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Vibronic Coupling in Dicyano-Complex-Bridged Mixed-Valence Complexes. Relaxation of Vibronic Constraints in Systems with Degenerate Bridging-Ligand and Electron-Transfer Excited States

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Intense near-infrared (NIR) absorption bands have been found in mixed-valence $Ru(NH_3)_5{}^{2+,3+}$ complexes bridged by *trans*-$Ru(py)_4(CN)_2$ and *cis*-$Os(bpy)_2(CN)_2$, $\epsilon_{max} \sim 1.5 \times 10^3$ cm^{-1} and $\Delta\nu_{1/2} \sim 5 \times 10^3$ cm^{-1} for bands at 1000 and 1300 nm, respectively. The NIR transitions implicate substantial comproportionation constants (64 and 175, respectively) characteristic of moderately strong electronic coupling in the mixed-valence complexes. This stands in contrast to the weakly forbidden electronic coupling of $Ru(NH_3)_5{}^{2+,3+}$ couples bridged by M(MCL)-$(CN)_2{}^+$ complexes (MCL = a tetraazamacrocyclic ligand) (Macatangay; et al. *J. Phys. Chem.* **1998**, *102*, 7537). A straightforward perturbation theory argument is used to account for this contrasting behavior. The electronic coupling between a cyanide-bridged, donor−acceptor pair, D−(CN$^-$)−A, alters the properties of the bridging ligand. Such systems are described by a "vibronic" model in which the electronic matrix element, H_{DA}, is a function of the nuclear coordinates, Q_N, of the bridging ligand: $H_{DA} = H_{DA}{}^\circ + bQ_N$. Electronic coupling in the dicyano-complex-bridged, D−[(NC)M(CN)]−A, systems is treated as the consequence of the perturbational mixing of the "local", D(NC)M and M(CN)A, vibronic interactions. If M is an electron-transfer acceptor, then the nuclear coordinates are assumed to be configured so that bQ_N is larger for D(NC)M but very small ($bQ_N \sim 0$) for M(CN)A. When the vertical energies of the corresponding charge-transfer transitions, E_{DM} and E_{DA}, differ significantly, a perturbation theory treatment results in $H_{DA} = H_{DA}H_{AM}/E_{ave}$ independent of M and consistent with the earlier report. When $E_{DM} \cong E_{DA}$, configurational mixing of the excited states leads to H_{DA} proportional to H_{DM}, consistent with the relatively intense intervalence bands reported in this paper. Some implications of the model are discussed.

Introduction

We have recently proposed a "selection rule" for the electronic matrix element in vibronically coupled donor/acceptor (D/A) complexes.[1] This proposal was based on the failure of the intervalence absorption to respond to configurational mixing with metal-to-ligand charge transfer (MLCT) states of the bridging ligand in some D/A complexes with dicyanometal complexes, $M^{III}(MCL)(CN)_2{}^+$ (MCL = a tetraazamacrocyclic ligand), as bridging ligands. In this report we show how this selection rule may be relaxed in simple D/A complexes.

The electronic coupling between an electron-transfer donor (D) and acceptor (A) (represented by the matrix element, H_{DA}) is a fundamental aspect of electron-transfer reactivity[2,3] and might in principle be useful in its manipulation. There have been many studies of electronic coupling in simple donor−acceptor (D/A) complex systems.[1,4−9] However, some of the most basic features of D/A coupling remain unresolved and controversial.

For example, it is commonly assumed that H_{DA} is independent of the nuclear coordinates (Condon approximation).[3,10] Yet, the CN$^-$-stretching frequency of cyanide-bridged M(CN)M′ complexes is shifted to low energy when M and M′ form a D/A pair,[11,12] opposite to the direction of the shift expected for the mechanical coupling of C−N, M−C, and N−M′ oscillators.[13] The magnitude of this shift has been found to increase with the oscillator strength of the donor/acceptor charge transfer (DACT) absorption.[11,14] This demonstrates that some nuclear coordinates are entangled with the electronic coordinates in the CN-bridged D/A complexes.

To systematically describe these systems, we have assumed that (a) the delocalization of electron density from the donor onto the bridging ligand, and/or from the bridging ligand onto the acceptor, weakens the C−N bonds and (b) a weakened C−N bond results in enhanced D and A coupling to the bridging ligand.[11,15] These assumptions can be accommodated in a simple, "vibronic" model for the bridge-enhanced D/A coupling, and this model has been demonstrated to be consistent with the proportionality between the shifts of ν_{CN} and the DACT

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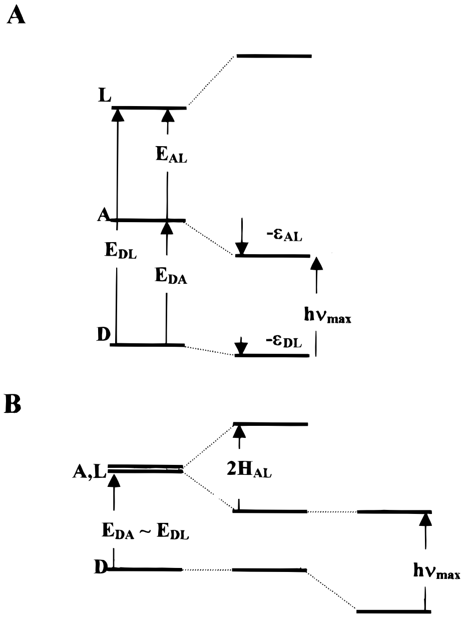

Figure 1. Schematic diagrams illustrating two types of behavior expected in donor−acceptor systems in which the bridging ligand mediates D/A electronic coupling. (A) illustrates the (diabatic) limit in which the three electronic states are clearly distinct with $E_{AL} \gg |H_{AL}|$; (B) is for $E_{AL} \sim 0$ and mixing of the electron-transfer excited state, A, and the perturbing charge-transfer excited state, L.

oscillator strength.[11,14,16,17] Neither these shifts of ν_{CN} nor the more recently observed configurational mixing independence of the intervalence absorption of $M^{III}(MCL)(CN)_2{}^+$-bridged, $Ru(NH_3)_5{}^{2+}/Ru(NH_3)_5{}^{3+}$ complexes is consistent with more the usual treatments of the influence of a bridging ligand on H_{DA}.

The bridging ligand (L) mediation of electron transfer is commonly attributed to superexchange coupling in which H_{DA} depends on the configurational mixing of the ground (D) and excited state (A) with an excited state of L (commonly an MLCT excited state).[2−4,8,18−22] Configurational mixing, illustrated by eqs 1a,b (the $\psi_i°$ are electronic wave functions for the unmixed

$$\psi_D = [\psi_D° + (H_{DL}°/E_{DL}°)\psi_L°]/(1 + \alpha_{DL}{}^2)^{1/2} \qquad (1a)$$

$$\psi_A = [\psi_A° + (H_{AL}°/E_{AL}°)\psi_L°]/(1 + \alpha_{AL}{}^2)^{1/2} \qquad (1b)$$

states and $\alpha_{JK} = H_{JK}°/E_{JK}°$), is expected to lower the energies of the two electron transfer states by an amount $\epsilon_{JL} = (H_{JL}°)^2/E_{JL}°$ (where J = D or A respectively for the electron transfer states and L designates the bridging ligand CT state which mixes with both);[23] see Figure lA. Since $E_{DL}° > E_{AL}°$ for the vertical transition, one expects that such configurational mixing will result in a decrease in the energy maximum, $h\nu_{max}$(IVCT), of the intervalence transition as in eq 2. The D/A matrix element, eq 3, reduces to a superexchange contribution, eqs 4, for such a three state-model if no other factors contribute.[3,18]

$$\Delta h\nu_{max} = (H_{AL}°)^2/E_{DL}° - (H_{DL}°)^2/E_{DL}° \cong (H_{DL}°)^2(E_{DL}° - E_{AL}°)/E_{DL}°E_{AL}° \qquad (2)$$

$$H_{DA} = \langle\psi_D|H|\psi_A\rangle \qquad (3)$$

If the matrix elements for mixing of the electron transfer states, A and D, with the bridging ligand state, L, are independent of the electron-transfer coordinates, then $H_{DL} = H_{AL}$.

$$H_{DA} = H_{DA}° + H_{DA}{}^{spx} + ... \qquad (4a)$$

$$H_{DA}{}^{spx} \cong H_{DL}°H_{AL}°/E_{av}\ (E_{av} = 2E_{AL}°E_{DL}°/(E_{AL}° + E_{DL}°)) \qquad (4b)$$

The "vibronic" coupling argument that we have used differs from the usual perturbation theory argument, sketched in the preceding paragraph, only in the added assumptions that the equilibrium nuclear coordinates of the electronic states are functions of the amount of charge delocalized onto the intervening ligands so that $H_{DA} = H_{DA}° + bQ_N$. The resulting algebraic formalism is essentially that of a "pseudo-Jahn−Teller" argument.[24,25] In this formalism, as in that of the preceding paragraph, energies of the electron transfer states are modified as a result of configurational mixing, $V_j \cong (V_j° + kQ_N{}^2/2 - \epsilon_{JL})$. In the "vibronic" model the ϵ_{JL} values are expanded in a Taylor's series around the relevant nuclear coordinates (the energy differences ϵ_{JL} are functions of the nuclear coordinates) to obtain eqs 5,[11,15−17] where $V_A°$ is the difference in energy

$$V_D \cong kQ_N{}^2/2 - \epsilon_{DL}° - aQ_N \qquad (5a)$$

$$V_A \cong V_A° + k(Q_N° - Q_N)^2/2 - \epsilon_{AL}° + a'Q_N \qquad (5b)$$

between the unmixed (diabatic), vibrationally equilibriated electron transfer states (PE minima at $Q_N = 0$ and $Q_N°$, respectively), k is a force constant, and a, and a' (and b) are linear vibronic coefficients from Taylor's expansions. This argument is based on the M/M′ coupling in an M(CN)M′ system. It does result in a functional relationship between the shifts in ν_{CN} and the MM′CT oscillator strength that is consistent with observations.[11,14,16,17] However, the net D/A coupling can be very complicated in complexes with more than one vibronically coupled D/A pair.[26,27]

The Ru^{II}/Ru^{III}, intervalence absorption in the $(NH_3)_5Ru^{II}$-$[NCM^{III}(MCL)CN]Ru^{III}(NH_3)_5{}^{6+}$ complexes is weak ($\epsilon_{max} = 120 \pm 40$ M^{-1} cm^{-1}), and the intensity is nearly independent of M.[1,28] To account for this, we have proposed a simple extension of the bimetallic vibronic model, of the last parargraph, for trimetallic, M(NC)M′(CN)M″ systems:[1,14] (1) The CN^--mediated, M/M″ and M′/M″ coupling is treated as a "local", D(NC)A(CN)A′, interaction as above. (2) The overall effect on ν_{CN}, in D(NC)A(CN)D systems,[14] or on M/M″ coupling, in D(NC)A(CN)A′ systems,[1] is treated in terms of the perturbational mixing of these local interactions. The assumption that $H_{DA} \cong H_{DA}° + bQ_N$ implies that the ground-state nuclear coordinates of the bridging CN^- are configured for strong (s) D/A coupling in the $D(CN)_sA'$ moiety. The optical

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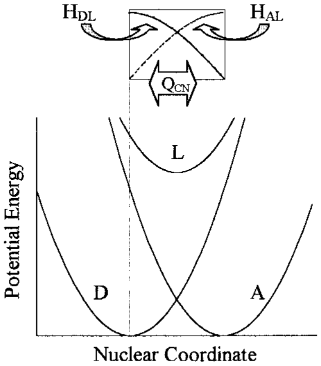

Figure 2. Three-state model for a $\mathrm{Ru^{II}{-}(NC){-}M^{III}{-}(CN){-}Ru^{III}} = \mathrm{D}$ system illustrating the variations of the coupling between the terminal (donor) and central (acceptor) metals when the coupling of the neighboring metals depends on the CN nuclear coordinates. $H_{DL} = H° + bQ_{CN}$ and $H_{AL} = H° + b'Q'_{CN}$, where bQ_{CN} and $b'Q'_{CN}$ achieve their maximum values at the D and A PE minima, respectively $\mathrm{A} = \mathrm{Ru^{III}{-}(NC){-}M^{III}{-}(CN){-}Ru^{II}}$; $\mathrm{L} = \mathrm{Ru^{III}(NC){-}M^{II}{-}(CN){-}Ru^{III}}$. The vertical dashed line qualitatively indicates the energies and matrix elements appropriate for the perturbational mixing of D, A, and L when the nuclear coordinates are those of the D potential energy minimum.

DA′CT transition leaves these coordinates fixed to generate an electron-transfer excited state as described in eq 6. According

$$[\mathrm{Ru^{II}(NC)_sM^{III}(CN)_wRu^{III}}]_D + h\nu \rightarrow {}^*[\mathrm{Ru^{III}(NC)_sM^{III}(CN)_wRu^{II}}]_A \quad (6)$$

to this model the $\mathrm{Ru^{II}/M^{III}}$ electronic coupling (H_{AL}) should be small in the excited state. The $\mathrm{CN^-}$ nuclear coordinates are expected to be between the s and w extremes in the vibrationally equilibriated MLCT excited state, $[\mathrm{Ru^{III}(NC)_iM^{II}(CN)_iRu^{III}}]_L$, and the $\mathrm{CN^-}$ nuclear coordinates of the two vibrationally equilibriated electron transfer states correspond to extrema of the antisymmetric combination of $\mathrm{CN^-}$ stretches in the MLCT excited state (L). In view of this and the symmetry of the electron-transfer system, H_{DL} and H_{AL} are expected to be complementary, or out of phase functions of the $\mathrm{CN^-}$ nuclear coordinates. Several functions can be used to express this complementarity. Among the simpler ones are $H_{DL} = (H_{DL}° + bQ_N° \cos\theta)$ and $H_{AL} = (H_{AL}° + bQ_N° \sin\theta)$ for $0 \leq \theta \leq \pi/2$. Figure 2 illustrates the expected relationship among H_{DL}, H_{AL}, the ground-state potential energies, and the nuclear coordinates. The resulting configurational mixing leads to an expression for H_{DA} that contains some terms (such as $(bQ_N°)^2 \cos\theta \sin\theta$) that are zero when evaluated in the ground-state coordinates. This is consistent with the observations in our earlier report.[1,28]

The specific functions employed (i.e., $\cos\theta$ and $\sin\theta$) illustrate the general features of the model but are not derived from it. In any event this simple "vibronic" model does suggest that there are conditions for which the matrix elements can approach zero and, thus, a "selecton rule" for H_{DA}. This paper examines conditions for the relaxation of this selection rule.

Experimental Section

Synthesis of Complexes. Syntheses of *trans*-$\mathrm{Ru^{II}(py)_4(CN)_2}$[29] and *cis*-$\mathrm{Os^{II}(bpy)_2(CN)_2}$[30] were based on literature reports.

***trans*-$\mathbf{[(py)_4Ru(CNRu(NH_3)_5)_2](PF_6)_6}$.** To a solution containing 0.540 g (0.8520 mmol) of $\mathrm{[Ru^{III}(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2}$ in 10 mL of methanol was added 0.100 g (0.2130 mmol) of *trans*-$\mathrm{Ru^{II}(py)_4(CN)_2}$. The resulting solution was stirred while covered from light, for approximately 1 h. The methanol was removed by rotoevaporation and the residue dissolved in a minimum of water. The complex was purified by column chromatography using Sephadex SP C-25 (swelled in water overnight) as the stationary phase, eluting with gradient concentrations of HCl. The monoruthenated complex was removed with 0.40 M HCl, and the desired bisruthenated complex was removed with 0.70 M HCl. The eluant solutions, containing the monoruthenated or bisruthenated complexes, after chromatography were concentrated by rotoevaporation. The resulting residue was dissolved in a minimal amount of water. An excess of $\mathrm{NH_4PF_6}$ was added to these solutions, and refrigeration overnight yielded a light pale blue powder for the monoruthenate and a darker blue powder for the bisruthenate. Typical yields were 20% and 45%, respectively. Anal. Calcd (found) for $\mathrm{C_{22}H_{50}N_{16}P_6F_{36}Ru_3{\cdot}3H_2O}$: C, 14.96 (14.90); H, 2.86 (2.90); N, 12.69 (12.70).

***trans*-$\mathbf{[(py)_4Ru(CN)(CNRu(NH_3)_5)](PF_6)_3}$.** To a solution containing 0.100 g (0.2130 mmol) of *trans*-$\mathrm{Ru(py)_4(CN)_2}$ in 25 mL of acetone was added 0.148 g (0.2342 mmol) of $\mathrm{[Ru(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2}$. The resulting solution was stirred, shielded from light, at room temperature for 1 h. The dark blue solution was vacuum filtered, and the solvent was removed from the filtrate by rotoevaporation. The residue was dissolved in distilled water and added to a column of Sephadex-SP C-25. The mixture was eluted with gradient concentrations of HCl. The desired monoruthenate was removed from the column with 0.40 M HCl. A small amount (approximately 5%) of the bisruthenate was removed from the column with 0.70 M HCl. Reduction of volume by rotoevaporation followed by the addition of excess $\mathrm{NH_4PF_6}$ resulted in a light blue precipitate. The product was collected by vacuum filtration, washed with distilled water and ether, and dried in vacuo (yield, 40%). Anal. Calcd (found) for $\mathrm{C_{22}H_{35}N_{11}P_3F_{18}{\cdot}5H_2O}$: C, 14.96 (14.90); H, 2.86 (2.90); N, 12.69 (12.70).

***cis*-$\mathbf{[(bpy)_2Os(CNRu(NH_3)_5)_2](PF_6)_6}$.** The bisruthenated complex was synthesized in a manner similar to the synthesis of *trans*-$\mathrm{[(py)_4Ru(CNRu(NH_3)_5)_2](PF_6)_6}$. However, problems did arise in the purification of the parent *cis*-$\mathrm{Os^{II}(bpy)_2(CN)_2}$ complex. The products of this synthesis typically contained three components (as shown in the cyclic voltammograms of the isolated material):[31] (1) unreacted starting material; (2) *cis*-$\mathrm{Os^{II}(bpy)_2(Cl)(CN)}$; (3) *cis*-$\mathrm{Os^{II}(bpy)_2(CN)_2}$. Separation of the three components by cation exchange chromatography was not possible since all three products are neutral in charge. However, ruthenation of the isolated product yielded materials that could be separated by cation exchange chromatography. The dichloro starting material does not yield a stable ruthenate, and the monocyano and dicyano species should yield the monoruthenate and bisruthenate, respectively. The amount of $\mathrm{[Ru^{III}(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2}$ was determined by assuming that the product was the pure dicyano complex. To a solution containing 0.343 g (0.5409 mmol) of $\mathrm{[Ru^{III}(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2}$ and 10 mL of methanol was added 0.050 g (0.0902 mmol) of "*cis*-$\mathrm{Os^{II}(bpy)_2(CN)_2}$". The resulting solution was stirred overnight, shielded from light. The methanol was removed by rotoevaporation, and the residue was redissolved in a minimal amount of

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(28) The Ru(II)/Ru(III) intervalence absorbancies of the $\mathrm{M(MCL)(CNRu(NH_3)_5)_2{}^{6+}}$ complexes differ by less than 50%.[1] On the basis of the 35/5 ratio of oscillator strengths (for M = Cr(III) and Rh(III)) for their Ru(II)/M(III) MM′CT absorptions,[15] the simple superexchange argument predicts a matrix element ratio of about 9/1 and a ratio of 80/1 for the oscillator strengths for the intervalence transitions. For the expression for H_{DL} and H_{AL} employed here, $\theta = 2\pi Q_N/a$, where the amplitude of the vibration is $a = (h/m\nu)^{1/2}/2\pi$, m is the reduced mass of the oscillator, and ν is the vibrational frequency. An alternative intepretation of the weak absorbancies of the $\mathrm{(NH_3)_5Ru^{II}[NCCr^{III}(MCL)CN]Ru^{III}(NH_3)_5{}^{6+}}$ complexes ($\epsilon_{max} = 160 \pm 12\ \mathrm{M^{-1}\ cm^{-1}}$) is that there is very strong antiferomagnetic coupling in the $\mathrm{Cr^{III}(CN^-)Ru^{III}}$ moieties. In such a case, the $\mathrm{Ru^{II}/Cr^{III}}$ and $\mathrm{Ru^{II}/Ru^{III}}$ CT transitions involve Ru(II)-donor electrons with different spin quantum numbers and so are uncorrelated. For this to be relevant, the magnetic coupling would have to be very large, $J \sim 290\ \mathrm{cm^{-1}}$, and we have no indication that this is the case. Furthermore, this mechanism cannot account for the relatively weak intervalence absorption in $\mathrm{(bpy)_2Ru^{II}(CNRu^{III}(NH_3)_5)_2{}^{6+}}$ ($\epsilon_{max} \sim 300\ \mathrm{M^{-1}\ cm^{-1}}$), whereas the vibronic argument proposed in the text can.

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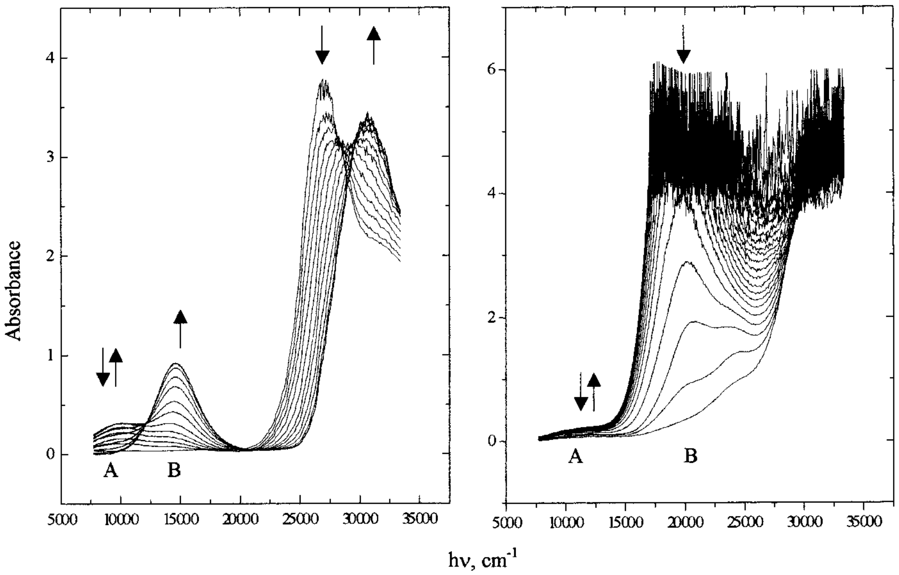

Figure 3. Comparison of the Fe^{3+} oxidations of the two $Ru(NH_3)_5{}^{2+}$ moieties in the *trans*-$Ru(py)_4(CN)_2$ (left) and *trans*-$Cr([14]aneN_4)(CN)_2{}^+$ (right) bridged complexes. The Cr-centered complex is 5−6 times more concentrated in order to display some absorbance of the MMCT(A) band at about 10×10^3 cm^{-1}. The MMCT absorption bands are labeled A and B as described in the text and Table 1.

water. The resulting mixture was vacuum filtered to remove any solid material, and the filtrate was purified by cation exchange chromatography using Sephadex SP C-25 and eluting with gradient concentrations of HCl. Unreacted *cis*-$Os^{II}(bpy)_2Cl_2$ was removed with water, the monoruthenated species was removed with 0.50 M HCl, and the bisruthated species was removed with 0.80 M HCl. Each solution was concentrated by rotoevaporation. The products precipitated from solution following the addition of an excess of NH_4PF_6 and overnight refrigeration. Typical yields were 10% monoruthenate and 30% bisruthenate, based on the starting amount of the dicyano intermediate. Anal. Calcd (found) for $C_{22}H_{46}N_{16}P_6F_{36}OsRu_2{\cdot}5H_2O$: C, 14.56 (14.51); H, 2.56 (2.60); N, 12.35 (12.33).

Absorption Spectroscopy (UV−Vis−NIR). Spectra of the ruthenated complexes were obtained in distilled water on an OLIS-modified Cary-14 spectrophotometer controlled by a Gateway 486/33 PC using OLIS software. Spectral deconvolutions were performed using SpectraCalc.[32] Redox titrations of the ruthenated complexes were performed in Ar-degassed, distilled water using either 0.10 M Ce^{4+} in 1.0 M H_2SO_4 or 0.10 M Fe^{3+} in 1.0 M HCl (Ar-degassed) as the oxidant. The procedures used have been described elsewhere.[11,15,33,34] The UV−vis−NIR spectrum of the complex was obtained after each 1−2 μL aliquot of oxidant was added. The absortivities of the Ru(II)/Ru(III) intervalence absorption bands were determined by fitting plots of absorbance versus redox titer to eq 7 (see Figures S1 and S2[35]), where n = equivalents of

$$\frac{A_n}{A_{\max}} = \frac{K_c - [K_c{}^2 - (2n - n^2)(K_c{}^2 - 4K_c)]^{1/2}}{K_c - 2(K_c)^{1/2}} \tag{7}$$

titrant added ($0 \le n \le 2$), $A_{\max}$ = absorbance maximum of the IV transition at $n = 1$, and K_c = comproportionation constant.[8]

Procedures used for the complexes with *cis*- and *trans*-$M_c(MCL)^{3+}$ centers are described elsewhere.[11,15,33,34]

Electrochemistry. Electrochemical measurements were performed, as described previously,[15,34] in acetonitrile (HPLC grade or better) with 0.10 M TEAP or 0.10 M TBAH as supporting electrolyte. Ferrocene (0.367 V vs SSCE) and diacetylferrocene (0.827 V vs SSCE) were used as internal standards.[36]

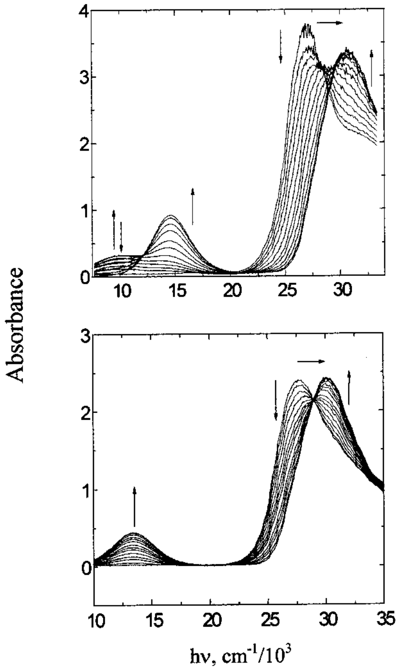

Figure 4. Comparison of the Fe^{3+} oxidations of the mono- (bottom) and bis- (top) ruthenates of *trans*-$Ru(py_4)(CN)_2$.

Infrared Spectroscopy. Infrared spectra were obtained as KBr pellets using a Nicolet 760SX FT-IR and a Nicolet 680 DSP Workstation.[11,14] IR spectra were the result of a minimum of 20 accumulations. Spectral grade KBr used for all pellets was obtained from Aldrich and used without further purification.

Results

The NIR−vis−UV spectra of mono- and bisruthenates of *trans*-$Ru(py)_4(CN)_2$ and *cis*-$Os(bpy)_2(CN)_2$ and the spectroscopic changes which accompany the oxidations of the terminal $Ru(NH_3)_5{}^{2+}$ moieties are presented in Figures 3−5. Important features of these spectra are included in Table 1. Since there is some ambiguity in the interpretation of the visible and NIR

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Table 1. Summary of Spectroscopic and Electrochemical Properties of Complexes

complex[a]	formal oxidn state: (M_t,M_c,M_t)	ν_{CN}[b] (cm^{-1})	selected NIR−vis−UV abss[c]			K_c[d]	(V) ($E_{1/2}$ ΔE_p[e,f] (mV))
			MMCT(A)	MMCT(B)	MLCT		
t-$Ru(py)_4(CN)_2$	(...,2,...)	2089, vw 2061, s					0.738 (109)
t-$Ru(py)_4(^{13}CN)_2$	(...,2,...)	2043, vw 2018, s					
t-$Ru(py)_4(CNRu(NH_3)_2)_2^{6+}$	(3,2,3)	2012 (sh) m 2063 (b), m		685 (4.2) [6.2]	372 (16.5) [∼6] 310 (sh, ∼9)	64 (op) 64 (echem)	1.294 (161)
t-$Ru(py)_4(CNRu(NH_3)_2)_2^{5+}$	(3,2,2)		1000 (1.5) [6.2]	700 (∼1.4)	350 (13.6)		0.046 (60)
t-$Ru(py)_4(CNRu(NH_3)_2)_2^{4+}$	(2,2,2)				330 (15.1) [∼7]		0.153 (68)
t-$Ru(py)_4(^{13}CNRu(NH_3)_5)_2^{6+}$	(3,2,3)						
t-$Ru(py)_4(CN)(CNRu(NH_3)_5)^{3+}$	(3,2)	2006 (b) s		746 (2.7) [6.5]	361 (14.9) [6.5]		1.08 (90)
t-$Ru(py)_4(CN)(CNRu(NH_3)_5)^{2+}$	(2,2)				332 (15.0) [6.5]		0.078 (67)
c-$Os(bpy)_2(CN)_2$	(...,2,...)	2045, s					0.41 (100)
c-$Os(bpy)_2(CNRu(NH_3)_5)_2^{6+}$	(3,2,3)	2045, m 1986, s		825 (5.8) [∼6.5] 670 (sh, ∼3.5)	526 (sh, ∼4.7)* 398 (9.1)	157 (op) 191 (echem)	
c-$Os(bpy)_2(CNRu(NH_3)_5)_2^{5+}$	(3,2,2)		<1300 (∼1.2)	808 (3.4)	∼395		−0.095 (67)
c-$Os(bpy)_2(CNRu(NH_3)_5)_2^{4+}$	(2,2,2)				341 (6)		0.035 (60)
t-$Cr([14]aneN_4)(CNRu(NH_3)_5)^{5+}$[f]	(2,3,2) 1996, w	2077, s		500 (7.6) [4.9]		7 ± 7	0.328 (82)
c-$Cr(Me_6[14]aneN_4)$-$(CNRu(NH_3)_5)^{5+}$[f]	(2,3,2)	2077, s 2075, s		525 (8.2) [5.1]		6 ± 4	0.320 (120)
c-$Ru(bpy)_2(CN)_2$[f]	(...,2,...)	2078, s 2062, s					0.793 (85)
c-$Ru(bpy)_2(CNRu(NH_3)_5)_2^{6+}$[f]	(3,2,3)	2057, s 2011, s		655 (6.0) [5.65]		15[g]	−0.037
c-$Fe(bpy)_2(CN)_2$[f]	(...,2,...)	2078, s 2070, s					0.445
c-$Fe(bpy)_2(CNRu(NH_3)_5)_2^{6+}$[f]	(3,2,3)	2033, s 2019, s		875 (6.58) [4.75]			0.00

[a] Abbreviations: *c* = cis; *t* = trans. Ligands: $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; $Me_6[14]aneN_4$ = 5,12-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; py = pyridine; bpy = 2,2′-bipyridine. [b] Abbreviations for relative intensities: s = strong; w = weak; m = medium; vw = very weak; sh = shoulder; b = broad. [c] For deconvoluted absorption bands: λ_{max} in nm (ϵ_{max} in $cm^{-1}/10^3$) [$\Delta\nu_{1/2}$ in $cm^{-1}/10^3$]). [d] Abbreviations for methods used to determine K_c: op, eq 1; echem, RT ln $K_c = \Delta E_{1/2}(Ru(NH_3)_5^{3+,2+})$). The spectroscopic determinations were performed in aqueous media, and the electrochemical measurements were performed in acetonitrile. [e] Potentials are for oxidation of the complex listed in the same row. [f] References 1, 11, 12, and 14−17.

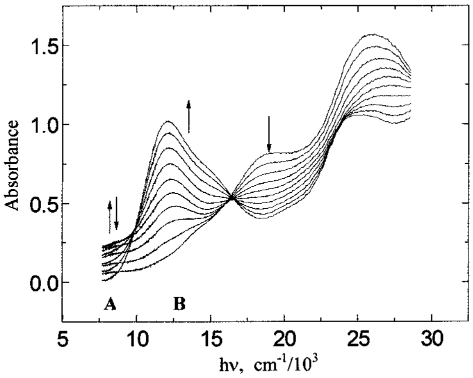

Figure 5. Absorption changes that accompany Fe^{3+} oxidations of the $Ru(NH_3)_5^{2+}$ moieties of *cis*-$Os(bpy)_2(CN)_2$. MMCT bands labeled A and B as described in the text.

absorbancies that depend on the oxidation states of the terminal $Ru(NH_3)_5$ moieties, we shall designate the observed bands as MMCT(A) for the NIR absorbance and MMCT(B) for the low-energy visible absorbance. These bands would traditionally be assigned as intervalence (IVCT or M_tM_tCT) and metal-to-bridging ligand (MLCT or M_tM_cCT) charge-transfer transitions, respectively. As discussed below, such an assignment would be misleading for these Ru(II)- and Os(II)-centered systems.

The observations on *trans*-$Ru(py)_4(CNRu(NH_3)_5)_2^{4+,5+,6+}$ are in striking contrast to our earlier observations on *trans*-M(MCL)-$(CNRu(NH_3)_5)_2^{5+,6+,7+}$ complexes.[1] Figure 3 illustrates this contrast for M = Cr(III) and MCL = 1,4,8,11-tetraazacyclotetradecane ($[14]aneN_4$ or cyclam). These complexes have comparable absorptivities for their Ru_t/M_c MMCT transitions (4.2×10^3 cm^{-1} for $Ru(NH_3)_5^{3+}/Ru(py)_4^{2+}$ and 7.6×10^3 cm^{-1} for $Ru(NH_3)_5^{2+}/Cr([14]aneN_4)^{3+}$), but the NIR bands of the half-oxidized complexes (i.e., the nominal $Ru(NH_3)_5^{2+,3+}$ intervalence bands) are more than 1 order of magnitude different in absorptivity: 1500 and 105 M^{-1} cm^{-1}, respectively.

A second striking feature of the *trans*-$Ru(py)_4(CNRu(NH_3)_5)_2^{4+,5+,6+}$ system is that the absorptivity per $Ru(NH_3)_5^{3+}$ of the MMCT(B) transition is smaller in the half-oxidized (3,2,2) than in the (3,2,3) complex with fully oxidized terminal pentaammine moieties: ∼1400 and 2100 M^{-1} cm^{-1}, respectively. Thus, the absorptivity of the MMCT(B) transition in the half-oxidized complex is about 50% of the value observed in the monoruthenate, Figure 4 and Table 1. However, MMCT absorption bands A and B have very similar absorptivities in the (3,2,2) mixed-valence complex.

While the NIR absorption appears to be comparably intense in the (3,2,2) $Os(bpy)_2(CNRu(NH_3)_5)_2^{5+}$ complex, the absorptivity per $Ru(NH_3)_5^{3+}$ of MMCT band B is greater in the (3,2,2) than in the (3,2,3) complex, Figure 5. This low-energy visible absorption, MMCT(B), exhibits a somewhat unusual shift to higher energy as the terminal Ru centers are oxidized, and a shoulder at 670 nm in the (3,2,3) complex is not present in the (3,2,2) complex. The intensity changes in the UV are more complicated.

The CN^--stretch region of the infrared is characterized by a single intense peak and a number of reproducible but very weak features for the *trans*-$Ru(py)_4(CN)_2$, Figure S3.[31] Since the related *trans*-$M(MCL)(CN)_2^+$ complexes and their bisruthenates have all exhibited a weak (symmetric) and a more intense (antisymmetric) combination of CN^- stretches,[14] we have prepared the $^{13}CN^-$-labeled complexes in order to identify the symmetric combination of CN stretches in the $Ru(py)_4$ complexes. The very weak feature that shifts in the isotopically substituted complexes has been so identified in Table 1.

We have been able to resolve two $Ru(NH_3)_5^{3+,2+}$ components in the electrochemistry of the bisruthenates of *trans*-$Ru(py)_4(CN)_2$ and *cis*-$Os(bpy)_2(CN)_2$ in acetonitrile (Table 1). This is unusual in this series of compounds,[14,16,17] and it suggests relatively strong coupling between the terminal ruthenium centers in the mixed-valence complexes. This is consistent with the relatively intense NIR absorption bands (in water) and the values of the comproportionation constants, K_c, inferred from them using eq 1, Table 1. The values of K_c inferred from MMCT absorption band A and from the separation of the two electrochemical components are in good agreement; see Table 1.

Discussion

We have found a dramatic contrast in the electronic coupling for $Ru(NH_3)_5^{2+,3+}$ D/A couples bridged by dicyanometalate complexes in which the terminal-$Ru(NH_3)_5$/central metal "MLCT" absorptivities are comparably strong. This is most clearly manifested in the 10−20-fold larger values of K_c found for the Ru(II)- and Os(II)-centered complexes reported here than for the Cr(III)-centered complexes. Furthermore, the much greater NIR absorptivity of the *trans*-$Ru_c(py)_4(CNRu_t(NH_3)_5)_2^{5+}$ (2,2,3) complex, which contrasts to that of the *trans*-M(MCL)$(CNRu(NH_3)_5)_2^{6+}$ (2,3,3) complexes,[1] is accompanied by a reduced intensity of the visible MMCT(B) absorption band. The unusually small absorptivities of the absorption bands assigned as IVCT bands in the $M(MCL)^{3+}$ complexes have been attributed to a vibronic interference effect[1] (see the Introduction). The behavior observed in the $Ru(py)_4^{2+}$-centered complex suggests a relaxation of the vibronic constraint that gives rise to such interference. On the other hand, Ferretti and co-workers have recently argued, on the basis of theoretical modeling, that the NIR absorbance in many $Ru(NH_3)_5^{2+}$/$Ru(NH_3)_5^{3+}$ complexes has been incorrectly assigned as an intervalence transition.[37,38] The effects of vibronic matrix element phase and the proper description of the electronic excited state are considered further in the discussion below.

A. General Comparisons. Despite the marked contrast in absorptivities of their MMCT bands, noted above, the *trans*-$Ru(py)_4(CN)_2$- and $Os(bpy)_2(CN)_2$-bridged complexes have a number of properties similar to those with $M(MCL)(CN)_2^+$ bridges. For example, there is a net shift of the CN stretch to lower energies when the central metal forms a donor/acceptor pair with the terminal $Ru(NH_3)_5^{n+}$ moieties.[11,14,16,17] The amplitudes of these shifts appear to be roughly consistent with the previously discussed correlation of oscillator strength of the MMCT(B) absorbancies with $\Delta\nu_{CN}$.[11,14,16,17] However, this is only a qualitative similarity since we do not have appropriate reference values of ν_{CN} for the present complexes.[14]

A contrast in behavior is that the shift in ν_{CN} (in the Ru_t^{III}/M_c^{II}/Ru_t^{III} complexes) appears to be in a single frequency. This feature is most surprising in the *cis*-$Os(bpy)_2(CNRu(NH_3)_5)_2^{6+}$ complex since it contrasts to observations on the *cis*-$Ru(bpy)_2(CN)_2$[11,39] and the *cis*-$Cr(MCL)(CN)_2^+$ [11,14] bridged complexes and since one CN stretching mode shifts relatively little in most trans complexes.[14] While the variations in the effect of electronic/nuclear entanglement appears to be more varied in cis complexes with strong D/A coupling than in their trans analogues, the sum of the shifts of the CN stretches remains correlated with variations in DACT oscillator strength.[14]

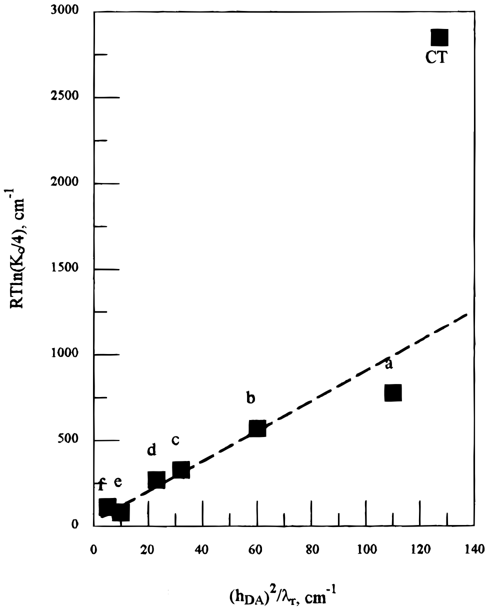

Figure 6. Correlation of the variations in the comproportionation constants for $[(NH_3)_5RuII]L[RuIII(NH_3)_5]$ complexes with stabilization energies based on eq 5. Bridging ligand L (r_{DA} = Ru(II)/Ru(III) separation in Å): a, *cis*-$Os(bpy)_2(CN)_2$ (7.35); b, *trans*-$Ru(py)_4(CN)_2$ (10.5); c, 4, 4′-bpy (11.3); d, *cis*-$Ru(bpy)_2(CN)_2$ (7.35); e, *cis*-$Cr(Me_6)$-[14]ane$N_4)(CN)_2^+$ (7.35); f, *trans*-Cr([14]ane$N_4)(CN)_2^+$ (10.5).

Figure 3 demonstrates the dramatically enhanced NIR absorptivities observed when *trans*-$Ru(py)_4(CN)_2$ rather than *trans*-$M(MCL)(CN)_2^+$ functions as a bridging ligand. However, these systems are all well-behaved, "class II"[40] systems insofar as (1) the comproportion constants, K_c, inferred from eq 1 and from electrochemical observations are in good agreement (Table 1) and (2) the values of K_c increase, as expected, with oscillator strength (Figure 6).[41] These factors are qualitatively different for the pyrazine-bridged Creutz−Taube ion (Table 2). One clear difference in the properties of these $M(L)(CN)_2^{n+}$-bridged complexes is that the MMCT(B) (or M_tM_cCT) excited state is the appreciably lower energy for the (3,2,3) and (3,2), Ru- and Os-centered complexes reported here than for the (2,3,2) and (2,3) Cr(III)-centered complexes.[15] The central ruthenium(II), Ru_c, to $Ru_t(NH_3)_5^{3+}$ absorption maximum in *trans*-$[(py)_4Ru(CNRu(NH_3)_5)_2]^{6+}$ occurs at 14.6 × 10^3 cm^{-1} while we would estimate that the $Ru(NH_3)_5^{2+}$/$Ru(NH_3)_5^{3+}$ CT absorption maximum should occur at about (13 ± 1) × 10^3 cm^{-1} (estimate based on an analysis of ion pair CT absorption spectra and self-exchange electron-transfer data[1,42,43]) in the limit of no bridge-mediated coupling. Thus, we estimate that $E_{DL}° \sim E_{DA}°$ for the $Ru(py)_4^{2+}$-centered mixed-valence complexes, while $E_{DL}° \gg E_{DA}°$ for the Cr-centered complexes. This suggests that the description of the "electron transfer" excited state (A) should be modified.

B. Simple Description of Systems with Nearly Degenerate MLCT and IVCT Excited States. The failure of the simple superexchange description of D/A coupling in $M(MCL)(CN)_2^+$-bridged systems[1] has been attributed to the cancellation in H_{DA}

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(41) For the compounds in Figure 6 (excluding the Creutz−Taube ion), $RT \ln(K_c/4) = a[2(H_{DA})^2/\lambda_r] + b$, where $a = 0.607 \pm 0.068$ and $b = -0.034 \pm 0.030$ with $r^2 = 0.95$.

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Table 2. Spectroscopic and Thermodynamic Properties of Selected $[Ru(NH_3)_5]_2(L)^{n+}$ Mixed-Valence Complexes

bridging ligand (L)	$\Delta E_{1/2}{}^{a}$ (mV)	K_c	H_{DL} (cm^{-1})	$H_{DA}{}^{b}$ (cm^{-1})
t-$Ru(py)_4(CN)_2{}^{c}$	107	64 ± 10	~200[d]	1550 ± 200
c-$Os(bpy)_2(CN)_2{}^{c}$	130	175 ± 15	~2500[d]	1700 ± 100
t-$Cr([14]aneN_4)(CN)_2{}^{+\,f}$	<100[e]	7 ± 7[g]	3900[e]	770 ± 700[h] (166)[g]
c-$Cr(Me_6[14]aneN_4)(CN)_2{}^{+\,f}$	<100[e]	6 ± 4[g]	~3500[e]	650 ± 600[h] (166)[g]
c-$Ru(bpy)_2(CN)_2$	70[i]	15[i]	3400[e]	~1200[h]
4,4′-bpy[j]	76[j]	20[j]	4200[k]	~1300[h]
pz[l]	390[l]	4×10^{6} [l]	9300[k]	3100 ± 100[m]

[a] See Table 1. [b] Determined from the average of $[(E_{DA}/2.3)RT\ \ln(K_c/4)]^{1/2}$ and eq 4 except as indicated. [c] This work. [d] Based on $Ru(bpy)_2(CN)_2$-centered complexes[11] with corrections for differences in absorptivity. [e] Data from ref 15 except as indicated. [f] Macrocyclic ligand abbreviations: $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; $Me_6[14]aneN_4$ = 5,12-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. [g] Reference 12. [h] $H_{DA} = [(E_{DA}/2.3)RT\ \ln(K_c/4)]^{1/2}$. [i] Bignozzi, C. A.; Roffia, S.; Scandola, F. *J. Am. Chem. Soc.* **1985**, *107*, 1644. Bignozzi, C. A.; Paradisi, C.; Roffia, S.; Scandola, F. *Inorg. Chem.* **1988**, *27*, 408. [j] Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3127. Also see ref 63. [k] Reference 60. [l] Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988. See also ref 4. [m] Average of estimates based on K_c and $E_{DA}/2$, where E_{DA} is the NIR absorption maximum (6.36×10^3 cm^{-1}).

of the in phase and out of phase vibronic matrix elements (see the Introduction and Figure 2) which are required for mixing the DACT state with the two different electron transfer states. The dicyano-complex-bridged D/A systems can be viewed as vibronically coupled, nonequivalent three-center D/A (or "mixed-valence") systems.[27,43−46] There has been relatively little systematic study of such systems. A particularly interesting limit for such a three-center system occurs when the vertical electron transfer and bridging ligand CT excited states are nearly degenerate. In this limit, the excited state wave functions should be significantly mixed (Figure 1B). However, this need not result in a valence delocalized ground state. The $Ru(py)_4(CN)_2$ and $Os(bpy)_2(CN)_2$ bridging ligands appear to be among the rare examples of this behavior.

The first order perturbation theory treatments of three state systems, as illustrated in Figure 1A and mentioned in the Introduction, are only valid when the matrix element, H_{AL}, is small with respect to the corresponding energy difference, E_{AL}. Since H_{DA} for $Ru^{II}(CN^-)Ru^{III}$ systems seems to run in the range of (2−4) × 10^3 cm^{-1} [15] (see Table 2), the unperturbed (or diabatic) vertical energy difference between the electron transfer and bridging ligand CT excited states, ~1.6×10^3 cm^{-1} based on the estimates in the preceding section, is apparently smaller than the coupling matrix element for these states. If $|H_{AL}| \geq E_{AL}$, then the simple, three-state perturbation theory approach based on Figure 1A is no longer useful. In this limit, the electron transfer and ligand-centered CT excited states are effectively degenerate as in Figure 1B. Thus, it is more appropriate to first consider the mixing of these two states and then to consider their perturbational mixing with the ground state. The limiting case of degenerate, vertical excited states is considered first. A more detailed discussion of the observations follows.

The first-order-corrected wave functions for a three-state system in the limit of a pair of degenerate excited states is represented in eqs 8 ($2^{1/2}\alpha_{DL}' \cong \alpha_{DL} = H_{DL}°/E_{DL}°$), and the qualitative consequences are illustrated in Figures 1B and 7. An important consequence of this simplest case mixing mechanism is that any phase difference in H_{DL} and H_{AL} will no longer be an issue in the D/A coupling (eq 8b). Consequently the intensity of the DACT transition should be appreciably greater than in those dicyano-complex-bridged compounds for which $|H_{DL}| < E_{DL}$. Thus, the $Ru(py)_4(CN)_2$-bridged mixed-valence complex demonstrates a means by which a vibronic (PJT) prohibition on D/A coupling is relaxed.

$$\psi_L = [(\psi_L° - \psi_A°)/2^{1/2} - \alpha_{DL}'\psi_D°\,]/(1 + \alpha_{DL}'^2)^{1/2} \qquad (8a)$$

$$\psi_A = [(\psi_A° + \psi_L°)/2^{1/2} - \alpha_{DL}'\psi_D°\,]/(1 + \alpha_{DL}'^2)^{1/2} \qquad (8b)$$

$$\psi_D = [\psi_D° + 2\alpha_{DL}'\psi_L°]/(1 + 4\alpha_{DL}'^2)^{1/2} \qquad (8c)$$

C. Application to the $Ru(py)_4(CN)_2$- and $Os(bpy)_2(CN)_2$-Bridged Complexes. 1. Intensities. The ~40% smaller absorptivity, per $Ru(NH_3)_5{}^{2+}$, of the MMCT(B) band in the mixed-valence complex than in *trans*-$Ru(py)_4(CNRu(NH_3)_5)_2{}^{6+}$ or in the monoruthenate might, in principle, be attributed to either (1) an "intensity stealing" effect, (2) some sort of symmetry effect, or (3) a difference in the nature of the electronic transition. Intensity stealing could be based on a naïve interpretation of eqs 2 since $H_{DA} \sim H_{DL}/2^{1/2}$ and this is roughly consistent with observations on these compounds (see section C3, below). However, one should expect a similar effect in the *cis*-$Os(bpy)_2(CN)_2$-bridged complexes and such an effect is not obvious.

There is an absorption feature at about 670 nm in the $Os(bpy)_2(CNRu(NH_3)_5)_2{}^{6+}$ complex that seems to disappear in the mixed-valence complex. The M_tM_cCT spectra of these Os complexes are the most complex that we have found in this class of compounds.[15] The two components noted may correspond to a separation of the symmetric and antisymmetric M_tM_cCT states in the $\{Ru^{III},Os^{II},Ru^{III}\}$ complex. Such a separation has not been observed in the other CN^--bridged complexes.[15] However, the strong terminal−terminal (Ru^{II}/Ru^{III}) coupling observed in the (3,2,2) ground state of the Os-centered mixed-valence complex should also be a characteristic of the (3,3,2) mixed-valence (M_tM_cCT) excited state. This would be expected to result in a related separation of the symmetric and antisymmetric $\{Ru^{II},Os^{III},Ru^{III}\}$ M_tM_cCT excited states.[47,48] The energy differences of the (the ground-state C_2) symmetry-adapted (2,3,3) ↔ (3,3,2) components of this mixed-valence excited state are expected to be comparable to $2H_{DL} = 3400$ cm^{-1}, where H_{DL} is derived from the oscillator strength of the ground-state Os(II)/Ru(III) DACT absorption (corrected for electron delocalization/relaxation effects as described previously[15]). Thus, the observed difference in absorption band

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energies, ~3 × 10^3 cm^{-1}, is close to simple expectation. No such separation of M_tM_cCT components is possible for the mixed-valence complex since the excited state has a formal {Ru^{II},Os^{III},Ru^{II}} configuration. Thus, a two component M_tM_cCT spectrum would be expected only in the cis Os(II)-centered (3,2,3) complex, and the absence of the 679 nm absorbance feature in the spectrum of the (3,2,2) mixed-valence complex is not readily attributed to "intensity stealing". The relative intensities of the components of the configurationally mixed transitions do not consistently fit very simple patterns.

Equations 2a,b do suggest a simple interpretation of the diminished intensity of the MMCT(B) band in the *trans*-$Ru(py)_2(CNRu(NH_3)_5)_2^{5+}$ complex. One expects that only one of the symmetric and antisymmetric combinations of M_tM_cCT bands will be observed in the spectrum of the *trans*-$Ru(py)_4(CN)_2$-bridged, axially symmetric (3,2,3) complex,[47,48] and we do observe only one band. That we observe two MMCT transitions (i.e., both the symmetric and antisymmetric) in the *trans*-$Ru(py)_4(CN)_2$-bridged mixed-valence complex is support for our inference that this system is valence localized and, consequently, not axially symmetric.[47−50] The diminished intensity of the higher energy component, relative to the oxidized (3,2,3) or to the (3,2) monoruthenate, could be interpreted as a weak residue of such a forbidden transition. However, the two MMCT components have nearly equal intensities in the mixed-valence complex, consistent with the simplest interpretation for an axially unsymmetrical, or electronically localized, system. Crutchley's recent paper[49] may provide an example of the spectroscopic consequences of the effective degeneracy and configurational mixing of bridging ligand (LMCT in this case) and electron transfer excited states in an axially symmetrical system.

2. Energies. Overall, the observed IVCT absorptivities in the $Ru(py)_4(CN)_2$- and $Os(bpy)_2(CN)_2$-bridged complexes are consistent with the interpretation (eqs 2) that the diabatic electron transfer and MLCT excited states are nearly degenerate in the mixed-valence systems. Further to this point, and if these states were degenerate (with respect to the vertical transition from the ground state), one would expect the resulting mixed (or adiabatic) states to differ in energy by about $2H_{DL}$. The observed energy differences are 4.3 and 4.4 × 10^3 cm^{-1} for the Ru- and Os-centered complexes, respectively (Tables 1 and 2). Within the uncertainties in the estimation of H_{DL} for these complexes (see Table 2), this is certainly consistent with expectation.

The energies of the unperturbed M_tM_cCT transitions of the mixed-valence, (3,2,2) complexes can be inferred from transitions in the oxidized, (3,2,3) or the respective monoruthenates. We estimate these transitions to occur at 15.8 and 12.1 × 10^{-1} cm^{-1}, respectively, for the Ru- and Os-centered complexes. The unperturbed (or diabatic) energy of the intervalence transition is not a readily accessible experimental parameter; however, plausible estimates are possible. For reasonably independent, valence localized complexes, this energy is well approximated by $E_{DL} \cong (\lambda_r +$ higher order terms),[23,42,51] where λ_r is a vibrational reorganizational parameter and the higher order terms are usually small. In principle the same reorganizational parameter may be estimated from electron-transfer self-exchange reactions[52−54] or from spectroscopic comparisons to related systems. Electron-transfer self-exchange data for the $Ru(NH_3)_6^{3+,2+}$ and $Ru(NH_3)_5py^{3+,2+}$ [55] indicate that λ_r is in the range of (10−14) × 10^3 cm^{-1} in water and that it is composed mostly of solvent contributions. A comparison of ion-pair charge-transfer spectra is consistent with these estimates.[43] The extrapolation to $H_{DL} = 0$ for a series of $M(MCL)(CNRu(NH_3)_5)_2^{6+}$ complexes suggests that $\lambda_r \cong 11.7 \times 10^3$ cm^{-1}.[1] Since, for the intervalence transition $h\nu_{max}$(IVCT) $\cong (\lambda_r - Dh\nu_{max})$, arguments summarized in the Introduction and eq 2 lead to eq 9, where we have assumed that $H_{DL} = H_{AL} < E_{AL} >$

$$h\nu_{obsd}(\mathrm{IVCT}) \cong \lambda_r + H_{DL}^2/E_{DL} - H_{DL}^2/[E_{DL} - \lambda_r + 2\lambda_r H_{DL}^2/(E_{DL} - \lambda_r)^2] \quad (9)$$

λ_r and we have taken account of the effect of the displacement of the ground-state potential energy minimum (the 3rd term of the denominator).[56] Iteration based on eq 9 yields $\lambda_r \cong 11.2 \times 10^3$ cm^{-1} for the (3,2,2) $Ru(bpy)_2(CNRu(NH_3)_5)_2^{5+}$ complex. For $\lambda_r \sim 11 \times 10^3$ cm^{-1}, $[h\nu_{obsd}(M_tM_cCT) - \lambda_r] \sim 4.3 \times 10^3$, 0.4 × 10^3, and 1.1 × 10^3 cm^{-1}, respectively, for $Ru(bpy)_2(CNRu(NH_3)_2)_2^{5+}$ [11] and its Fe(II)[11] and Os(II) analogues on the basis of their M_tM_cCT parameters (Table 1). Thus, only for the Ru(II)-centered complex is E_{AL} estimated to be larger than H_{AL}. The relatively low energies and the large absorptivities of the Fe(II)- and Os(II)-centered complexes are consistent with the mixing mechanism proposed above (eqs 2 and 8) and $H_{AL} > E_{AL}$.

Fewer pertinent comparisons are available for the *trans*-$Ru(py)_4(CNRu(NH_3)_5)_2^{5+}$ complex. Nevertheless, this complex exhibits many of the same features of its lowest energy CT band as the Os-centered complex discussed in the preceding paragraph, and we attribute this to the same excited-state configurational mixing mechanism. This mechanism would require λ_r in the range of (13−14) × 10^{-1} cm^{-1} for this complex if $H_{DL} \sim 2000$ cm^{-1}. While this seems a little large for this class of complexes, it is within the plausible range noted above.

A striking feature of Figure 3a is the series of changes in absorption maxima and in absorptivity of the Ru_c/py MLCT transition which accompany the successive oxidations of $Ru(NH_3)_5^{3+}$ moieties. A number of factors can contribute to the systematic shift of the MLCT transition to higher energy with this oxidation.[15] One of these is the possibility of configurational mixing with lower energy, $Ru(NH_3)_5^{3+}$-dependent CT excited states. Any such mixing should contribute to the stabilization of the electron-transfer excited state and, thus, lower its energy. This could lead to a smaller value of λ_r than that estimated above. We have no evidence that this is a significant effect in these systems.

3. Donor−Acceptor Electronic Coupling. Equations 3 and 8 can be combined to estimate H_{DA} for these complexes as in eq 10. Parameters from Tables 1 and 2 result in $H_{DA} = 1.4 \times 10^3$ cm^{-1} for *trans*-$Ru(py)_4(CNRu(NH_3)_5)_2^{5+}$.

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(50) This observation contrasts to a recent report by Crutchley and co-workers[49] that a single absorption band was found in a 2,5-dichloro-1,4-dicyanamidobenzene dianion bridged mixed-valence complex in which the IVCT and the bridging ligand LMCT states were effectively degenerate. A value of $K_c = 3.5 \times 10^5$ was inferred from electrochemical measurements.

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(56) For an electron-transfer coordinate Q with respect to which the localized (diabatic) potential energy minima occur at $Q = 0$ and Q_0, the three-state model leads to new PE minima displaced by $\pm Q_m = \alpha_{DA}^2 Q_0$, respectively, from the diabatic minma. For $\lambda_r = {}^1/_2 k Q_0^2$, E_{AL}(obsd) $\cong E_{AL}^\circ + 2\alpha_{AL}^2\lambda_r = E_{DL}^\circ - \lambda_r + 2\alpha_{AL}^2\lambda_r$. Substitution of $H_{AL} = H_{DL}$ and rearrangement leads to eq 7. Equation 8 is obtained by assuming complete mixing of the excited states.

$$H_{DA} \cong H_{DL}/[2(1 + \alpha_{DL}^2)]^{1/2} \qquad (10)$$

Other estimates of H_{DA} are possible. For example, for a two-state model the value can be based on the oscillator strength of the lowest energy CT transition, eq 11[23,52] and $r_{DA} = 10.5$ Å

$$H_{DA} = (0.0205/r_{DA})[\epsilon_{max}\Delta\nu_{1/2}(h\nu_{max})]^{1/2} \qquad (11)$$

(the metal−metal distance). This results in $H_{DA} \cong 505$ cm^{-1}. Values of H_{DA} based on eq 11 are often inappropriately small,[57−62] and this is the case for several of the complexes in Table 1.[15] The discrepancy in this system is expected to be unusually large due to the delocalization of electron density between the nominal M_tM_cCT and IVCT excited states (thus reducing r_{DA}).

In principle, an estimate of H_{DA} might be based K_c since the RT *ln* K_c is expected to increase with perturbational stabilization energy, $\epsilon_{DA} = H_{DA}^2/E_{DA}$.[8,23,63] In fact, estimates of ϵ_{DA} based on eq 6 correlate very well with RT *ln* K_c, Figure 6, for all the complexes mentioned in this paper except the Creutz−Taube ion. However, the slope of this correlation is more than 1 order of magnitude too small. For example, even the value of $H_{DA} \sim 1400$ cm^{-1} found from eq 4 leads to $2\epsilon_{DA} \sim 326$ cm^{-1}, a value which is much smaller than RT *ln* $K_c = 857$ cm^{-1} on the basis of experimental observations (Table 1). Of course, other factors also contribute to K_c. Important among these are the following: (1) a statistical factor ($K_c \rightarrow 4$ if no other factors contribute);[8] (2) changes in the densities of vibrational states and spin multiplicity that accompany the oxidation and reduction;[64] (3) changes in electrostatic repulsion[8,63] and solvation;[15] (4) changes in magnetic coupling.[16,49] In the systems compared in Figure 6 the changes in the densities of states and spin multiplicities (we have found that the magnetic coupling between terminal Ru(NH_3)$_5^{3+}$ moieties in the Ru(bpy)$_2$(CN)$_2$-bridged complex is very small[65]) can be assumed to be reasonably constant. Magnetic coupling to the central metal might play a role for the Cr(III) centered complexes,[16] but the consistency of the electrochemical data (a single CV wave is observed in the bisruthenates with $\Delta E_{1/2}(\mathrm{Ru(NH_3)_5}^{3+,2+}) < 30$ mV)[15−17,33,65,66] and IPCT absorptivity[1] in these complexes indicates that this is not a significant factor. The correlation in Figure 6 suggests that the major factors contributing to $K_c/4$ are functions of the fraction of charge delocalized, α_{DA}^2, in the ground state of the mixed-valence complex (note that $\epsilon_{DA} \cong \alpha_{DA}^2\lambda_r$). Since there are significant variations in the amount of charge delocalized through this series of compounds (from less than ~0.05% for the Cr(III)-centered complexes to ~2% for the Ru(py)$_4$(CN)$_2$-bridged complexes) differential solvation effects may be very important.[15] This contribution varies as $\partial\Delta G_{ds} \cong -\alpha_{DA}^2\lambda_s/3$[15] (for the systems considered here the solvent contribution to the reorganizational energy is $\lambda_s \cong \lambda_r$, and $Z = 3$ is the effective charge). This would lead to RT *ln*(K_c/4) $\cong 2.3\alpha_{DA}^2\lambda_r$ and $H_{DA} \cong 1.7 \times 10^3$ cm^{-1} for the Ru(py)$_4$(CN)$_2$-bridged mixed-valence complex, in good agreement with the estimate based on eq 4.

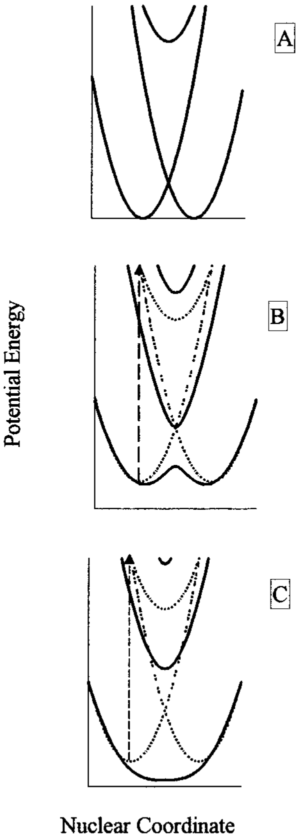

Figure 7. Qualitative potential energy surfaces (single nuclear coordinate) representing different limits of bridge mediated electronic coupling in mixed-valence systems: A, adiabatic limit of no mixing ($H_{DA} = 0$; $H_{DL} = 0$); B, limit of degenerate (diabatic) electron transfer and MLCT excited states with $|H_{DL}| > E_{AL}$; C, delocalized limit with $|H_{DL}| > \lambda_r/(2\sqrt{2})$. Dotted curves represent the diabatic states in (B) and (C). The vertical arrows designate the degeneracy of the diabatic states. Solid lines represent the mixed or diabatic states.

The Ru$_t$(II)/Ru$_t$(III) electronic coupling is clearly much stronger for the Os-, Fe-, and Ru-centered than for the M(MCL)-(CN)$_2^+$-bridged complexes (estimates as above imply more than 10-fold greater values of H_{DA} for these than for the MCL based systems; see Table 2). The physical property which distinguishes these complexes is that the M_tM_cCT excited state is lower in energy for the former and comparable to the energy expected for the electron-transfer excited state. The excited-state mixing mechanism proposed above readily accounts for the enhanced electronic coupling.

D. Concerning the Extent of Electronic Delocalization in the Ground States of the M(L)(CN)$_2$-Bridged Complexes. The mixing of MLCT and IVCT excited states, as discussed above, need not imply that the ground states are valence delocalized. This is evident from consideration of simple, representative potential energy surfaces as in Figure 7. For simplicity, all states are assumed to have similar force constants, and the diabatic IVCT and MLCT states are assumed to be degenerate at the coordinates of the ground-state PE minimum. For the coordinates of the electron-transfer transition state of such a symmetrical mixed-valence system, the diabatic electron-transfer states are degenerate (in the absence of mixing with the bridging ligand excited state), symmetric, and antisymmetric combinations of the localized electron-transfer states (referenced to their PE minima) with energy $E_{et}^{\ddagger} = \lambda_r/4$.[52,53] The MLCT excited state will have an energy of $E_{DL} - \lambda_r/4$ for the

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coordinates of the transition state. If, as in the simplest model of the present systems (with degenerate excited states), there is a single MLCT state, this state will be either symmetric or antisymmetric and mix with only one of the electron-transfer states. This mixing will lower the energy of that electron-transfer state by approximately $H_{DL}^2/(\lambda_r/2)$. More generally if $H_{DL}^2/[E_{DL} - \lambda_r/2] > \lambda_r/4$, one expects the mixed-valence system to be delocalized.

The mixed-valence system considered here should exhibit localized behavior if $|H_{DL}| < \sim \lambda_r/(2\sqrt{2})$.[67] For the Ru(py)$_4(CN)_2$- and M(bpy)$_2(CN)_2$-bridged systems, we estimate that $\lambda_r \cong 12 \times 10^3$ cm^{-1}so that $|H_{DL}|$ would have to be greater than about 4.2×10^3 cm^{-1} in order that the ground states would be delocalized. This does not appear to be the case (see the previous section). Of course, the observed properties of these systems which would be symptomatic of delocalization (bandwidth and K_c) contrast appropriately with those of the delocalized pyrazine-bridged mixed-valence analogue,[4] see Tables 1 and 2. In general, the IVCT and MLCT states will not be exactly degenerate at the coordinates of the ground-state PE minimum and their energy difference will be a factor in the observed properties.

The secular determinant for such a three-state system at the electron-transfer transition state can be written as in eq 12[1]

$$\begin{vmatrix} V_L^{\ddagger} - \epsilon & bQ_s & bQ_a \\ bQ_s & -\epsilon & 0 \\ bQ_a & 0 & -\epsilon \end{vmatrix} = 0 \qquad (12)$$

(assuming vibronic coupling only between the terminal and central metals). It is useful to consider the application of these arguments to the pyrazine- and 4,4′-bpy-bridged mixed-valence complexes. For Ru(NH$_3$)$_5$pz^{2+}, H_{DL} has been estimated to be 9.3×10^3 cm^{-1} [60] and (in the ground-state coordinates) $E_{DL} = 17.65 \times 10^3$ cm^{-1}.[22] For $\lambda_r \sim 11 \times 10^3$ cm^{-1}, $V_L^{\ddagger} \cong 12.15 \times 10^3$ cm^{-1} so that $E_-^{\ddagger} \sim -5.0 \times 10^3$ cm^{-1} consistent with a delocalized ground state. Similarly, the experimental parameters for [Ru(NH$_3$)$_5$]$_2$(4,4′bpy)$^{5+}$ [63] give $E_-^{\ddagger} \cong 1.5 \times 10^3$ cm^{-1}, consistent with a significantly localized ground state.

Conclusions

Experimental observations on the (py)$_4$Ru(CNRu(NH$_3$)$_5$)$_2$$^{5+}$ and the Os(bpy)$_2$(CNRu(NH$_3$)$_5$)$_2$$^{5+}$ complexes have served to illuminate several issues important in the study of mixed-valence complexes: (1) the conditions for observation of significant values of the electronic matrix element (H_{DA}) in electron-transfer systems (a selection rule issue); (2) the role of configurational mixing in reducing the Franck−Condon barrier to electron transfer; (3) the proper classification of low energy electron-transfer optical absorption bands.

Work presented elsewhere[1,12] has provided evidence that a vibronic selection rule can disallow a superexchange contribution to H_{DA} in M(MCL)(CN)$_2$$^+$-bridged mixed-valence complexes. The present work demonstrates that this selection rule is relaxed when the vertical IVCT (Ru(II)/Ru(III)) and bridging ligand MLCT (Ru(II)/M(III)) diabatic excited states are approximately degenerate. The configurational mixing of these diabatic excited states results in elimination of one of the vibronic matrix elements (H_{AL}) and a strongly allowed transition. Under these circumstances $H_{DA} \cong H_{DL}[2(1 + \alpha_{DL}^2)]^{1/2}$.

If this configurational mixing is sufficiently strong in the electron-transfer transition state of a chemically degenerate system, then the resulting ground-state stabilization energy, $\epsilon_{DL}^{\ddagger} = (H_{DL}^{\ddagger})^2/E_{DL}^{\ddagger}$, can be larger than the Franck−Condon barrier for electron transfer ($\lambda_r/4$). If this is the case, the mixed-valence system will have a valence-delocalized ground state. An approximate (first-order perturbation theory, three-state model) condition for valence localization is $H_{DL} < (\lambda_r/2\sqrt{2})[2h\nu(\text{MLCT})/\lambda_r - 1]^{1/2}$.[67] This condition is consistent with valence localization in the above complexes and the 4,4′-bpy bridged systems studied by Taube and co-workers. It is also consistent with valence delocalization in the Creutz−Taube ion.

Configurational mixing between electron-transfer and bridging ligand CT excited states tends to remove the distinction between MLCT and IVCT excited states. When the corresponding diabatic states approach degeneracy (with respect to vertical transitions from the ground state), this configurational mixing results in two states of mixed composition and neither can be rigorously assigned as "the" intervalence transition. The *trans*-Ru(py)$_4$(CN)$_2$- and *cis*-Os(bpy)$_2$(CN)$_2$-bridged mixed-valence complexes provide examples of this limit.

The *trans*-Ru(py)$_2$(CN)$_2$- and Os(bpy)(CN)$_2$-bridged mixed-valence complexes nicely demonstrate that the vibronic constraints on H_{DA} for Ru(NH$_3$)$_5$$^{2+}$/Ru(NH$_3$)$_5$$^{3+}$ complexes with dicyano-complex-bridging ligands can be relaxed in the limit that the electron-transfer and the mediating bridging ligand charge-transfer excited states are nearly degenerate. It would certainly be difficult to apply a simple "through bond" model to describe the electronic coupling in these systems.

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Supporting Information Available: Fits of eq 1 to the NIR MMCT absorbance changes and infrared spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(67) If the electron transfer and MLCT excited states are degenerate for the ground-state nuclear coordinates of a valence localized mixed-valence system, then their energy PE($Q = 0$) = λ_r. For the coordinates, $Q^{\ddagger}$, of the transition state the two electron transfer states (i.e., the symmetric and antisymmetric combinations of the two localized states) have diabatic energies $E_{et}^{\ddagger} = \lambda_r/4$ with respect to the localized (diabatic) ground state. For simplicity, assuming that all force constants are equal, the perturbing MLCT excited state will have an energy $E_L^{\ddagger} = \lambda_r - \lambda_r/4 = 3\lambda_r/4$ with respect to the localized ground state. Symmetry-allowed configurational mixing will decrease the energy of one of the electron transfer states by $H_{DL}^2/(E_L^{\ddagger} - E_{et}^{\ddagger}) = 2H_{DL}^2/\lambda_r$. Then the effective barrier to delocalization becomes $(\lambda_r/4 - 2H_{DL}^2/\lambda_r)$ and the stated limiting conditions follow. More generally, if the MLCT and electron-transfer ground states are not degenerate at $Q = 0$, then the condition for delocalization becomes $H_{DL}^2/(E_L - \lambda_r/2) \geq \lambda_r/4$ or, approximately, $H_{DL}^2/(h\nu(\text{MLCT}) - \lambda_r/2) \geq \lambda_r/4$.