MLCT excited states and charge delocalization in some ruthenium–
ammine–polypyridyl complexes

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Abstract

The ab initio calculations of polypyridine \( \pi^* \)-orbital energies are the basis for assignment of the lowest energy, highest intensity metal-to-ligand charge transfer (MLCT) transitions in simple ammine–polypyridyne–ruthenium(II) complexes. A gaussian analysis of the absorption and emission spectra of these complexes enables the evaluation of reorganizational energies for the vertical MLCT transitions from component bandwidths and from apparent vibronic progressions. The observed bandwidths are about half of the widths expected in the limit of no metal–ligand mixing. The excited state-ground state mixing coefficient, \( \alpha_{DA} \), is inferred to be about 0.3 in \([\text{Ru(NH}_3)_3\text{bpy}]^{2+}\) based on this observation and a perturbation theory argument. These estimated reorganizational energies are combined with the observed ambient Stokes shifts to determine that the excited state electron exchange energy, \( K_{e,i} \), is small (600–1200 cm\(^{-1}\) for 2,2’-bipyridine complexes; \( \sim 1500 \text{ cm}^{-1} \) for 2,3-bis-(2-pyridyl)pyrazine complexes), but significant. This and the observation that the N–H stretching frequency increases as the vertical MLCT energy (or \( \alpha_{DA}^2 \)) decreases suggests that there is significant charge delocalization in these complexes.

Keywords: Ammine–polypyridyne–ruthenium(II) complexes; Vertical MLCT energy; Metal-to-ligand charge transfer (MLCT)

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1. Introduction

1.1. General comments

The spectroscopic and electrochemical properties (P) of most transition metal donor–acceptor complexes (C) can be represented as the sum of the properties of the isolated donor (D) and acceptor (A) components modified by a generally small correction (\(\Gamma\)) for the changes in properties that result from the electronic mixing of the donor and acceptor [1–8]; in simplest general form,

\[
P(C) = P(D) + P(A) = \Gamma(D/A) \tag{1}
\]

Electron transfer systems in the limit that the donor and acceptor are very strongly mixed can exhibit unique properties that do differ markedly from those of the separated donor and acceptor. In principle, the degree to which these modifications in properties are important can be correlated to the amount of electronic charge delocalized between the donor and acceptor. Thus, it is generally believed that very strong D/A mixing can lead to electron delocalization over an extended array of donors and acceptors, and this delocalization might facilitate the flow of electrons in molecular-scale electronic devices [9–12]. On the other hand, very strong D/A mixing can lead to selection rules and interference effects when several donors and acceptors are connected [13–15]. The interference effects are not well documented, but they appear to be a function of the symmetry (or phase) properties of the bridging ligand orbitals that mediate the D/A mixing [13,16].

The extent of D/A mixing can significantly alter several physical and chemical properties of D/A complexes without invalidating correlations to the properties of the constituents, as represented in Eq. (1). Increased mixing results in: increased ground state stabilization [17]; shifts in electrochemical redox potentials [7]; changes in the energies and bandwidths of electronic absorptions and emissions [3,18,20–22]; shifts in ‘spectator’ ligand vibrational frequencies; etc. The changes in the energy of the molecule that result from D/A mixing are a combination of coulombic and electron exchange contributions. It is the coulombic contributions that are correlated with electron delocalization [23]. In strongly coupled systems, one expects both kinds of contributions to be important [23,24]. Clearly, the design of systems that are effective in delocalizing electrons depends on an understanding of how one can optimize the coulombic contributions.

1.2. Ruthenium–polypyridyl complexes

Polypyridyl complexes of ruthenium(II) are among the simplest and most extensively investigated of strongly mixed D/A systems, and 2,3-bis(2-pyridyl)pyrazine (dpp) is one of the most commonly used linkers for assembling arrays of such metal complexes [25–38]. 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 [39–42]. The bridging ligand mediated super-exchange mixing that leads to electronic delocalization between the bridged metals [43–45] does not necessarily imply appreciable electron delocalization onto the bridging ligand nor does it necessarily invalidate Eq. (1) as an approach to the properties of the complex system. We have been examining the spectroscopic and electrochemical properties of several series of ruthenium polypyridyl complexes [18,46] This report focuses on the simplest of these systems.

Since calculations by Lever and Gorelsky [24] have suggested that bpy is a poor electron acceptor ligand, it seems possible that there should be significant contrasts in the properties of simple bpy and dpp complexes if there is indeed appreciable delocalization of electron density into the LUMO of dpp. In this report, we summarize a detailed comparison of the spectroscopic and electrochemical properties of very simple bpy and dpp complexes.

2. Some general aspects of spectroscopic and electrochemical correlations

2.1. Excited state–ground state mixing in a two state system; perturbation theory approach

To relate the effect of D/A mixing on the absorption and emission maxima, we set,

\[
h^\text{max}_{\text{abs}} = E^0_{\text{DA}} = E^0_{\text{DA}} + \lambda_{\text{reorg}} \tag{2a}
\]

\[
h^\text{max}_{\text{emis}} = E^0_{\text{DA}} = E^0_{\text{DA}} + \lambda'_{\text{reorg}} \tag{2b}
\]

where \(E^0_{\text{DA}}\) is the energy difference between the 0th vibrational levels of the two potential energy (PE) surfaces, \(\lambda_{\text{reorg}}\) and \(\lambda'_{\text{reorg}}\) are the respective vibrational reorganizational parameters. In the limit of very weak electronic coupling, \(\lambda_{\text{reorg}} = \lambda'_{\text{reorg}}\). For a two state system with quadratic PE functions, and for \(E_0\) the difference in the nuclear coordinates for the ground and excited state PE minima in the absence of configurational mixing, these minima are displaced by \(\pm \sqrt{\lambda_{\text{reorg}}E_0} \) and \(\pm \sqrt{\lambda'_{\text{reorg}}E_0} \), respectively, as a consequence of the mixing; where, \(E_0 = H_{\text{II}}/E_{\text{I}}\). The matrix elements are defined in terms of the electronic wave functions, \(H_{\text{I}} = \langle \psi_I | H | \psi_I \rangle\), and we assume that \(H_{\text{DA}} = H_{\text{AD}}\). The ground state stabilization, \(E_{\text{gs}}\), and the excited state destabilization, \(E_{\text{ds}}\), that result from the mixing are given by Eqs. (3) and (4) (the third term in the denominator takes account of the shift in PE minima) [17].
If we assume that the electron exchange contributions are small and that \( \lambda_{\text{reorg}} \lambda_{\text{reorg}} \ll E_{\text{BA}}^{(0)} \), then the \( \varepsilon_i \) are approximately related as in Eq. (5),

\[
\varepsilon_i \approx \varepsilon_0 + x_i^2 (\lambda_{\text{reorg}} + \lambda_{\text{reorg}}^2) + \ldots
\]  

The displacement of the PE minima results in a correlated decrease in the reorganizational energy for a strongly coupled system [19–21,41,47]. Free energy quantities are generally easier to evaluate than, and can be substituted for energy quantities in expressions dealing with vertical transitions. For \( \lambda_{\text{DA}}^{(0)} \) the reorganizational free energy in the limit that \( z_{\text{DA}} = 0 \),

\[
\lambda_{\text{reorg}}^{(0)} = \frac{1}{2} (\lambda_{\text{reorg}} + \lambda_{\text{reorg}}^2)
\]

In the two state limit, with \( z_{\text{DA}} = z_{\text{DA}}, \) the reorganizational free energy appropriate to the absorption (emission) bandwidth should decrease in the reorganizational energy for a \( \lambda_{\text{DA}}^{(0)} \) as in Eq. (9).

A generally small correction term is necessary here because the species involved in the electrode processes differ from those in the light absorption process [7,58,18]. Eq. (9) is similar in form to Eq. (1), and while the potentials in this equation are determined on the complex (not the separate components), their values are typically shifted less than one hundred mV from those of the equivalent, separated donor and acceptor; this is very small compared with the approximately 2.5 eV vertical energy difference. Thus, even in these systems many properties of the complexes are well represented as a sum of the properties of the donor and the acceptor plus a relatively small perturbational correction term. On the other hand, the reorganizational parameters in Eq. (10) are much smaller than expected for \( \lambda_{\text{DA}}^{(0)} \) based on the properties of the separated donor and acceptor [18]. This is readily attributed to the large attenuation of reorganizational energies expected with even modest charge delocalization, as in Eqs. (8) and (9) (in the electrochemical comparisons the attenuation is about half that predicted by these equations owing to the contributions of \( \eta_{\text{DA}} \) [18]).

2.3. Effects of configurational mixing on electrochemical properties

When metal–ligand mixing is appreciable, it should have an effect on every term in Eq. (9). When the half-wave potentials are determined for the metal–ligand complex, the oxidation of the metal and the reduction of the ligand each contain a contribution that results from the mixing, as in Eqs. (10)–(13),

\[
(A_n M^{n+1})^+, L]^{n+1} + e^- \xrightarrow{\text{sol}} [A_n M^n, L]^{n+} + E_{1/2}^- \quad (10)
\]

\[
F_{1/2}^+ = F_{1/2}^-(M^{n+1})^+[M^{n+}] + e^+ - \partial g_{\text{sol}}^+ \quad (11)
\]

\[
F_{1/2}^+ = F_{1/2}^-(L)[L]^e + e^- - \partial g_{\text{sol}}^- \quad (12)
\]

In these equations, \( \partial g_{\text{sol}}^X \) is a stabilization energy (or a difference of stabilization energies) that results from metal–ligand mixing and \( \partial g_{\text{sol}}^X \) is the solvation free energy difference of the combined and separated metal and ligand. Eqs. (11) and (13) are only useful when \( F_{1/2}^+(M^{n+1})^+[M^{n+}] > FE_{1/2}^-(L)[L]^e - 1 \) eV,

and the electrochemical measurements of the complexes

\[
\eta_{\text{DA}} = \frac{2}{E_{\text{BA}}} - \frac{1}{E_{\text{BA}}} = \frac{1}{E_{\text{BA}}} - \frac{1}{E_{\text{BA}}}
\]
can be considered to be slightly perturbed metal oxidations and ligand reductions. The difference between the differences in the solvational contributions of the complex couple and the separated components to the electrochemistry, \(|\delta g_{\text{sol}} - \delta g_{\text{mol}}|\), is usually much smaller (a related discussion can be found elsewhere [59]). The chemical species involved in the electrochemical processes, Eqs. (10) and (12), are different from those in the light absorption process [7,58].

The ground state stabilization energy that results from M/L mixing is [17],

\[ [(A_m M^{n^+}), L]^{n^+} + h\nu_{\text{abs}} \rightarrow [(A_m M^{(n+1)^+}), L]^{(n+1)^+} \]  

These species are related through the electron transfer equilibrium,

\[ [(A_m M^{n^+}), L]^{n^+} + [(A_m M^{n^+}), L]^{n^+} \]  

\[ \Rightarrow [(A_m M^{(n+1)^+}), L]^{(n+1)^+} + [(A_m M^{(n+1)^+}), L]^{(n+1)^+} \]  

Direct measurements of the equilibrium constant for Eq. (16), \( K_{\text{ML}} \), are usually not possible for metal–poly(pyridyl) complexes, but simple perturbation theory arguments can be used to generate useful estimates and trends. The ground state stabilization energy that results from M/L mixing is [17], \( \eta_{\text{t}} = H_{\text{ML}}/E_{\text{ML}} \), the destabilization of the MLCT excited state at its potential energy minimum is \( \eta_{\text{d}} = H_{\text{ML}}/E_{\text{ML}} \) (see Eqs. (3) and (4)). If \( K_{\text{el}} \) represents the strictly electrostatic contribution to \( K_{\text{DA}} \), and for \( \Delta K_{\text{exch}} \), the difference in exchange integral contributions (see Section 2.3.1) then Eq. (16) can be used.

\[ \text{RT} \ln K_{\text{DA}} = -\eta_{\text{t}} + \eta_{\text{d}} + \text{RT} \ln K_{\text{el}} + \Delta K_{\text{exch}} \]  

In view of these considerations, Eq. (9) has the form,

\[ h\nu_{\text{max}} = F\Delta E_{1/2} + \text{RT} \ln K_{\text{DA}} + \chi_{\text{reorg}}^{\text{ML}} + \Delta (\delta g_{\text{sol}}) \]  

Values of the reorganizational free energies in Eqs. 9 (or 17) can be referenced to the self-exchange bimolecular electron transfer processes in Eqs. (18) (for the limit in which there is very little electron delocalization),

\[ M^{(n+1)^+} + *M^{n^+} \Rightarrow M^{n^+} + *M^{(n+1)^+} \]  

\[ L + *L \Rightarrow L^- + *L \]  

(a) (the asterisk denotes a labeled species), \( \chi_{\text{reorg}}(M^{(n+1)^+}, M^{n^+}) \) and \( \chi_{\text{reorg}}(L, L^-) \), respectively; the reorganizational free energies can in principle be obtained from the activation free energies, \( \chi_{\text{reorg}}(X^+, X) = \chi_{\text{reorg}}^{X}(1/4) \Delta G_{X}^\phi \) of the reaction indicated [1–3,19,20]. Then,

\[ \chi_{\text{reorg}}^{X}(0) = \frac{1}{2}(\chi_{\text{reorg}}^{X} + \chi_{\text{reorg}}^{\text{A}}) \]  

2.3.1. General features of the exchange energy contributions

Measurements of all energy quantities mentioned contain some exchange energy contribution. Most discussions have presumed that these contributions are small compared with coulombic contributions; e.g., the ground state stabilization energy is a sum of coulomb and exchange terms, \( \eta_{\text{tot}} = [H_{\text{ML}}/E_{\text{ML}}] + K_{\text{DA}} \). At issue is how these exchange contributions affect the evaluation of delocalized electron density. The exchange energy stabilizes a closed shell system (i.e. the ground state, g) [23], destabilizes the singlet excited state (e) [23] and presumably stabilizes radical species (r1 and r2). The exchange integral itself is positive, and the contributions [quantities in brackets] may be written as follows for electrochemical measurements,

a) \( (M^+, L) + e^- \rightarrow (M, L), [-K_g + K_e] \)

b) \( (M, L) + e^- \rightarrow (M, L^-), [-K_{r2} + K_g] \)

c) \( F\Delta E_{1/2} \), \( [2K_g - K_{r2} - K_{r1}] \)

d) \( h\nu_{\text{max}}, [K_g + K_e] \)

e) \( \text{RT} \ln K_{\text{DA}}, [-K_{r1} - K_{r2} + K_g - K_e] \)

Thus, for a comparison of \( h\nu_{\text{max}} \) to \( F\Delta E_{1/2} \), these quantities differ in their exchange contributions by \( [K_g - K_e - K_{r1} - K_{r2}] \). Since the stabilization energy, \( \eta_{\text{d}} \), as discussed above is assumed to be related to a coulomb-like delocalization of charge, \( \Delta K_{\text{exch}} = [K_g - K_e - K_{r1} - K_{r2}] \) should be added to Eq. (17) when the terms in Eq. (16) are evaluated as coulombic contributions.

Eq. (17) may be rewritten as,

\[ h\nu_{\text{max}} \geq F\Delta E_{1/2} + \chi_{\text{reorg}}^{\text{ML}}(1 - 2x_{\text{ML}}) - \text{RT} \ln K_{\text{el}} + \Delta K_{\text{exch}} + \ldots \]  

for the electrochemical comparisons (using Eq. (16) in an estimate of RT ln \( K_{\text{DA}} \) \( \chi_{\text{reorg}}^{\text{ML}} \approx \chi_{\text{reorg}}^{\text{ML}}(1 + 2x_{\text{ML}}) \); this assumes that free energy quantities may be substituted for energy quantities in the perturbational correction terms.

3. Computational results and the assignment of MLCT transitions

3.1. 2.2′-bipyridine

Ab initio calculations have been performed at the HF/LANL2DZ level of theory [60] on the ligands configured for bidentate coordination. The calculations indicate that there are several ligand \( \pi^* \)-orbitals in a relatively small energy range. This is a necessary consequence of the fact that the two lowest energy \( \pi^* \)-orbitals of pyridine and pyrazine are correlated with the \( e_{2g} \) set of degenerate \( \pi^* \)-orbitals of benzene (Fig. 1). In one of each pair of orbitals both nodal planes orthogonal to the ring pass between the atoms; this is the \( \pi \)-type orbital. In the other orbital, one of the orthogonal nodal planes passes through two ring atoms; this is the \( \beta \)-type orbital.
The four lowest energy \( \pi^* \)-orbitals of 2,2\(^\prime\)-bipyridine (bpy) correspond to symmetric and antisymmetric combinations of \( \alpha \)- and \( \beta \)-type pyridine orbitals (Fig. 2; note that in bpy the orthogonal nodal planes of the component pyridine \( \beta \)-type orbitals do not pass through the nitrogen atoms). These combinations have \( a_2 \) and \( b_1 \) symmetry in \( C_2 \). Both of the lowest energy \( \pi^* \)-orbitals have \( b_1 \) symmetry; these orbitals can be represented as \( (\alpha/C_2)/a \) and \( (\beta/C_2)/a \) combinations of pyridine orbitals. It has long been recognized that the symmetric and antisymmetric combinations of pyridine \( \pi^* \)-orbitals are responsible for the dominant MLCT absorption features of ruthenium(II)/bipyridine complexes [61,62] but it has not been commonly recognized that the dominant observed, lowest energy transitions in involve the same combination (symmetric with respect to the \( \sigma_{zx} \) reflection) of the different \( (\alpha \) and \( \beta \)) pyridine \( \pi^* \)-orbital types. This situation arises because there is relatively little energy difference between the parent pyridine LUMO and LUMO+1 and there is more mixing between the \( \alpha \) than the \( \beta \) pyridine \( \pi^* \)-orbitals. The small difference in energy of these \( \pi^* \)-orbitals has important consequences in many polypyridine complexes.

3.2. 2,3-bis-(2-pyridyl)Pyrazine

The LUMO of pyrazine is an \( \alpha \)-type \( \pi^* \)-orbital, but this correlates with the LUMO+1 of dpp; in terms of the pyridine and pyrazine \( \pi^* \)-orbital types defined above, the LUMO+1 is the additive combination of the \( \alpha \)-type pyrazine \( \pi^* \)-orbital with \( \beta \) and \( \beta' \) orbitals from the pendant pyridines (Fig. 3) [18]. The LUMO of dpp \( (\beta+\alpha+\alpha') \) correlates with the \( \beta\pi^* \)-orbital of pyrazine. Owing to the py/pz mixing, the orbital coefficients are significant at the pyrazine moiety in the LUMO of dpp, but they have the opposite phase of the orbital coefficients at the nitrogens in the pz LUMO. This contrast in the nitrogen orbital phases could be important in the ligand mediated coupling of metals bridged by pz and dpp.

The [Ru(NH\(_3\))\(_4\)dpp]\(^{2+}\) complex has three strong MLCT absorptions in the UV–vis spectral region. The LUMO of dpp is implicated in the lowest energy transition and the LUMO+1 in the second lowest [18].

4. The effect of D/A configurational mixing on absorption and emission bandwidth

4.1. General considerations

Eq. (6) predicts an attenuation of bandwidth as D/A configurational mixing increases. The significance of bandwidth in limiting cases was addressed long ago by Hush in his discussion of mixed valence systems [19,20]. One expects a very narrow bandwidth in a completely delocalized system (i.e. for the normalized mixing coefficient \( \gamma_{DA} = (1/2)/\sqrt{2} \); roughly analogous to a \( \pi/\pi^* \) transition. More systematically, the bandwidth is related to the vibrational reorganization energy, \( \lambda_{\text{reorg}} \).
that is required to transform the nuclear coordinates of the vibrationally equilibrated excited state (energy $E_{DA}^{00}$) to the nuclear coordinates of the ground state, as in Eq. (21) for a gaussian absorption or emission band [3,19,20,63],

$$
\Delta v_{1/2} = \sigma + 4[K_B T \lambda_{\text{reorg}} \ln 2]^{1/2}
$$

(21)

In this expression, $\Delta v_{1/2}$ is the full width at half height, $\sigma$ is related to the standard deviation from the mean of the sum ($E_{DA}^{00} + \lambda_{\text{reorg}}$) under the conditions of measurement, and it is assumed that for all the vibrational modes that contribute to the displacement of the minima of the ground and excited states, $h v_{\text{vib}} < 4k_B T$. In order for a gaussian analysis to be applicable, the absorbance must be properly scaled. For this purpose, the absorption spectrum resulting from a single electronic transition may be fitted to, [64]

$$
e(v_{abs}) = \frac{8N_A \pi^3}{3000h^2 c v_{abs} \ln 10} n^3 H_{DA}^2 (\Delta \mu_{DA})^2 (FC)$$

(22)

where $FC = \Sigma_j F_j \exp[-E_{DA}^{00} - h v_{abs} + jh v_h + \lambda_s^2/4\lambda_s K_B T]$ and $F_j = S_j \exp(-S)/[4! (4\pi \lambda_s K_B T)^{1/2}]$ and $S = \lambda_h/h v_h$.

This equation is based on the assumption that a single high frequency vibration contributes to the excited state distortion, $\lambda_{\text{reorg}} = (\lambda_s + \lambda_h)$ with $\lambda_s < 4k_B T$ and $\lambda_h >$
4k_B T and ΔH_DA is the difference in ground and excited state dipole moments. Thus, a plot of $[\chi(v_{\text{abs}}) \times v_{\text{abs}}]$ versus $v_{\text{abs}}$ can be represented as a progression of gaussian components separated by $h\nu_B$ and with maxima at,

$$h\nu_{\text{max}}(j) = E_{DA}^\text{0} + \lambda_a + jh\nu_B$$  \hspace{1cm} (23)

The vibronic progressions are not well resolved in the ambient solution absorption or emission spectra of most Ru(II)–polypyridyl complexes since: (a) $\Delta V_{1/2}$ tends to be comparable to or larger than $h\nu_B$; (b) there is a distribution of solvates and $\sigma$ may be greater than zero; (c) several high frequency vibrational modes may contribute to the distortion [65] and their overlapping progressions may result in broadened absorption or emission band envelopes. Absorption spectra are further complicated in heavy metal complexes by the small energy differences between electronic states involving different metal orbitals, and some absorption band envelopes will contain more than one electronic component. Emission spectra are rarely complicated by multiple electronic components. In any event, the absorption or emission bandwidth is the most direct measure of the reorganizational energy $\lambda_a$; $\lambda_B$ can be inferred from vibronic progressions. The attenuation of reorganizational energies as represented in Eq. (6) is greatly simplified and idealized. For example, the attenuation of $\lambda_a$ and $\lambda_B$ with D/A mixing could be very different. Addressing these issues requires careful deconvolution of the absorption or emission band envelopes. Certainly, no meaningful conclusions can be based on approaches that disregard band-shape and component contributions.

4.2. Experimental observations

The scaled absorption spectrum of [Ru(NH_3)4bpy]^2+ is presented in Fig. 4. The non-gaussian shapes of the absorption envelopes of the two dominant MLCT bands clearly require at least four gaussian bands (two each) for a proper fit. The minor components, a and b in Fig. 4, are probably some combination of vibronic and electronic contributions. Similar gaussian analyses have been made for the absorption and the 77 K emission of several related bpy and dpp complexes [5,18]. The maxima and bandwidths of the first major components are summarized in Table 1. These gaussian components are interpreted in terms of Eq. (22) with $j = 0$; the values of the Huang–Rys parameter $S$ are obtained from the ratio of the intensity at the maximum of the first two principle gaussian components in the 77 K emission, and $h\nu_B$ is the energy difference between the maxima of these components. The parameters extracted in this analysis are most likely the convolution of several vibronic contributions: resonance Raman data for [Ru(NH_3)4bpy]^2+ indicate that there are several contributing high frequency modes (apparently 7 with $h\nu_B > 1000$ cm$^{-1}$) [65].

There is no particular trend in the ambient absorption or emission bandwidths with the transition energy. The ambient emission bandwidths are generally somewhat smaller than the absorption bandwidths, as expected [21] (Eqs. (8) and (9)), but electronic transitions convoluted into the absorption may contribute to this. On the other hand, $\chi_{\text{reorg}}$ has been estimated to be about $8 \times 10^3$ cm$^{-1}$ for [Ru(bpy)3]^2+ and about $9 \times 10^3$ cm$^{-1}$ for [Ru(NH_3)4bpy]^2+ [18]. This would make the observed absorption and emission bandwidths less than one-half of that based on $\chi_{\text{reorg}}$ consistent with Eqs. (8) and (9) and 5–10% electron delocalization. Similarly, the square of the ratio of ambient absorption and emission bandwidths can be combined with Eqs. (8) and (9) to estimate that $x_{\text{AD}}^2 \approx 0.17$ and $x_{\text{DA}}^2 \approx 0.078$ for [Ru(NH_3)4bpy]^2+. Based on the differences in the energies of the absorption maxima, this implies that $x_{\text{DA}}^2 \approx 0.09$ for [Ru(NH_3)4bpy]^2+.

One expects many of the solvent contributions to $\chi_{\text{reorg}}$ to be frozen out at 77 K [56]. The smaller values of $x_{\text{AD}}^2$ (about 26% of the ambient values) also contribute to smaller 77 K emission bandwidths than those observed in ambient fluid solution. Electroabsorption measurements suggest that $H_{\text{DA}} \approx 10 \times 10^3$ cm$^{-1}$ for Ru(II)/py MLCT absorptions [66]; a similar value for Ru(II)/bpy and Eq. (7) predicts very large broadband attenuation effects as $E_{\text{AD}}$ (or $h\nu_{\text{max}}$) approaches this value.

5. The Stokes shifts and electron exchange energy contributions

The singlet-triplet energy difference, $E_{\text{ST}}$, arises from a difference in exchange energies, and it may be estimated from the observations and parameters discussed above,

$$E_{\text{ST}} = h\nu_{\text{max}}(\text{abs}) - h\nu_{\text{max}}(\text{em}) - [\lambda_{\text{reorg}}^\text{DA} + \lambda_{\text{reorg}}^\text{AD}]$$

$$= 2\kappa_{\text{exch}}$$  \hspace{1cm} (24)

We have noted that the reorganizational energy for emission is generally smaller than that for absorption. The (deconvoluted; for transitions with $j = 0$) absorption and emission maxima are listed in Table 1, and the corresponding bandwidths enable us to estimate values of $\lambda_{\text{reorg}}^\text{H}$ (we assume that the sum of the reorganizational free energies, as defined in Eqs. (6)–(8), is equivalent to the sum of the reorganizational energies in Eq. (24)). This results in a value of $2\kappa_{\text{exch}} \approx (3.3 \pm 0.7) \times 10^3$ cm$^{-1}$ for [Ru(NH_3)4bpy]3^2+. However, the values of $\lambda_{\text{reorg}}$ used in this estimate are not exactly consistent with equations Eqs. (6)–(8); these equations, combined with $\lambda_{\text{reorg}}^\text{AD}$ imply that the absorption bandwidth should have
been about 25% larger than observed and $2K_{\text{exch}} \approx 2300$ cm$^{-1}$. These estimates compare well with a value of $2K_0 = 2800$ cm$^{-1}$ interpolated from values calculated for [Ru(NH$_3$)$_4$bpy]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ by Lever and Gorelsky [24].

The smaller than expected absorption bandwidth is more of a problem for [Ru(bpy)$_3$]$^{2+}$: the ambient absorption bandwidth is smaller than or equal to the ambient emission bandwidth (this is unique among the complexes that we have examined, and contrary to expectation (20% larger absorption bandwidth) based on Eqs. (7), (8) and (21) with $\sigma = 0$). We suspect that this is a consequence of the appreciable electronic delocalization that results from the configurational mixing between the three degenerate, localized Ru(III)/bpy$^-$ configurations in the Franck–Condon excited state. For [Ru(bpy)$_2$]$^{2+}$, $2K_{\text{exch}} \approx 2000$ cm$^{-1}$ based on the observed bandwidths, and $2K_{\text{exch}} \approx 500$ cm$^{-1}$ based on Eqs. (7), (8) and (21) and the emission bandwidth. The average of these values, $2K_{\text{exch}} = 1300 \pm 800$ cm$^{-1}$ is comparable to the value of $2K_{\text{exch}} = 1460$ cm$^{-1}$ that Lever and Gorelsky have calculated for [Ru(bpy)$_3$]$^{2+}$ [24]. These estimates indicate that there are substantial exchange energy contributions (less than or equal to 10% of the total) to the MLCT excited state energies. As noted above, the percentage contribution of exchange terms to the perturbational stabilization of the ground state should be about the same as the percentage contribution of exchange energies to the ground state-excited state energy difference. Coulomb terms, correlated with fractional electron delocalization, should dominate the ground state stabilization energy that results from ground state-excited state configurational mixing.

Fig. 4. Scaled absorption spectra of [Ru(NH$_3$)$_4$bpy]$^{2+}$ in water and acetonitrile ([absorbance] $\times \nu_{\text{obs}}$ vs. $\nu_{\text{obs}}$). The upper spectrum is the band envelope in water; the lower spectra include the results of a Gaussian fitting procedure. For these spectra, the heavy black line is the experimental absorption envelope, and the superimposed solid white line is the sum of the Gaussian fitting components. The Gaussian components (energies in cm$^{-1}$), $h\nu_{\text{max}}$ [Å$\nu_{\text{inc}}$] in H$_2$O: MLCT 1, 19 100 [2400]; MLCT 2, 27,400 [4400]; a, 20 800 [1870]; b, 23,100 [3400]. In CH$_3$CN: MLCT 1, 19 000 [2200]; MLCT 2, 27 400 [4200]; a, 20 800 [2100]; b, 23 400 [2700]. There are several minor components: at least some are electronic; from “unmixed” d$\pi$ orbitals.
The above analysis is based on a simple perturbation theory model involving two electronic states. The energies involved are relatively small, and we have already noted that these systems are probably too complicated for this to be rigorously correct. Other approaches to measuring some of the quantities discussed here seem to confirm this point. Photoacoustic and thermal lensing calorimetries have been used to make relatively direct estimates of the MLCT energy of [Ru(bpy)]$_2$$^{2+}$ [67,68]:

\[ E_{\text{MLCT}}^{0} = \Delta h v_{\text{abs max}} \approx \chi_{\text{reorg}}^{2} + 2 \chi_{\text{DA}}^{2} \]

This difference, \( \sim 600 \text{ cm}^{-1} \), is about one-third of the value for \( \chi_{\text{reorg}}^{2} \approx 1800 \text{ cm}^{-1} \) inferred from the emission bandwidth. The accumulated uncertainties (\( \sim 900 \text{ cm}^{-1} \)) are comparable to the discrepancy, clearly indicating that the available spectroscopic measurements involve energies that are too large to definitively address the size of \( E_{\text{ST}} \). However, the comparison does raise some important issues: (a) spin-orbit coupling in this complex is known to split the MLCT state into components, and the higher energy components have the largest emission efficiencies [69,70]. This would have the effect of subtracting a term, whose magnitude is probably in the range of 200–600 cm$^{-1}$, from the right-hand side of Eq. (26). (b) \( \sigma \) in Eq. (21) may not be small (the simplest assumption). If \( \sigma \) were to make a significant contribution to the bandwidth, then our estimates of \( \lambda_{\text{reorg}}^{2} \) would be too large, while our estimates of \( \chi_{\text{DA}}^{2} \) and \( 2 \kappa_{c} \) would be too small.

At present, the perturbation theory-two state model arguments used in most of this paper seem to provide the most consistent overall basis for dealing with the

\[ h v_{\text{max}}^{\text{emis}} \approx \lambda_{\text{reorg}}^{2} + 2 \chi_{\text{DA}}^{2} \]

Table 1
Spectroscopic parameters for some ammine–polypyridine ruthenium(II) and related complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>( h v_{\text{max}}^{\text{emis}} ) (( \Delta ))</th>
<th>( h v_{\text{abs max}}^{\text{emis}} ) (( \Delta ))</th>
<th>( \Delta h v_{\text{abs max}}^{\text{emis}} )</th>
<th>( \Delta h v_{\text{max}}^{\text{emis}} )</th>
<th>( \Delta h v_{\text{abs max}}^{\text{emis}} )</th>
<th>( \Delta h v_{\text{max}}^{\text{emis}} )</th>
<th>( S(\lambda_{\text{max}}^{\text{emis}}) )</th>
<th>( v_{\text{NH}}^{\text{emis}} )</th>
<th>( f ) (( \lambda_{\text{DA}}^{2} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NH$_3$)$_2$(bpy)$_2$][PF$_6$]$_2$</td>
<td>13.78</td>
<td>14.62</td>
<td>20.4</td>
<td>6.7</td>
<td>0.6</td>
<td>3357</td>
<td>3258</td>
<td>0.27</td>
<td>0.09</td>
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<td>[Ru(NH$_3$)$_3$(bpy)$_2$][PF$_6$]$_2$</td>
<td>16.2</td>
<td>17.2</td>
<td>21.7</td>
<td>5.5</td>
<td>0.9</td>
<td>3250</td>
<td>3328</td>
<td>0.27</td>
<td>0.078</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_6$][PF$_6$]$_2$</td>
<td>18.4</td>
<td>20.8</td>
<td>20.8</td>
<td>6.3</td>
<td>0.7</td>
<td>3250</td>
<td>3328</td>
<td>0.27</td>
<td>0.06</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_2$(bpy)$_2$][PF$_6$]$_2$</td>
<td>14.5</td>
<td>15.6</td>
<td>20.8</td>
<td>6.3</td>
<td>0.7</td>
<td>3250</td>
<td>3328</td>
<td>0.27</td>
<td>0.06</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$dpp][PF$_6$]$_2$</td>
<td>18.6</td>
<td>20.8</td>
<td>20.8</td>
<td>6.3</td>
<td>0.7</td>
<td>3250</td>
<td>3328</td>
<td>0.27</td>
<td>0.06</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$dpp][PF$_6$]$_2$</td>
<td>19.01</td>
<td>21.7</td>
<td>21.7</td>
<td>5.5</td>
<td>0.9</td>
<td>3357</td>
<td>3258</td>
<td>0.27</td>
<td>0.078</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$dpp][PF$_6$]$_2$</td>
<td>19.5</td>
<td>21.7</td>
<td>21.7</td>
<td>5.5</td>
<td>0.9</td>
<td>3357</td>
<td>3258</td>
<td>0.27</td>
<td>0.078</td>
</tr>
<tr>
<td>[Ru(NH$_3$)$_4$dpp][PF$_6$]$_2$</td>
<td>19.5</td>
<td>21.7</td>
<td>21.7</td>
<td>5.5</td>
<td>0.9</td>
<td>3357</td>
<td>3258</td>
<td>0.27</td>
<td>0.078</td>
</tr>
</tbody>
</table>

a Data from [18] except as indicated. Peak maxima and bandwidths of the first major component of a gaussian fit of the (corrected and scaled)absorption or emission using Grams 32. The tetraazamacrocyclic ligands are: MCL (1) = 1,4,8,11-tetraazacyclotetradecane (cyclam), MCL (2) = 5,12-neso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta).

b In DMSO–H$_2$O (1/1).

c Energy difference between the lowest energy principle absorption component and the highest energy emission component in the gaussian fit.

d Ratio of the intensities of the peak maxima of the first two principle components in a gaussian fit of the 77 K emission spectrum.

e In KBr pellet.

f \( f = [\Delta h v_{\text{abs max}}^{\text{emis}} - \Delta h v_{\text{max}}^{\text{emis}}] / [\Delta h v_{\text{max}}^{\text{emis}}] \).

g Based on components in a gaussian analysis of the emission. Several high frequency modes may be superimposed in the resolved gaussian component. Based on weighted average of \( v_{\text{NH}}^{\text{emis}} \).

h \( \lambda_{\text{DA}}^{2} \) based on bandwidth analysis for [Ru(NH$_3$)$_2$(bpy)$_2$]$^{2+}$ and corrected by means of the ratio of the squares of the absorption maxima for the other polypyridine complexes. Estimated from band envelope.

i From [72].

j \( \chi_{\text{DA}}^{2} \) based on parameters from [59].

k Macatangay, A.V., private communication and [72].
ambient spectroscopic observations. Future more sensitive experimental approaches may better define the limitations of this approach.

6. Shifts in spectator ligand vibrational frequencies as an indicator of delocalized charge

The N–H stretching frequency is very sensitive to cationic charge [71]; it is about 200 cm$^{-1}$ higher for [Ru(NH$_3$)$_6$]($\text{L}_n$)$_2^{2+}$ than for [Ru(NH$_3$)$_6$]$^{3+}$. The actual values of N–H stretching frequencies are also sensitive to the counterion in the solid-state salt [71]. The N–H stretching frequencies for the hexafluorophosphate salts of several ammine–polypyridyl complexes of ruthenium(II) are presented in Table 1. The shifts are very substantial. Previous work [59] has shown that there is relatively little electron delocalization in the cyanuro-thenates of rhodium and chromium complexes with tetraaza-macroyclic ligands, [M(III)(MCL)(CN)Ru-(II)(NH$_3$)$_3$)$_2$]$^{3+}$; about 3.5%/Ru for M = Cr and about 0.3%/Ru for M = Rh. The PF$_6^-$ salts of these complexes [72] are probably good comparisons to the N–H stretching frequencies of NH$_3$ coordinated to Ru(II) in the polypyridyl complexes. For convenience in this discussion, we define a parameter $0 \leq f \leq 1$,

$$f = \frac{[v_{\text{NH}}(\text{Ru(II)})]_{\text{ref}} - v_{\text{NH}}(\text{sample})}{[v_{\text{NH}}(\text{Ru(II)})]_{\text{ref}} - v_{\text{NH}}(\text{Ru(III)})]}$$

This parameter increases as the energy of the lowest energy MLCT component decreases, qualitatively as one would expect for significantly increasing delocalization of charge with D/A mixing in the series of Ru(II)–amine–polypyridyl complexes. Of course, the charge delocalized can never exceed 0.5, the dependence of $f$ on $\sigma_{DA}$ is bound to be complicated and the uncertainties are substantial. Nevertheless, figure 5 illustrates that the N–H stretch shifts significantly in the direction expected, and that the stretching frequencies are lowest for those complexes for which we infer the largest amount of delocalized charge. The substantial shifts imply substantial charge delocalization. A line of the least slope (illustrated in Fig. 5) that passes within the estimated error limits of $f$ is consistent with our inferences for $\sigma_{DA}$ if it is equal to $f$.

7. Conclusions

The work summarized here has used a variety of experimental and theoretical approaches to address some basic issues in the excited state properties of polypyridyl complexes of ruthenium(II).

a) Ab initio calculations have shown that both of the two lowest energy $\pi^*$-orbitals of the ligands contribute to the MLCT transitions observed in the UV–vis spectral region. The two lowest energy MLCT transitions of [Ru(NH$_3$)$_3$bpz]$^{2+}$ correspond to symmetric combinations of the two lowest energy $\pi^*$-orbitals of the constituent pyridine moieties. The LUMO of coordinated dpp correlates with the LUMO$+1$ of pyrazine, and the orbital coefficients at the nitrogen atoms of this LUMO are antisymmetrically related. This suggests that bridging ligand properties of dpp may not be a simple combination of those of pyrazine, slightly modified by pyridine.

b) The reorganizational energies inferred from gaussian bandshape analyses, combined with the ambient Stokes shifts imply that the excited state electron exchange energy, $K_{\text{exch}}$, is reasonably significant.

c) The trend of the N–H stretching frequencies of coordinated ammonia with MLCT transition energies suggests that the large mixing coefficients in these complexes are associated with substantial charge delocalization in the ground state.

d) The emission and absorption bandwidths are about half of those expected in the limit of no metal/ligand mixing. There is some indication that the band-
widths decrease as the transition energy decreases. This can be discussed in terms of the perturbational shifts of the excited and ground state potential energy surfaces because of metal/ligand mixing.

e) The attenuation of reorganizational energies with metal/ligand mixing is also a factor in optical/electrochemical comparisons.

Acknowledgements

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References


