Figure 1. Low energy visible, near-infrared spectrum of a solution containing $[Ru(NH_3)_5py]^{3+}$ (3.0×10^{-3} M) and $[Fe(CN)_6]^{4-}$ (1.5×10^{-3} M) in H_2O at pH 5 (22 ± 2 °C).

head-to-tail 1,5-dienes is now at our disposal. Further aspects of these ate complexes are under active investigation.
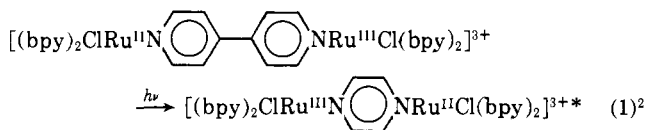
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Outer-Sphere Intervalence Transfer

Sir:

In mixed-valence complexes where there are localized redox sites, low energy absorption bands are often observed which can be assigned to intervalence transfer (IT) transitions (e.g., eq 1).[1] The observation of an IT transition is of real value in

$$[(bpy)_2ClRu^{II}N\bigcirc{-}\bigcirc NRu^{III}Cl(bpy)_2]^{3+}$$

$$\xrightarrow{h\nu} [(bpy)_2ClRu^{III}N\bigcirc NRu^{II}Cl(bpy)_2]^{3+*} \quad (1)^2$$

gaining insight into related thermal electron-transfer processes (eq 2). The electronic resonance energy or electron tunneling matrix element arising from electronic coupling between sites can be determined from the band intensity and the band energy
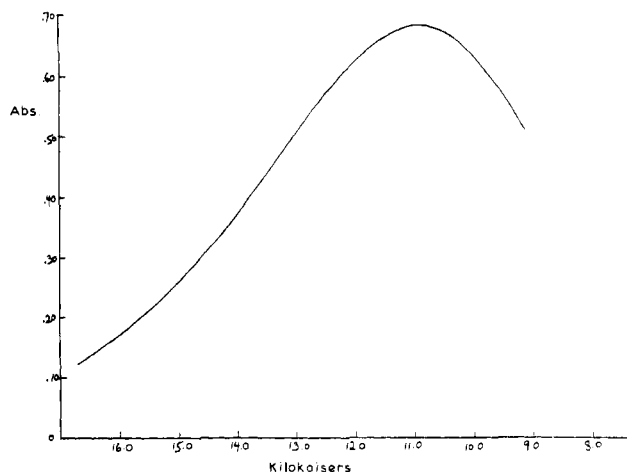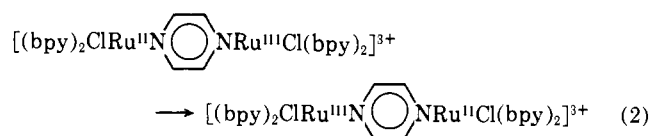
and band shape give information about the vibrational barrier to electron transfer.[2a,b,3]

$$[(bpy)_2ClRu^{II}N\bigcirc NRu^{III}Cl(bpy)_2]^{3+}$$

$$\longrightarrow [(bpy)_2ClRu^{III}N\bigcirc NRu^{II}Cl(bpy)_2]^{3+} \quad (2)$$

There is no a priori requirement that IT transitions be confined to cases where there are chemically linked donor and acceptor sites. In fact, the observation of such a transition for an outer-sphere case could be of even greater value given the absence of the structural definition provided by a bridging ligand.

It has been suggested that outer-sphere IT transitions should appear in mixed-valence solids and in concentrated solutions containing complexes of the same metal in different oxidation states.[1a,3] In practice the experiments in solution are difficult both because of the low oscillator strengths expected for the bands[1a,3] and because of the low formation constants expected for like-charged ion pairs.

Miralles, Armstrong, and Haim have investigated the kinetics of reduction of $M(NH_3)_5py^{3+}$ (Co, Ru; py is pyridine) by $Fe(CN)_6^{4-}$ in aqueous solution.[4] For $[Co(NH_3)_5py]^{3+}$, electron transfer is sufficiently slow that an initial ion pair between $Co(NH_3)_5py^{3+}$ and $Fe(CN)_6^{4-}$ is detectable kinetically. Since the charge types favor ion pairing, similar ion combinations are reasonable candidates for observing outer-sphere IT transitions and we have investigated a series of them.

In sufficiently concentrated aqueous solutions (0.001 to 0.003 F) containing $Ru(NH_3)_5py^{3+}$ and $Fe(CN)_6^{4-}$, a new absorption band appears in the near-infrared at 915 nm (Figure 1).[5] The band only appears in solutions containing both the Ru(III) and Fe(II) ions and its intensity grows as the concentration of the two ions increases. An estimate of $K_{1P} \simeq 3 \times 10^3$ for the ion-pair formation constant (eq 3) can be made and compares reasonably well with the experimentally measured value for the Co(III)–Fe(II) ion pair, $[Co(NH_3)_5py,Fe(CN)_6]^{-}$.[4,6] Using this value of K_{1P}, $\epsilon_{max} = 40 \pm 5$ M^{-1} cm^{-1} can be estimated for the near-infrared band. As expected, the bandwidth at half-maximum, $\Delta\bar\nu_{1/2}$ (6.5 ± 0.3 kK) is larger than the value predicted for IT bands by Hush using a single oscillator model ($\Delta\bar\nu_{1/2} = (2310\ \bar\nu_{max})^{1/2} = 4.8$ kK).[1a,b] In fact, the ratio $\Delta\bar\nu_{1/2}(obsd)/\Delta\bar\nu_{1/2}(calcd) = 1.3$ is typical of values found for dimeric mixed-valence ions.[9] It seems clear that the origin of the band is an outer-sphere, metal-metal charge transfer (MMCT) or IT transition (eq 4).
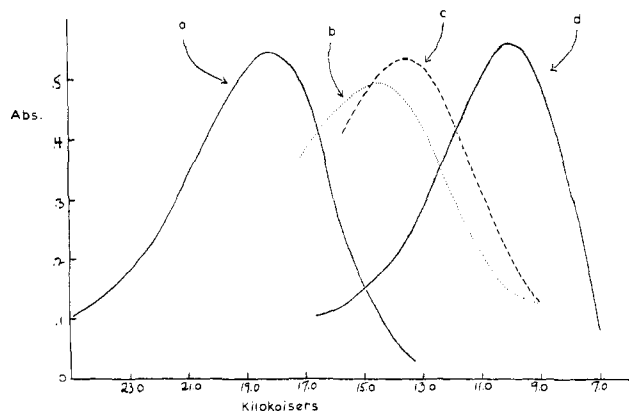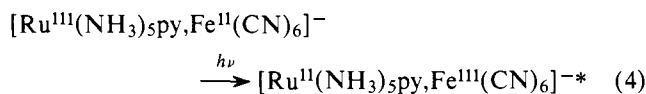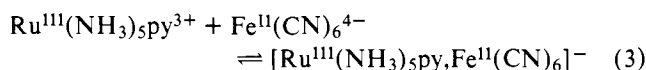
Figure 2. Solid-state spectra for the various mixed salts in Nujol mulls: a, $[Ru(NH_3)_6]_4[Ru(CN)_6]_3 \cdot 5H_2O$; b, $[Ru(NH_3)_5py]_4[Ru(CN)_6]_3 \cdot 7H_2O$; c, $[Ru(NH_3)_6]_4[Fe(CN)_6]_3 \cdot 5H_2O$; d, $[Ru(NH_3)_5py]_4[Fe(CN)_6]_3 \cdot 7H_2O$.

$$Ru^{III}(NH_3)_5py^{3+} + Fe^{II}(CN)_6^{4-}$$
$$\rightleftharpoons [Ru^{III}(NH_3)_5py,Fe^{II}(CN)_6]^- \quad (3)$$

$$[Ru^{III}(NH_3)_5py,Fe^{II}(CN)_6]^-$$
$$\xrightarrow{h\nu} [Ru^{II}(NH_3)_5py,Fe^{III}(CN)_6]^{-*} \quad (4)$$

In principle, there are a series of anion–cation pairs appropriate for solution studies, but in practice they tend to form sparingly soluble microcrystalline salts.[10] However, the salts themselves are of interest since they represent examples of outer-sphere, mixed-valence solids. They are brightly colored and form rapidly when nearly colorless solutions of the Ru(III) and Fe(II) ions are mixed. The salts isolated include $[Ru(NH_3)_5py]_4[Fe(CN)_6]_3 \cdot 7H_2O$, $[Ru(NH_3)_5py]_4[Ru(CN)_6]_3 \cdot 7H_2O$, $[Ru(NH_3)_6]_4[Fe(CN)_6]_3 \cdot 5H_2O$, and $[Ru(NH_3)_6]_4[Ru(CN)_6]_3 \cdot 5H_2O$.

Elemental analyses[11] show that the salts are extensively hydrated. Solid-state infrared spectra (KBr pellets) are essentially the sum of the spectra of salts of the separate ions. Each of the salts has a new absorption band at relatively low energies (Figure 2) which is the origin of its color. The transitions leading to the observed absorption bands are no doubt outer-sphere IT in nature as in eq 4, but the donor and acceptor sites are held in fixed lattice sites (eq 5). For the system $Ru(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$, solution reduction potentials for the M(III)/(II) couples $Ru(NH_3)_5py^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ (0.060 and 0.161 V, respectively, at pH 5 in 0.1 M KCl vs. the SCE) show that the redox asymmetry is slight but that the Ru(III),Fe(II) formulation is favored within the ion pair in solution (eq 3). The solid $[Ru(NH_3)_5py]_4[Fe(CN)_6]_3 \cdot 7H_2O$ also contains Ru(III) and Fe(II) as shown by the absence of the intense $\pi^*(py) \leftarrow d\pi(Ru(II))$ CT band in the visible which is a characteristic of the $Ru(NH_3)_5py^{2+}$ ion.

$$Ru^{III}(NH_3)_5L,M^{II}(CN)_6$$
$$\xrightarrow{h\nu} Ru^{II}(NH_3)_5L,M^{III}(CN)_6^* \quad (5)$$
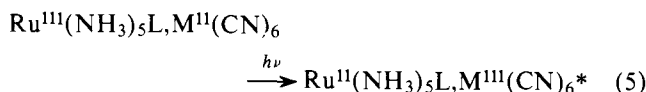
The assignment of the absorption bands in the solid state to outer-sphere charge transfer is supported by the data in Figure 3 where band energies at λ_{max} (E_{CT}) are plotted against $\Delta E_{1/2}$, the difference in solution reduction potentials for the $[Ru(NH_3)_5L]^{3+/2+}$ (L = NH$_3$, py) and $M(CN)_6^{3-/4-}$ (M = Fe, Ru) couples. Although solution data are of limited value in describing energetics in the solid state, the band energies do increase roughly linearly as the redox asymmetry between donor and accpetor sites increases, which is expected for an IT transition.[1]

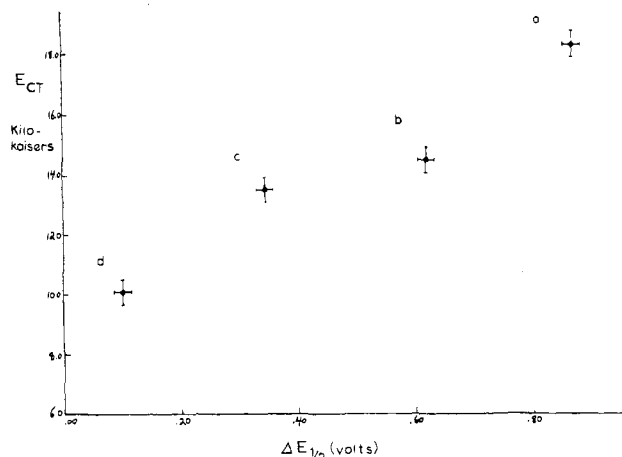From the properties of the IT band for the ion pair

Figure 3. Solid-state absorption maxima E_{CT} vs. $\Delta E_{1/2}$, the difference in reduction potentials for the $[Ru(NH_3)_5L]^{3+/2+}$ (L = py, NH$_3$) and $[M(CN)_6]^{3-/4-}$ (M = Fe, Ru) couples in H$_2$O at pH 5. Points are labeled as given in Figure 2.

$[Ru^{III}(NH_3)_5py,Fe^{II}(CN)_6]^-$ in solution, it is possible to estimate the extent of orbital mixing between the donor and acceptor sites (α) and the degree of ground-state delocalization (α^2, eq 6)[1a,b] In eq 6, d is the internuclear separation between redox sites which is ~ 8.5 Å[8] and using that value gives $\alpha^2 = 1.4 \times 10^{-4}$. This value is reasonable given the range found for mixed-valence dimers, e.g., $\alpha^2 = 1.9$–3.8×10^{-4} for **1**, which

$$[(bpy)_2ClRu^{II}N\bigcirc\!\!-\!\!\bigcirc NRu^{III}Cl(bpy)_2]^{3+}$$
1
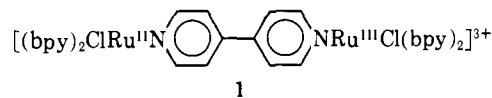
demonstrates that orbital overlap in the outer sphere can be of the same magnitude as in mixed-valence dimers where the redox sites are held in close proximity by a bridging ligand. Although quantitative data are not available for the $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5py^{3+}$ salts, it is apparent from their colors that the pyridyl group is not essential for significant overlap between the donor and acceptor sites, at least in the solid state.

$$\alpha^2 = \frac{(4.24 \times 10^{-4})\epsilon_{max}\Delta\bar{\nu}_{1/2}}{\bar{\nu}_{max}d^2} \quad (6)$$

Using the value for α^2 and eq 7,[12] it is possible to calculate the electronic resonance energy (β or J) arising from orbital mixing and therefore to obtain a measure of the splitting at the intersection between surfaces (2 J) for the thermal barrier to electron transfer within the ion pair, eq 8.[1,13] The value calculated ($\beta \le 0.37$ kcal/mol) is in the same range as values calculated for intramolecular electron transfer in **1** (0.40–0.57 kcal/mol). The magnitude of the value is of interest in the context of semiclassical electron-transfer theory[14] since it suggests that perturbation of the vibrational barrier to electron transfer by electronic delocalization is small and yet the splitting at the intersection between the $[Ru^{III}(NH_3)_5py,Fe^{II}(CN)_6]^-$ and $[Ru^{III}(NH_3)_5py,Fe^{III}(CN)_6]^-$ vibrational energy surfaces is sufficiently large that electron transfer is adiabatic.

$$\beta \le \alpha\bar{\nu}_{max} \quad (7)$$
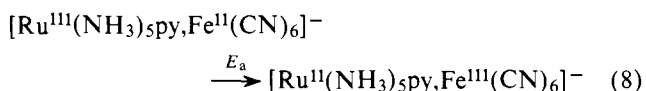
$$[Ru^{III}(NH_3)_5py,Fe^{II}(CN)_6]^-$$
$$\xrightarrow{E_a} [Ru^{II}(NH_3)_5py,Fe^{III}(CN)_6]^- \quad (8)$$

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(5) Concentrated solutions containing the two ions are unstable over a period of time. With time, a new band grows in at ~1190 nm and the near-infrared spectrum shifts to longer wavelengths. The new absorption band may arise because of the formation of a mixed-valence cyano-bridged ion, a possibility which is currently under investigation. The spectrum in Figure 1 was obtained by rapid mixing in a Cary 17 spectrophotometer so that the extent of the subsequent reaction was negligible.

(6) The value for K_{IP} was arrived at using the following equations[7]

$$K_0 = \frac{4\pi Na^3}{3000}\exp(-U(a)/kT)$$

$$U(a) = Z_1 Z_2 e^2/Da(1 + \kappa a)$$

$$\kappa = \left(\frac{8\pi Ne^2\mu}{1000\, Dk_B T}\right)^{1/2}$$

where N is Avogadro's number, Z_1 and Z_2 are the ion charges, e is the unit electron charge, μ is the ionic strength, k_B is Boltzmann's constant, a is the distance of closest approach (~8.5 Å),[8] and D is the bulk dielectric constant. K_{IP} and μ were arrived at by iterative calculations starting from the formal concentrations of the metal ions employed.

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(8) Estimated from crystallographic data on $Fe(CN)_6^{4-}$ [8a] and $Ru(NH_3)_6^{3+}$ [8b] and the known van der Waals radii for N and H:[8c] (a) A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals", Academic Press, New York, N.Y., 1976, p 104; (b) H. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971); (c) "Handbook of Chemistry and Physics", 53rd ed, CRC, Cleveland, Ohio, 1973, p D146.

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(10) Studies currently in progress indicate that it will be possible to make solution measurements on a number of ion pairs between complexes of Ru(III) and $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, or $Os(CN)_6^{4-}$.

(11) Calcd for $[Ru(NH_3)_5py]_4[Fe(CN)_6]_3\cdot7H_2O$: C, 25.03; H, 5.16; N, 32.26. Found: C, 24.62; H, 4.90; N, 31.86. Calcd for $[Ru(NH_3)_5py]_4[Ru(CN)_6]_3\cdot7H_2O$: C, 23.29; H, 4.80; N, 30.03. Found: C, 23.19; H, 4.60; N, 29.80. Calcd for $[Ru(NH_3)_6]_4[Fe(CN)_6]_3\cdot5H_2O$: C, 14.04; H, 5.33; N, 38.23. Found: C, 14.07; H, 5.30; N, 38.00. Calcd for $[Ru(NH_3)_6]_4[Ru(CN)_6]_3\cdot5H_2O$: C, 12.90; H, 4.90; N, 35.13. Found: C, 12.88; H, 4.65; N, 32.86.

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Photoelectrochemical Cells Based on Electron-Transfer Quenching of Excited States

Sir:

Electron-transfer quenching of molecular excited states is a common reaction[1] and one which can lead to significant conversion of excited-state energy into stored chemical redox energy on a transient basis. The excited states of metal complexes like $Ru(bpy)_3^{2+}$ (bpy is 2,2'-bipyridine) are especially appealing in this regard because the complexes absorb light appreciably in the visible, well-characterized, ground-state, one-electron oxidation and reduction products are known, and the excited states have been shown to undergo both oxidative and reductive quenching (e.g., eq 1 and 2).
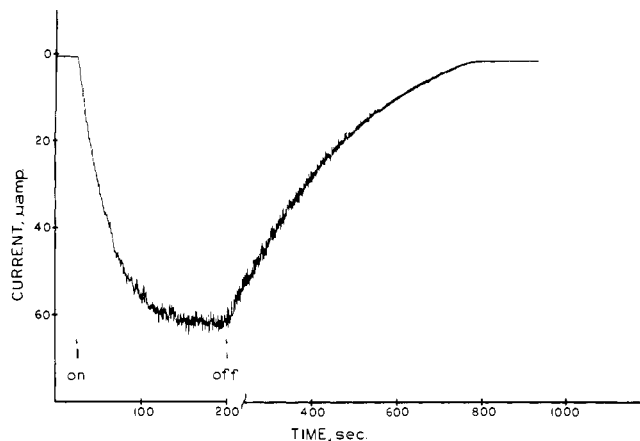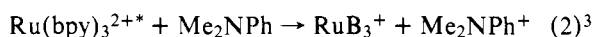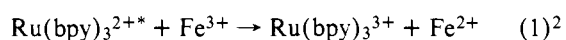
$$Ru(bpy)_3^{2+*} + Fe^{3+} \rightarrow Ru(bpy)_3^{3+} + Fe^{2+} \quad (1)^2$$

$$Ru(bpy)_3^{2+*} + Me_2NPh \rightarrow RuB_3^+ + Me_2NPh^+ \quad (2)^3$$

Figure 1. Time dependence of the photocurrent following irradiation at 453 nm of a cell consisting of $[Ru(bpy)_3^{2+}] = 8.6 \times 10^{-8}$ M and $[Co(C_2O_4)_3^{-3}] = 2.5 \times 10^{-3}$ M in 1 N H_2SO_4 in the photolyzed cell compartment and $[Fe^{2+}] = [Fe^{3+}] = 0.01$ M in 1 N H_2SO_4 in a second compartment.

The redox properties of the excited state $Ru(bpy)_3^{2+*}$ have been used in electrochemical cells to demonstrate direct excited-state quenching at semiconductor electrodes.[4] The difference in quenching (eq 1) and back-electron-transfer rates, $Ru(bpy)_3^{3+} + Fe^{2+} \rightarrow Ru(bpy)_3^{2+} + Fe^{3+}$, has also been utilized in a photogalvanic cell.[5] We would like to point out that there are a number of additional electrochemical-excited-state experimental configurations which can be exploited and that the photoelectrochemical cells which result may be useful in providing models for a variety of approaches to solar energy conversion based on molecular excited states.

Demas and Adamson[6] have shown that $Ru(bpy)_3^{2+*}$ undergoes net oxidative quenching by tris(oxalato)cobalt(III) in acid solution to give Co^{2+} with a quantum efficiency of ~0.85.

$$6H^+ + Ru(bpy)_3^{2+*} + Co(C_2O_4)_3^{3-}$$
$$\rightarrow Ru(bpy)_3^{3+} + Co^{2+} + 3H_2C_2O_4 \quad (3)$$
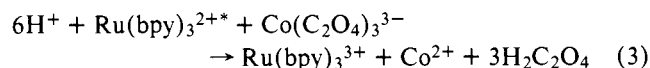
Photolysis at 453 nm (±10 nm) of a solution containing $Ru(bpy)_3^{2+}$ (5×10^{-5} M) and $Co(C_2O_4)_3^{3-}$ (2×10^{-3} M) in 1.0 N H_2SO_4 and a platinum electrode causes a rapid increase in potential as $Ru(bpy)_3^{3+}$ is produced. The potential increases exponentially and after a few seconds reaches a limiting value of 1.015 V which is that expected for the $Ru(bpy)_3^{3+/2+}$ couple vs. SCE. At the concentration level used, $Ru(bpy)_3^{2+}$ absorbs an appreciable amount of light from the ultraviolet through much of the visible region of the spectrum. Making corrections for the amount of light absorbed, essentially identical results were obtained at 405, 500, and 546 nm. The absence of a wavelength dependence is expected since $Ru(bpy)_3^{2+*}$ is known to form with an efficiency of ~1 following photolysis throughout much of the ultraviolet and visible.[7] The initial slopes of the potential curves are dependent on the absorbance of the solution as well as on the output of the irradiating lamp. The long term stability of the cell is limited because of slow oxidation of oxalic acid by $Ru(bpy)_3^{3+}$, but there are two points worth noting. The first is that this or a related system may be useful for chemical actinometry since the total number of photons absorbed over a broad wavelength range can be determined by simple potential measurements. The usefulness of the present system below 400 nm is limited by the photoreactivity of $Co(C_2O_4)_3^{3-}$,[8] but other, less photoactive quenchers could also be used.

The second point is that the stored chemical redox energy in the cell can be withdrawn as a current during and following photolysis. In Figure 1 is shown a photocurrent vs. time plot for a photoelectrochemical cell consisting of an illuminated