; $Na_3[Fe(CN)_5(py)]$, 56028-27-4; $[(CN)_5Fe(4\text{-CNpy})Rh(NH_3)_5]$, 81230-42-4; $Na_3K_2[(CN)_5Fe(4\text{-CNpy})Co(CN)_5]$, 81230-45-7; $Na_3[Fe(CN)_5(4,4'\text{-bpy})]$, 66269-64-5; $Na_3[Fe(CN)_5(isn)]$, 37475-71-1; $Na_6[[Fe(CN)_5]_2\text{-}4,4'\text{-bpy}]$, 66269-60-1; $Na_3[Fe(CN)_5(pz)]$, 37475-70-0; $Na_3K_2[(CN)_5Fe(4,4'\text{-bpy})Co(CN)_5]$, 81230-44-6; $Na_3[Fe(CN)_5(4\text{-CNpy})]$, 65637-45-8; $Na_3[Fe(CN)_5B]$ (B = acetylpyridine), 65848-96-6; $[(CN)_5Fe(4,4'\text{-bpy})Rh(NH_3)_5]$, 70649-69-3; $Na_6[[Fe(CN)_5]_2pz]$, 66269-62-3; $Na_2[Fe(CN)_5B]$ (B = *N*-methyl-4,4′-bipyridinium), 84823-80-3; $Na_3K_2[(CN)_5Fe(pz)Co(CN)_5]$, 81230-43-5; $[(CN)_5Fe(pz)Rh(NH_3)_5]$, 71050-65-2; $Ru(NH_3)_5(4\text{-CNpy})$, 70982-10-4; $Ru(NH_3)_5(pz)$, 19471-65-9; $Ru(NH_3)_5(4,4'\text{-bpy})$, 54714-01-1; $[(NH_3)_5Ru(4\text{-CNpy})Rh(NH_3)_5](ClO_4)_5$, 84823-81-4; $[(NH_3)_5Ru(pz)Rh(NH_3)_5](ClO_4)_5$, 41557-40-8; $[Ru(NH_3)_5B]^{3+}$ (B = 4-cyanopyridinium), 70982-09-1; $[(NH_3)_5Ru(4,4'\text{-bpy})Rh(NH_3)_5](ClO_4)_5$, 84823-83-6; $[[Fe(CN)_5]_2\text{-}4,4'\text{-bpy}]^{5-}$, 66402-51-5; $[(CN)_5Fe(4,4'\text{-bpy})Co(CN)_5]^{4-}$, 84823-84-7; $[[Fe(CN)_5]_2\text{-}4,4'\text{-bpy}]^{4-}$, 84823-85-8; $[(CN)_5Fe(4,4'\text{-bpy})]^{2-}$, 84823-86-9; $[(CN)_5Fe(4,4'\text{-bpy})Rh(NH_3)_5]^+$, 84823-87-0; $[[Fe(CN)_5]_2pz]^{5-}$, 51321-23-4; $[(CN)_5Fe(pz)Co(CN)_5]^{4-}$, 84823-88-1; $[[Fe(CN)_5]_2pz]^{4-}$, 57574-93-3; $[(CN)_5Fe(pz)]^{2-}$, 61332-65-8; $[(CN)_5Fe(pz)Rh(NH_3)_5]^+$, 84823-89-2; $[(CN)_5Fe(N\text{-Mepz})]^-$, 61363-44-8; $[(CN)_5Fe(N\text{-Mepz})]^{2-}$, 37475-66-4; $[[(NH_3)_5Ru]_2\text{-}4,4'\text{-bpy}]^{5+}$, 54065-65-5; $[[(NH_3)_5Ru]_2\text{-}4,4'\text{-bpy}]^{4+}$, 36451-88-4; $[(NH_3)_5Ru(4,4'\text{-bpy})]^{3+}$, 54714-03-3; $[(NH_3)_5Ru(4,4'\text{-bpy})Rh(NH_3)_5]^{6+}$, 84823-90-5; $[(NH_3)_5RuB]^{4+}$ (B = 4,4′-bipyridinium), 84823-91-6; $[(NH_3)_5RuB]^{3+}$ (B = 4,4′-bipyridinium), 36645-25-7; $[[(NH_3)_5Ru]_2\text{-}4,4'\text{-bpy}]^{6+}$, 53964-47-9; $[[(NH_3)_5Ru]_2pz]^{5+}$, 35599-57-6; $[[(NH_3)_5Ru]_2pz]^{4+}$, 26253-76-9; $[(NH_3)_5Ru(pz)]^{3+}$, 38139-16-1; $[(NH_3)_5Ru(pz)Rh(NH_3)_5]^{6+}$, 48170-09-8; $[(NH_3)_5RuB]^{4+}$ (B = *N*-methyl-4,4′-bipyridinium), 38192-67-5; $[(NH_3)_5RuB]^{3+}$ (B = *N*-methyl-4,4′-bipyridinium), 19441-21-5; $[[(NH_3)_5Ru]_2pz]^{6+}$, 38900-60-6; $[(NH_3)_5Ru(N\text{-Mepz})]^{3+}$, 48135-76-8; $[(NH_3)_5Ru(N\text{-Mepz})]^{4+}$, 48135-77-9; $[(CN)_5Fe(H_2O)]^{3+}$, 19413-97-9; $[(CN)_5Fe(py)]^{3+}$, 61332-63-6.

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