Solvent-Dependent Studies of Intervalence Transfer of Mixed-Valence Complexes Containing Ferrocenylpyridine and Rutheniumammines

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Two heterobimetallic complexes of $[Fc(4\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (**1**) and $[Fc(3\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (**2**) (Fc(4-Py) = 4-ferrocenylpyridine, Fc(3-Py) = 3-ferrocenylpyridine) have been synthesized and characterized for the purpose of investigating optical and thermal electron transfer. The mixed-valence species generated in situ using ferrocenium hexafluorophosphate as the oxidant show Robin and Day class II behavior, and the oxidized sites are ruthenium centered. $\Delta E_{1/2}°$, $E_{1/2}°(\mathrm{Fe^{III}/Fe^{II}}) - E_{1/2}°(\mathrm{Ru^{III}/Ru^{II}})$, an estimate of ΔE_o that is an energetic difference between the donor and acceptor sites, changes sharply with variation of solvents. Good linear relationship exists between $\Delta E_{1/2}°$ and Gutmann solvent donor number (DN) and $\Delta E_{1/2}°$ versus DN plots yield a slope of 20.4 ± 1.6 mV/DN for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{2+/3+/4+}$ and a slope of 21.1 ± 2.2 mV/DN for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{2+/3+/4+}$. The solvent-dependent IT bands were found to vary almost exclusively with $\Delta E_{1/2}°$. The continuum dielectric approximation is found to be adequate, and the $(E_{op} - \Delta E_o)$ versus $(1/\epsilon_{op} - 1/\epsilon_s)$ plot yields a straight line with a slope of 3848 ± 1444 and an intercept of 4265 ± 227 cm^{-1} for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$. The corresponding values for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$are 2328 ± 1560 and 6712 ± 100 cm^{-1}. The thermal electron transfer (the reverse of the optical process, viz., $\mathrm{Ru^{II}} \rightarrow \mathrm{Fe^{III}}$ electron transfer) is adiabatic for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ but somewhat nonadiabatic ($\kappa \approx 0.6$) for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$. The thermal transfer rate constants of both complexes decrease exponentially with increasing solvent donor number and show close magnitude in all solvents despite $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ having apparently a shorter through-space distance and lower activation energies. However, these calculated k_{th} values should be used with caution because no experimental data as measured by flash photolysis techniques are available.

Introduction

Usually a class II or class III mixed-valence complex[1] features the characteristics of having an intervalence transfer (IT), metal-to-metal charge transfer, in the visible−near-IR spectrum that is absent in its isovalent states. One of the major differences between valence-trapped (class II) and valence-delocalized (class III) mixed-valence species is the effect of solvent on the intervalence transitions. Only the former shows solvent dependence.[2] According to Hush theory,[3] activation energy for optical electron transfer can be expressed as

$$E_{op} = \chi_{in} + \chi_s + \Delta E_o \qquad (1)$$

where χ_{in} and χ_s are inner-sphere and solvent reorganization energies and ΔE_o is an energetic difference between the donor and acceptor sites. When a continuum dielectric approximation is used for the medium, the solvent reorganization energy χ_s can be expressed as

$$\chi_s = e^2(^1/_2a_1 + {}^1/_2a_2 - 1/r)(1/\epsilon_{op} - 1/\epsilon_s) \qquad (2)$$

where e is the electronic charge transferred, a_1 and a_2 are radii of spherical donor and acceptor sites whose metal−metal separation is r, and ϵ_{op} and ϵ_s are the optical and static dielectric constants of the medium, respectively.

In contrast to other aspects of mixed-valence chemistry in the literature,[2,4] relatively little data of asymmetric, especially heteronuclear mixed-valence, species have been obtained on the solvent dependence of intervalence transfer, despite their importance in providing vital information on vibrational reorganization energies and solvent reorganization energies of the mixed-valence species. This is primarily due to a lack of (1) substitution inertia,[5,6] (2) solubility in solvents of a wide range of Gutmann donor number (DN),[7] or donicity, (3) strongly localized, yet appreciably electronic coupled class II systems to offer observable IT bands,[8,9] (4) a wide “window” in visible and near-IR spectra that stays away from the influences of MLCT (metal-to-ligand charge transfer) and solvent absorption,[10,11] and (5) electrochemical reversibility.[12] Nevertheless, studies on a number of symmetric, valence-trapped mixed-valence species have confirmed the correlation predicated by

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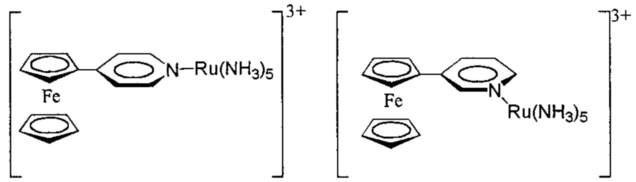
theory.[13−19] Modulation of IT bands via solvents have also been carried out for asymmetric class II species and, therein, situations become more complex due to the fact that ΔE_o is also solvent-dependent.[10,20] Treating ΔE_o as a constant, as these were not available in their studies, Laidlaw and Denning[12] failed to find a linear relationship between E_{op} and solvent dielectric function ($1/\epsilon_{op} - 1/\epsilon_s$). Using miscalculated values for ($1/\epsilon_{op} - 1/\epsilon_s$), although the corrected data still supported the same conclusion, Díaz and Arancibia[21] found the plot of ($E_{op} - \Delta E_o$) versus ($1/\epsilon_{op} - 1/\epsilon_s$) of [Cp(dppe)Fe-($\mu$-CN)-Fe(dppe)Cp] $(PF_6)_2$ to be linear for four solvents. It should be noted that such a correlation was first reported for $[(bpy)_2Ru^{II}(Cl)pyzRu^{III}(NH_3)_5]^{4+}$,[10] but a later study on the same compound did not confirm this relationship.[22] The controversy may have something to do with the quality of spectra, because IT bands of systems containing $Ru^{II}-L-L-Ru^{III}$ (L−L = bridging aromatic heterocycles) are usually found on the low-energy tail of MLCT bands. The difficulties to deconvolve IT bands from overlapping MLCT bands are recognized.[23] In this work, we attempted to calculate the inner-sphere and solvent reorganization energies of $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ and $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ (Fc(4-Py) = 4-ferrocenylpyridine, Fc(3-Py) = 3-ferrocenylpyridine) by carrying out solvent-dependent studies and using Hush theory. These two complexes meet all requirements for solvent-dependent studies and have one great advantage over previous systems; that is, their IT bands are free from interference of $Ru^{II}(d\pi)$ to $L(\pi^*)$ charge transfer.



Experimental Section

General Methods and Chemicals. ^1H NMR spectra were obtained in acetone-d_6 on a Bruker Aspect-3000 (300 MHz) spectrometer. All chemical shifts are reported in parts per million downfield from tetramethylsilane. DMF and DMSO were dried over 4 Å molecular sieves, and benzonitrile was dried over $MgSO_4$. Acetone was dried over 4 Å molecular sieves and distilled to collect the fraction between 56 and 57 °C. Other solvents were dried according to established procedures[24] by distillation under N_2 from appropriate drying agents: acetonitrile from CaH_2; nitrobenzene from P_2O_5; DMA, methanol, and ethanol from CaO. Chemicals were obtained from the following sources: acetone-d_6 from MSD, Al_2O_3 from Fluka, and the rest from Aldrich.

Preparation of $[Fc(4\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (1). 4-Ferrocenylpyridine, Fc(4-Py), was prepared as previously described,[8] and $[Ru(NH_3)_5OH_2](PF_6)_2$ was generated from $[Ru(NH_3)_5Cl]Cl_2$[25] via a procedure outlined by Taube.[26] To 5 mL of degassed acetone solution of $[Ru(NH_3)_5OH_2](PF_6)_2$ (100 mg, 0.20 mmol) under argon was added a solution of Fc-(4-Py)(100 mg, 0.38 mmol), and the reaction mixture was stirred for 10 min. Then, 100 mL of ether was added to the solution, and the system was kept at 0 °C for 30 min. The precipitate thus formed was filtered, washed with ether, recrystallized in acetone, and dried under reduced pressure to give 80 mg (53% yield) of red powder. ^1H NMR (acetone-d_6) δ 2.56 (s, 12H, equatorial ammine), 3.04 (s, 3H, axial ammine), 4.06 (s, 5H, free Cp), 4.48 (t, 2H, substituted Cp), 4.92 (t, 2H, substituted Cp), 7.43 (m, 2H, pyridine), 8.60 (m, 2H, pyridine). Anal. Calcd for $C_{15}H_{28}F_{12}N_6P_2FeRu$: C, 24.37; H, 3.82; N, 11.37. Found: C, 25.03; H, 3.90; N, 11.05.

Preparation of $[Fc(3\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (2). The same procedure for the preparation of complex **1** was used here starting from $Ru(NH_3)_5OH_2](PF_6)_2$ (100 mg, 0.20 mmol) and 3-ferrocenylpyridine, Fc(3-Py), 100 mg, 0.38 mmol. The purified product was a yellow powder and weighed 85 mg (57% yield). ^1H NMR (acetone-d_6) δ 2.61 (s, 12H, equatorial ammine), 3.05 (s, 3H, axial ammine), 4.07 (s, 5H, free Cp), 4.41 (t, 2H, substituted Cp), 4.89 (t, 2H, substituted Cp), 7.24, 7.92, 8.59, 8.86 (m, 1H, 1H, 1H, 1H, pyridine). Anal. Calcd for $C_{15}H_{28}F_{12}N_6P_2FeRu$: C, 24.37; H, 3.82; N, 11.37. Found: C, 25.10; H, 3.82; N, 10.93.

CV. Cyclic voltammetric experiments were carried out with the use of a Princeton Applied Research (PAR) model 273 electrochemistry system and a standard three-electrode configuration. The working electrode (Beckman no. 39273) was a platinum inlay electrode with a surface area of 0.28 cm^2. Its surface was polished to a mirror-bright finish with polishing alumina before each experiment. The auxiliary electrode was a Pt-wire. Potentials were measured against a PAR-KO103 nonaqueous reference electrode (Ag/0.1 M $AgNO_3$ in CH_3CN) located inside a reference electrode bridge tube with a Vycor tip (PAR-K0065) to prevent contamination of test solution by reference electrode filling solution. Solutions were $1.0 \times 10^{-3}-5 \times 10^{-4}$ M in complex, 0.1 M in $(Bu_4N)PF_6$, and purged with Ar for 15 min prior to each measurement. The scan rates were 200 mV/s. The $E_{1/2}°$ values were calculated from the average of the cathodic and anodic potentials.

Spectroscopic Studies. UV−vis and near-IR spectra were recorded at 298 ± 0.5 K with a Shimadu 3101 PC spectrophotometer equipped with a thermostated cell holder. Solutions for near-IR measurements were prepared by mixing 1 mL each of the oxidant (2×10^{-3} M ferrocenium hexafluorophosphate) and the reductant (ca. 1×10^{-3} M of complex **1** or **2**) in a sidearmed flask containing the solvents chosen. The reactions were controlled at 298 ± 0.5 K for 2 h. The resulting solution was then transferred to a 1 cm matched quartz cell capped with a septum using the syringe technique. Intervalence charge transfer (IT) spectra were recorded and analyzed with ORIGIN, a Gaussian fitting program.[27]

Results and Discussion

Electrochemistry. Both complexes **1** and **2** showed two reversible redox couples at pt electrode in all solvents studied. Table 1 summarizes half-wave potentials and comproportionation constants K_c calculated from the following equations:

$$\text{(II, II)} + \text{(III, III)} \rightleftharpoons 2\text{(II, III)} \qquad K_c \tag{3}$$

$$\Delta E_{1/2}° = (RT/F) \ln K_c \tag{4}$$

The sensitivity of mixed-valent states to solvents can be easily seen from the range of K_c, a span of 9 orders of magnitude for both complexes. Note that the corresponding values of $[Fc(3\text{-}Py)Ru(NH_3)_5](PF_6)_3$ are 1−2 orders of magnitude smaller than

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Table 1. $E_{1/2}°$ Values and Comproportionation Constants of $[Fc(4\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (**1**) and $[Fc(3\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (**2**) in Different Solvents[a]

solvent	$(E_{1/2}°)_1$,[b] mV	$(E_{1/2}°)_2$,[b] mV	$\Delta E_{1/2}°$,[c] mV	K_c[d]
DMSO	−491 (−466)	208 (146)	699 (612)	6.66×10^{11} (2.25×10^{10})
DMA	−431 (−384)	271 (215)	702 (599)	7.48×10^{11} (1.35×10^{10})
DMF	−409 (−382)	254 (195)	663 (572)	1.64×10^{11} (6.22×10^{9})
C_2H_5OH	−65 (−6)	336 (255)	401 (261)	6.06×10^{6} (2.60×10^{4})
CH_3OH	−95 (−54)	321 (240)	416 (294)	1.09×10^{7} (9.39×10^{4})
CH_3COCH_3	−135 (−85)	297 (238)	432 (323)	2.03×10^{7} (2.91×10^{5})
PC[e]	−141 (−93)	254 (179)	395 (272)	4.80×10^{6} (3.99×10^{4})
CH_3CN	−39 (−6)	305 (222)	344 (228)	6.59×10^{5} (7.19×10^{3})
benzonitrile	30 (50)	365 (226)	335 (176)	4.64×10^{5} (9.48×10^{2})
nitrobenzene	134 (145)	348 (225)	214 (80)	4.17×10^{3} (2.26×10^{1})
nitromethane	110 (141)	260 (219)	150 (174)	3.45×10^{2} (1.79×10^{1})

[a] Data for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ are in parentheses. [b] The values of $E_{1/2}°$ were measured against the a PAR−KO103 nonaqueous reference electrode, Ag/0.1 M $AgNO_3$ in CH_3CN, located inside a reference electrode bridge tube with Vycor tip (PAR-K0065). These values are the average of the potentials for peak anodic and cathodic currents in the cyclic voltammograms recorded at 200 mV/s. [c] $\Delta E_{1/2}°$ ($\Delta E_{1/2}° = E_{1/2}°(Fe^{III}/Fe^{II}) - E_{1/2}°(Ru^{III}/Ru^{II})$). [d] Calculated from eqs 3 and 4. [e] Propanediol-1,2-carbonate.

Table 2. Electronic Spectra of Ferrocenylpyridyl-Pentaammineruthenium Complexes[a]

complex	band maxima, nm	$10^{-3}\epsilon_{max}$, $M^{-1}\ cm^{-1}$
3-PyFc	238	14.3
	280	13.1
	340	1.44
	454	0.39
$[Fc(3\text{-}Py)Ru(NH_3)_5](PF_6)_2$	238	14.9
	282	15.2
	376[b]	5.24
	418	8.05
$[Fc(3\text{-}Py)Ru(NH_3)_5](PF_6)_3$	253	12.7
	284	11.5
	370	2.44
	1015	0.025
4-PyFc	242	11.37
	280	8.26
	342	1.30
	466	0.38
$[Fc(4\text{-}Py)Ru(NH_3)_5](PF_6)_2$	248	14.8
	280	10.8
	438	12.6
$[Fc(4\text{-}Py)Ru(NH_3)_5](PF_6)_3$	250	12.5
	285	13.8
	396	3.32
	1092	0.61

[a] Spectra taken in CH_3CN. [b] Shoulder.

$[Fc(4\text{-}Py)Ru(NH_3)_5](PF_6)_3$ in all solvents, indicating that distance-dependent electrostatic interaction is not the major factor[28] here. Analogous observations have been found in diferrocenylbenzene systems.[29] To confirm ruthenium to be the first metal oxidized in these complexes, another two similar pentaammineruthenium(II) complexes, $[3\text{-}PhPyRu(NH_3)_5](PF_6)_2$ and $[4\text{-}PhPyRu(NH_3)_5](PF_6)_2$, were synthesized[30] and studied in CH_3CN. They both showed $E_{1/2}°$ values at −10 mV, which is very close to $(E_{1/2}°)_1$ of $[Fc(3\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (**2**) and $[Fc(4\text{-}Py)Ru(NH_3)_5](PF_6)_2$ (**1**). By contrast, $E_{1/2}°$ values of free ligands Fc(3-Py) and Fc(4-Py), 128 and 172 mV, respectively, are lower than $(E_{1/2}°)_2$ values (222 and 305 mV) of the corresponding binuclear complexes, suggesting moderate electronic couplings between ruthenium and iron centers.

UV−Vis Spectra. The UV−vis spectra of Fc(4-py)/Fc(3-py) and $[Fc(4\text{-}Py)Ru(NH_3)_5]^{n+}$/$[Fc(3\text{-}Py)Ru(NH_3)_5]^{n+}$ ($n = 2$, 3) are summarized in Table 2.

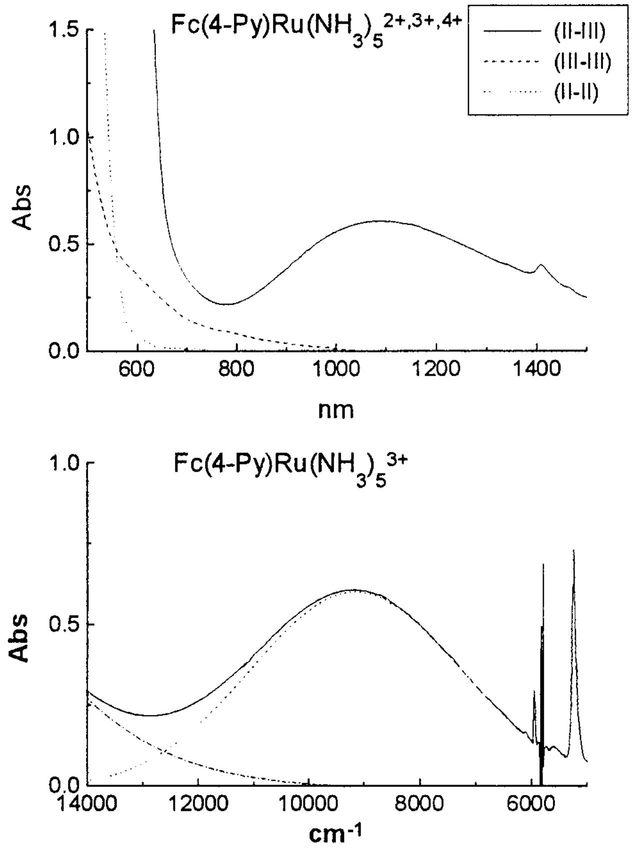

Figure 1. NIR spectra of $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$, 9.76×10^{-4} M in CH_3CN, taken in 1 cm matched quartz cells and its Gaussian fitting employing OREGIN, MICROCAL.

According to the extensively discussed electronic spectra of ferrocene,[31] the shorter wavelength bands (200−300 nm) were assigned to Fe(dπ) → Cp(π*) charge transfer, $\pi \rightarrow \pi^*$ transitions, or a combination of these, and the long-wavelength band at 440 nm was assigned to d−d transition within the ligand field formalism. An analogous conclusion may be drawn for shorter wavelength bands (230−350 nm) and longer wavelength bands (450−460 nm) of Fc(3-Py) and Fc(4-Py). The 418 nm ($\epsilon = 8.05 \times 10^3\ M^{-1}\ cm^{-1}$) band in $[Fc(3\text{-}Py)Ru(NH_3)_5]^{2+}$ and 438 nm ($\epsilon = 1.26 \times 10^4\ M^{-1}\ cm^{-1}$) band in $[Fc(4\text{-}Py)Ru(NH_3)_5]^{2+}$, which are absent in their corresponding free ligands and in 3+ species, are assigned to Ru^{II}(dπ) to Cp(π*) charge

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Table 3. Data for Intervalence-Transfer Bands and Hush Parameters of $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ and $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ in Different Solvents[a]

solvent	DN[b]	$1/\epsilon_{op} - 1/\epsilon_s$[c]	ν_{max}, cm^{-1}	ϵ_{max}, $M^{-1}\ cm^{-1}$	$\Delta\nu_{1/2}$, cm^{-1}	$\Delta E_{1/2}°$,[d] mV	H_{AB},[e] cm^{-1}	$\alpha^2 \times 10^{-3}$ [c]	χ_s,[f] cm^{-1}	χ,[g] cm^{-1}
DMSO	29.8	0.436	11698 (13 123)[h]	380 (27)	3671 (4332)	699 (612)	335 (143)	0.82 (0.12)	1678 (1015)	5943 (7727)
DMA	27.8	0.458	11486 (12 612)	340 (28)	3743 (4454)	702 (599)	318 (145)	0.76 (0.13)	1762 (1066)	6927 (7778)
DMF	26.6	0.463	11422 (12 788)[h]	360 (30)	3674 (5260)	663 (579)	323 (164)	0.80 (0.16)	1782 (1078)	6047 (7790)
C_2H_5OH	20	0.500	9622 (9815)	590 (23)	3642 (4910)	401 (261)	378 (122)	1.5 (0.15)	1924 (1164)	6189 (7876)
CH_3OH	19	0.536	9661 (10 314)	550 (30)	3661 (4938)	416 (294)	367 (143)	1.4 (0.19)	2062 (1248)	6328 (7960)
CH_3COCH_3	17	0.494	9777 (10 507)	560 (32)	3670 (4761)	432 (323)	373 (146)	1.4 (0.19)	1901 (1150)	6166 (7862)
PC[i]	15.1	0.482	9417 (10 091)	500 (28)	3800 (5247)	395 (272)	352 (141)	1.4 (0.19)	1855 (1122)	6120 (7834)
CH_3CN	14.1	0.526	9160 (9856)	610 (25)	3788 (4794)	344 (228)	382 (126)	1.7 (0.16)	2024 (1224)	6289 (7936)
benzonitrile	11.9	0.389	8742 (−)[j]	700 (−)[j]	3776 (−)[j]	335 (176)	400 (−)[j]	2.1 (−)[g]	1497 (906)	5762 (7618)
nitrobenzene	4.4	0.387	7224 (−)[j]	810 (−)[j]	3881 (−)[j]	214 (80)	396 (−)[j]	3.0 (−)[g]	1489 (901)	5754 (7613)
nitromethane	2.7	0.498	6952 (−)[j]	880 (−)[j]	3997 (−)[j]	150 (74)	411 (−)[j]	3.5 (−)[g]	1916 (1159)	6181 (7871)

[a] Data for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ are in parentheses. [b] Taken from ref 7. [c] Calculated from: *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995. [d] $\Delta E_{1/2}°$ ($\Delta E_{1/2}° = E_{1/2}°(Fe^{III}/Fe^{II}) - E_{1/2}°(Ru^{III}/Ru^{II})$) is taken as ΔE_o. [e] Calculated from eq 6 where a through-space distance of 7.8 Å from crystallographic data was used for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ and an estimated average of 5.6 Å was used for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$. [f] Solvent reoganization energy calculated from the slope of Figure 3. [g] Total vibronic energy calculated from the slope and intercept of Figure 3. [h] Shoulder. [i] Propandiol-1,2-carbonate. [j] Not observed.

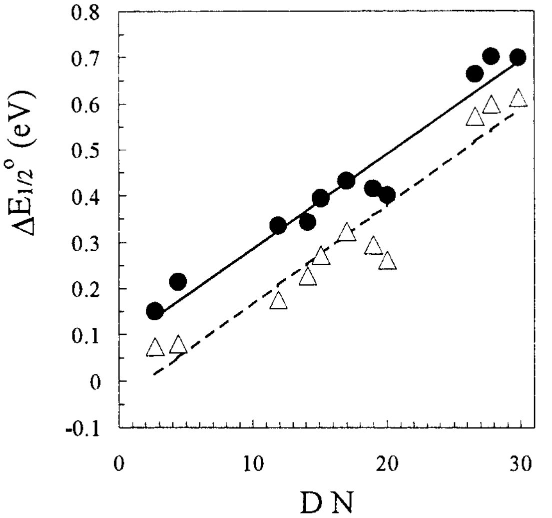

Figure 2. $\Delta E_{1/2}°$ ($\Delta E_{1/2}° = E_{1/2}°(Fe^{III}/Fe^{II}) - E_{1/2}°(Ru^{III}/Ru^{II})$) vs Gutmann solvent donor number: $[Fc(4\text{-}Py)Ru(NH_3)_5]^{2+/3+/4+}$(circles) with a slope of 20.4 ± 1.6 mV/DN and an intercept of 83 ± 45 mV; $[Fc(3\text{-}y)Ru(NH_3)_5]^{2+/3+/4+}$(triangles) with a slope of 21.1 ± 2.2 mV/DN and an intercept of −44 ± 57 mV.

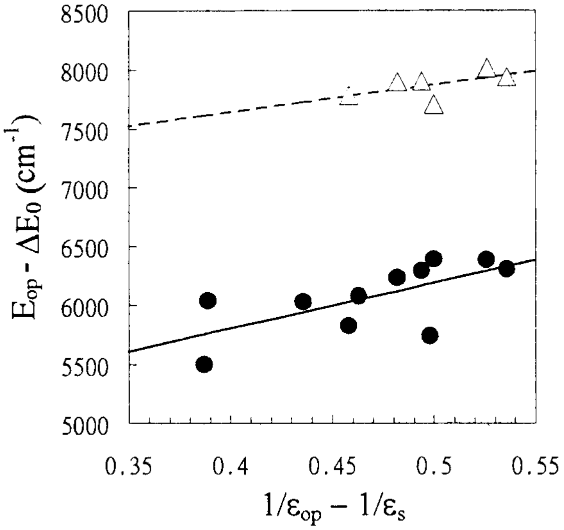

Figure 3. Plot of ($E_{op} - \Delta E_o$) versus ($1/\epsilon_{op} - 1/\epsilon_s$): $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$(circles) with a slope of 3848 ± 1444 and an intercept of 4265 ± 227 cm^{-1}; $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ (triangles) with a slope of 2328 ± 1560 and an intercept of 6712 ± 100 cm^{-1}.

transfer. These assignments were also supported by the reported MLCT spectra of pentaammineruthenium(II) complexes of pyridine and other aromatic nitrogen heterocycles.[32−35] Upon oxidation, these bands disappear, suggesting ruthenium to be the first metal center oxidized.

NIR Spectra. Figure 1 shows a near-IR spectrum of $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ taken in CH_3CN and the corresponding Gaussian fitting. As indicated in Table 1, $(E_{1/2}°)_1$ values that correspond to redox potentials of $Ru^{II/III}$ have a range of 600 mV in various solvents. By contrast, $(E_{1/2}°)_2$ values that correspond to $Fe^{II/III}$ redox potentials of ferrocenyl moiety only have a span of 150 mV. The redox potentials were found to vary linearly as a function of solvent donicity. Figure 2 shows correlation obtained between $\Delta E_{1/2}°$ ($\Delta E_{1/2}° = E_{1/2}°(Fe^{III}/Fe^{II}) - E_{1/2}°(Ru^{III}/Ru^{II})$) and solvent donor number.[7] For $[Fc(4\text{-}Py)Ru(NH_3)_5]^{2+/3+/4+}$ we find a slope of 20.4 ± 1.6 mV/DN, an intercept of 83 ± 45 mV with a correlation coefficient 0.948. For $[Fc(3\text{-}Py)Ru(NH_3)_5]^{2+/3+/4+}$, the corresponding values are 21.1 ± 2.2 mV/DN, −44 ± 57 mV, and 0.919, respectively.

The consequence of $Ru^{II}(d\pi) \rightarrow \pi^*$ back-donation toward solvent donicity is clearly shown in this figure where π back-donation is less extensive in low donor number solvents. Similar observations have been previously reported.[22,36]

From equations 1 and 2, it is clear that for an asymmetric system the ($E_{op} - \Delta E_o$) versus ($1/\epsilon_{op} - 1/\epsilon_s$) plot should be linear if a continuum dielectric approximation is adequate. Realizing the influence of the ionic association effect,[19,37] we chose all concentrations in this study to be $\approx 1 \times 10^{-3}$ M. Figure 3 shows such a plot. The least-squares fit of the straight line yields a slope of 3848 ± 1444, an intercept of 4265 ± 227 cm^{-1} for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$, and corresponding values of 2328 ± 1560 and 6712 ± 100 cm^{-1} for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$. Considering $\Delta E_{1/2}°$ ($\Delta E_{1/2}° = E_{1/2}°(Fe^{III}/Fe^{II}) - E_{1/2}°(Ru^{III}/Ru^{II})$) values to be taken as an approximate measure of ΔE_o, we feel the trends in Figure 3 are interpretable and produce useful insight into vibrational reorganization energies and solvent reorganization energies for the mixed-valence chromophores in different solvents. Solvent reorganization energy χ_s and total vibronic energy χ calculated from the slope and intercept are summarized in Table 3. Using eq 2 and $a_1 = 4.69$ Å (value for $Ru(NH_3)_5Py$

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Table 4. Rate Constants and Activation Energies for Thermal Electron Transfer of $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ and $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ in Different Solvents[a]

solvent	DN[b]	ν_{el}, s^{-1}	κ	ΔG^*, kcal/mol	k_{th}, s^{-1}
DMSO	29.8	3.3×10^{13} (5.4×10^{12})	0.98 (0.58)	15.2 (14.6)	3.7×10^{1} (5.5×10^{1})
DMA	27.8	2.8×10^{13} (5.5×10^{12})	0.97 (0.59)	15.3 (14.2)	3.2×10^{1} (1.2×10^{2})
DMF	26.6	3.1×10^{13} (7.1×10^{12})	0.98 (0.67)	14.9 (14.0)	1.3×10^{2} (1.9×10^{2})
C_2H_5OH	20	4.2×10^{13} (3.8×10^{12})	0.99 (0.48)	9.3 (8.6)	7.9×10^{5} (1.2×10^{6})
CH_3OH	19	3.9×10^{13} (5.6×10^{12})	0.99 (0.60)	9.5 (9.1)	5.2×10^{5} (5.9×10^{5})
CH_3COCH_3	17	4.1×10^{13} (5.5×10^{12})	0.99 (0.58)	9.8 (9.6)	3.3×10^{5} (2.8×10^{5})
PC[c]	15.1	3.6×10^{13} (5.2×10^{12})	0.99 (0.57)	9.2 (8.8)	9.6×10^{5} (9.9×10^{5})
CH_3CN	14.1	4.2×10^{13} (4.1×10^{12})	0.99 (0.50)	8.3 (8.3)	4.1×10^{6} (2.1×10^{6})
benzonitrile	11.9	4.8×10^{13} (−)[d]	0.99 (−)[d]	7.9 (−)[d]	8.1×10^{6} (−)[d]
nitrobenzene	4.4	4.8×10^{13} (−)[d]	0.99 (−)[d]	5.6 (−)[d]	3.6×10^{8} (−)[d]
nitromethane	2.7	4.9×10^{13} (−)[d]	0.99 (−)[d]	4.8 (−)[d]	1.4×10^{9} (−)[d]

[a] Data for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ are in parentheses. [b] Taken from ref 7. [c] Propandiol-1,2-carbonate. [d] Not observed.

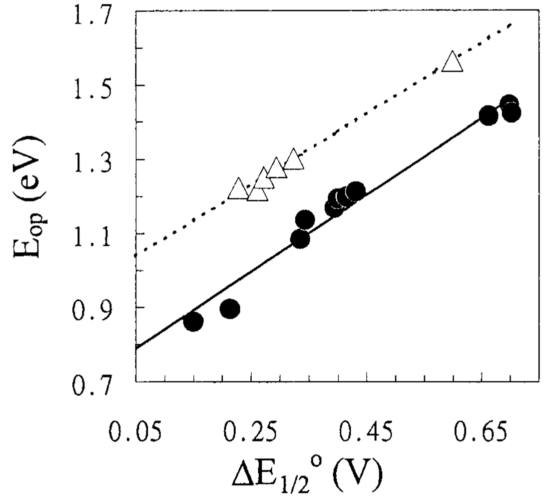

Figure 4. E_{op} vs $\Delta E_{1/2}°$ ($\Delta E_{1/2}° = E_{1/2}°(Fe^{III}/Fe^{II}) - E_{1/2}°(Ru^{III}/Ru^{II})$) as solvent is varied for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$(circles) and $[Fc(3\text{-}Py)\text{-}Ru(NH_3)_5]^{3+}$(triangles).

moiety calculated from ref 38), $a_2 = 5.76$ Å (crystallographic distance from ferrocenyl Fe to N of Fc(4-Py)), and $r = 7.8$ Å (through-space crystallographic distance between Fe and Ru in $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$, the calculated slope has a value of 7.57 kK. The calculation is quite sensitive to the chosen values a_1, a_2, and r, and the calculated slope would approach to the observed value as a_2 has a value larger than the estimated 5.76. It should be noted that χ values obtained from Figure 3 agree well with those calculated from the equation derived by Hush,[39] especially for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ where the deviations are around 5% for most solvents and 10% for low donor number solvents such as nitromethane and nitrobenzene:

$$\Delta\nu_{1/2} = [16(\ln 2)k_bT\chi]^{1/2} = 47.9\chi^{1/2}\ \text{cm}^{-1} \text{ at } 298\ \text{K} \qquad (5)$$

$\Delta\nu_{1/2}$ refers to half-bandwidth at IT band maximum.

Figure 4 shows that E_{op} changes as $\Delta E_{1/2}°$ is varied. For $[Fc\text{-}(4\text{-}Py)Ru(NH_3)_5]^{3+}$, we find a slope of 1.04 ± 0.06 eV/V with a correlation coefficient 0.968 and for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$a slope of 0.96 ± 0.05 eV/V with a correlation coefficient of 0.991. The data indicate that E_{op} is increasing with $\Delta E_{1/2}°$ in such a way that $(1/\epsilon_{op} - 1/\epsilon_s)$ is solvent independent. This is ascribed to the fact that the slight variations of solvent reorganization energy are overwhelmed by the sharp changes of $\Delta E_{1/2}°$.

Summarized also in Table 3 are the metal−metal interaction parameters H_{AB} and the delocalization parameters α^2 calculated from eqs 6 and 7

$$H_{AB} = (2.05 \times 10^{-2})\left[\frac{\epsilon_{max}\Delta\nu_{1/2}}{\nu_{max}}\right]^{1/2}\frac{\nu_{max}}{\gamma}\ \text{cm}^{-1} \qquad (6)$$

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\epsilon_{max}\Delta\nu_{1/2}}{\nu_{max}\gamma^2} \qquad (7)$$

where ν_{max} is IT band maximum in cm^{-1}, ϵ_{max} is the molar absorptivity in M^{-1} cm^{-1} at the band maximum, and r is intermetallic separation. To carry out the calculation through-space distances were used for r. For $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$, r was estimated to be 7.8 Å from the crystallographic data[40] of Fc(4-Py) and a Py-Ru^{III} distance[35] of 2.0 Å. For $[Fc(3\text{-}Py)Ru\text{-}(NH_3)_5]^{3+}$, r was estimated to be 5.6 Å from the configuration where the cyclopentadienyl ring is coplanar with the pyridine mean plane and the same Py−Ru^{III} distance. The corresponding values of H_{AB} are two to three times larger for $[Fc(4\text{-}Py)Ru\text{-}(NH_3)_5]^{3+}$ than for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ in all solvents and agree well with the π-mediated interaction rule.[35]

Rate constants for thermal electron transfer were also calculated and listed in Table 4. The relevant equations[2] are (8)−(10)

$$\nu_{el} = \frac{2.3 \times 10^{10}H_{AB}^2}{\chi^{1/2}} \qquad (8)$$

$$\kappa = \frac{2\left[1 - \exp\left(\frac{-\nu_{el}}{2\nu_n}\right)\right]}{2 - \exp\left[\frac{-\nu_{el}}{2\nu_n}\right]} \qquad (9)$$

$$k_{th} = \kappa\nu_n \exp(-\Delta G^*/RT) \quad \text{and}$$

$$\Delta G^* = \frac{(\chi + \Delta E_o)^2}{4\chi} - H_{AB} \approx \frac{(\chi + \Delta E_{1/2})^2}{4\chi} - H_{AB} \qquad (10)$$

where κ is an adiabaticity factor, ΔG^* is the activation energy for thermal electron transfer, ν_{el} and ν_n are electronic and nuclear frequencies at 298 K, and a value of 5×10^{12} s^{-1} is taken for ν_n. Figure 5 shows a log k_{th} versus DN plot, and the linear relationship suggests the decrease in thermal rate constants is mainly due to solvent donicity. As indicated in Table 4, the

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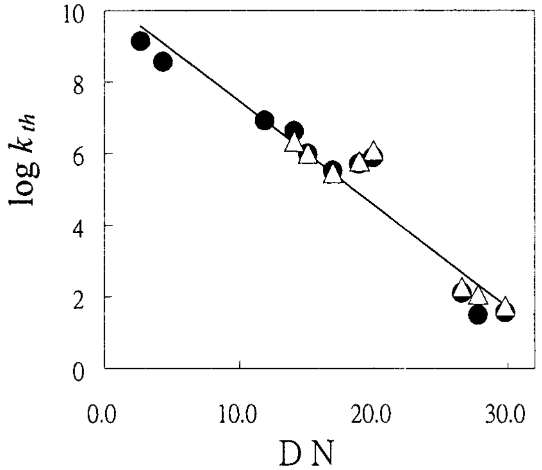

Figure 5. ln k_{th} vs Gutmann solvent donor number for $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$(circles). Triangles are for $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ and are not fitted for linear regression.

thermal transfers of $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ in all solvents examined are adiabatic, whereas the transfers of $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ are somewhat nonadiabatic. As a result, both complexes show close thermal transfer rates despite $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ having a shorter metal−metal separation and lower activation energies. It should be noteworthy that the thermal electron transfers correspond to the reverse of the optical process, viz., $Ru^{II} \rightarrow Fe^{III}$ electron transfer, and that the calculated values of k_{th} are meaningful only if they are in comparison with experimental values as measured by flash photolysis techniques.

In conclusion, IT bands of $[Fc(4\text{-}Py)Ru(NH_3)_5]^{3+}$ and $[Fc(3\text{-}Py)Ru(NH_3)_5]^{3+}$ are solvent-dependent, and they vary almost exclusively with $\Delta E_{1/2}°$ ($\Delta E_{1/2}° = E_{1/2}°(Fe^{III}/Fe^{II}) - E_{1/2}°(Ru^{III}/Ru^{II})$) that decrease linearly with Gutmann solvent donor number.

Acknowledgment. We gratefully acknowledge support from the National Science Council.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles for Fc(4-Py), 4-ferrocenylpyridine. This material is available free of charge via the Internet at http://pubs.acs.org.

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