Characteristics and Properties of Metal-to-Ligand Charge-Transfer Excited States in 2,3-Bis(2-pyridyl)pyrazine and 2,2'-Bipyridine Ruthenium Complexes. Perturbation-Theory-Based Correlations of Optical Absorption and Emission Parameters with Electrochemistry and Thermal Kinetics and Related Ab Initio Calculations

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The absorption, emission, and infrared spectra, metal (Ru) and ligand (PP) half-wave potentials, and ab initio calculations on the ligands (PP) are compared for several \([L_n Ru(PP)]^{2+}\) and \([\{L_n Ru\}dpp\{RuL'_n\}]^{4+}\) complexes, where Lₙ and L'ₙ = (bpy)₂ or (NH₄)₄ and PP = 2,2'-bipyridine (bpy), 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq), or 2,3-bis(2pyridyl)benzoquinoxaline (dbp). The energy of the metal-to-ligand charge-transfer (MLCT) absorption maximum \((h\nu_{max})\) varies in nearly direct proportion to the difference between Ru III/RuII and (PP)/(PP') half-wave potentials, \(\Delta E_{1/2}\), for the monometallic complexes but not for the bimetallic complexes. The MLCT spectra of \([\{NH_4\}_4Ru(dpp)]^{2+}\) exhibit three prominent visible–near-UV absorptions, compared to two for \([\{NH_4\}_4Ru(bpy)]^{2+}\), and are not easily reconciled with the MLCT spectra of \([\{NH_4\}_4Ru\}dpp\{RuL'_n\}]^{4+}\). The ab initio calculations indicate that the two lowest energy \(\pi^*\) orbitals are not much different in energy in the PP ligands (they correlate with the degenerate \(\pi^*\) orbitals of benzene) and that both contribute to the observed MLCT transitions. The LUMO energies calculated for the monometallic complexes correlate strongly with the observed \(h\nu_{max}\) (corrected for variations in metal contribution). The LUMO computed for dpp correlates with LUMO + 1 of pyrazine. This inversion of the order of the two lowest energy \(\pi^*\) orbitals is unique to dpp in this series of ligands. Configurational mixing of the ground and MLCT excited states is treated as a small perturbation of the overall energies of the metal complexes, resulting in a contribution \(\epsilon_s\) to the ground-state energy. The fraction of charge delocalized, \(\alpha_{DA}^2\), is expected to attenuate the reorganizational energy, \(\chi_{reorg}\), by a factor of approximately \((1 - 4\alpha_{DA}^2 + \alpha_{DA}^4)\), relative to the limit where there is no charge delocalization. This appears to be a substantial effect for these complexes (\(\alpha_{DA}^2 \approx 0.1\) for Ru II/bpy), and it leads to smaller reorganizational energies for emission than for absorption. Reorganizational energies are inferred from the bandwidths found in Gaussian analyses of the emission and/or absorption spectra. Exchange energies are estimated from the Stokes shifts combined with perturbation-theory-based relationship between the reorganizational energies for absorption and emission values. The results indicate that \(\epsilon_s\) is dominated by terms that contribute to electron delocalization between metal and PP ligand. This inference is supported by the large shifts in the N–H stretching frequency of coordinated NH₃ as the number of PP ligands is increased. The measured properties of the bpy and dpp ligands seem to be very similar, but electron delocalization appears to be slightly larger (10–40%) and the exchange energy contributions appear to be comparable (e.g., \(\sim 1.7 \times 10^3\) cm⁻¹ in [Ru(bpy)₂dpp]²⁺ compared to \(\sim 1.3 \times 10^3\) cm⁻¹ in the bpy analogue).

Introduction

There has been a great deal of interest in the properties of covalently linked, polymeric transition metal complexes. These compounds can often be assembled in supramolecular arrays that might be useful in applications such as the collection of light energy and its transformation into chemically useful forms, the conduction of charge in molecular level devices, and other unique chemical properties.¹–⁴
of the simplest linkers commonly used in assembling metals into such arrays is 2,3-bis(2-pyridyl)pyrazine (dpp).\(^5\)\(^{-18}\) This molecule can function as a bidentate ligand to two metals simultaneously, and the relatively low-energy LUMO of the pyrazine moiety is expected to facilitate electronic delocalization between the bridged metals.\(^19\)\(^{-22}\) Partly for these reasons, we began some systematic studies of dpp-bridged complexes several years ago.\(^23\) At that time we also thought that such polypyridyl types of bridging ligands might exhibit some of the features characteristic of the mixing of bridging ligand nuclear properties with donor–acceptor (D/A) electronic properties that have been found for cyanide-bridged donors and acceptors\(^24\)\(^{-30}\) and, if not similar, that their properties could provide an instructive contrast between different classes of strongly coupled transition metal donor–acceptor complexes. As our work has progressed, it has become evident that complexes with dpp ligands have some unexpected spectroscopic and chemical properties. Related features have been noted in earlier work. For example, several research groups have noted that the bidentate coordination of two metals by dpp results in some twisting of the pyrazine ring.\(^5\)\(^{11,13,15}\) It has also been observed that the electrochemical properties of the dpp-bridged complexes do not correlate with bond order in the same manner as those of related complexes,\(^9\) in order to fit the bond order correlation, bonds of the pyridine moieties had to be included for dpp but not for closely related ligands.

The difference in the electrochemical potential for oxidation of the donor (Ru\(^6\) in systems reported here) and the potential for reduction of a linked acceptor ligand (e.g., a polypyridyl ligand) commonly correlates strongly with the lowest energy MLCT absorption maximum as in eq 1.\(^{31\)\(^{-36}\)

\[
h_{\text{max}}(\text{MLCT}) = F(D/A) + \eta_{\text{DA}}
\]

where \(F\) is Faraday’s constant and the potentials are determined in the assembled complex.\(^{31,32}\) In the experimental correlations of monometallic complexes, the \(\eta_{\text{DA}}\) cross term has been commonly found to be small, \(\sim (0-2) \times 10^3\) cm\(^{-1}\), for poly(pyridine acceptors).\(^{31,33\)\(^{-35}\) In contrast, \(\eta_{\text{DA}}\) has been found to be \(\sim 5 \times 10^3\) cm\(^{-1}\) for some pyrazine-bridged bimetallic complexes.\(^{37}\) The general success of eq 1 has led to the proposal that \(h_{\text{max}}(\text{MLCT})\) can be represented as the sum of independent contributions of the donor, \(F(D)^n\), and the acceptor, \(F(A)^m\), with a small correction for cross terms, \(\Gamma_{\text{DA}}\), as in eq 2.\(^{31}\)

\[
h_{\text{max}}(\text{MLCT}) = F(D)^n + F(A)^m + \Gamma_{\text{DA}}
\]
relations among $\Gamma_{DA}$, $\eta_{DA}$, energy gaps, and the nuclear reorganizational parameters$^{31,38-40}$ in the weakly coupled limit to aid in the evaluation of the more complicated systems. The deviations from this limit can be expressed in terms of a perturbation theory parameter, $\alpha_{DA}$ (\(\alpha_{DA} = H_{DA}/E_{DA}\)), which can be interpreted as the fraction of electron density delocalized. For example, the absorption bandwidth in the weakly coupled, two-state limit is proportional to the square root of the electron-transfer reorganizational energy,$^{39,41}$ but in strongly coupled systems the bandwidth should decrease with $\alpha_{DA}^{-2}$ $^{21,39,41-44}$ as succinctly expressed in eq 3.$^{44}$

$$\lambda_{\text{reorg}} \approx \lambda_{\text{reorg}}^{\text{ca}} (1 - 4\alpha_{DA}^{-2})$$  (3)

where $\lambda_{\text{reorg}}^{\text{ca}}$ is the reorganizational energy defined for the limit of weak coupling.

We initially sought to gain insight into the origin of the complexities of the charge-transfer properties of dpp-containing complexes by means of a careful comparison to the “much better understood” bipyridine complexes.$^{45}$ Calculations reported by Lever and Gorelsky$^{46,47}$ indicated that there is very little electron delocalization in the bipyridine (bpy) complexes and that large electron exchange energies account for some properties commonly attributed to electron delocalization in these complexes.$^{48}$ Since electroabsorption measurements indicate similar extents of metal–ligand mixing in \([\text{Ru(NH}_3])_2\text{L}]^{2-}\) complexes with L = pyridine and pyrazine,$^{49}$ this raised the possibilities (a) that Coulomb and exchange terms may contribute differently to $\alpha_{DA}$ in dpp and bpy complexes and (b) that there is less electron delocalization in the dpp complexes than is generally supposed. The first possibility should lead to some differences in physical properties, and we have found that \([\text{Ru(NH}_3)_4\text{dpp}]^{2+}\) and some dpp-bridged complexes do have unexpected spectroscopic features. Unfortunately, not all the relevant properties of the bipyridine complexes seem to be as well understood as we had supposed;\(^{50,51}\) this is illustrated by recent estimates of the bipyridine complexes and (b) that there is less electron delocalization in \([\text{Ru(NH}_3)_4\text{bpy}]^{2+}\).

The combination of these experimental issues has led us to perform ab initio computations on dpp and some related ligands. On the basis of the computations and the experimental observations, we propose that some of the unusual spectroscopy and chemistry associated with the dpp ligand may be a consequence of a difference in the nature of the LUMO of dpp from that expected based on pyrazine.

### Experimental Section

**A. Materials.** The ligands (see Figure 1) dpp (2,3-bis(2-pyridyl)pyrazine) and dpb (2,3-bis(2-pyridyl)benzoquinoxaline) were synthesized according to literature procedures.$^{43,54}$ The dpp ligand (2,3-bis(2-pyridyl)pyrazine), \(\text{NH}_4\text{PF}_6\), \(\text{KPF}_6\), and Sephadex C-25 ion-exchange resin were purchased from Aldrich and used without further purification. All solvents used were reagent or spectroscopic grade. Tetraethylammonium hexafluorophosphate (TBAAH) was purchased from Aldrich and dried in a vacuum oven before use. \(\text{RuCl}_3\cdot3\text{H}_2\text{O}\) was purchased from Strem Chemicals or from Acros and used as received. \(\text{Ru(bpy)}_3\text{Cl}_2\cdot\text{H}_2\text{O}\) was purchased from Strem Chemicals and used without further purification.

Preparative solutions were deaerated by passing an argon gas stream through two chromous scrubbers (0.1 M \(\text{CrCl}_3\cdot6\text{H}_2\text{O}\) in 1 M \(\text{HCl}\) over \(\text{Zn}/\text{Hg}\)) and then through a \(\text{CaSO}_4\) column. Distilled water was deionized prior to distillation by passing through two

(48) Very recent DFT calculations by Gorelsky and Lever suggest that there is about 10% electron delocalization in the ground state of \([\text{Ru(NH}_3])_2\text{bpy}]^{2+}\). This calculation also seems to be consistent with the $\pi^*\text{ orbital sequence that we have inferred below. Lever, A. B. P.; Gorelsky, S. I. Private communication, October, 23, 2001.}$
(50) The properties of concern here deal with the amount of electron density delocalized, the absorption and emission bandwidths, the sequence of MLCT excited states, the exchange energy, etc. Our studies of \([\text{Ru(NH}_3])_2\text{bpy}]^{2+}\) and related complexes are briefly summarized in this report. A preliminary report has been submitted,\(^{31}\) and a full report is being prepared.
B. Synthesis of Compounds. The starting materials [Ru
\textsuperscript{II}(NH\textsubscript{3})\textsubscript{5}-Cl]Cl\textsubscript{2}
\textsuperscript{55} cis-[(NH\textsubscript{3})\textsubscript{5}Ru\textsubscript{II}(Cl)\textsubscript{2}Cl]\textsuperscript{4+}, and [Ru
\textsuperscript{II}(NH\textsubscript{3})\textsubscript{5}(O\textsubscript{2}SCF\textsubscript{3})\textsubscript{2}]O\textsubscript{2}-
SCF\textsubscript{3}]\textsuperscript{57} were synthesized according to literature procedures. The
following compounds were prepared by slightly modified literature
procedures (see pages S2 and S3\textsuperscript{58}):
(a) ([bpy]\textsubscript{2}Ru-dpp)[PF\textsubscript{6}]\textsubscript{2}\textsuperscript{12}
(b) ([bpy]\textsubscript{2}Ru-μ-η\textsubscript{1}-dpp[Ru(bpy)]\textsubscript{2}[PF\textsubscript{6}]\textsubscript{2}\textsuperscript{12}
(c) [Ru(NH\textsubscript{3})\textsubscript{4}O(H\textsubscript{2}O)]-(PF\textsubscript{6})\textsubscript{2}\textsuperscript{59}
(d) [Ru(NH\textsubscript{3})\textsubscript{4}(dpq)][PF\textsubscript{6}]\textsubscript{2}\textsuperscript{60}
(e) ([bpy]\textsubscript{2}Ru(dpq))[PF\textsubscript{6}]\textsubscript{2}\textsuperscript{12}
The skeletal structures of the ligands are shown in Figure 1.

\[[\text{NH}_3\text{H}_3\text{Ru(dpp)}]/\text{Ru(NH}_3\text{)}_4]\text{Cl}_2\cdot 0.25 g (0.9 mmol) sample of
\text{cis}-(\text{NH}_3\text{H}_3\text{Ru(dpp)}\text{Cl}) and a 3-fold molar excess of ligand dpp
(0.071 g, 0.3 mmol) were reacted in 20 mL of an argon deaerated
ethanol/water mixture in the presence of freshly made Zn/Hg.
The reaction was carried out in an argon atmosphere in the absence
of light. The yellow reaction mixture was warmed (50°C) and
constantly stirred for 3 h. The blue-violet reaction mixture was
filtered, and solid NH\textsubscript{4}PF\textsubscript{6} was added until the precipitation was
completed. The crude product was isolated after being chilled for
30 min. The crude product was recrystallized from water. Typical
yields were ~40%.

\[[\text{bpy}_2]\text{Ru(dpp)}/\text{Ru(NH}_3\text{)}_4]\text{Cl}_2\cdot 100 mg (0.11 mmol) sample of
\text{[(bpy)_2Ru(dpp)]/PF}_6\textsubscript{2} was dissolved in 6 mL of argon deaerated
distilled water. A 38 mg (0.137 mmol) sample of \text{cis}-(\text{NH}_3\text{H}_3\text{Ru}^\text{III},
Cl\textsubscript{2}Cl\textsubscript{2} was dissolved separately in 8 mL of argon degassed
distilled water and reduced with Zn/Hg for about 1/2 h under argon,
wrapped with aluminum foil for protection from light. After this
time the reduced ruthenium solution was added to the deaerated
([bpy]_2Ru-
\text{Cl}_2)\text{Cl}_2 solution. The resulting solution was shielded from light
and allowed to react under argon at room temperature for 12 h.
The initial brown-orange solution changed to blue-purple during this
the crude product was isolated as the PF\textsubscript{6}\textsuperscript{- salt by adding
solid NH\textsubscript{4}PF\textsubscript{6}. The product was purified by ion-exchange chroma-
tography using Sephadex SPC-25 resin and eluted with increasing
concentrations of acids. The desired product was eluted with 0.5
M HCl as a blue-purple solution. The solvent was removed by rotary
evaporation, and the product was isolated as a chloride salt.
Precipitation as the PF\textsubscript{6}\textsuperscript{- salt gave a very low yield. The typical
yield of the chloride salt was about 30%.

\[[\text{NH}_3\text{H}_3\text{Ru(dpp)}]/\text{PF}_6\textsubscript{2}\cdot In a typical experiment, a 2-fold excess
of dpq ligand (115 mg, 0.4 mmol) and \text{[(NH}_3\text{H}_3\text{Ru}^\text{III}-
\text{Cl}_2][PF\textsubscript{6}]\textsubscript{2} were dissolved separately in 8 mL of argon
degassed distilled water. The solution was sonicated for a few
seconds between polishing cycles. After 10 min with stirring, the
solution was filtered, and the solid NH\textsubscript{4}PF\textsubscript{6} was added until the
precipitation was completed. The crude product was isolated after
being chilled for 30 min. The crude product was recrystallized from
water. Typical yields were ~40%.

Chem. 1986, 25, 4233.}
\text{(56) Salaymeth, F.; Berhause, S.; Yusof, R.; de la Rosa, R.; Fung, E. Y.;
Matamoros, R.; Law, K. W.; Zhen, Q.; Kober, E. M.; Curtis, J. C.
Inorg. Chem. 1993, 32, 3895.}
\text{(57) Dixon, N. E.; Lawrence, A.; Lay, P. A.; Sargeson, A. M.; Taube, H.
Inorg. Synth. 1986, 24, 243.}
\text{(58) Supporting material, see paragraph at end of paper.}
\text{(59) Callahan, R. W.; Brown, G. M.; Meyer, T. J. Inorg. Chem. 1975, 74,
1443.}
\text{(60) Gould, I. R.; Noukakis, D.; Luis, G.-J.; Young, R. H.; Goodman, J.
\text{(61) Galactic Industries Corporation, Salem, NH.}
\text{(62) Song, X.; Lei, Y.; VanWallendal, S. V.; Perkovic, M.; Jackman, D.
Endicott, J. F.; Rilema, D. P. J. Phys. Chem. 1993, 97, 3225.}
in the MLCT excitation energies can be obtained from Koopman’s theorem, i.e., from the orbital energies of the free ligands in the conformations indicated. Even though accurate excitation energies cannot be obtained from the orbital energies alone, changes in the energies of the unoccupied orbitals of the ligands should parallel trends in the MLCT excitation energies that are due to differences in the ligands. To obtain approximate values of the metal-independent variations of MLCT energies for systematic comparison to the calculated ligand orbital energies, we have subtracted the $M^{II}/M^{III}$ half-wave potentials from the observed absorption band energies.

**Results**

**Infrared Spectroscopy.** Infrared spectra were obtained as KBr pellets using a Nicolet 760SX FT-IR and a Nicolet 680 DSP workstation. Spectral grade KBr used for all pellets was obtained from Aldrich and used without further purification. The KBr and all samples were dried in a vacuum oven at $80^\circ C$ for several hours.

**G. Molecular Orbital Calculations.** Computations were carried out with the Gaussian series of electronic structure programs. Geometries were fully optimized at the HF/6-31G level of theory. This consists of the Los Alamos pseudopotentials on heavy atoms and the D95V all-electron basis on first- and second-period atoms. To simulate the change in conformation of the ligands on complexation, the dpp, dpq, and dpb ligand geometries were also optimized with one and two Zn$^{2+}$ bound. An estimate of the trends

<table>
<thead>
<tr>
<th>complex [(D)(A)]</th>
<th>$\lambda_{max}$ (nm) ($\epsilon_{max}$, 10$^3$, M$^{-1}$ cm$^{-1}$)</th>
<th>$\Delta\nu_{12}$/10$^3$, cm$^{-1}$</th>
<th>solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(bpy)(Ru)(bpy)]$^{2+}$</td>
<td>452 ± 1 (14.23)$^b$</td>
<td>455 [1.9]$^c$</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>[(bpy)(en)(Ru)(bpy)]$^{2+}$</td>
<td>451 ± 1$^c$</td>
<td>496$^d$</td>
<td>1:1 DMSO/H$_2$O</td>
</tr>
<tr>
<td>[(bpy)(NH$_3$)(Ru)(bpy)]$^{2+}$</td>
<td>490 (9.5)$^d$</td>
<td>345 (8.8)$^d$</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>[(en)(Ru)(bpy)]$^{2+}$</td>
<td>515 (3.96)$^d$</td>
<td>365 (7.85)$^d$</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>[(NH$_3$)$_2$(Ru)(bpy)]$^{2+}$</td>
<td>522 (4.4)$^d$</td>
<td>366 (7.1)$^d$</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>[(bpy)(Ru)(dpp)]$^{2+}$</td>
<td>478 (10)</td>
<td>426 (12)</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>[(NH$_3$)$_2$(Ru)(dpp)]$^{2+}$</td>
<td>463 (sh, 11.5)$^d$</td>
<td>439 (12)$^d$</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>[(bpy)(Ru)(dpq)]$^{2+}$</td>
<td>546 (4.5)</td>
<td>456 ± 2 (4.8)</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>[(bpy)(Ru)(dpb)]$^{2+}$</td>
<td>530 (3.5)</td>
<td>423 (3.1)</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>[(NH$_3$)$_2$(Ru)(dpb)]$^{2+}$</td>
<td>517</td>
<td>426</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>[(bpy)(Ru)(dpb)]$^{2+}$</td>
<td>591 (2.8)</td>
<td>438 (1.3)</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>[(NH$_3$)$_2$(Ru)(dpb)]$^{2+}$</td>
<td>619 (4.9)</td>
<td>427 (3.1)</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>[(bpy)(Ru)(dpp)]$^{2+}$</td>
<td>466</td>
<td>430</td>
<td>CH$_3$CN</td>
</tr>
</tbody>
</table>

Table 2. MLCT Spectra of Bimetallic Complexes

| complex [(D, D′)](A) | \( \lambda_{\text{max}}(\text{nm}) \) | \( (\epsilon_{\text{max}} \cdot M^{-1} \cdot \text{cm}^{-1})^{1/2} \) | \( |\Delta\nu_{1/2}, \text{cm}^{-1}|^{1/2} \) | solvent |
|----------------------|----------------|------------------|------------------|--------|
| [(bpy)_2Ru,Ru(bpy)_2(dpdp)]^{2+} | 520 (21) | 417 ± 2 (17) | 330 (26) | H₂O |
| [(NH₃)₄Ru,Ru(NH₃)₄(bpy)]^{2+} | 536 (7) | 429 (5) | 318 (25) | H₂O |
| [(NH₃)₂Ru,Ru(NH₃)₂(bpy)]^{2+} | 556 (19) | 368 (9.8) | 318 (25) | H₂O |
| [(bpy)_2Ru,Ru(bpy)_2(dpdp)]^{2+} | 606 (12.8) | 530, 426 | 424 (8), 393 (10), 350 (17) | H₂O |
| [(NH₃)₂Ru,Ru(NH₃)₂(dpdp)]^{2+} | 640 (4) | 531 (9) | 424 (8), 393 (10), 350 (17) | H₂O |
| [(NH₃)₂Ru,Ru(NH₃)₂(dpdp)]^{2+} | 660 (14) | 531 (9) | 424 (8), 393 (10), 350 (17) | H₂O |
| [(NH₃)₄Ru,Ru(NH₃)₄(dpdp)]^{2+} | 680 (5) | 578 (5) | 318 (25) | CH₃CN |
| [(bpy)_2Ru,Ru(bpy)_2(dpdp)]^{2+} | 646 | 410 | 368 | H₂O |

\(^{a}\) 1 cm path; 298 K. Uncertainty in \( \lambda_{\text{max}} \) is about ±1 nm except as noted. Uncertainties in extinction coefficient and bandwidth are about ±10%. Estimates are based on band envelopes except as indicated. \(^{b}\) Estimate based on Gaussian deconvolution (this work). \(^{c}\) Average for this work and refs 8 and 12. \(^{d}\) This work and ref 7.

Table 3. Half-Wave Potentials of the Complexes

<table>
<thead>
<tr>
<th>complex <a href="A">(D)</a></th>
<th>( E_{1/2}, \text{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(bpy)_2Ru(dpdp)]^{2+}</td>
<td>1.26 ± 0.01 (^{b})</td>
</tr>
<tr>
<td>[(NH₃)₄Ru(dpdp)]^{2+}</td>
<td>0.56 (^{d})</td>
</tr>
<tr>
<td>[(bpy)_2Ru(dpdp)]^{2+}</td>
<td>0.76 (^{d})</td>
</tr>
<tr>
<td>[(NH₃)₂Ru(dpdp)]^{2+}</td>
<td>0.88 (^{d})</td>
</tr>
<tr>
<td>[(bpy)_2Ru(dpdp)]^{2+}</td>
<td>1.28 (^{d})</td>
</tr>
<tr>
<td>[(NH₃)₂Ru(dpdp)]^{2+}</td>
<td>1.45 (^{d})</td>
</tr>
<tr>
<td>[(bpy)_2Ru(dpdp)]^{2+}</td>
<td>1.56, 1.38 (±0.05) (^{f})</td>
</tr>
<tr>
<td>[(NH₃)₂Ru(dpdp)]^{2+}</td>
<td>0.76 (^{d})</td>
</tr>
<tr>
<td>[(bpy)_2Ru(dpdp)]^{2+}</td>
<td>1.38, 0.89 (^{f})</td>
</tr>
<tr>
<td>[(NH₃)₂Ru(dpdp)]^{2+}</td>
<td>1.44 (^{d})</td>
</tr>
</tbody>
</table>

\(^{a}\) Sweep rate, 100–200 mV/s; electrolyte, 0.1 M TBAE or TBAH; Ag/AgCl reference electrode; ambient conditions. \(^{b}\) Average of values is listed in the following works. Juri, A.; Barigelletti, F.; Campagna, S.; Balzani, V.; Belser, P.; von Zewerovsky, A. Coord. Chem. Rev. 1988, 84, 85. \(^{c}\) Reference 82. \(^{d}\) This work.

Table 4. Comparison of Computed Orbital Energies (LUMO and LUMO + 1) and MLCT Energy Maxima (Bands 1 and 2) of [(NH₃)₄Ru(L)]^{2+}

<table>
<thead>
<tr>
<th>ligand (L)</th>
<th>orbital</th>
<th>parent ring</th>
<th>free ligand</th>
<th>constrained with one metal</th>
<th>constrained with two metals</th>
<th>( h\nu_{\text{max}} )^{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>LUMO</td>
<td>15.39</td>
<td>15.5</td>
<td>19.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bpy</td>
<td>LUMO + 1</td>
<td>21.62</td>
<td>21.7</td>
<td>22.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dpp</td>
<td>LUMO</td>
<td>17.6 (A)</td>
<td>17.9 (A)</td>
<td>12.1 (β)</td>
<td>10.3 (β)</td>
<td>18.48</td>
</tr>
<tr>
<td>dpp</td>
<td>LUMO + 1</td>
<td>22.0 (β)</td>
<td>19.1 (β)</td>
<td>16.7 (A)</td>
<td>16.0 (A)</td>
<td>21.83</td>
</tr>
<tr>
<td>dpq</td>
<td>LUMO</td>
<td>11.6 (α)</td>
<td>11.9 (A)</td>
<td>10.5 (A)</td>
<td>9.8 (A)</td>
<td>16.9</td>
</tr>
<tr>
<td>dpq</td>
<td>LUMO + 1</td>
<td>21.1 (β)</td>
<td>16.5 (β)</td>
<td>13.4 (β)</td>
<td>11.5 (β)</td>
<td>22.8</td>
</tr>
<tr>
<td>dpq</td>
<td>LUMO</td>
<td>7.2 (α)</td>
<td>7.8 (A)</td>
<td>6.2 (α)</td>
<td>5.3 (A)</td>
<td>16.5</td>
</tr>
<tr>
<td>dpq</td>
<td>LUMO + 1</td>
<td>20.3 (β)</td>
<td>16.8 (β)</td>
<td>14.0 (β)</td>
<td>11.9 (β)</td>
<td>17.3</td>
</tr>
</tbody>
</table>

\(^{e}\) All energies are in units of cm⁻¹/10¹. Computations were performed at the HF/LANL2DZ level of theory. \(^{f}\) From absorption envelope in acetonitrile.

addition, multiple intensity contributions on the high-energy side of band 1 and the low-energy side of band 2, compensation for them requires a minimum of two relatively minor Gaussian components, as shown in the Gaussian fits at the top and middle of Figure 2. The transition energies, bandwidths, and intensities of the major and minor components were essentially the same in water and in acetonitrile. These minor fitting components a and b cannot be purely vibronic; the energy differences and intensities required are too large for a simple vibronic progression. Resonance Raman data for this complex\(^{64}\) can be used to construct an absorption profile for the lowest energy MLCT band including the apparent vibronic contributions, shown at the bottom of Figure 2, and this profile requires additional electronic components (such as component a) in order to match the observed spectrum. The report of Streiff et al.\(^{65}\) that components of band 1 are resolved in a 77 K methanol/ethanol glass is further support for this analysis. We tentatively assign the most intense component to the \( d\tau_m \) orbital that has the largest overlap with the bpy LUMO.
ab initio calculations indicate that the LUMO and LUMO + 1 of coordinated bpy both have b1 (C2v) symmetry.50,66–70 Both \( \pi^* \) orbitals would mix with the \( d\pi_m(b_1) \) orbital, and both transitions would be \( \pi \)-allowed.

We have resolved three distinct principle MLCT bands for \([\text{Ru(NH}_3)_4\text{dpp}]^{2+}\). The resulting absorption envelope was different in acetonitrile than in water (Figure 3). The Grams 32 based spectral deconvolution indicates that this difference is attributable to a smaller bandwidth of MLCT 1 in acetonitrile; the ratio of integrated band intensities (MLCT 1/MLCT 2) is nearly the same (0.73 in acetonitrile and 0.71 in water). The energies and integrated intensities of the principle MLCT bands do not appear to be significantly different in the two solvents. We have treated the component structure of this complex as similar to that of \([\text{Ru(NH}_3)_4\text{bpy}]^{2+}\) but with one additional, major MLCT band (Figure 3).

The three intense MLCT transitions observed for the \([\text{Ru(NH}_3)_4\text{dpp}]^{2+}\) complex in the visible–near-UV region, where only two are observed for \([\text{Ru(NH}_3)_4\text{bpy}]^{2+}\), suggest that there are more low-energy \( \pi^* \) acceptor orbitals in dpp than in bpy. If the energy differences were simply transferable, then the second Ru\(^{II}\)/dpp MLCT transition in \([\text{Ru(bpy)2}(\text{dpp})]^2+\) would occur at 24.6 \( \times 10^3 \) cm\(^{-1}\), very similar to the energy expected for the Ru\(^{II}\)/bpy transition. In acetonitrile the lowest energy MLCT absorption maxima of the mononuclear complexes, \([\text{Ru(NH}_3)_3\text{Li}]^{2+}\) and \([\text{Ru(bpy)}_2\text{Li}]^{2+}\), correlate well with changes in the constituent half-wave potentials (Figure 4; slope = 0.9 ± 0.2, intercept = (3 ± 3) \( \times 10^3 \) cm\(^{-1}\), \( r^2 = 0.9 \); omitting the point for \([\text{Ru(bpy)}_2\text{dpb}]^{2+}\)). The bimetallic complexes that contain Ru\(^{II}\)-(NH\(_3\))\(_4\) deviate dramatically from this correlation.

The minimized structures calculated for the free ligands all have the pendant pyridines arranged with nitrogen atoms adjacent, and their rings are twisted by about 130° from the ideal orientation for coordination (see Figure 5). When the ligands are constrained to adopt a structure appropriate for
bidentate coordination (modeled in the calculations by binding to Zn²⁺), the pyridine rings are splayed and the pyrazine moiety is twisted (see Figure 1). The changes shown in Figure 5 are also representative of dpq and dpb. In the unconstrained geometries, the LUMO’s of dpp, dpq, and dpb correlate with the LUMO’s of pyrazine, quinoxaline, and benzoquinoxaline (Figures 6 and 7) and the nodal pattern is designated by \( \alpha \) in Table 4. Likewise, the LUMO +1's correlate and their nodal pattern is designated by \( \beta \) in the Table. As can be seen from Table 4, the conformations of the 2-pyridyl substituents have very little effect on the energy of the LUMO, but they can lower the LUMO +1 energy significantly. In conformations suitable for bidentate coordination, the pyridyls are more nearly coplanar with the rest of the ring system and can interact more strongly. The

Figure 4. Correlation of band I absorption maxima with the difference in the half-wave potentials for Ru²⁺ oxidation and ligand (L) reduction (\( F \) is Faraday’s constant) in acetonitrile: solid squares for \([\text{Ru(bpy)}_2(L)]^{2+}\) complexes, solid circles for \([\text{Ru(NH}_3)_4(L)]^{2+}\) complexes (L as indicated on the figure); open circles for bimetallic complexes (BB, \([\text{Ru(bpy)}_2\text{Ru(NH}_3)_4(dpp)]^{4+}\); AB, \([\text{Ru(bpy)}_2\text{Ru(NH}_3)_4(dpp)]^{4+}\); AA, \([\text{Ru(NH}_3)_4(dpp)]^{4+}\). The ligand reduction potential used for AA was interpolated from the values observed for monometallic complexes \([\text{Ru(bpy)}_2(dpp)]^{4+}\) and \([\text{Ru(bpy)}_2\text{Ru(NH}_3)_4(dpp)]^{4+}\). The solid line is drawn with a slope of 1.0 and a zero intercept.

(66) The details of this assignment will be discussed elsewhere. In brief, there are two principle issues: (a) the \( \pi^* \) orbital sequence corresponding to the observed dominant MLCT bands and (b) the assignment of the minor electronic components. In regard to issue a: (1) the lowest energy \( \pi^* \) orbitals of pyridine do not differ greatly in energy and correlate with the degenerate orbitals of the LUMO of benzene (we label the \( \pi^* \) orbital with a nodal plane passing through two atoms as \( \beta \), the other as \( \alpha \)); the ab initio calculations indicate that the two lowest energy \( \pi^* \) orbitals of planar bpy are of the form \( (\alpha + \alpha) \) and \( (\beta + \beta) \). This contrasts with the more common assignment of \( (\alpha + \alpha) \) and \( (\alpha - \alpha) \), respectively, based either on the simplifying neglect of the higher energy pyridine orbital²⁶⁷,⁷⁸ or on semiempirical MO calculations.⁴⁵,⁶⁴ Other sequences have also been proposed.⁶⁹ In regard to issue b: In a simple orbital model of the complex, one of the d\( \tau \) orbitals (labeled \( d_{\tau \alpha} \); note that the \( C_2 \) symmetry axis bisects the Cartesian angles of the metal complex, and symmetry adaption of the usual Cartesian \( d_{\tau} \) orbital set is required) mixes with the bpy LUMO, resulting in electron delocalization and a decrease in the energy of \( d_{\tau \alpha} \) (this is illustrated in Figure S4 of Supporting Information). The electron density delocalized from \( d_{\tau \alpha} \) to the bpy LUMO in the ground state could increase the electron-electron repulsions for transitions involving the other d\( \tau \) orbitals, leading to an energy higher than expected on the basis of only orbital energy considerations. There are, of course, lower energy, very weak absorption contributions that probably are the convolution of hot band and triplet contributions, and there may be MLCT bands at energies outside the spectral window presented in Figure 2.


Figure 5. Minimized stereochemistries of dpp: top, free ligand; middle, constrained to coordinate one metal; bottom, constrained to bridge two metals. The Zn atoms have been highlighted in dark-gray.
interaction is greater for LUMO + 1, and its energy is lowered more. In dpp, the LUMO and LUMO + 1 are close in energy, and the effect of twisting one or both pyridyls into bidentate conformations is to push the energy of the original LUMO + 1 below that of the original LUMO, inverting their order. In dpq and dbp, the LUMO and LUMO + 1 separation (in the pyrazine moiety) is larger and the order is not inverted, despite the strong interaction between the pyridyls and the LUMO + 1’s.

The calculated orbital energies of these ligands changed dramatically when Zn\(^{2+}\) was bound. This was most pronounced for the LUMO with the maximum orbital coefficients on the pyrazine nitrogens (e.g., the LUMO of pyrazine) and resulted in a change of the sequence of LUMOs in the dpp ligand. This is clearly an electrostatic effect of the vacuum calculation with a bare Zn\(^{2+}\) ion, and its relevance to the spectra of coordination complexes in the condensed phase is not clear. In contrast, the MLCT energies correlate well with the LUMO energies calculated with the ligands configured for coordination but without the dipositive metal (Figure 8).

Emission band energies and N–H stretching frequencies are summarized in Table 5. The ambient (DMSO/H\(_2\)O) emission spectra of [Ru(NH\(_3\))\(_2\)(bpy)\(_2\)]\(^{2+}\) and [Ru(bpy)\(_3\)]\(^{2+}\) were fit to three Gaussian components (Figure S5\(^{58}\)). Emission bandwidths were smaller, and the vibronic structure was better resolved in glasses at 77 K than in ambient solutions, as illustrated for [Ru(bpy)\(_2\)dbp]\(^{2+}\) in Figure 9.

The N–H stretching regions of the infrared for the PF\(_6^–\) salts of the ammine complexes were complicated by the O–H stretching frequencies of water. Extensive drying and careful handling of the samples reduced the O–H contribution. The N–H bands of the tetraammines were broad with little indication of structure and were very similar in energy; the band maxima (selected by the instrument program) varied over about a 40 cm\(^{-1}\) range depending on sample preparation. The [Ru(NH\(_3\))\(_2\)(bpy)\(_2\)]\(^{2+}\) complex exhibited two relatively sharp bands of very different intensity; both bands were significantly higher in frequency than the N–H stretches of the tetraammines (about 30 and 100 cm\(^{-1}\)).

Discussion

In the course of this study we have found a number of features of the dipyridylpyrazine class of ligands that have been a challenge to understand, even without the conceptual problems that are intrinsic to linked mixed-valence systems. The synthesis of complexes with a variety of second metals has been difficult, probably as a consequence of the
accompanied by stereochemical distortions. Three visible near-UV MLCT transitions of roughly comparable intensity are observed in [(NH₃)₄Ru²⁺] and [(NH₃)₆Ru²⁺]²⁺, but only two are observed in this energy region for [(NH₃)₄Ru²⁺] and [(NH₃)₆Ru²⁺]²⁺. The lowest energy transition is about 4 times as intense in the dimer as in the monomer. In a comparison of the lowest energy MLCT states of the donor and the acceptor, respectively, in the limit that coupling goes to zero, but all other conditions are the same.

A. Spectroscopic, Kinetic, and Electrochemical Correlations in Simple D/A Systems. A.1. General Features and Expectations. Donor—acceptor complexes typically give rise to an optical absorption whose energy can be related to ionization energies and electron affinities or to electrochemical potentials. When there is strong electronic coupling between the donor and the acceptor, manifested by an intense charge-transfer absorption band, this can result in configurational mixing which perturbation theory analysis alters the properties of both the donor and the acceptor. In a simple perturbation theory analysis, the ground state is stabilized by an amount $\Delta E = [\langle H_{DA}\rangle^2/(1 + \alpha_{DA}^2)]/E_{DA}$, where $H_{DA} = \langle \psi_e|H|\psi_o\rangle$ is the electronic coupling matrix element, $\langle \psi_e|H|\psi_e\rangle$ and $\langle \psi_o|H|\psi_o\rangle$ are the unmixed excited and ground-state wave functions (in our treatment they represent the isolated donor and the isolated acceptor in the same medium), and $H$ is a Hamiltonian operator; the Franck–Condon (FC) excited state is destabilized by an equal amount. This mixing alters the properties of the donor-metal and acceptor-ligand in the complex relative to those of the isolated donor and acceptor. The magnitude of this change in properties depends on both the donor and the acceptor and is not easily factored into individual contributions of the components. In the simplest perturbation theory limit, eqs 4a and 4b

$$\psi_G = \frac{\psi_D^0 + \alpha_{DA}\psi_A^0}{1 + \alpha_{DA}^2}$$

$$\psi_E = \frac{\psi_A^0 - \alpha_{AD}\psi_D^0}{1 + \alpha_{AD}^2}$$

where $\alpha_{DA} = H_{DA}E_{DA}$, molecular properties can be interpreted in terms of the fraction of charge delocalized, $\alpha_{DA}^2/(1 + \alpha_{DA}^2)$, between the donor and acceptor (for simplicity, we omit the normalization factors in the remaining discussion; all $\alpha_{DA}$ and $H_{DA}$ parameters below are understood to be normalized). The mixing could alter either the Coulomb or the exchange integral terms.

Table 5. Ambient Emission, N–H Stretching Frequencies, and Derived Parameters of Am(m)ine—Polypyridine—Ruthenium(II) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$h\nu_{max}$(cm⁻¹)</th>
<th>$\Delta \nu/\nu$</th>
<th>$\chi_{exc}^{(D0)}$</th>
<th>$\Delta h\nu$</th>
<th>$f$</th>
<th>$E_{DA}^{(0f)}$</th>
<th>$\lambda_f$</th>
<th>$\alpha_{DA}^{2b}$</th>
<th>$E_{ST}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(NH₃)₄Ru²⁺]Cl₃</td>
<td>3307</td>
<td></td>
<td></td>
<td>13.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(NH₃)₄Ru²⁺]Cl₂</td>
<td>3315, 3210</td>
<td></td>
<td></td>
<td>13.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(NH₃)₆Ru²⁺]PF₆²⁺</td>
<td>3185</td>
<td></td>
<td></td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(NH₃)₆Ru²⁺]PF₄Cl₂</td>
<td>3360 ± 20</td>
<td>11.2</td>
<td>0.6 ± 0.2</td>
<td>16.9</td>
<td>2.1</td>
<td>0.09</td>
<td>(15.1)</td>
<td>(1.4)</td>
<td>3.8</td>
</tr>
<tr>
<td>[(NH₃)₆Ru²⁺]PF₄Cl₂</td>
<td>3250 ± 20</td>
<td></td>
<td></td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.2 ± 0.5</td>
</tr>
<tr>
<td>[(NH₃)₆Ru²⁺]PF₆Cl₂</td>
<td>3557, 3258</td>
<td>9.1</td>
<td>0.2 ± 0.1b</td>
<td>(15.1)</td>
<td>3.8</td>
<td>0.09</td>
<td>(1.4)</td>
<td></td>
<td>3.2 ± 0.5</td>
</tr>
<tr>
<td>[(NH₃)₆Ru²⁺]PF₆Cl₂</td>
<td>3185</td>
<td>6.5</td>
<td></td>
<td>(15.1)</td>
<td>3.8</td>
<td>0.09</td>
<td>(1.4)</td>
<td></td>
<td>3.2 ± 0.5</td>
</tr>
<tr>
<td>[(NH₃)₆Ru²⁺]PF₆Cl₂</td>
<td>3240</td>
<td>5.6</td>
<td></td>
<td>(18.0)</td>
<td>0.9</td>
<td>0.07</td>
<td>(1.8)</td>
<td></td>
<td>3.1 ± 0.8</td>
</tr>
<tr>
<td>[(Ru(bpy)₂dpp)]PF₆³⁻</td>
<td>16.2 [2.0]</td>
<td>6.8</td>
<td>5.6</td>
<td>(18.0)</td>
<td>3.9</td>
<td>0.07</td>
<td>(1.8)</td>
<td></td>
<td>3.1 ± 0.8</td>
</tr>
<tr>
<td>[(Ru(bpy)₂dpp)]PF₆³⁻</td>
<td>3250 ± 20</td>
<td>6.6</td>
<td></td>
<td>(14.0)</td>
<td>3.9</td>
<td>0.07</td>
<td>(1.8)</td>
<td></td>
<td>3.1 ± 0.8</td>
</tr>
<tr>
<td>[(Ru(bpy)₂dpp)]PF₆³⁻</td>
<td>3241</td>
<td>6.6</td>
<td></td>
<td>(14.0)</td>
<td>3.9</td>
<td>0.07</td>
<td>(1.8)</td>
<td></td>
<td>3.1 ± 0.8</td>
</tr>
<tr>
<td>[(Ru(bpy)₂dpp)]PF₆³⁻</td>
<td>14.5 [1.8]</td>
<td>~6.8</td>
<td></td>
<td>(14.0)</td>
<td>3.9</td>
<td>0.07</td>
<td>(1.8)</td>
<td></td>
<td>3.1 ± 0.8</td>
</tr>
</tbody>
</table>

energies or vibrational frequencies are sensitive to the energy difference of nuclear and electronic relaxation. Terms about D/A mixing. Values of reorganizational parameters are used to characterize charge-transfer processes, and variations in these parameters are expected to result in variations in molecular bond lengths and angles, in solvation energy, and in certain vibrational frequencies. The correlated variations in the nuclear reorganization and electrochemical parameters are used to characterize charge-transfer processes, and variations in these experimental parameters are often used to extract information about D/A mixing. Values of reorganizational energies or vibrational frequencies are sensitive to the electronic charge distribution, while the singlet–triplet energy difference ($E_{ST}$) is mostly dependent on exchange terms ($E_{ST} \approx 2K_{exch}$; there should also be small contributions of nuclear and electronic relaxation).

Figure 9. Emission of [Ru(bpy)$_2$dppe]$_2^{2+}$ in DMSO/H$_2$O; top, ambient solution; bottom, 77 K glass. For the Gaussian components in ambient solution (energies in cm$^{-1}$), $h\nu_{max}$ [$\Delta v_{1/2}$] values are the following: 14 200 [1843]; 13 000 [1505]; 12 100 [1219]. For the major Gaussian components in 77 K glass (energies in cm$^{-1}$), $h\nu_{max}$ [$\Delta v_{1/2}$] values are the following: 15 700 [1157]; 14 300 [1404]; 13 000 [1222]. The scaled experimental spectrum is a heavy dark line, and the fitted spectrum (sum of the Gaussian components) is the superimposed white line.

Variations in the charge distribution within a molecule are expected to result in variations in molecular bond lengths and angles, in solvation energy, and in certain vibrational frequencies. The correlated variations in the nuclear reorganization and electrochemical parameters are used to characterize charge-transfer processes, and variations in these experimental parameters are often used to extract information about D/A mixing. Values of reorganizational energies or vibrational frequencies are sensitive to the electronic charge distribution, while the singlet–triplet energy difference ($E_{ST}$) is mostly dependent on exchange terms ($E_{ST} \approx 2K_{exch}$; there should also be small contributions of nuclear and electronic relaxation).

A.2. Characterization of MLCT Excited States. The absorption of light to form the Franck–Condon excited state leaves the nuclei fixed, and this excited state will be vibrationally excited. In the limit that a high-frequency mode ($h\nu > 4k_BT$) is excited and that there is a continuum of low-frequency modes ($h\nu < 4k_BT$ usually associated with the solvent), the absorptivity at a frequency $\nu_{abs}$ for the process in eq 5,

$$D - A + h\nu \rightarrow D^\cdash - A^-$$

(5)

can be expressed as in eq 6.

$$\epsilon(\nu_{abs}) = \frac{8N_A \tau^3}{3000h^2 c \nu_{abs}} \ln 10 \nu_{abs}^2 (\Delta \mu_{DA})^2 (FC)$$

(6)

$$FC = \sum_j F_j \exp \left[ -\frac{(E_{DA}^{00} - \hbar \nu_{abs} + j\hbar \nu + \lambda_v)^2}{4\lambda_h k_B T} \right]$$

$$F_j = S^{1/2} \exp(-S) \frac{\hbar \nu}{j!(4\pi \lambda_h k_B T)^{1/2}}$$

$$S = \frac{\lambda_h}{\hbar \nu}$$

where $E_{DA}^{00}$ is the energy difference between the zeroth vibrational levels of the ground and excited state, $\lambda_v$ is the energy required to change the nuclear coordinates of the vibrationally equilibrated excited state (VEqES) into those of the ground-state PE minimum, and the reorganizational energy contributions corresponding to $\hbar \nu$ and $h\nu_{abs}$ to $\lambda_{reorg}$ are $\lambda_h$ and $\lambda_v$, respectively. The energy of the absorption maximum is equal to the free energy change that occurs during the absorption of light. The dominant contributions to this process, based on the maximum of the FC function, are given by either eq 7a or eq 7b,

$$h\nu_{max} = E_{DA}^{00} + \lambda_{reorg} + ...$$

(7a)

$$h\nu_{max} = |\Delta G_{DA}^{00}| + \chi_{reorg} + ...$$

(7b)

provided the terms on the right-hand side of these equations are internally consistent: energy quantities for eq 7a and free energy quantities for eq 7b ($\chi_{reorg} = \lambda_h + \lambda_v$, analogous to the components of $\lambda_{reorg}$). $\Delta G_{DA}^{00}$ is the free energy difference between the vibrationally equilibrated ground and excited states, and $\chi_{reorg}$ is the free energy change associated with the change from the nuclear coordinates of the VEqES to those of the ground state. The experimental evaluations of free energy quantities are usually easier than of energy quantities, and most correlations of the components of optical


(78) Note that the use of eq 6 assumes that $H_{DA}$ and $\Delta \mu_{DA}$ are constant through the absorption band.
transition energies are in terms of electrode potentials determined for oxidation or reduction of the D/A system (eq 1).


A.3.a. Kinetic Parameters. The reorganizational parameters in eq 7b are often interpreted in terms of the component, electron-transfer activation free energies (from rate constant data). This interpretation of the parameters is fundamentally based on the assumption that there is very little configurational mixing between donor and acceptor. Homogeneous solution electron-transfer kinetic data or ion pair charge-transfer spectra can be the bases for useful estimates of the reorganizational free energy, $\chi_{\text{reorg}}(DA)$, in the limit of little electronic mixing (see Figure S6). The reorganizational free energy is the sum of metal-fragment and ligand-fragment contributions and $\chi_{\text{reorg}}(DA(0)) = 1/2(\chi_N(0) + \chi_L(0))$. We have used aqueous self-exchange electron-transfer data to estimate values of $\chi_{\text{reorg}}(DA)$ and these values as the bases for estimating $\chi_N(0)$ for several complexes (Table 5).

A.3.b. Effect of Ground State–Excited State Mixing on Nuclear Reorganizational Energies. In the simple two-state limit (parabolic ground state and excited state PE surfaces with the same force constants), the excited state–ground state mixing results in a reorganizational potential energy (PE) minima that are related as in eq 15 (see page S9). The recombination of eqs 10 and 11 leads to eqs 5 and 12

$$-\Delta G_{DA} = \frac{F}{2} \Delta E_{1/2}^{DA} - RT \ln K_{DA}$$

where $\Delta E_{1/2}^{DA} = E_{1/2}^{A} - E_{1/2}^{D}$ and $F$ is Faraday’s constant. Substitution of eq 12 into eq 7b leads to

$$h\nu_{\text{max}} = -F\Delta E_{1/2}^{DA} + RT \ln K_{DA} + \chi_{\text{reorg}}(a) + ...$$

Direct measurements of $K_{DA}$ are not usually feasible for covalently linked D/A systems, but simple perturbation theory arguments lead to useful estimates. If the stabilization energy of the ground state that results from D/A mixing is $\epsilon_s = H_{DA}^2/2E_{DA}$, the destabilization of the VEQS is $\epsilon_d = H_{AD}^2/2E_{AD}$. If $K_d$ represents the strictly electrostatic contribution to $K_{DA}$, the difference in exchange integrals (see page S8), then eq 14 can be used:

$$RT \ln K_{DA} = -\epsilon_s + \epsilon_d + RT \ln K_d + \Delta K_{\text{exch}}$$

If we set $h\nu_{\text{max}} = E_{DA} = [E_{DA}^{00} + \chi_{\text{reorg}}(a)], E_{AD} = [E_{DA}^{00} - \chi_{\text{reorg}}(a)],$ assume that $H_{DA} = H_{AD}$, and allow for the effect of the shift in the PE minima that results from D/A mixing $(\alpha_{DA}x_0$ and $-\alpha_{AD}x_0$, respectively) for the ground and excited states, then $\epsilon_s$ and $\epsilon_d$ are related as in eq 15 (see page S9).

$$\epsilon_d = \epsilon_s + 2\alpha_{DA}^2\chi_{\text{reorg}}(a) + ...$$

Equation 13 may be rewritten as in eq 16.

$$h\nu_{\text{max}} = -F\Delta E_{1/2}^{DA} + \chi_{\text{reorg}}(a)(1 + 2\alpha_{DA}^2) + RT \ln K_d + \Delta K_{\text{exch}} + ...$$

where we have assumed that free energy quantities may be substituted for energy quantities in the perturbational correction terms. The reorganizational parameter in eq 16 has the same meaning as that in eq 7b, and the correction terms arise only because $F\Delta E_{1/2}$ is not the same free energy quantity as $\Delta G_{DA}^{00}$ in eq 7b.

A.3.d. Electrostatic Contributions. The contributions of $K_d$ may also be important. These can be factored into intermolecular and intramolecular contributions. The former amounts to an ion pair association constant and is expected to be small in high dielectric media. The intramolecular Coulombic term is the largest term for the $D^+-A^-$ species in eq 11.

B. Strongly Coupled Systems and the Ru(bpy) Complex. Arguments presented above indicate that charge

(79) Note that $\chi_{\text{reorg}}(DA) = 1/2(\chi_{\text{reorg}}(D) + \chi_{\text{reorg}}(A))$ and that each reorganizational energy contribution is the sum of contributions ($\chi_N^0$ and $\chi_L^0$) from the low-frequency (largely solvent) and high-frequency (molecular) vibrational modes, respectively, that correlate with the solvational and structural differences of the ground and excited states.

(80) Equation 3, when applied to emission, implies similar mixing at both minima; this would only be the case for the two-state limit if the minima have the same PE or if $\lambda_{\text{reorg}}$ is very small; see page S9 of Supporting Information and ref 81.

delocalization can attenuate both the low-frequency and the high-frequency vibrational contributions to the reorganization free energy in strongly coupled systems. Conversely, the attenuation of these vibrational contributions to the reorganizational energy could be a measure of the amount of charge delocalized.

**B.1. MLCT Spectra of [Ru(NH₃)₆]bpy³⁺.** The MLCT absorption spectra of this complex in water and acetonitrile are very similar, but the resolved Gaussian bandwidth of the dominant lowest energy component is about 10% larger in water.

![Equation 17](image)

(Equation 17, (where \( \sigma \) is the standard deviation from the mean values of \( E_{DA} \) and \( \lambda_{reorg} \); see page S10) with \( \sigma = 0 \) implies that \( \lambda_s \approx 2.1 \times 10^3 \) in water, significantly smaller than even the value of \( \lambda_{reorg} \) in Table 5. Since \( \lambda_{D} = \lambda_{E}^{\text{obs}} + \lambda_{S} \) and assuming that \( \lambda_{E}^{\text{obs}} = \lambda_{reorg} \lambda_{D} \approx 900 \) cm⁻¹ (see below), with \( \lambda_s \approx \lambda_{reorg} \) in eq 8, an iterative fit implies about 9% delocalization of electron density in this complex.

There is also evidence for attenuation of the reorganizational energy in the emission spectra of Ru(Am)₆–bpy(bpy)₆⁺ complexes \(^{82,83} \) (Am = am(m)ine). The observed bandwidths imply that \( \lambda_s(e) \approx 1.8 \) and 1.4 cm⁻¹/10³, respectively, smaller and in the opposite order of the estimated values of \( \lambda_{reorg} \) (Table 5). This ordering of \( \lambda_s(e) \) is consistent with the greater value of \( \alpha_{DA} \) expected for the ammine complex and the resulting greater attenuation of reorganizational parameters.

The intensity contributions of the high-frequency modes are also attenuated; the intensity ratios of the first and second Gaussian components with frequencies in the range 1300–1400 cm⁻¹, and in the opposite order of the estimated values of \( \lambda_{reorg} \).

**B.2. Concerning the Exchange Integral Contribution.**

In principle, the exchange integral can be estimated from the absorption–emission energy difference,

![Equation 18](image)

(Equation 18, \( E_{ST} \) is the singlet–triplet energy difference) provided the reorganizational energies are known. The deconvoluted absorption and emission maxima are summarized in Tables 1 and 5, and when combined with the values of \( \lambda_{reorg}(e) \approx 1900 \) cm⁻¹ and \( \lambda_{reorg}(e) \approx 1400 \) cm⁻¹ from the observed (deconvoluted) bandwidths and eq 18, indicate that \( 2K_{exch} \approx (3.3 \pm 0.7) \times 10^3 \) cm⁻¹ for [Ru(NH₃)₆(bpy)]³⁺ (for an uncertainty of about 10% in each bandwidth). However, these values of \( \lambda_{reorg} \) are not consistent with eqs 8 and 9; these equations, combined with \( \lambda_{reorg}(f) \), imply that the absorption bandwidth should have been about 25% larger than observed and \( 2K_{exch} \approx 2300 \) cm⁻¹. This is even more of a problem for [Ru(bpy)]³⁺: \( \Delta_{1/2}(abs) \approx \Delta_{1/2}(em) \), contrary to expectation based on eqs 8, 9, and 17 (\( \Delta_{1/2}(abs) \approx 1.5 \Delta_{1/2}(em) \)). This behavior is probably a consequence of more extensive inter-ring configurational mixing (and charge delocalization) in the Franck–Condon excited state (see section B.4) than in the emitting state. For [Ru(bpy)]³⁺, \( K_{exch} \approx 2000 \) cm⁻¹ based on the observed bandwidth (probably an upper limit), and \( 2K_{exch} \approx 500 \) cm⁻¹ based on the emission bands and eqs 8, 9, and 17. These estimates are comparable to the values that Lever and Gorelský \(^{46} \) calculated, \( K_{exch} \approx 1460 \) cm⁻¹ for [Ru(bpy)]³⁺ and (interpolated from calculated values) 2800 cm⁻¹ for [Ru(NH₃)₆(bpy)]³⁺; the ordering of the experimental estimates of \( K_{exch} \) is consistent with the calculations.

**B.3. N–H Stretch as an Indicator of Charge Delocalization.** It is well-known that N–H stretching frequencies are very sensitive to the charge on a metal center. Unfortunately, they are also sensitive to the counterion and to other environmental factors. However, the difference in \( \nu_{NH} \) for [Ru(NH₃)₆]³⁺ and [Ru(NH₃)₆]³⁺ is sufficiently large, about 175 cm⁻¹, such that shifts in this frequency can be used as an indicator of the effective charge density on the metal. For this purpose, we define a fractional shift, \( f \), for a complex:

![Equation 19](image)

These parameters are quite large for all the polypyridylamine complexes in this study (Table 5). In the simplest interpretation \( f \) is proportional to the amount of charge delocalized from Ru⁴⁺ to the polypyridine ligand. Certainly the order of values of \( f \), increasing with [\( \chi_{max} \) (MLCT) 1]⁻², is consistent with this interpretation (Figure S12). Appreciable charge delocalization is implied by the observed shifts in N–H stretching frequencies.

**B.4. Electrochemical Observations on Polypyridine Complexes.** We have inferred that eq 16 is appropriate for correlations involving the lowest energy MLCT transition. However, the first bipyridine ligand reduction of a series of \([L₆–₂Ru⁴⁺(bpy)₆] \) complexes (L an am(m)ine) occurs at increasingly negative potentials as \( n \) decreases (Table 3). This suggests significant electronic coupling between the bipyridine rings. Equation 20

![Equation 20](image)

can be used to take account of ligand–ligand coupling (the vertical energy for moving the electron from one ring to another is the electron-transfer reorganizational energy, \( \lambda_i \)).
Ruthenium Complexes

There are three nondegenerate solutions of the secular equation. This is qualitatively consistent with observation. If the first reduction of \( [\text{NH}_3\text{Ru(bpy)}]^2+ \) is at \( E_i^< \), then this argument suggests that the first reduction of \([\text{Ru(bpy)}]^2+\) will occur at \( (E_{\text{ir}}^< - 2(H_{\text{BB}})^{1/2})/\lambda_e \) in the limit that \( \lambda_e > H_{\text{BB}} \) (the general solution is \( \lambda = [\lambda_e^2 - 1/4(\lambda_e^2 + 8H_{\text{BB}})^{1/2}] \)). The related treatment of \([\text{NH}_3\text{Ru(bpy)}]^2+\) predicts that the first ligand reduction will occur at \( (E_{\text{ir}}^< - (H_{\text{BB}})^{1/2})/\lambda_e \); see also Dodsworth et al.\(^6\) The predicted trend in reduction potentials is qualitatively in accord with the observations. After taking account of the stabilization arising from Ru\(III\) bpy mixing and of the statistical effect contributed by the different numbers of polypyridyl rings in these complexes (for \([\text{Ru(bpy)}]^2+\) compared to \([\text{Ru(NH}_3]^2+\) and assuming that \( \lambda_e \) and \( H_{\text{BB}} \) are the same in each complex and that no other factors contribute, then the electrochemical observations indicate that each bipyridine—bipyridine interaction confers about \( \epsilon_{\text{d}}(\text{BB}) \approx -0.1 \text{ eV} \). This can be a basis for estimating \( \lambda_{\text{reorg}}^{-1}. \) If we note that a \([\text{bpy}])^2+\) complex is a mixed-valence complex in which the donor (bpy\(^-\)) and acceptor (bpy) are bridged by Ru\(^{III}\), then statistical superexchange arguments\(^72,73,87\) predict that \( H_{\text{BB}} \approx H_{\text{ML}}^{1/2} \) \( (E_{\text{ML}})_{\text{ave}} \), for \( H_{\text{ML}} \approx 7(1 \pm 10^3 \text{ cm}^{-1}) \) (eq 8; assuming that \( H_{\text{ML}} \) is independent of the distortion in the bpy\(^-\) ring; \( E_{\text{ML}} \) for \( H_{\text{ML}} \approx 7(1 \pm 10^3 \text{ cm}^{-1}) \)) results in a calculated decrease in the energy of the \( \beta-\text{LUMO} \) of about 2 \( \text{ eV} \). This can be interpreted as a stabilization energy of \( \epsilon_{\text{d}}(\text{PP}) \approx 7 \times 10^3 \text{ cm}^{-1} \) resulting from py—pz configurational mixing with the \( \beta-\text{LUMO} \) of pz and very little mixing with the \( \alpha-\text{LUMO} \). However, neither the \( \alpha-\text{LUMO} \) nor the \( \beta-\text{LUMO} \) changes much in energy when the second pyridine rotates into position for coordination of a second metal. This suggests that the stereochemical repulsion energy, which results in twisting of the pz ring, is approximately equal to \( -\epsilon_{\text{d}}(\text{PP}) \). The net result is little change in LUMO energy, and this correlates with the observation that there is little difference in \( h\mu_{\text{max}} \) for band I of the monometallic and bimetallic ammine complexes. The \( 1.8 \times 10^3 \text{ cm}^{-1} \) lower energy of band I in \([\text{bpy}]_2\text{Ru}^{III}\) compared to \([\text{bpy}]_2\text{Ru}^{III}\) is attributable in part to the \( 1 \times 10^3 \text{ cm}^{-1} \) lower energy expected to result from bpy/dpp configurational mixing when the second metal Ru(bpy)\(^2+\) moity is coordinated to dpp (see Discussion, section B.4).

C. Application to the dpp Complexes. The dpp and bpy ligands of monometallic complexes exhibit very similar properties in each of the comparisons that we have made of monometallic complexes in this study. Many points made in the preceding section apply with only minor differences to the complexes containing the dpp ligand.

C.1. Features of MLCT Absorption Spectra. Several puzzling features of the spectra and electrochemistry noted above involve the comparison of monometallic and bimetallic complexes. Explanations for most of these observations can be based on the hypotheses that (a) the lowest energy MLCT band in the monometallic complexes involves the \( \beta-\text{LUMO} \), (b) band II of the monometallic complexes involves the \( \alpha-\text{LUMO} \), and (c) the \( \alpha-\text{LUMO} \) mediates very strong electronic coupling between Ru(II) and Ru(III) centers in the excited state, giving rise to a very large Jahn—Teller splitting of band II in bimetallic complexes. To accommodate the observations, the postulated explanations require that the \( \beta-\text{LUMO} \) contributes little to the Ru\(^{III}\)/Ru\(^{II}\) coupling.

C.2. Relevant Features of the ab Initio Calculations. It appears that orbitals of \( \alpha \) and \( \beta \) types are similar in energy in most polypyridyl complexes and that both orbital types contribute to the low-energy MLCT transitions. The energies calculated for the LUMOs of bpy, dpp, dpq, and dpb correlate with the observed band I energies of the monometallic complexes (Figure 8; slopes of 1.0 ± 0.2 and 0.6 ± 0.1, respectively, for the ammine and bipyridine complexes when \( \Delta E_{\text{MLCT}} \) is subtracted from \( h\mu_{\text{max}} \) for the comparisons of donor energy; this “correction” omits some contributions that result from metal—ligand mixing). The LUMO computed for the dpp ligand has \( \beta \) symmetry, while the LUMOs of dpq and dpb have \( \alpha \) symmetry. The strong correlation of the calculated LUMO and the observed band I MLCT transition energies (Figure 8) is support for this inversion of the order of LUMOs in dpp. Note that this approach to the assignment is consistent with the arguments used throughout this paper that the properties of the complexes can be described as the sum of (1) the properties of the isolated metal, (2) the properties of the isolated ligand, and (3) perturbation theory based correction terms.

The rotation of one pyridine from a position nearly orthogonal to the pyrazine ring (dihedral angles of 75°) to a position appropriate for bidentate coordination of a metal (dihedral angle of 21°) results in a calculated decrease in the energy of the \( \beta-\text{LUMO} \) of about 7 \( \times 10^3 \text{ cm}^{-1} \), while the energy of the \( \alpha-\text{LUMO} \) changes by only about 1 \( \times 10^3 \text{ cm}^{-1} \). This can be interpreted as a stabilization energy of \( \epsilon_{\text{d}}(\text{PP}) \approx 7 \times 10^3 \text{ cm}^{-1} \) resulting from py—pz configurational mixing with the \( \beta-\text{LUMO} \) of pz and very little mixing with the \( \alpha-\text{LUMO} \). However, neither the \( \alpha-\text{LUMO} \) nor the \( \beta-\text{LUMO} \) changes much in energy when the second pyridine rotates into position for coordination of a second metal. This suggests that the stereochemical repulsion energy, which results in twisting of the pz ring, is approximately equal to \( -\epsilon_{\text{d}}(\text{PP}) \). The net result is little change in LUMO energy, and this correlates with the observation that there is little difference in \( h\mu_{\text{max}} \) for band I of the monometallic and bimetallic ammine complexes. The \( 1.8 \times 10^3 \text{ cm}^{-1} \) lower energy of band I in \([\text{bpy}]_2\text{Ru}^{III}\) compared to \([\text{bpy}]_2\text{Ru}^{III}\) is attributable in part to the \( 1 \times 10^3 \text{ cm}^{-1} \) lower energy expected to result from bpy/dpp configurational mixing when the second metal Ru(bpy)\(^2+\) moity is coordinated to dpp (see Discussion, section B.4).

C.3. Electron Delocalization and Electron Exchange Contributions. We can make qualitative inferences and semiquantitative estimates of the significance of electron delocalization in the ground states of some of the dpp complexes. The N—H stretching frequencies imply that very similar amounts of electron density are delocalized in comparable bpy and dpp complexes. The emission spectra imply that \( \lambda_e \) is about 400 cm\(^{-1}\) smaller for \([\text{bpy}]_2\text{Ru}^{III}\) than for \([\text{bpy}]_2\text{Ru}^{III}\); this suggests somewhat larger values of \( H_{\text{LO}} \) or smaller values of \( \lambda_{\text{reorg}}^{-1} \) for the dpp complex. The differences in the energies of the lowest energy deconvoluted emission components differ only slightly from the respective

\( ^{(84)} \) Since \( E_{\text{ST}} \) is roughly comparable to the spin—orbit coupling energy for these complexes, we have assumed that \( \lambda_{\text{reorg}}^{-1} \approx \lambda_e^{-1} \) in these estimates.

\( ^{(85)} \) Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds; Wiley: New York, 1997; Part B.


differences in metal and ligand half-wave potentials (the difference is larger for the dpp complex). These observations and the stronger attenuation of $\lambda_{\text{c}}$ (eqs 3 and 8) suggest that both $E_{\text{ST}}$ and $\lambda_{\text{reorg}}$ are somewhat larger in the dpp complex.

Arguments presented above and observations summarized in Tables 1 and 5 indicate that $E_{\text{ST}} \approx (h\nu_{\text{max}} - h\nu_{\text{em}}) - \lambda_{\text{reorg}} \approx 2K_{\text{exch}} \approx (3.4 \pm 1.0) \times 10^3 \text{ cm}^{-1}$ for the MLCT excited state of [Ru(bpy)2dpp]$^{2+}$. This contrasts with an estimate of $2K_{\text{exch}} \approx (1.3 \pm 0.8) \times 10^3 \text{ cm}^{-1}$ for [Ru(bpy)3]$^{2+}$ (Table 5).

C.4. Spectroscopic Splittings That Result from RuII/RuIII Electronic Coupling. We have observed the RuII/RuIII MMCT transition at $6.4 \times 10^3 \text{ cm}^{-1}$ in the [(NH3)4RuII]$^2-$ (dpp)$^{5+}$ complex. This is comparable to the excited-state splitting (Jahn–Teller) of about $9.2 \times 10^3 \text{ cm}^{-1}$ proposed here for the vertical transition. It is not possible to examine this issue in the complexes containing Ru(bpy)2 complexes because the RuII/bpy MLCT transition is expected at about the energy predicted for band II.

This suggests that the $\pi^*$ orbitals of $\alpha$ symmetry are much more effective at mediating RuII/RuIII electronic coupling than are those of $\beta$ symmetry. We have assigned bands I and II in the monometallic complexes as MLCT transitions involving the LUMOs of $\alpha$ and $\beta$ symmetry ($\alpha$ higher energy only for the dpp complexes). These bands are roughly comparable in intensity, and this implies roughly comparable metal–ligand mixing ($H_{\text{ML}}(\text{I}) \sim H_{\text{ML}}(\text{II})$). This is reasonably consistent with the significant orbital contributions calculated at the pyrazine nitrogen atoms in both symmetries (Figure 3). As a consequence, simple superexchange arguments would imply roughly comparable metal–metal mixing. However, in the $\alpha$ symmetry the N-atom orbital phases are symmetrically related (with respect to a C2 axis perpendicular to the pyrazine moiety), while in the $\beta$ symmetry they are antisymmetrically related. Thus, the orbitals of two metals coupled by means of a $\pi^*$ orbital with $\beta$ symmetry would be expected to be out of phase, and this might result in very little metal–metal mixing. This is reminiscent of the bridging ligand phase effects observed in cyanide-bridged complexes.

C.5. Optical/Electrochemical Comparison. We have observed much larger values of $(h\nu_{\text{max}} - F\Delta E_{1/2})$ for the dpp-bridged dimers than for the monomers (Table 3 and Figure 4). Arguments presented above demonstrate that this difference cannot be attributed to a large difference in reorganizational energies. Observations, such as the very similar values of $\nu_{\text{SH}}$ for monometallic and bimetallic tetraammine complexes, are consistent with very little difference in electron delocalization in the ground state. The band I energies of the bimetallic complexes do not vary in proportion to variations in $E_{1/2}(\text{RuIII})$ for the dimer. There are several, not necessarily exclusive, possible interpretations of this behavior: (1) the stabilization energy contributions, $\epsilon_s$, that result from metal–ligand mixing enter differently into the transition energy for monometallic and bimetallic complexes, (2) the observed transition is not properly classified as an MLCT transition, or (3) the optical excitation involves a metal HOMO different from that accessed electrochemically. The first possibility is the most straightforward. The shift of the ground-state PE minimum ($\alpha_{\text{ML}}\gamma_{\text{ML}}\gamma_{\text{X}}$) in the monometallic complexes compensates partly for the effects of ground-state stabilization and vertical excited-state destabilization, $\epsilon_s$, while in the dimer there should be little shift of the ground-state PE minimum (Figure 10). In terms of the arguments above, the absorption of the symmetric dimer should occur at approximately $\lambda_{\text{reorg}}(4\alpha_{\text{ML}}\gamma_{\text{ML}}\gamma_{\text{X}}) + 2.8\epsilon_{\text{ML}} - H_{\text{MM}}(1 - 4\alpha_{\text{ML}}\gamma_{\text{ML}}\gamma_{\text{X}})$ higher energy than the monomer (relative to the values of $F\Delta E_{1/2}$). Values of $H_{\text{MM}}(1 - 4\alpha_{\text{ML}}\gamma_{\text{ML}}\gamma_{\text{X}}) + 2.8\epsilon_{\text{ML}}$ for ammine complexes are reasonably consistent with the implications of the MLCT absorption/emission properties discussed above. Pyrazine-bridged bimetallic Os complexes have been reported to have similar values of $(h\nu_{\text{max}} - F\Delta E_{1/2})$.

We believe that the other two possibilities are less likely. The amount electron density delocalization seems small enough that the MLCT classification is still useful in the dimers. It is unlikely that the electrochemical oxidations access markedly different metal HOMOs in the monomers and the dimers.

Conclusions

Overall, our observations indicate that there is appreciable charge delocalization in RuII–polypyridyl complexes and that this has some striking effects on the trends in the properties of these complexes. The bandwidth of the lowest energy MLCT absorption of [Ru(NH3)4bpy]$^{2+}$ implies about 10%

Figure 10. Illustration of the effects on the ground state of mixing with one (top) and two degenerate-coupled (bottom) excited states. For mixing with a single excited state, the shift of the ground-state PE minimum partially compensates for the effects of ground-state stabilization. With two degenerate excited states, the ground-state PE minimum does not shift and $\epsilon_s$ contributes more strongly to $h\nu_{\text{max}}$.

delocalization of electron density between metal and ligand, provided the distribution of solvent environments does not affect the bandwidth in a manner different from its effect on the reorganizational energy. The fraction of electron density delocalized is similar, but probably slightly larger (10–40%), in the dpp analogue. Electron exchange energy does appear to play a role in these systems, more in the dpp than in the bpy complexes. The lowest energy MLCT excited states of \([\text{Ru}(\text{bpy})_2(\text{dpp})]^2^+\) and \([\text{Ru}(\text{NH}_3)_4(\text{dpp})]^2^+\) complexes populate the \(\pi\)-LUMO rather than the more commonly expected \(\sigma\)-LUMO. This means that the lowest energy \(\pi^*\) orbital of dpp differs in symmetry from that of the parent pyrazine ring, and this feature is unique to the dpp ligand in the series considered. Similarly, the ligand reductions of the dpp complexes predominately involve the \(\pi\)-LUMO, and this readily accounts for the previously observed deviations of the electrochemical reductions of dpp complexes from a correlation with bond order, since the \(\pi\)-LUMOs mix more strongly with the pyridyl moieties than do the \(\sigma\)-LUMOs. The \(\sigma\)-LUMOs would be involved in ligand reductions of all but the dpp complexes.

Spectroscopic, electrochemical, and computational observations on a series of Ru\(\text{II}-\)polypyridyl complexes have led to the following conclusions.

1. The LUMO and LUMO + 1 of dpp, bpy ligands, and closely related ligands are not greatly different in energy.
2. The changes in electron exchange contributions that result from configurational mixing are smaller than the stabilization energies associated with electron delocalization. The fraction of electrons delocalized seems to be similar in bpy and dpp complexes that differ only in these ligands, but the exchange contribution appears to be significantly larger for complexes with dpp ligands.
3. The MLCT excited-state spectra of dpp-bridged complexes can be complicated by large “intervalance” splittings mediated by one, but not both, of the lowest energy \(\pi^*\) orbitals. This difference in mediation of Ru\(\text{II}/\text{RuIII}\) coupling suggests a bridging ligand orbital phase effect on the superexchange coupling.
4. The connection between the different species involved in the electrochemical and photochemical processes can be made by means of an electron-transfer equilibrium constant, \(K_{DA}\), and the contributions to \(K_{DA}\) can assessed in terms of perturbation theory based arguments.

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**Supporting Information Available:** Table of elemental analyses, description of synthesis of complexes, figure of spectral assignments for \([\text{Ru}(\text{NH}_3)_3(\text{bpy})]^2^+\), ambient emission spectra of \([\text{Ru}(\text{NH}_3)_2(\text{bpy})]^2^+\) and \([\text{Ru}(\text{bpy})_2]^2^+\), figure comparing IPCT transition energies to electron-transfer parameters, paragraph describing exchange energy contributions, paragraph describing perturbation theory stabilization energies, paragraph describing the extraction of reorganizational energies from bandwidths, and figure relating N–H stretching frequencies to variations in MLCT energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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