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Electrochemical Variational Study of Donor/Acceptor Orbital Mixing and Electronic Coupling in Cyanide-Bridged Mixed-Valence Complexes

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Introduction

Cyanide-bridged mixed-valence complexes featuring metal(III) pentaammine acceptor sites and metal(II) hexacyano donor sites have been investigated extensively by Vogler et al.,[1] Haim and Burewicz,[2] Shepherd et al.,[3] and others.[4] These complexes are interesting examples of strongly covalently linked redox systems which, nevertheless, exist in valence-localized form. As mixed-valence species, they display fairly intense intervalence (or metal-to-metal) charge-transfer transitions ($\epsilon \approx 3000$ M^{-1} cm^{-1}), which tend to be shifted toward the visible region from the near-infrared on account of substantial redox asymmetry.[1–3]

Our own interests center on bridge-mediated charge-transfer kinetics. We have recently succeeded[5] in obtaining (by femtosecond transient absorbance spectroscopy) a direct measure of the thermal kinetics (k_{ET}) of the highly exothermic back-electron-transfer reaction which follows intervalence excitation in one of these complexes, $(H_3N)_5Ru\text{–}NC\text{–}Fe(CN)_5^-$:

$$(H_3N)_5Ru^{III}N{\equiv}CFe^{II}(CN)_5^- \xrightarrow{h\nu} (H_3N)_5Ru^{II}N{\equiv}CFe^{III}(CN)_5^- \qquad (1a)$$

$$(H_3N)_5Ru^{II}N{\equiv}CFe^{III}(CN)_5^- \xrightarrow{k_{ET}} (H_3N)_5Ru^{III}N{\equiv}CFe^{II}(CN)_5^- \qquad (1b)$$

We have also recently found that *complete* mode-by-mode descriptions of the Franck–Condon structural changes accompanying reactions like eq 1 can be obtained from a time-dependent analysis of intervalence-enhanced Raman scattering spectra.[4–6]

With the available structural, kinetic, and thermodynamic information, the only additional ingredient needed to complete the picture of intramolecular electron transfer is a knowledge of initial-state/final-state electronic coupling. From the work of Burewicz and Haim,[2] one estimate of the size of the coupling element (H_{if}) is, in fact, already available. For the reaction in eq 1a, they report $H_{if} = 1500$ cm^{-1}, on the basis of a Hush–Mulliken analysis[7,8] of the oscillator strength for intervalence absorption.[2] While the absorption measurements were no doubt done with considerable care, we were reluctant to make use of the derived H_{if} estimate without further corroboration. Our concern stemmed from three recent reports[9–11] which have called into question the quantitative reliability of the Hush analysis for intervalence and related charge-transfer transitions. The purpose of this paper is to report on an alternative electrochemical investigation of electronic coupling as well as donor/acceptor orbital mixing—with particular emphasis on comparisons to the oscillator strength method.

As background, we note briefly that the electrochemical method, as developed by Curtis and co-workers,[9] is an experimental variational approach. Electrochemically significant structural changes are introduced at one of the two available redox sites in a binuclear system. From the electrochemical response at the second (unperturbed) site, Mulliken-type mixing parameters can be readily extracted. To elaborate, the Curtis analysis[9] assumes (following Mulliken[8]) that the true initial and final electronic states (Ψ_i and Ψ_f) for charge transfer can be expressed as linear combinations of zeroth-order states (i.e. fully valence-localized states, ψ_1 and ψ_2):[12]

$$\Psi_i \approx a\psi_1 + b\psi_2 \qquad (2a)$$

$$\Psi_f \approx b\psi_1 - a\psi_2 \qquad (2b)$$

$$\rho = b/a \qquad (3)$$

In eqs 2 and 3, mixing (or valence delocalization) is complete when ρ is unity but is completely absent when ρ is zero. We further note that in the limit of small orbital overlap ($S_{12} \ll 1$; eq 4) the squares of the coefficients themselves describe directly the net fractional distributions of charge at the donor and acceptor sites:[13]

$$a^2 + b^2 \pm 2abS_{12} = 1 \qquad (4)$$

The key extension by Curtis was to show that, under appropriate conditions,[14] ρ may be obtained directly from the slope (m) of a plot of the *change* in donor formal potential (E_2) versus the *change* in acceptor formal potential (E_1) as redox structural perturbations are introduced at the acceptor site:[9,14]

$$\partial E_2/\partial E_1 = m = \rho^2 = b^2/a^2 \qquad (5)$$

We have applied the analysis by preparing the series $L(NH_3)_4Ru^{III}N{\equiv}CFe^{II}(CN)_5^-$ and changing the identity of the ligand, L, which is trans to the bridging cyanide. While still observing valence localization, we find significantly greater donor-acceptor mixing than implied by oscillator strength measurements.

Experimental Section

Syntheses. $[(H_3N)_5Ru\text{–}NC\text{–}Fe(CN)_5]Na$ was prepared by a literature method[1b] and purified (removal of trimeric species) by passage through a cation-exchange column (Dowex 50W-X8; Na$^+$ form).

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[12] In our study, ψ_1 describes the fully-localized redox state $L(H_3N)_4Ru^{III}N{\equiv}CFe^{II}(CN)_5^-$, while ψ_2 describes the fully-localized redox state $L(H_3N)_4Ru^{II}N{\equiv}CFe^{III}(CN)_5^-$.

[13] In Hush's notation,[7] b^2 is designated α^2 and a^2 is $(1 - \alpha^2)$ in the limit of small S_{12}.

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[*t*-(py-x)Ru(NH_3)$_4$(SO_4)]Cl (py-x = Pyridine, 4-Methylpyridine, 3-Chloropyridine). These intermediate species were prepared by a literature method.[15]

[*t*-(py)(NH_3)$_4$Ru–NC–Fe(CN)$_5$]Na. This compound was prepared by adding an equimolar amount (ca. 0.1 mmol) of $K_4Fe(CN)_6$ to [*t*-(py)-(NH_3)$_4$Ru(SO_4)]Cl dissolved in 50 mL of water. After 24 h, the reaction mixture was filtered, and the filtrate was run through a Dowex 50W-X8 column in the Na^+ form. The sample volume was reduced to ca. 10 mL by rotary evaporation. A 20-mL portion of methanol was added. After 20 min, the resulting crude product was collected by vacuum filtration on a glass frit. At this point, cyclic voltammetry experiments indicated significant contamination with $Fe(CN)_6^{n-}$. We found, however, that the contaminant could be efficiently removed by passage of the sample through a gel permeation column (Bio-Gel P-2). A blue-green band was collected, and the partially purified product was precipitated again by the addition of a 2-fold excess of methanol. At this stage, studies by rotating-disk voltammetry showed the sample to be free of electroactive impurities. Limiting currents, however, were appreciably smaller than expected on the basis of voltammetry for [(H_3N)$_5$Ru–NC–Fe(CN)$_5$](Na), implying significant contamination with an electro*inactive* substance. Subsequent analysis for Fe, Ru, Na, Cl, and S indicated substantial Na_2SO_4. The compound is best formulated, therefore, as [*t*-(py)(NH_3)$_4$Ru–NC–Fe-(CN)$_5$]Na·Na_2SO_4·$2H_2O$. Anal. Found: C, 19.24; H, 4.12; N, 22.49; Ru, 15.27; Fe, 8.44; Na, 10.57; S, 5.10; Cl, <0.52. Calcd: C, 19.98; H, 3.20; N, 23.30; Ru, 15.28; Fe, 8.45; Na, 10.43; S, 4.85; Cl, 0. (Note that, for elemental analyses, it is important that an appropriate catalyst be used to liberate C and N from the iron center.)

[*t*-(4-Mepy)(H_3N)$_4$Ru–NC–Fe(CN)$_5$]Na·2.5Na_2SO_4·$2H_2O$. This complex was prepared and partially purified essentially as described above. Elemental analysis indicated contamination by approximately 2 equiv of Na_2SO_4, but electrochemical measurements revealed that no electroactive impurities were present. Anal. Found (multiple determinations, single preparation): C, 14.28, 16.08, 15.54; H, 3.00, 3.06; N, 15.94, 16.81, 16.51; Na, 14.54. Calcd: C, 16.22; H, 2.61; N, 17.34; Na, 15.53.

[*t*-(3-Cl-py)(NH_3)$_4$Ru–NC–Fe(CN)$_5$]Na·6.5Na_2SO_4·$3H_2O$. This complex was likewise prepared and partially purified essentially as described above. It was obtained, however, only in heavily contaminated form (Na_2SO_4). (No other impurities were detected.) Anal. Found: C, 7.15; H, 1.48; N, 9.69; Na, 21.71. Calcd: C, 8.84; H, 1.48; N, 10.31; Na, 21.53.

Measurements. Formal potentials were obtained by differential-pulse voltammetry (PAR 174A polarographic analyzer, Houston Omnigraphics X-Y recorder) in water containing 0.1 M NaCl. The working electrode was a glassy-carbon disk, the counter electrode was platinum, and the reference was saturated (NaCl) calomel. Rotating-disk measurements were made with a Pine Instruments rotator. Visible and near-infrared absorption spectra were recorded in matched 1-cm cells on an OLIS-modified Cary 14 spectrophotometer.

Results and Discussion

Figure 1 shows a plot of E_f(Fe) versus E_f(Ru) for the four cyanide-bridged mixed-metal complexes. As one would expect, E_f(Ru) shifts positively as NH_3 is replaced first by 4-methylpyridine and then by progressively more strongly electron-withdrawing ligands. Note, however, that the indirectly perturbed redox site also shifts significantly in potential. Figure 2 shows that the difference quantity (E_f(Fe) – E_f(Ru)) correlates linearly, with roughly unit slope, with the corresponding optical intervalence energy (eq 1a). A one-to-one energy correlation would be expected, of course, if trans-ligand variations serve chiefly to change the redox asymmetry of the optical ET process.[16]

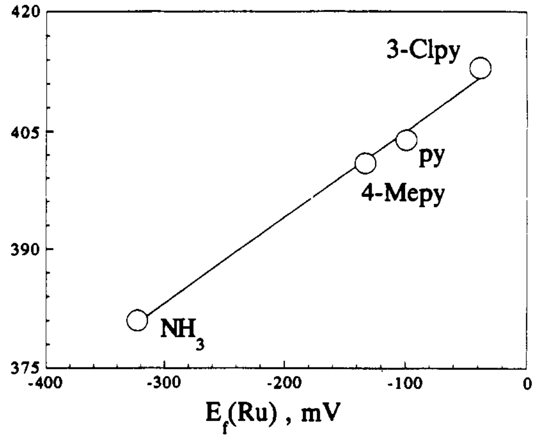

Figure 1. E_f(Fe) versus E_f(Ru) for complexes of the type *t*-L(NH_3)$_4$-Ru–NC–Fe(CN)$_5^{0/-/2-}$ where L = NH_3, 4-Mepy, py, or 3-Cl-py. Unitless slope = 0.11.

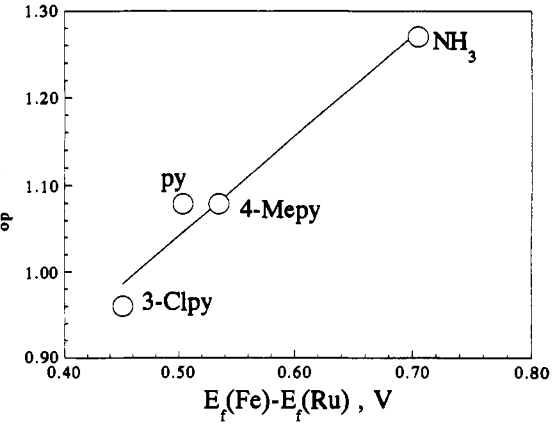

Figure 2. Site-to-site electrochemical potential difference (E_f(Fe) – E_f(Ru)) versus optical intervalence charge-transfer energy for complexes of the type *t*-L(NH_3)$_4$Ru–NC–Fe(CN)$_5^{0/-/2-}$ where L = NH_3, 4-Mepy, py, or 3-Cl-py.

Returning to Figure 1, the unitless slope is 0.11. From eq 5 the slope also should equal b^2/a^2, in the limit of small S_{12}. Imposing the normalization condition (eq 5), we derive $b^2 = 0.10$ and $a^2 = 0.90$, implying that roughly 10% of a valence electronic charge has already been transferred from iron to ruthenium in the electronic ground state.

For comparison, Burewicz and Haim report $b^2 = 0.022$ for (H_3N)$_5$Ru(NC)Fe(CN)$_5^-$, on the basis of an oscillator strength measurement for the electronic transition in eq 1.[2] (Alternatively, an evaluation of the intervalence oscillator strength for *t*-(py(H_3N)$_4$Ru(NC)Fe(CN)$_5^-$ yields $b^2 = 0.032$ and $H_{if} = 1560$ cm^{-1}.) While both approaches (spectral and electrochemical) lead to the conclusion that the cyanide mixed-valence species are predominantly valence localized, the 3–5-fold difference in residual delocalization determined by the two methods is disconcerting. We note that previous studies of metal–ligand mixing in Ru(NH_3)$_4$L^{2+} (L = 2,2′-bipyridine or 1,10-phenanthroline)[11] and metal–metal mixing in the Creutz–Taube ion[9] and in a series of halide-bridged copper dimers[10] have revealed similar discrepancies between oscillator strength estimates and other measures of orbital mixing. Furthermore, in the studies

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(14) Appropriate conditions are simply those that minimize additional sources of influence of perturbations at one redox site upon the formal potential at another. Several possible effects (other than mixing) have been catalogued and discussed by Sutton and Taube (*Inorg. Chem.* **1981**, *20*, 3125). The most important are (1) variable electrostatic effects, which can be minimized by conserving redox-site charge and size as structural perturbations are made, and (2) variable back-bonding effects, which can be minimized via an appropriate choice of site to perturb. To explain further, in mixed-valence systems, in particular, ancillary ligands may compete effectively with bridging ligands for dπ electron density (via back-bonding) and thereby perturb π^* electron density on the bridge. This, in turn, may influence the formal potential at the remote redox site (via a mechanism different from the mixing phenomenon we seek to probe). Obviously, the effect will be most important when the ligand bridge is short (CN^-, pyrazine, etc.) and when the potential of the indirectly perturbed site is measured under conditions where the directly perturbed site is effective at back-bonding. We have minimized the effect by measuring remote-site potentials (Fe(II/III)) in the presence of various Ru^{III}L (rather than Ru^{II}L) species. (Recall that Ru(III) is *in*effective (especially in comparison to Ru(II)) in back-bonding even to strongly accepting ligands.)

(15) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

(16) See, for example: Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3002.

cited, the oscillator strength method has generally *under*estimated b^2 by a factor of 5 or more. On the other hand, for the first two cases, at least (i.e. $Ru(NH_3)_4L^{2+}$ and the Creutz–Taube ion), the electrochemical method has shown fairly good agreement with independent mixing parameter measurements.[9,11] For the present series, an independent measure of b^2 is unavailable. Nevertheless, it is tempting to conclude (on the basis of earlier studies) that the spectral method is again underestimating the extent of orbital mixing. We will proceed, therefore, by examining at least some of the assumptions commonly made in the oscillator strength analysis (while not necessarily ruling out limitations in the electrochemical analysis[9,14] as the ultimate source of error).

A limiting expression for the relationship between absorption spectral parameters and H_{if} is

$$|H_{if}| = 2.06 \times 10^{-2}(\epsilon_{max}(\Delta\bar{\nu}_{1/2})E_{op}^{MMCT})^{1/2}/eR \qquad (6)$$

where $\Delta\bar{\nu}_{1/2}$ is the half-width of the MMCT absorption, e is the amount of charge transferred, and R is the charge-transfer distance. The mixing parameter, b^2, is then typically obtained from

$$b^2 \approx (H_{if}/E_{op}^{MMCT})^2 \qquad (7)$$

As a starting point, it is often assumed that e is identically the unit electronic charge and that the distance of intervalence transfer is the geometric metal-to-metal separation distance (ca. 5.2 Å in our case[2]). If, for the sake of argument, the electrochemical findings are accepted at face value, then the first assumption would be less than fully correct. Thus, the observation of ca. 10% valence delocalization in the electronic ground state implies net optical transfer of just 80% of the unit charge (assuming 10% delocalization in the intervalence excited state as well). This in turn leads to an upward revision by more than 50% for the value of H_{if}^2 and therefore b^2. Note, however, that the electrochemical and spectral estimates of orbital mixing still differ by a factor of 2–3.

The two estimates can be further reconciled if it is additionally assumed that the actual charge-transfer distance, R, is less than the distance between metal ions—exact agreement resulting when R is 3.0 Å ($L = NH_3$). While diminution of R by the needed 40% (from the nominal geometric value) is obviously an arbitrary exercise here, it is not without experimental precedent. For example, recent work by Boxer and Oh[17] on the electronic Stark effect spectroscopy of $(H_3N)_5Ru^{II}$–4,4′-bipyridine–$Ru^{III}(NH_3)_5^{5+}$ shows that the actual distance for intervalence transfer (directly measured) is only ~45% of the geometric distance between the nominal donor and acceptor ions. Clearly, Stark-effect measurements, if they could be applied here as well, would be most valuable in testing our hypothesis.[18] In any case, it is worth noting that the electrochemical analysis does *not* require the charge-transfer distance as in input parameter.

A corollary to the electrochemical observation of apparently enhanced donor/acceptor orbital mixing is a substantially revised estimate for H_{if}. From eq 7, on the basis of $b^2 = 0.10$ and $E_{op}^{MMCT} = 10\,200$ cm^{-1}, H_{if} is ca. 3200 cm^{-1}. For comparison, the total Franck–Condon reorganization energy (λ) may be crudely estimated as 6800 cm^{-1} (Hush analysis[7] of absorption bandwidth[2]).[19] For symmetrical mixed-valence complexes, an H_{if}/λ ratio of ~0.5 or greater should lead to complete valence delocalization. If the electrochemical estimate of H_{if} is correct, then the observation of strong valence *localization* in the $L(NH_3)_4Ru(NC)Fe(CN)_5^-$ series points in a compelling—perhaps obvious—way to the important additional role played by redox asymmetry and/or other factors in trapping valencies.

To summarize, widely divergent estimates of b^2 or orbital mixing are obtained from independent optical and electrochemical experiments. For $(L)(H_3N)_4Ru$–NC–$Fe(CN)_5^-$ species, at least, the differences can be rationalized by noting that the geometric distance between nominal donor and acceptor metal ions could, in principle, significantly exceed the true charge-transfer distance. If so, then the optical analysis would significantly underestimate both H_{if} and the extent of orbital mixing.

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(18) We note that Stark-effect measurements actually yield the product of e and R. When this is combined with data for eqs 6 and 7 (three equations, total), however, unique solutions for the three unknowns (e, R, and H_{if}) should be obtainable. (Recall for eq 7 that the mixing parameter, b^2, may be equated approximately with $(1 - e^2)/2$.)

(19) An alternative bandwidth analysis,[5] based on somewhat different assumptions, has yielded λ(total) = 5600 cm^{-1}.