Inorganic Chemistry

Communication

Observations on the Low-Energy Limits for Metal-to-Ligand Charge-Transfer Excited-State Energies of Ruthenium(II) Polypyridyl Complexes

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The 77 K emission spectral maxima of bis(bipyridine)ruthenium(II) complexes are found to approach a limit at energies below about 14 000 cm^{-1}. There is also evidence for related low-energy excited-state limits in some other classes of ruthenium polypyridyl complexes. The shapes of the vibronic sidebands found in these limits differ from those of complexes that emit at higher energies. These low-energy excited states are not simple "charge-transfer" excited states and are analogous to $\pi\pi^*$ excited states. The observations are consistent with effective ground state/excited state mixing matrix elements in the range of $(5-10) \times 10^3$ cm^{-1} for ruthenium polypyridine complexes.

The lowest-energy electronic excited states of $[M(L)_{6-2n}(PP)_n]^{n+}$ complexes with polypyridyl (PP) ligands are facile electron-transfer donors in a variety of processes.[1-6] Such electron-transfer reactivity depends on the differences in the energies and molecular geometries between the excited states and their ground states, and these are generally inferred from various measurements on the respective ground-state complexes and/or different levels of computational modeling. However, the energies ($E_{ge}^{0'0}$) of the lowest-energy metal-to-ligand charge-transfer (MLCT) excited states are generally difficult to determine: (1) the lowest-energy absorption bands of bis(bipyridine) complexes contain overlapping electronic origins, and only the weak lowest-energy-resolved contribution, MLCT$_{lo}$, is related to the HOMO → LUMO transition;[7] (2) observed ambient absorption maxima contain unresolved contributions from vibronic sidebands;[8-10] (3) the MLCT emissions of many complexes fall in the near-IR (NIR) range, and their determination requires somewhat specialized detectors;[8-10] (4) estimates of $E_{ge}^{0'0}$ based on electrochemical oxidations and reductions ($F\Delta E_{1/2}$) assume that $E_{ge}^{0'0} \approx -F\Delta E_{1/2}$, whereas a recent examination of the relationship between absorption spectra and $F\Delta E_{1/2}$ of $[Ru(L)_2(bpy)_2]^{m+}$ complexes (for a wide range of ancillary ligands L) has shown that for the MLCT$_{lo}$ component (and for calculated HOMO → LUMO transitions) $\phi \approx 0.7$[7] in correlations such as

$$h\nu_{\max}(\text{abs}) \approx -\phi F\Delta E_{1/2} + \lambda + S \quad (1)$$

(λ is a nuclear reorganizational energy,[11-13] and S represents entropic, electrostatic, and other contributions).[14] The observation that ϕ is significantly smaller than 1.0 in eq 1 can be attributed to a relative decrease of excited-state charge-transfer character as a consequence of ground-state/excited-state configurational mixing and suggests that, at sufficiently low energies, MLCT excited states will approach a limit that is nearly independent of $F\Delta E_{1/2}$.[7] While the inference of a low-energy limit based on currently available absorption spectra and eq 1 is equivocal, such low-energy MLCT excited-state limits are more clearly manifested in the emission energies of the same complexes.

Equation 1 is based on simple models for the limit of weak donor and acceptor mixing $|H_{DA}/E_{ge}^d|^2 < 0.1$, where H_{DA} is an effective mixing matrix element and E_{ge}^d is the vertical energy difference between the ground and excited states in the absence of such configurational mixing.[15-17] However, excited states in systems in which $|H_{DA}/E_{ge}^d|^2 > 0.1$ may approach a delocalized limit that is not appropriately treated

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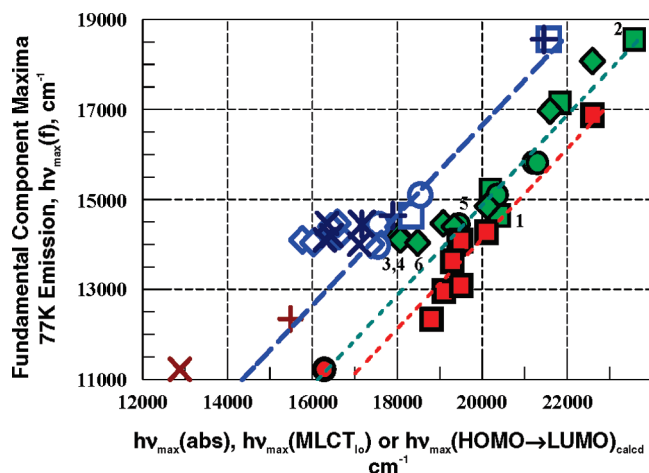
Figure 1. Relationships between ambient MLCT absorption maxima and the fundamental components of the 77 K emissions of ruthenium(II) bis- and mono(bipyridine) complexes. The red and green points are for the maxima of the observed MLCT absorption bands, $h\nu_{max}(abs)$, for $[Ru(L)_4bpy]^{m+}$ and $[Ru(L)_2(bpy)_2]^{m+}$, respectively; the open blue points are for the resolved lowest energy (MLCT$_{lo}$) contributions to the lowest-energy absorption bands.[7] For the squares, $m = +2$, circles, $m = +1$, and diamonds, $m = 0$. The respective $h\nu_{max}$ values calculated by time-dependent density functional theory for the HOMO → LUMO transitions[7] (with ground-state coordinates) are indicated by +, *, and ×. The dashed lines are drawn with slopes of 1.0. For details, see Figure S1 in the Supporting Information, SI.[23] The absorption and emission measurements were performed in the same solvents (ethanol/methanol or butyronitrile). The numbers are for complexes whose vibronic sidebands are shown in Figure 2.

as a simple charge-transfer excited state.[18] For $|H_{DA}/E_{ge}^d|^2 >$ 0.1, the transition energy for a two-state system should vary qualitatively as

$$h\nu_{max}(abs) \approx [(E_{ge}^d)^2 + 4(H_{DA})^2]^{1/2} \qquad (2)$$

The effective values of H_{DA} for ruthenium(II) polypyridyl complexes have been estimated from a range of studies to be about $(5-10) \times 10^3$ cm^{-1},[19-22] and this suggests very significant departures from simple correlations when $h\nu_{max}(MLCT) < \sim 14 \times 10^3$ cm^{-1} for these complexes. The absorption and emission maxima for a two-state system can be represented as

$$h\nu_{max}(abs) \approx E_{ge}^{0'0} + \lambda$$

$$h\nu_{max}(emis) \approx E_{ge}^{0'0} - \lambda' - 2K_{exch} \qquad (3)$$

where K_{exch} is an exchange energy contribution and the primes allow for any differences in the corresponding parameters. Thus, for the emission, E_{ge}^d in eq 2 should be replaced with $E_{eg}^d \approx E_{ge}^{0'0} - 2K_{exch} - \lambda - \lambda'$, consistent with the 4000−7000 cm^{-1} lower energies of the emission than the absorption

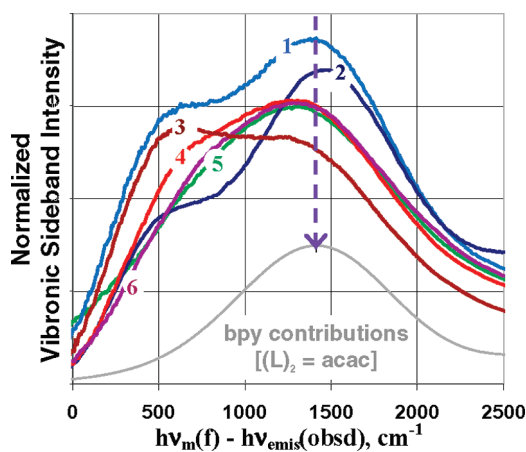(18) Ferretti, A.; Lami, A.; Villani, G. *Inorg. Chem.* **1998**, *37*, 2799.
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Figure 2. Comparison of the emission sidebands of $[Ru(L)_2(bpy)_2]^{m+}$ complexes with $(L)_2 = (NH_3)_2$, 1; $(CH_3CN)_2$, 2; CO_3^{2-}, 3; malonate, 4; acac$^-$, 5; oxalate, 6. The vibronic sidebands are the differences between the observed 77 K emission spectra and the fitted fundamental components as described previously[8-10] and illustrated in Figure S3 in the SI.[23] The vibronic sideband spectra are normalized with respect to the integrated emission intensity; note that correcting for the low-frequency vibronic contributions ($\sim$500 cm^{-1}) would bring the medium-frequency amplitude of 4 closer to those of 3, 5, and 6.

maxima of these complexes.[9,10] Figure 1 shows that the emission energies approach a limiting value more clearly than do the MLCT absorption energies. These observations are consistent with eq 2, the expected differences in the absorption and emission energies and large values for the effective mixing matrix elements.

The differences between the absorption and emission behavior have several sources: (1) $E_{ge}^d > E_{eg}^d$; (2) it is likely that K_{exch} is different in the diabatic and highly delocalized limits; (3) $h\nu_{max}(f)$ is an estimate of $E_{eg}^{0'0}$.[8-10] The principal uncertainties in $h\nu_{max}(f)$ arise when the bandwidths are very large (fwhh > $\sim$900 cm^{-1})[9] and/or there are significant sideband contributions from low-frequency vibrational modes, which can lead to overestimates of $h\nu_{max}(f)$.[9,10] Uncertainties can also arise in correlations of $h\nu_{max}(abs)$ when the vibronic sideband contributions to the ambient spectra[7,8] vary from complex to complex and when the absorption spectra are strongly solvent-dependent (see Figure S2 in the SI).[23] These uncertainties do not seem to be systematic in the excited-state energies: they are important for some complexes in all regions of Figure 1. The horizontal displacements of the red and green data points correspond to the differences between the calculated maxima of the HOMO → LUMO transitions in Figure 1 and the observed absorption maxima.[7]

The emission bandshapes of the complexes vary systematically with the excited-state energies (see Figure S3 in the SI):[23] (1) for $h\nu_{max}(abs) > \sim 19\,000$ cm^{-1}, the vibronic sidebands arising from medium-frequency ($\sim$bpy) modes decrease systematically with excited-state energies by at least 2-fold over the range used in Figure 1;[8-10] (2) the amplitudes of medium-frequency sidebands vary less with $h\nu_{max}(abs)$ when it is less than $\sim 19\,000$ cm^{-1} (Figure 2), and there appears to be a tendency of vibronic sideband contributions in the 1000−1200 cm^{-1} range to become more important for the lower-energy excited states. A detailed analysis of

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variations in the bandshapes is complicated by the electronic mixing between different excited states, each of which has a different set of characteristic distortion modes (e.g., resulting in different vibronic amplitudes near 500 cm^{-1}; see Figure 2).[8-10] The vibronic envelope that results from distortions in the bpy vibrational modes is estimated for [Ru(acac)(bpy)$_2$]$^+$ in Figure 2 based on resonance Raman parameters reported[25] for [Os(bpy)$_3$]$^{2+}$;[9,26] the vertical dashed arrow indicates its energy maximum.

The values of $-F\Delta E_{1/2}$ for the [Ru(L)$_2$(bpy)$_2$]$^{m+}$ complexes with $h\nu_{max}$(abs) $\leq 19\,000$ cm^{-1} also decrease monotonically[7] in the region where values of $h\nu_{max}(f) \sim 14\,000$ cm^{-1}, suggesting that ϕ in eq 1 decreases appreciably at low excited-state energies; however, the complexes L = CN$^-$ and NO$_2^-$ do not correlate well with the other complexes for which $h\nu_{max}$(abs) $> 19\,000$ cm^{-1} (Figure S4 in the SI),[23] possibly because of their relatively large bandwidths (fwhh $> \sim 10^3$ cm^{-1}) and/or to their sensitivity to the solvent and the different solvents used in their spectroscopic and electrochemical measurements.

Preliminary observations indicate closely related behavior for ruthenium(II) complexes containing 2,3-bis-(pyridyl)pyrazine with a smaller limiting emission energy ($\leq 10\,000$ cm^{-1}); Figure S4 in the SI.[23]

These observations indicate that the nominally MLCT excited states of many ruthenium(II) polypyridyl complexes tend to be highly delocalized with little charge-transfer character when their absorption and emission energies approach or are in the NIR region. As a consequence, the electron-transfer reactivity of such excited states is not readily extrapolated from that of complexes with higher-energy MLCT excited states.

Supporting Information Available: Details for Figure 1, solvent-dependent absorption maxima, comparisons of 77 K emission spectra, and emission spectral/electrochemical correlations. This material is available free of charge via the Internet at http://pubs.acs.org.

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