

## Electrochemical and Spectral Probes of Metal/Ligand Orbital Mixing in $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$ and $\text{Ru}(\text{NH}_3)_4(\text{phen})^{2+}$

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An electrochemical variational method (de la Rosa, et al. *Inorg. Chem.* **1985**, *24*, 4229) has been used to examine experimentally the extent of metal/ligand orbital mixing and electronic coupling in complexes of the type  $\text{Ru}^{\text{II}}(\text{NH}_3)_4\text{L}^{2+}$  (L = 2,2'-bipyridine or 1,10-phenanthroline). From the experiments, strong localization of  $d\pi$  electrons at the ruthenium metal center is indicated. Nevertheless, some mixing of  $d\pi(\text{Ru})$  and  $\pi^*(\text{bpy}; \text{phen})$  is detected, implying a significant degree of delocalization (ca. 25%). These results differ substantially from those derived from metal-to-ligand charge-transfer (MLCT) oscillator strength measurements. The latter indicate less than 2% delocalization. The difference is particularly surprising in view of the fact that both approaches derive from Mulliken charge-transfer theory and the two are employed at similar (but not identical) levels of approximation. The origin of the discrepancies is unclear, but may be related to the choice of charge-transfer distance which must necessarily be made in the optical analysis. Independent estimates of electronic delocalization, based on partial oxidation-state markers in vibrational Raman spectra, corroborate the electrochemical findings.

### Introduction

Donor/acceptor orbital mixing and closely related concepts such as electronic resonance and initial-state/final-state electronic coupling are of considerable importance in charge-transfer-based chemical reactions. For example, they play major roles in determining (1) thermal electron-transfer probabilities (adiabaticity),<sup>1</sup> (2) optical charge-transfer probabilities (oscillator strengths),<sup>2</sup> (3) charge-transfer excited-state lifetimes,<sup>3</sup> and (4) charge or valence localization and delocalization.<sup>4</sup> A convenient and simple theoretical representation of the donor/acceptor orbital mixing problem is Mulliken's perturbation analysis.<sup>2</sup> In this analysis the true initial and final electronic states ( $\Psi_i$  and  $\Psi_f$ ) are written as linear combinations of zeroth-order states (i.e. valence-localized states,  $\Psi_1$  and  $\Psi_2$ ):

$$\Psi_i \approx a\Psi_1 + b\Psi_2 \quad (1a)$$

$$\Psi_f \approx b\Psi_1 - a\Psi_2 \quad (1b)$$

$$\rho = b/a \quad (2)$$

Note that in this formulation the extent of mixing is given simply by the ratio of wave function coefficients ( $\rho$ ). Thus  $\rho$  is unity when mixing is complete and zero when it is completely absent. Furthermore, in the limit of small overlap ( $S_{12} \ll 1$ ; eq 3), the squares of the coefficients themselves describe directly the fractional distributions of charge at the donor and acceptor sites.

$$a^2 + b^2 \pm 2abS_{12} = 1 \quad (3)$$

The most common experimental approach to the assessment of mixing parameters ( $a$ ,  $b$ , and  $\rho$ ) is to determine charge-transfer oscillator strengths ( $f$ ) from optical absorption spectra. If the charge-transfer dipole length is known and if  $S_{12}$  is not too large, then it is a simple matter to extract  $a^2$  and  $b^2$  from an integrated spectrum (see below).<sup>2</sup> The spectral approach can be difficult to implement, however, if there exist multiple, overlapping electronic transitions. A further problem is the known inadequacy of the analysis for strongly coupled systems.<sup>2</sup> More recently, evidence has begun to appear which calls into question the quantitative validity of the spectral analysis even for moderately coupled systems.<sup>5</sup>

Recently, an alternative approach, based on electrochemical methods, has been developed.<sup>6</sup> The essence of this approach experimentally is to introduce an electrochemically significant

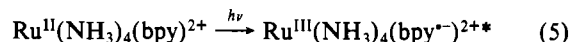
structural or environmental change at the nominal donor site and then to track the redox response at the acceptor (or vice versa). Curtis and co-workers have shown that, in the limit of small  $S_{12}$  (see below),  $\rho$  can be readily derived from the slope ( $m$ ) of a plot of acceptor (or donor) formal potential ( $E_2$ ) versus donor (or acceptor) potential ( $E_1$ ):

$$\partial E_2 / \partial E_1 = m = \rho^2 = b^2 / a^2 \quad (4)$$

Equation 4, as written, applies to the case where the perturbation is introduced at the donor site (1) and followed at the acceptor site (2).

Thus far, the electrochemical method has been applied to only a few chemical systems;<sup>6,7</sup> all consist of inorganic (metal complex) donors and acceptors bridged by difunctional organics. In the initial studies, Curtis and co-workers found good agreement between their electrochemical results and currently accepted<sup>8,9</sup> experimental descriptions of orbital mixing and electronic structure for the chemical systems in question (Creutz-Taube ion analogues).<sup>6</sup> By inference, however, there was disagreement between the electrochemical results<sup>6</sup> and optically derived (oscillator strength) results.<sup>10</sup> More specifically, the electrochemical experiment indicated appreciably stronger electronic coupling and appreciably greater orbital mixing for the nominal donor and acceptor sites than did the spectral experiment.

In view of the remarkable simplicity and apparent success of the electrochemical approach, we have been interested in applying and testing it with other types of charge-transfer systems. We report here an electrochemical study of metal/ligand orbital mixing in two closely related systems,  $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$  (bpy = 2,2'-bipyridine) and  $\text{Ru}(\text{NH}_3)_4(\text{phen})^{2+}$  (phen = 1,10-phenanthroline). Our interest in these particular systems stems, in part, from an earlier study of Franck-Condon effects (vibrational reorganization) accompanying MLCT excitation (eq 5) in  $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$ .<sup>11</sup>



As suggested by eq 4, we find (by the electrochemical method) strong localization of  $d\pi$  electrons at the ruthenium metal center in the ground electronic configuration. Nevertheless, some mixing of  $d\pi(\text{Ru})$  and  $\pi^*(\text{bpy}; \text{phen})$  orbitals is detected, leading to a significant degree of electronic delocalization (ca. 25%). Perhaps, more importantly, the degree of mixing detected is several times greater than implied by oscillator strength measurements. An independent spectroscopic measurement, however, supports the electrochemical findings. These results, together with possible

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(3) See, for example: Meyer, T. J. *Pure Appl. Chem.* **1986**, *53*, 1193.

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(6) de la Rosa, R.; Chang, P. J.; Salaymeh, F.; Curtis, J. C. *Inorg. Chem.* **1985**, *24*, 4229.

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explanations for the discrepancies, are presented in the following sections.

### Experimental Section

**Materials.** The following solvents were commercially acquired and used as received: acetonitrile (AN), propylene carbonate (PC), acetone (AC), formamide (FA), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and benzonitrile (BN). Tetraethylammonium perchlorate (TEAP) was purchased from GFS Chemicals and used as received.

$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  was prepared by adding solid  $\text{NH}_4\text{PF}_6$  to a stirring aqueous solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  purchased from GFS Chemicals.

$[\text{Ru}(\text{NH}_3)_4(\text{bpy})](\text{PF}_6)_2$  and  $[\text{Ru}(\text{NH}_3)_4(\text{phen})](\text{PF}_6)_2$  were prepared by the method of Curtis and co-workers<sup>12</sup> and purified as outlined by Doorn and Hupp.<sup>11</sup> Since these are well-characterized compounds, purity was judged chiefly by electrochemistry and UV-vis absorption spectroscopy. We note that the former is fairly sensitive for the detection of unwanted  $\text{Ru}(\text{NH}_3)_2\text{L}_2^{2+}$  as well as various oxo-bridged ruthenium-amine impurities.

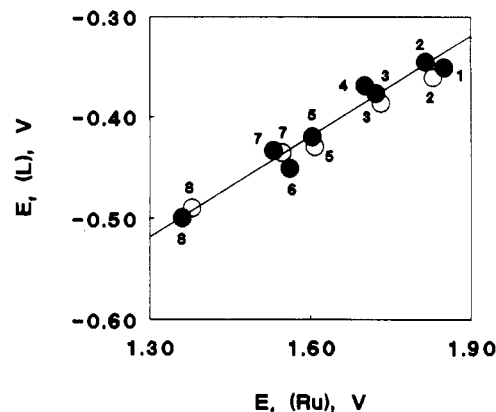
**Measurements.** Formal potentials ( $E_f$ ) were obtained primarily by cyclic voltammetry by using either a PAR 174A or 264 A polarographic analyzer and a Houston Omnigraphic 2000 X-Y recorder. Some of the voltammetry peaks, however, were partially obscured by electrochemical oxidation or reduction of the solvent. In those cases, differential-pulse voltammetry (PAR 174A) was employed. The working electrode in all cases was a glassy-carbon disk. The counter electrode was a platinum wire. A saturated (NaCl) calomel electrode was employed as a reference. The electrochemical cell was a two-compartment cell of conventional design. The supporting electrolyte in all experiments was 0.1 M TEAP. The concentration of the metal complex was typically about 1 mM. In a few cases, however, concentrations as high as 5 mM were required in order to resolve electrochemical peaks adequately.

In order to facilitate comparisons of formal potentials obtained in different solvents and to avoid complications associated with liquid-junction effects, an internal reference redox couple<sup>13</sup> was employed. The couple chosen was  $\text{Ru}(\text{bpy})_3^{2+/+}$ —a ligand-based redox couple. Our reasoning in choosing this system as a redox standard was 2-fold. First, we anticipated (on the basis of the available electrochemical<sup>14</sup> and spectroscopic<sup>15</sup> charge-transfer data) that this couple would display an approximately solvent-independent  $E_f$ . Second, and more importantly,  $\text{Ru}(\text{bpy})_3^{2+}$  should effectively mimic the  $\text{Ru}(\text{NH}_3)_4\text{L}^{2+}$  species with regard to charge and chemical identity of the reduction site. Consequently, any undesirable residual redox effects associated, for example, with solvent-variable ion-pairing or with specific solvation at the bpy (or phen) site of the sample would tend to be compensated by the reference. In the  $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$  experiments,  $\text{Ru}(\text{bpy})_3^{2+}$  was added directly to the sample cell. In the  $\text{Ru}(\text{NH}_3)_4(\text{phen})^{2+}$  experiments, however, interferences sometimes occurred. Consequently, both the sample and reference were separately measured (in each solvent) versus ferrocenium/ferrocene; the resulting formal potentials for  $\text{Ru}(\text{NH}_3)_4(\text{phen})^{3+/2+/+}$  were then converted to the  $\text{Ru}(\text{bpy})_3^{2+/+}$  scale.

Visible-region absorption spectra for  $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$  in acetonitrile, DMF, and DMSO as solvent were obtained with matched 1-cm cells by using a Perkin-Elmer 330 spectrophotometer.

### Results

In order to implement the orbital-mixing analysis (eqs 1–3), we require electrochemical data for a two-site system ( $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{n+}$  or  $\text{Ru}(\text{NH}_3)_4(\text{phen})^{n+}$ ) in which one site is systematically perturbed. In previous work,<sup>6</sup> the perturbation has been introduced via ligand substituents (i.e., a series of compounds containing ligands of varying electron-donating or electron-withdrawing strength has been employed). In the present study,<sup>7</sup> we have taken advantage of the known strong hydrogen-bond-donating (electron-pair-accepting) ability of the coordinated amine ligands to introduce a more subtle variation: Following previous work from our own laboratory<sup>7,16</sup> and elsewhere,<sup>17</sup> we



**Figure 1.**  $E_f(\text{Ru}^{3+/2+})$  vs  $E_f(\text{L}^{0/-})$  in various solvents: filled circles, L = bpy; open circles, L = phen. Key to solvents: (1) acetonitrile; (2) propylene carbonate; (3) acetone; (4) formamide; (5) *N,N*-dimethylformamide; (6) *N,N*-dimethylacetamide; (7) dimethyl sulfoxide; (8) hexamethylphosphoramide.

varied  $(\text{NH}_3)_4\text{Ru}^{\text{III/II}}$  potentials by systematically varying the hydrogen-bond-accepting (electron-pair-donating) ability of the solvent. This then permitted a single chemical compound (instead of a series) to be used in each electrochemical investigation of metal/ligand coupling.

Figure 1 presents  $E_f$  data for  $\text{Ru}(\text{NH}_3)_4\text{L}^{2+/+}$  (ligand based) versus  $\text{Ru}(\text{NH}_3)_4\text{L}^{3+/2+}$  (metal based) in nine solvents. As noted in the Experimental Section, the potentials are plotted versus  $\text{Ru}(\text{bpy})_3^{2+/+}$  as an internal electrochemical reference. In the plot we observe nearly identical behavior for L = bpy and L = phen. Indeed, for both systems the formal potentials change significantly and systematically as the solvent is changed. Thus  $E_f$  increases (shifts positively) as the solvent basicity (in a Lewis sense) decreases. More importantly, the values for  $E_f(2+/1+)$  (the unperturbed site) track those for  $E_f(3+/2+)$  (the perturbed site).<sup>18</sup> The slope of the plot (for either complex) is  $0.34 \pm 0.02$ .

Analysis of the slope (in the limit where  $S_{12} = 0$ ) leads to a value of  $0.58 \pm 0.02$  for the mixing parameter,  $\rho$ . If we impose the additional condition that  $a^2 + b^2$  equal unity (eq 3), then we find (for both systems)  $a^2 = 0.75$  and  $b^2 = 0.25$  (or  $a = 0.86$  and  $b = 0.5$  in eq 1). In other words, significant metal/ligand orbital mixing exists and fully 25% of an electronic charge has already been effectively redistributed from  $d\pi$  (ruthenium) to  $\pi^*$  (bpy or phen) in the electronic ground state.<sup>19</sup>

An alternative measure of mixing is available from metal-to-ligand charge-transfer (MLCT) absorption spectra. The absorption data can be used to determine both the oscillator strength,  $f$ , and the transition moment,  $\mu$ , via the following:<sup>2,20</sup>

$$f \approx (4.6 \times 10^{-9}) \epsilon_{\text{max}} \nu_{1/2} \quad (6)$$

$$\mu = [f / (1.085 \times 10^{-5}) \nu_{\text{max}}]^{1/2} \quad (7)$$

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(18) We note here that  $\rho$  can also be determined by varying  $E(2+/1+)$  and observing changes in  $E(3+/2+)$ .  $E(2+/1+)$  is perturbed by changing the substituents of L. For  $\text{Ru}(\text{NH}_3)_4\text{L}^{3+/2+/+}$  (L = 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, 5-amino-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline) in DMSO, a plot of  $E(3+/2+)$  vs  $E(2+/1+)$  has a slope of 0.46. From the slope,  $\rho$  is estimated as 0.68 and  $a^2$  as 0.68, in fair agreement with the results derived from metal-centered perturbation (Figure 1).

(19) Expressed in this way, it is clear that the putative mixing measurement could equally well be described as a quantitative metal-ligand back-bonding measurement. This perspective clarifies at least some of the assumptions inherent to the electrochemical analysis. The two most important ones are that Ru(III) does not contribute significant electron density (via back-bonding) to neutral bpy or phen and likewise that bpy and phen radical anions do not accept significant  $d\pi$  electron density from Ru(II).

Table I. Spectral Data and Calculated Parameters (Mulliken Analysis)

solvent	$\epsilon_{\max}$ , M <sup>-1</sup> cm <sup>-1</sup>	$\nu_{1/2}$ , cm <sup>-1</sup>	$\nu_{\max}$ , cm <sup>-1</sup>	$f^a$	$\mu^b$	$B^c$ , cm <sup>-1</sup>	$\Delta$ , cm <sup>-1</sup>	$\rho^d$
acetonitrile	3410	3200	19 120	0.050	0.49	2284	18 520	0.12
DMF	3740	3300	18 120	0.057	0.54	2350	17 440	0.13
DMSO	3480	3300	17 830	0.053	0.52	2240	17 200	0.13

<sup>a</sup> Calculated from eq 6. <sup>b</sup> Calculated from eq 7. <sup>c</sup> Calculated from eqs 8 and 7. <sup>d</sup> Calculated from eq 10.

In the equations,  $\epsilon_{\max}$  is the extinction coefficient (M<sup>-1</sup> cm<sup>-1</sup>),  $\nu_{1/2}$  is the absorption bandwidth at half-height (cm<sup>-1</sup>), and  $\nu_{\max}$  is the energy of the transition at the absorption maximum (cm<sup>-1</sup>).

The transition moment is also given by<sup>2,20</sup>

$$\mu = 2^{1/2}BR/\Delta \quad (8)$$

where  $\Delta$  is the excited-state/ground-state separation energy,  $B$  is the interaction energy, and  $R$  is the transition dipole length in angstroms. (In our calculations  $R$  was taken as 2.84 Å, the crystallographically determined distance from the metal center to the center of bipyridine in Ru(bpy)<sub>3</sub><sup>2+</sup>.<sup>21</sup>)

In the limit where  $\Delta^2/4 \gg B^2$ , the absorption maximum is given approximately by<sup>2,20</sup>

$$h\nu_{\max} = \Delta + 2B^2/\Delta \quad (9)$$

It can further be shown that

$$\rho = -B/\Delta \quad (10)$$

With this in mind, absorption spectra were collected for Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup> in three solvents: CH<sub>3</sub>CN, DMF, and DMSO. Table I lists the relevant spectral parameters. Insertion of these into eqs 6 and 7 leads to estimates for  $f$  and  $\mu$  (Table I). Values for  $B$  and  $\Delta$  were then obtained by simultaneously solving eqs 8 and 9. Insertion of these into eq 10 yields  $\rho = 0.13$ . From eq 4 the values for  $a^2$  and  $b^2$  are then 0.02 and 0.98, implying virtually complete localization of the transferring electron on ruthenium in the electronic ground state.

## Discussion

Surprisingly, the results of the two methods differ considerably. The electrochemical approach indicates substantial mixing of zero-order states and therefore significant electronic delocalization, whereas the spectral method suggests that the system is almost completely localized. This is especially puzzling in view of the fact that both analyses derive from Mulliken theory and that the two are used at similar (but not identical) levels of approximation. We are forced, therefore, to one (or both) of the following conclusions: (1) the two experiments measure different quantities or (2) one (or both) of the methods gives quantitatively incorrect results.

The possibility that *significantly* different quantities are being measured seems remote.<sup>22</sup> One might expect a slightly smaller  $\rho$  value from an optical experiment because of a slightly larger initial-state/final-state energy gap, but the effect should be slight. To elaborate, in the optical experiment  $h\nu_{\max}$ , strictly speaking,

must contain contributions not only from  $B$  and  $\Delta$  (see eq 9) but also from solvent and internal reorganization (Franck-Condon) terms. In the electrochemical experiment, on the other hand, these terms are absent, since the system is evaluated in a vibrationally relaxed form. A reasonable guess for the magnitude of the MLCT reorganization energy in Ru(NH<sub>3</sub>)<sub>4</sub>L<sup>2+</sup> would be  $\sim 2500$  cm<sup>-1</sup> ( $\sim 0.28$  eV).<sup>11,23</sup> Assuming  $B$  remains unchanged, diminution (hypothetically) of  $\Delta$  by this amount would lead to an increase in  $\rho$  of only about 10–15%. Clearly, this is insufficient to reconcile the optical and electrochemical findings.

Evaluation of the second hypothesis (i.e., that one or both methods give incorrect results) requires a reliable independent measure of valence or charge localization. One approach that has gained acceptance is variable oxidation-state vibrational spectroscopy. Van Duyne and co-workers have shown, for example, that the frequencies of several Raman-active modes in TCNQ<sup>2-/-/0</sup> (TCNQ = tetracyanoquinodimethane) shift linearly (incrementally) with formal oxidation state.<sup>24</sup> They have further shown, with TTF-TCNQ and related charge-transfer salts, that these shifts are also accurate predictors of *fractional* oxidation states.<sup>25</sup>

Closer to our own work, Caspar and co-workers<sup>26</sup> have argued that excited-state ( $\nu_e$ )/ground-state ( $\nu_g$ ) vibrational frequency shifts can be employed to identify the fraction ( $x$ ) of electronic charge effectively transferred upon MLCT excitation within various osmium and ruthenium bipyridine complexes. They proposed the expression

$$\frac{\nu_e - \nu_g}{\nu(1-) - \nu(0)} = x \quad (11)$$

In the expression  $\nu(0)$  is a C=C or C=N ring stretching frequency for neutral bipyridine and  $\nu(1-)$  is a stretching frequency for the free anion (Li<sup>+</sup> salt). In the context of our experiments,  $x$  would equal  $a^2 - b^2$ , in the limit of small orbital overlap (small  $S_{12}$ ).

In principle, eq 11 could be used directly to determine  $x$ ,  $a^2$ ,  $b^2$ , and  $\rho$  for Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup> if both  $\nu_g$  and  $\nu_e$  were available. Unfortunately, we have been able to observe only the ground-state vibration.<sup>11</sup> Nevertheless, estimates of  $x$  for Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup> are still possible on two counts. First, we note that, for the species evaluated by Caspar and co-workers,  $\nu_g$  by itself varies with  $\nu_e - \nu_g$  and therefore can be taken as a measure of  $x$ . To illustrate the point, Figure 2 shows a plot of  $\nu_g$  versus  $x$  for five related bipyridine complexes. Extrapolation of the plot to the known values for  $\nu_g$  for Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup> yields a range of estimates for  $x$ . At the upper end, in acetonitrile as solvent,  $x = 0.74$  ( $\nu_g = 1558$  cm<sup>-1</sup>). At the lower end, in HMPA as solvent,  $x = 0.57$  ( $\nu_g = 1548$  cm<sup>-1</sup>).

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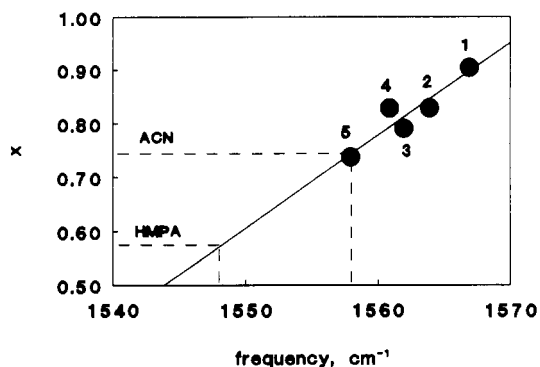
(22) A reviewer has suggested that the electrochemical measurement might differ from the spectral measurement by responding to all  $d\pi/\pi^*$  interactions. It seems clear, however, that when metal-based perturbations are probed electrochemically at the ligand, the probe is effectively confined to the lowest lying  $\pi^*$  orbital, where thermal electron injection (from the electrode) is occurring. On the other hand, this single  $\pi^*$  level presumably does respond in some sense to all three  $d\pi$ (Ru) orbitals. The reverse experiment in which perturbations are introduced at the ligand (via substituents) and monitored at the metal center (see footnote 18) presumably would measure mixing between all  $\pi^*$  levels and the highest lying  $d\pi$ (Ru) orbital. This distinction might account for the slightly greater degree of mixing inferred from that experiment. Note, however, that the ability of the higher lying  $\pi^*$  levels to mix with the metal center will be weighted heavily by the relative  $d\pi/\pi^*$  separation energy. Consequently, these types of interactions should be less important than the interaction with the lowest available  $\pi^*$  level. (The next highest MLCT transition (Ru-bpy) is at 25 700 cm<sup>-1</sup> in CH<sub>3</sub>CN as solvent.)

(23) A reviewer has pointed out that this energy is much less than the reorganization energy one might estimate from the sum of kinetic barriers to electron self-exchange for Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>3+/2+</sup> and bpy<sup>0/-</sup>. The comparison is inappropriate, however, for two important reasons: (1) the self-exchange reactions are bimolecular and therefore will overestimate by a factor of 2 the vibrational reorganization energy for a single metal-ligand charge transfer and (2) the bimolecular reactions are accompanied by significant solvent reorganization; this component should be almost negligible for the intramolecular MLCT reaction. (It is worth noting that our Raman-based estimates of internal reorganization are quantitatively consistent with independent estimates based on low-temperature emission analyses (see refs 11 and 26).)

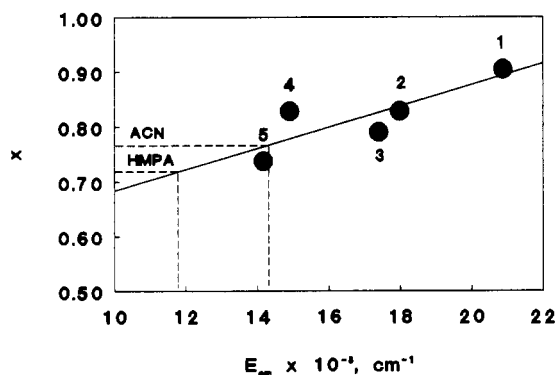
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**Figure 2.** Ground-state vibrational frequency vs  $x$  for various complexes: (1) Os(bpy)(P<sub>2</sub>)<sub>2</sub><sup>2+</sup>; (2) Os(bpy)<sub>2</sub>P<sub>2</sub><sup>2+</sup>; (3) Ru(bpy)<sub>3</sub><sup>2+</sup>; (4) Ru(bpy)<sub>2</sub>(en)<sup>2+</sup>; (5) Os(bpy)<sub>3</sub><sup>2+</sup> (P<sub>2</sub> = (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); en = H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>). Data are from ref 26. Dotted lines illustrate the determination of  $x$  (by extrapolation) for Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup> in acetonitrile (ACN) and hexamethylphosphoramide (HMPA).



**Figure 3.** Emission energy vs  $x$ .<sup>26</sup> See Figure 2 for key to complexes and solvents.

Alternatively, values of  $x$  can be derived from the known linear correlation<sup>26</sup> between this quantity and the emissive MLCT energy gap (see Figure 3).<sup>27</sup> Again, there is a complication in that Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup> is nonemissive at room temperature in conventional solvents. The gap can be estimated, however, by noting (experimentally as well as theoretically) the expected close relationship between emission energy and  $E_f(3+/2+) - E_f(2+/1+)$ .<sup>28,29</sup> Using the systems in Figures 2 and 3 as a guide, we obtain from electrochemical data<sup>25</sup> a set of emission energies ranging from 11 800 cm<sup>-1</sup> (HMPA) to 14 300 cm<sup>-1</sup> (CH<sub>3</sub>CN). Extrapolation of the plot in Figure 3 then yields  $x$  values ranging from 0.72 to 0.77 for Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup>. The corresponding values for  $a^2$  and  $b^2$  are 0.86 and 0.14;  $\rho$  is estimated as 0.40 (HMPA data).

It is worth noting that the two Raman-based approaches yield reasonably self-consistent results. More importantly, the vibrational spectroscopic measurements clearly corroborate the elec-

trochemical interpretation. While the corroboration is satisfying, it begs the question of why the familiar spectral method yields such disparate results. It is tempting to respond that when mixing becomes as substantial as it apparently does in Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>4</sub>(phen)<sup>2+</sup>, it is simply unrealistic to expect a perturbational or variational method (Mulliken theory) to yield satisfactory quantitative results. The flaw in this "explanation", as we see it, is that the electrochemical method is also derived from Mulliken theory and yet does appear to give fairly accurate results. One factor which may possibly account (in part) for the apparent mixing differences is the choice of charge-transfer distance,  $R$ , in the optical analysis. Consideration of eqs 1–3 and 6–10 reveals that  $b^2$  (optical) scales essentially with  $R^{-2}$ . For simplicity, we have equated  $R$  with the geometric metal-center to ligand-center distance—a choice which appears to be appropriate (or nearly appropriate) for Ru(bpy)<sub>3</sub><sup>2+</sup>.<sup>27</sup> When ancillary polypyridyl ligands are replaced by ammonias, however, the effective charge-transfer distance can be shortened. We note that the ability of ammonia ligands to compete with bipyridine for ground-state  $d\pi$ (Ru) electron density should be almost nonexistent, leaving the chromophore somewhat polarized along the Ru–bpy axis and causing the ground-state charge center to be shifted somewhat away from the metal center. Experimental precedent for such an effect can be found in the recent Stark-effect studies of Oh and Boxer.<sup>30</sup> For example, for metal-to-metal charge transfer in (NH<sub>3</sub>)<sub>5</sub>Ru<sup>II</sup>-4,4'-bipyridine-Ru<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup>, they report a transition dipole length which is only 45% as great as the nominal ruthenium–ruthenium separation distance. Force fitting of the optical data for Ru(NH<sub>3</sub>)<sub>4</sub>L<sup>2+</sup> to the electrochemical or Raman results would require  $R \approx 0.7$  Å. If one further appreciates that  $R$  in eq 8 is really the product distance and change and notes that the electrochemical experiment suggests net transfer of just 50% of an electronic charge, then a physical charge-transfer distance of ca. 1.4 Å is required. In view of Boxer's work, this may not be unrealistic. Clearly, it would be valuable at some point to carry out direct charge-transfer transition–dipole length measurements on the tetraammineruthenium polypyridyl systems.

To conclude, for metal-to-ligand charge transfer in Ru(NH<sub>3</sub>)<sub>4</sub>L<sup>2+</sup>, we find that the electrochemical method of Curtis et al.<sup>6</sup> yields a surprisingly accurate picture of metal/ligand orbital mixing and partial charge-transfer effects, at least to the extent that independent vibrational measurements can be accepted as "true" charge-transfer measurements. Perhaps more surprisingly, a conventional oscillator strength analysis of the same systems appears to yield gross underestimates of mixing and charge-transfer effects. The origin of the discrepancies is unclear but may be related to the choice of charge-transfer distance, which must necessarily be made in the optical analysis. It is worth noting that the oscillator strength approach has yielded similarly unsatisfactory results for the well-known Creutz–Taube ion ((H<sub>3</sub>N)<sub>5</sub>Ru–pyrazine–Ru(HN<sub>3</sub>)<sub>5</sub><sup>5+</sup>)<sup>6,8</sup> and for a series of halide-bridged Cu(I/II) mixed-valence complexes.<sup>5</sup> The latter were recently investigated by Solomon and co-workers; they observed factor-of-10 differences between  $b^2$  values derived from ESR hyperfine structure measurements and those derived from a Hush-type oscillator strength analysis.<sup>5</sup> We intend to report shortly on yet another class of compounds which yields disparate electrochemical versus spectral charge-transfer results. In the mean time, skepticism, or at least caution, would seem advisable in the quantitative interpretation of optical charge-transfer (orbital mixing) experiments.

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- (27) Yet another alternative involves the measurement, by Stark spectroscopy, of the difference between ground- and excited-state dipole moments. For example, from the difference measurement and a knowledge of the excited-state dipole length, Boxer and Oh (*J. Am. Chem. Soc.* **1989**, *111*, 1130) derive a value of  $x = 0.65/f$  for Ru(bpy)<sub>3</sub><sup>2+</sup>. ( $f$  is a local-field correction and typically lies between 1 and 1.3.)
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- (29) While ref 28 describes linear correlations between emission energies and  $\Delta E_f$  based on spectator-ligand variations, it should be noted that excellent emission energy/formal potential correlations have been found as well by using solvent (H-bonding) perturbations. Representative examples: Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> (Fung, et al. *Inorg. Chem.* **1988**, *27*, 1294); Ru(bpy)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub><sup>2+</sup> (Doorn, S. K. Ph.D. Dissertation, Northwestern University, 1990).

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