

described.<sup>7b</sup> The working electrode was a gold disk (0.5-mm diameter). PhCl, PPhSPh, and the various catalysts were from commercial origin with the exception of diethyl phenyl phosphite which was synthesized according to the literature.<sup>16</sup> The solution of benzenethiolate and diethyl

phosphite ions were prepared by reduction of the conjugated acids by potassium.

**Registry No.** PhSPh, 139-66-2; PhCl, 108-90-7; naphthalene, 91-20-3; diethyl phenyl phosphite, 4894-60-4; 2-methylnaphthyl ether, 93-04-9; 1-methylnaphthyl ether, 2216-69-5; phenyl radical, 2396-01-2; benzenethiolate ion, 13133-62-5; diethyl phosphite ion, 62305-77-5.

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## Mixed-Ligand Poly(pyridine) Complexes of Ruthenium(II). Resonance Raman Spectroscopic Evidence for Selective Population of Ligand-Localized <sup>3</sup>MLCT Excited States

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**Abstract:** The resonance Raman spectra of the series of mixed-ligand complexes, Ru(bpy)<sub>3-N</sub>(DMB)<sub>N</sub><sup>2+</sup> (where N = 0-3 and bpy and DMB are 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine, respectively), are reported for both the ground and excited metal-to-ligand charge-transfer (MLCT) electronic states. In both sets of spectra, vibrational bands associated with the unsubstituted ligand in the mixed-ligand complexes (N = 1 and 2) are more intense than the corresponding bands from 2:1 and 1:2 mixtures of Ru(bpy)<sub>3</sub><sup>2+</sup> and Ru(DMB)<sub>3</sub><sup>2+</sup>. Conversely, those bands associated with DMB ligand in the N = 1 and 2 mixed-ligand complexes are less intense than those from the 2:1 and 1:2 mixtures of the N = 0 and 3 complexes. These results are discussed in terms of localized excited states (both <sup>1</sup>MLCT and <sup>3</sup>MLCT) and indicate that, in the <sup>3</sup>MLCT state, the optical electron preferentially resides on a bpy ligand rather than on a DMB ligand, on the vibrational time scale. In addition to the Raman spectra, excited-state decay times, quantum yields, and emission energies are given. These data allow estimation of the summed nonradiative decay rate constants for the series of complexes from which a modified energy gap law plot is constructed. For complexes containing a bpy ligand, linear behavior is observed. These results imply that a substantial degree of selectivity can be induced into the charge-transfer excited states by a relatively mild chemical modification.

The metal-to-ligand charge-transfer (MLCT) excited states of Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine) continue to attract wide interest. A number of recent studies have suggested that these largely triplet<sup>1</sup> MLCT excited states are ligand-localized; that is, they are properly formulated as [Ru<sup>3+</sup>(bpy)<sub>2</sub>(bpy<sup>-</sup>)]<sup>2+</sup>. A summary of these studies includes the following.

(1) The temperature dependence of the ESR spectrum of Ru(bpy)<sub>3</sub><sup>1+</sup>, where the redox orbital involved in the 2+/1+ reduction is thought to be similar to the optical orbital involved in the MLCT excited state, has been interpreted in terms of ligand-to-ligand intramolecular electron transfer, implying localized orbitals.<sup>2,3</sup>

(2) The absorption spectrum of Ru(bpy)<sub>3</sub><sup>m</sup>, where m = 1+, 0, or 1-, contains features associated with both the (Ru-bpy) and the bpy<sup>-</sup> chromophores.<sup>4</sup>

(3) The absorption spectrum of \*Ru(bpy)<sub>3</sub><sup>2+</sup> (\* indicates the <sup>3</sup>MLCT excited state) has similarities to Na<sup>+</sup>(bpy<sup>-</sup>).<sup>5</sup>

(4) Carlin and DeArmond have employed photoselection data to present a strong case that excitation is localized in a single-ligand ring.<sup>6</sup>

(5) The time-resolved resonance Raman (TR<sup>3</sup>) spectrum of the excited state is characterized by two sets of bands, one associated with the fully reduced coordinated ligand and the other corresponding to the Ru<sup>III</sup>-bpy fragment.<sup>7,8</sup> In fact, the same frequency shifts observed in proceeding from the neutral to the anion radical form of bpy in the MLCT excited state of Ru(bpy)<sub>3</sub><sup>2+</sup> are seen

in the resonance Raman (RR) spectrum of the MLCT excited state of a Re(I) compound that contains only one bipyridine, fac-ClRe(CO)<sub>3</sub>(bpy).<sup>9</sup>

(6) Finally, Angel et al. have recently shown that the RR spectrum of [Ru<sup>II</sup>(bpy)<sub>2</sub>(bpy<sup>-</sup>)]<sup>1+</sup> is a composite of the spectra of the n = 1- and 2+ spectra.<sup>10</sup>

Inasmuch as the localized formulation of the excited state seems now firmly established, it is of interest to investigate the effects of subtle modifications of the parent structure on the stability of the electronic states and pertinent photophysical processes. A few recent studies are relevant to this issue. For a series of "mixed-ligand" complexes of this type, (RuL<sub>3-N</sub>L'<sub>N</sub>)<sup>2+</sup>, where L and L' are distinct diimine ligands and N = 0, 1, 2, and 3, it has been generally observed that emission occurs only from the lowest <sup>3</sup>MLCT state.<sup>11-14</sup> In addition, Ferguson et al.<sup>15</sup> and Ford et al.<sup>16</sup>

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report data for  $[\text{Ru}(\text{bpy})_2(\text{bpy}') ]^{2+}$  complexes, where bpy is a bipyridine derivative bearing electron-withdrawing substituents. Their results imply that the optical electron is localized on the bpy' ligand as a result of the enhanced stability of its anion radical relative to that of bpy.

We have recently reported a reasonably detailed analysis of the RR spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$ .<sup>17</sup> The essential purpose of the present paper is to demonstrate the utility of RR spectroscopy for probing the excited states of "mixed-ligand" complexes and to determine the effects of relatively slight chemical modification of the bipyridine ligand. The series of complexes chosen for this study contains 2,2'-bipyridine and its dimethyl derivative, 4,4'-dimethyl-2,2'-bipyridine (DMB), i.e.,  $\text{Ru}(\text{bpy})_{3-N}(\text{DMB})_N^{2+}$  where  $N = 0, 1, 2,$  and  $3$ . We report the ground- and excited-state resonance Raman spectra of the series as well as those of 2:1 and 1:2 mixtures of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{DMB})_3^{2+}$ . These investigations are supplemented by measurements of the excited-state lifetimes, emission energies, and emission quantum yields of the complexes, and the results are discussed in terms of selective population of particular <sup>3</sup>MLCT states.

### Experimental Section

**Materials.**  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  and 4,4'-dimethyl-2,2'-bipyridine were used as received. 2,2'-Bipyridine was sublimed prior to use. Water was doubly distilled.

**Preparation of Compounds.**  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  was prepared by literature methods.<sup>18</sup> In an identical manner,  $\text{Ru}(\text{DMB})_2\text{Cl}_2$  was prepared. For the tris complexes, approximately 0.5 mmol of  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  or  $\text{Ru}(\text{DMB})_2\text{Cl}_2$  was dissolved by refluxing in aqueous ethanol (ca. 25 mL of a 1:1 mixture) for 1 h. To this solution, 1.1 equiv of DMB or bpy, dissolved in a minimum of ethanol, was added, and the resulting mixture was gently refluxed for an additional 3 h. Approximately 50% of the solvent was removed by distillation, and the concentrated solution was cooled overnight in ice. The addition of a small quantity of a cold saturated solution of NaCl precipitated the red complexes. These were filtered and dried in vacuo at 60–70 °C.

The complexes were purified by column chromatography on Sephadex LH-20 (Pharmacia Fine Chemicals) when using ethanol as eluant. Typically 100 mg of complex was dissolved in a minimum of ethanol and loaded into a 1.5 cm × 30 cm column. Flow rates were less than 0.5 mL/min. The bright-orange, luminescent fraction was collected and dried under a stream of nitrogen. All complexes were chromatographed at least twice prior to use.

**Physical Measurements.** UV-visible spectra were recorded at room temperature on a Beckman 26 spectrophotometer. <sup>1</sup>H NMR spectra were obtained in D<sub>2</sub>O solution on a Varian 390 spectrometer at room temperature. Lifetime measurements were obtained from nitrogen-purged, room-temperature solutions in Pyrex tubes with the use of Photochemical Research Assoc. fluorescence lifetime instrumentation employing single-photon counting techniques. The excitation wavelength was either 313 or 380 nm while the emission was collected at 610 nm. Lifetimes were determined from the slope of the exponential decay which was linear for at least 3τ. Emission spectra and quantum yields were obtained on a Spex Fluorolog 2 spectrofluorimeter with excitation at 380 or 436 nm. Quantum yields were determined in water relative to  $\text{Ru}(\text{bpy})_3^{2+}$  as standard and were calculated from eq 1,<sup>19,20</sup> where  $I_x$  and  $I_s$

$$\phi_x = \phi_s(I_x/I_s)(A_s/A_x) \quad (1)$$

are the integrated emission intensities of the unknown and standard, respectively, and  $A_x$  and  $A_s$  are the corresponding absorbances of the optically dilute solutions at the excitation wavelength.

Raman spectra were obtained from aqueous solutions which were typically 0.5–1.0 mM in metal complex and 0.5 M in internal standard.

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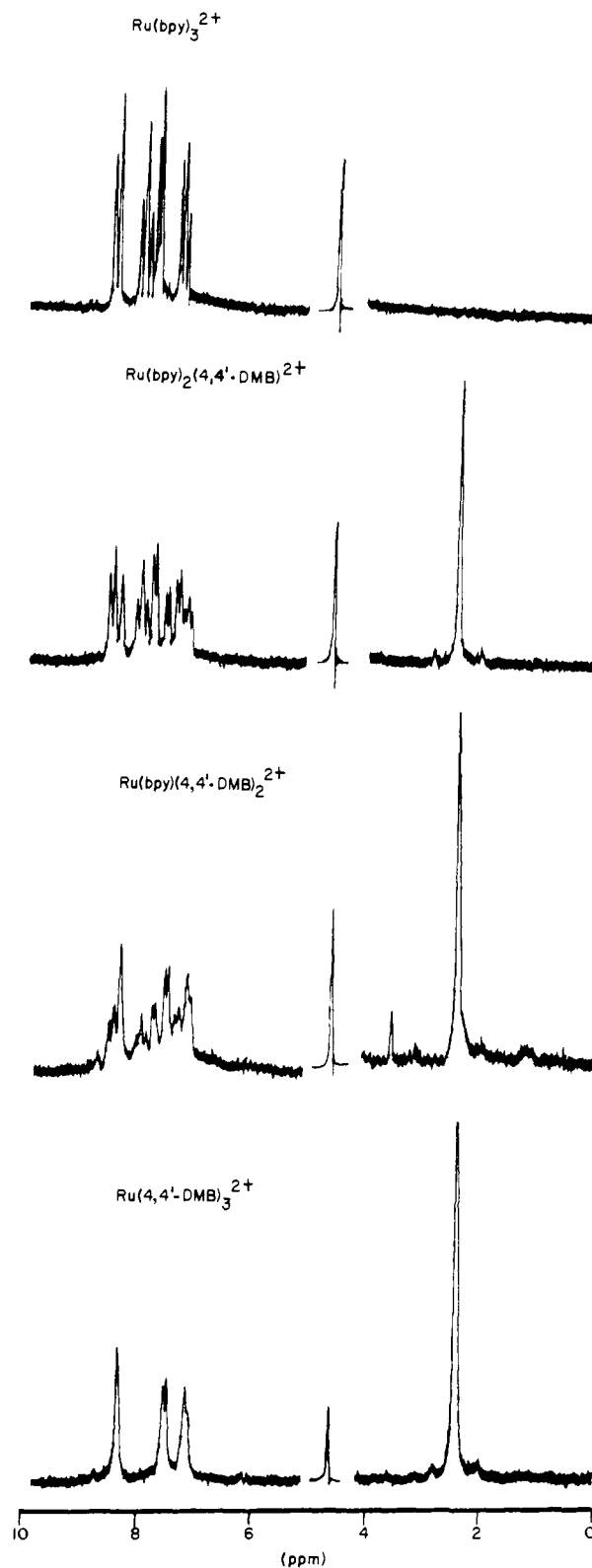


Figure 1. <sup>1</sup>H NMR spectra of  $\text{Ru}(\text{bpy})_{3-N}(\text{DMB})_N^{2+}$  ( $N = 0-3$ ) in D<sub>2</sub>O. The peak at 4.62 ppm is due to HOD.

$\text{Na}_2\text{SO}_4$ . Solutions were purged with nitrogen or argon for 15 min and sealed prior to excitation. Resonance Raman spectra of the electronic ground states were obtained by using 457.9-nm excitation from a CW argon ion laser as described previously,<sup>17</sup> while those of the lowest electronic excited state were obtained by employing the 354.7-nm third harmonic line of a Nd:YAG laser (Quanta Ray DCR-1) typically operated at a 10-Hz repetition rate, yielding 7-ns, 5-mJ pulses. The scattered radiation was collected at 90° to the excitation and focused onto the entrance slit of a Spex 1400 double monochromator. The monochromator gratings were blazed at 750 nm; therefore, the spectra were

**Table I.** Chemical Shifts and Coupling Constants for Ru(bpy)<sub>3-N</sub>(4,4'-DMB)<sub>N</sub><sup>2+</sup> Complexes in D<sub>2</sub>O

N	chemical shifts, ppm <sup>a</sup>								coup const, Hz
	bpy				4,4'-DMB				
	H3	H4	H5	H6	H3	CH <sub>3</sub>	H5	H6	
0	8.49 (dd) <sup>b</sup>	7.97 (ddd)	7.31 (ddd)	7.75 (dd)					$J_{3,4} = 8.7, J_{3,5} = 1.0, J_{4,5} = 6.7, J_{4,6} = 1.5, J_{5,6} = 5.1$
1	8.51	7.99	7.32	7.78	8.34	2.45	7.15	7.54	
2	8.48	7.94	7.29	7.72	8.30	2.41	7.11	7.50	
3					8.31 (s)	2.42 (s)	7.10 (d)	7.49 (d)	$J_{5,6} = 4.5$

<sup>a</sup> Relative to HOD resonance at 4.62 ppm. <sup>b</sup> Multiplicity of signal.

**Table II.** Electronic Absorption Spectral Data for Ru(bpy)<sub>3-N</sub>(4,4'-DMB)<sub>N</sub><sup>2+</sup> Complexes in Water at 25 °C<sup>a</sup>

complex	dπ → π <sub>1</sub> *	π → π <sub>1</sub> *	π → π <sub>2</sub> *
Ru(bpy) <sub>3</sub> <sup>2+</sup>	452	285	242
Ru(bpy) <sub>2</sub> (4,4'-DMB) <sup>2+</sup>	454	285	243
Ru(bpy)(4,4'-DMB) <sub>2</sub> <sup>2+</sup>	456	285	245
Ru(4,4'-DMB) <sub>3</sub> <sup>2+</sup>	459	285	247

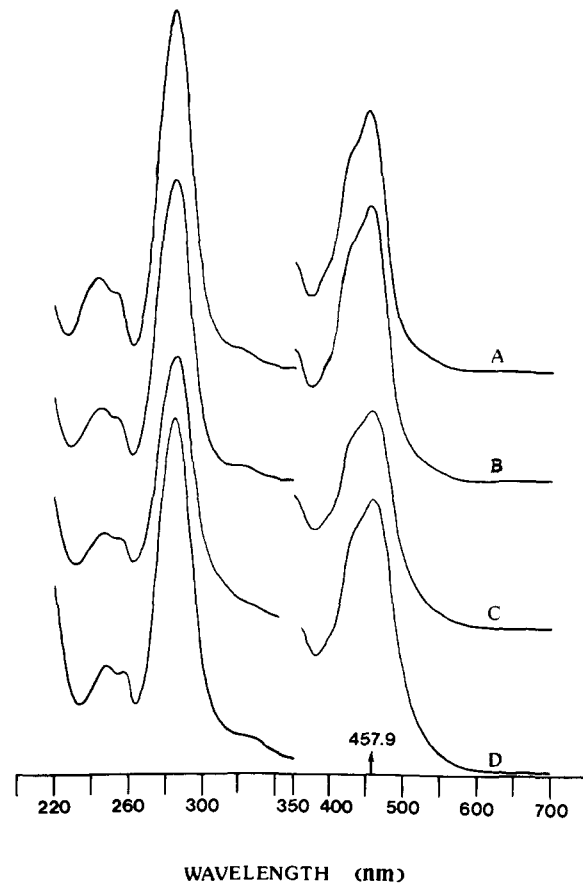
<sup>a</sup> λ<sub>max</sub> in nanometers. Error limits ±1 nm.

taken in the second order. A CuSO<sub>4</sub> solution, placed between the collection lens and entrance slits, was used to filter the intense first-order luminescence of the sample. The output of the PMT was processed by a gated amplifier (Quanta Ray DGA-1) with a 100-μs gate width. The gated amplifier output was sent to a voltage-to-frequency converter and finally to a Data General Corp. Nova 2 computer. Solutions were contained in either circulating capillary tubes or spinning NMR tubes.

### Results and Discussion

**NMR Spectra.** The <sup>1</sup>H NMR spectra of the series are given in Figure 1, and the measured chemical shifts and coupling constants are listed in Table I. In these spectra, resonances due to both types of ligands are apparent since the chemical shifts of the protons of the DMB ligand are lower than those for the unsubstituted bipyridine. There is no evidence of induced asymmetry in the spectra of the mixed-ligand species as a result of lowering the molecular symmetry from D<sub>3</sub> to C<sub>2</sub>. Thus, the <sup>1</sup>H NMR spectra of these species appear as simple weighted averages of the N = 0 and 3 complexes. These results are consistent with those reported for the series Ru(bpy)<sub>3-N</sub>(phen)<sub>N</sub><sup>2+</sup> by Pillings and co-workers<sup>22</sup> (phen is 1,10-phenanthroline) in their reexamination of earlier NMR studies of this series<sup>21</sup> where the chemical shifts of the 3,3'-protons of bpy and the 4,7-protons of phen were reported to vary with N. Furthermore, we have obtained the <sup>1</sup>H NMR spectra of the Ru(phen)<sub>3-N</sub>(5,6-DMP)<sub>N</sub><sup>2+</sup> series (5,6-DMP is 5,6-dimethyl-1,10-phenanthroline). The measured chemical shifts of the 4,7-protons of both types of ligands remain constant as N varies. Interestingly, there is a splitting in the signals from the 2,9-protons for the two mixed species (N = 1 and 2) relative to the N = 0 and 3 complexes. In the spectrum of the N = 1 complex, an asymmetry in the resonances due to the 2,9-protons of the phenanthroline ligand occurs, while in the N = 2 species the asymmetry occurs in the 2,9-protons of the 5,6-DMP ligand. This effect is undoubtedly due to the lowering of the molecular symmetry in the mixed-ligand species. However, it should be stressed that this effect is observed only for these protons which are α to the nitrogen atoms and thus evidently arises from the proximity of these protons to neighboring ligands. It thus appears from consideration of the NMR spectral data that there is no strong electronic coupling between ligands and that any induced asymmetry is due simply to the juxtaposition of protons α to the nitrogen atoms to a different ligand. The fact that this asymmetry is observed in phenanthroline and not bipyridine complexes probably reflects the rigidity of the former ligand.

**Electronic Absorption Spectra.** The electronic absorption spectra for the bpy/DMB series of complexes are shown in Figure 2 and the corresponding spectral parameters are summarized in Table II. Inspection of these reveals that substitution for bpy by DMB causes a systematic red shift in the position of the



**Figure 2.** Electronic absorption spectra in water: (A) Ru(bpy)<sub>3</sub><sup>2+</sup>, (B) Ru(bpy)<sub>2</sub>(DMB)<sup>2+</sup>, (C) Ru(bpy)(DMB)<sub>2</sub><sup>2+</sup>, and (D) Ru(DMB)<sub>3</sub><sup>2+</sup>.

absorption maximum in the region of the MLCT band. However, methyl substitution has essentially no effect on the energy of the ligand-localized π-π\* transition located at 285 nm. It should be noted that the intensities of the MLCT absorption bands in Ru(bpy)<sub>3</sub><sup>2+</sup> (ε<sub>452</sub> = 1.46 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>)<sup>23</sup> and Ru(DMB)<sub>3</sub><sup>2+</sup> (ε<sub>459</sub> = 1.43 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>)<sup>24</sup> are virtually identical.

There is now general agreement regarding the assignment of the dominant features of the electronic absorption spectra of these complexes. First, the paper by Kober and Meyer<sup>1</sup> demonstrates the validity in the description of the terminal states in the MLCT transition as largely singlet in character. In addition, Kober, Sullivan, and Meyer have recently shown, on the basis of the solvent dependence of the energy of the MLCT band in Ru(bpy)<sub>3</sub><sup>2+</sup>, that the <sup>1</sup>MLCT state is ligand-localized.<sup>26</sup>

In the case of mixed-ligand complexes, such as the series studied here, it is to be expected that the spectra should consist of bands assignable to different dπ-π\* and π-π\* transitions characteristic

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**Table III.** Reduction Potentials, Volts vs. SCE<sup>a</sup>

bpy	-2.10 (0/1-)	
DMB	-2.20 (0/1-)	
Ru(bpy) <sub>3</sub> <sup>2+</sup>	+1.26 (3+/2+)	-1.28 (2+/1+)
Ru(DMB) <sub>3</sub> <sup>2+</sup>	+1.10 (3+/2+)	-1.37 (2+/1+)

<sup>a</sup>Data taken from ref 5a and 29.

of the individual ligands. It is therefore satisfying that the general features of the spectra of the present series of complexes are readily understood on the basis of the ligand-localized model and the known relative basicities and  $\pi^*$  orbital energies by bpy and DMB.

From the  $pK_a$  values,<sup>27</sup> DMB ( $pK_a = 5.3$ ) is seen to be a stronger  $\sigma$  donor than bpy ( $pK_a = 4.4$ ) as a result of the electron-donating ability of the methyl groups and thus stabilizes the  $Ru^{3+}$  state to a greater extent than does bpy as is reflected in the 3+/2+ reduction potentials given in Table III. The increased donor strength of DMB relative to bpy will give rise to a general increase in the  $d\pi$  orbital energies in  $Ru(DMB)_3^{2+}$  and the mixed-ligand complexes relative to their energies in  $Ru(bpy)_3^{2+}$ . On the other hand, the  $\pi^*$  orbital energy for bpy is lower than that for DMB as can be seen (Table III) from the reduction potentials both for the free ligands and for the (2+/1+) tris complexes (reduction occurs in an orbital largely localized on the ligand).<sup>2,3,28</sup> In fact, as has been shown by Saji and Aoyagui,<sup>29</sup> the energy of the visible absorption band is well correlated with  $\Delta E_{1/2} = E_{1/2}(2+/1+) - E_{1/2}(3+/2+)$  since the MLCT may be viewed as an internal redox process.

Given these differences in ligand properties and the ligand-localized model, the data of Table II are easily interpreted. For a mixed-ligand complex, the lowest energy  $d\pi-\pi^*$  transition is associated with the ligand containing the lowest  $\pi^*$  level, i.e., bpy. Thus,  $\lambda_{max}$  for  $Ru(bpy)_3^{2+}$  occurs at 452 nm. Upon replacement of one bpy ligand by DMB (i.e.,  $Ru(bpy)_2(DMB)^{2+}$ ),  $\lambda_{max}$  shifts to lower energy as a result of the increase in energy of the  $d\pi$  orbitals owing to the increased donor strength of DMB. In the case of the mixed-ligand complex,  $Ru(bpy)(DMB)_2^{2+}$ , the lowest energy transition is still associated with the bpy ligand but the  $d\pi$  orbitals are yet higher in energy, thus giving rise to a red shift relative to  $Ru(bpy)_2(DMB)^{2+}$ . In the case of  $Ru(DMB)_3^{2+}$ , the MLCT transition involves the  $\pi^*$  orbital of DMB rather than that of bpy, but now the  $d\pi$  orbitals are sufficiently destabilized so that the  $\lambda_{max}$  is again red-shifted relative to those of the other complexes in the series.

It is interesting to note that, according to the above interpretation, although the MLCT transition localized on DMB occurs at a lower energy than that localized on bpy for the corresponding tris complexes, in the mixed-ligand complexes it is blue-shifted relative to the bpy-localized MLCT transition. It is worth pointing out that the electronic absorption spectra of related mixed-ligand complexes can be interpreted in a similar fashion.<sup>11-13,21-23</sup>

**Ground-State Resonance Raman Spectra.** Excitation within the MLCT band results in strong resonance enhancement for each of the complexes studied. As has been pointed out previously,<sup>17,30-38</sup>

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**Table IV.** Summary of Intensities of RR Bands in  $Ru(bpy)_3 \cdot N(4,4'-DMB)_N^{2+}$  ( $N = 1, 2$ ) Complexes Relative to 2:1 and 1:2 Mixtures of  $Ru(bpy)_3^{2+}$  and  $Ru(4,4'-DMB)_3^{2+}$ <sup>a</sup>

band, cm <sup>-1</sup>	ground state	excited state
$Ru(bpy)_2(4,4'-DMB)^{2+}$		
1621	0.35	2.45
1607	1.69	0.74
1452		0.12 <sup>b</sup>
1429		1.58
$Ru(bpy)(4,4'-DMB)_2^{2+}$		
1621	0.79	1.33
1607	1.85	1.07
1452		0.42
1429		1.14

<sup>a</sup>See text for explanation of data. <sup>b</sup>Contains a large uncertainty, band essentially hidden in noise of the spectrum.

$\sim 11 A_1$  modes associated with core stretching and  $\delta(CCH)$  in-plane bending are observed between 1000 and 1650 cm<sup>-1</sup>. As can be seen from Figure 3, the RR spectrum of  $Ru(DMB)_3^{2+}$  is quite similar to that of  $Ru(bpy)_3^{2+}$  although significant differences do exist. The origin of these differences and a description of the vibrational assignments are of little concern for the purposes of the present work. The importance of these few differences lies in the fact that they permit a clear distinction to be made between RR scattering from particular ligands in the mixed ligand complexes, the most efficiently exploitable difference being the pair of bands at 1608 cm<sup>-1</sup> [ $Ru(bpy)_3^{2+}$ ] and 1621 cm<sup>-1</sup> [ $Ru(DMB)_3^{2+}$ ].

This effect is quantitatively demonstrated for each of the mixed-ligand complexes in Figure 4. Here, the bands at  $\sim 1600$  cm<sup>-1</sup> are shown for the series of complexes. These spectra were acquired from solutions which were isoabsorbing at the visible MLCT absorption maxima ( $A = 0.75$  in 0.1-cm cells). The intensities of these bands are compared with that of the 983-cm<sup>-1</sup> band due to 0.5 M Na<sub>2</sub>SO<sub>4</sub> internal standard. Also shown in the figure are the spectra for the 2:1 and 1:2 mixtures of  $Ru(bpy)_3^{2+}$  and  $Ru(DMB)_3^{2+}$  which also have a total absorbance of 0.75 (per millimeter). These complexes are substantially inert to thermal substitution, and so the integrity of each of the tris species is preserved. A summary of the intensities of these ground-state bands for the mixed-ligand complexes relative to the intensities for the synthetic mixtures is given in Table IV (ground state). These data were derived as follows. The intensity of each band relative to the SO<sub>4</sub><sup>2-</sup> band was obtained for each tris species to arrive at an enhancement factor for each band (with 457.9-nm excitation). Corresponding enhancement factors were determined for the synthetic mixtures. It is noted that the observed enhancements of the bands in the synthetic mixtures were found to agree to within 6-10% of the expected value based on the enhancement factors for the tris complexes and the relative amounts of each ligand present in the mixture. Next, the corresponding enhancement factors were obtained for the bands in the spectra of the mixed-ligand complexes. The data given in Table IV represent the ratios of the enhancement factors for the mixed-ligand complexes to the factors for the synthetic mixtures. Thus, the value of 0.35 for the 1621-cm<sup>-1</sup> (DMB) band indicates that for the mixed-ligand complex,  $[Ru(bpy)_2(DMB)]^{2+}$ , the enhancement of the DMB band is substantially less than for  $Ru(DMB)_3^{2+}$ . Conversely, the value of 1.69 for the 1608-cm<sup>-1</sup> (bpy) band shows that the enhancement factor has increased relative to its value for  $Ru(bpy)_3^{2+}$ .

These intensity variations in the ground-state RR spectra are readily explained on the basis of the interpretation of the electronic spectra discussed in the previous section. In the case of the mixed-ligand complex,  $[Ru(bpy)_2(DMB)]^{2+}$ , the MLCT transition associated with the DMB ligand is now blue-shifted relative to its energy in  $Ru(DMB)_3^{2+}$ ; i.e., it now is further displaced from the 457.9-nm excitation line. This results in smaller enhancement factors (35%) for the DMB bands. On the other hand, for this complex, the MLCT transition associated with bpy is red-shifted relative to its energy in  $Ru(bpy)_3^{2+}$ , resulting in an increase (170%)

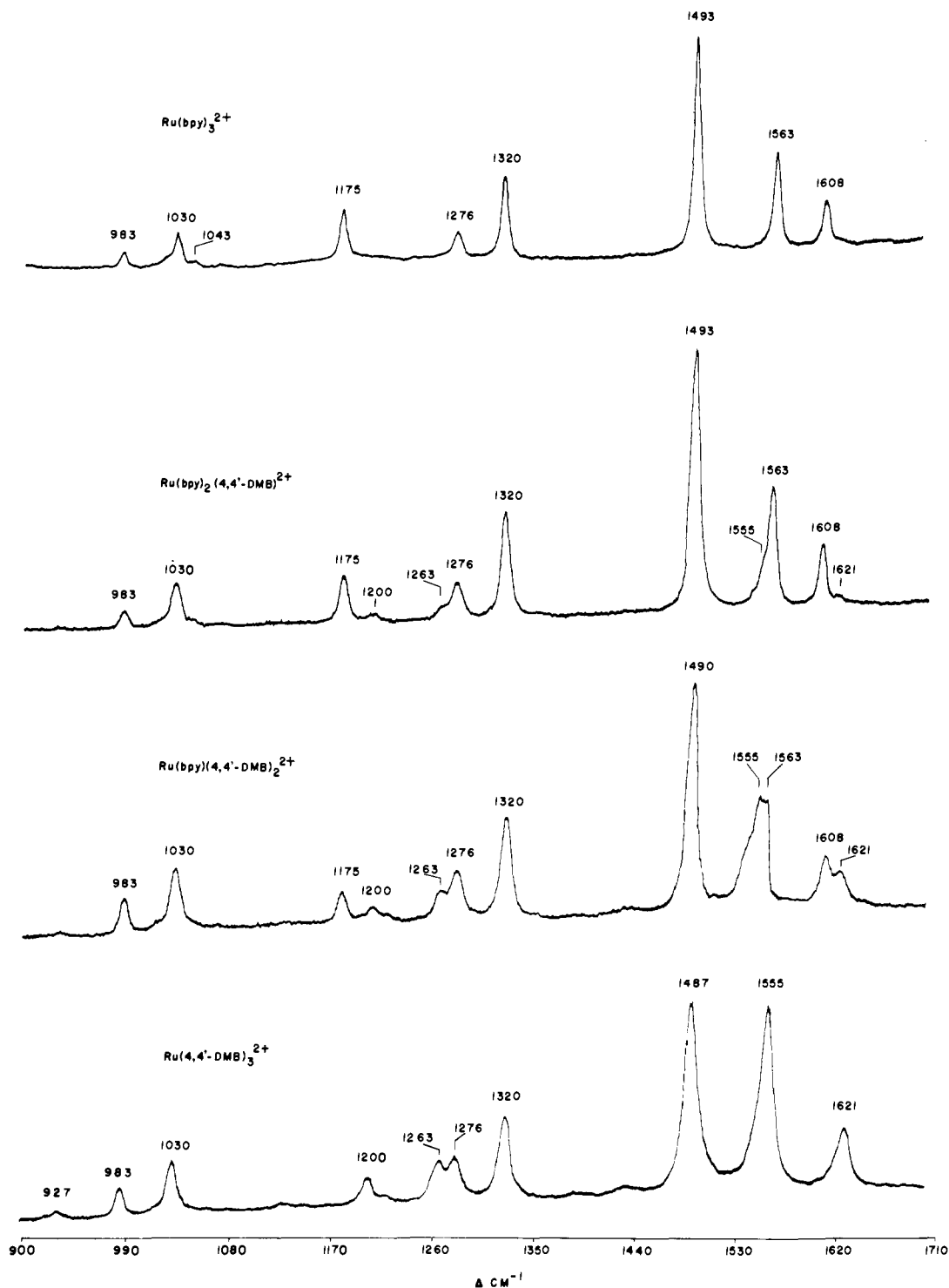
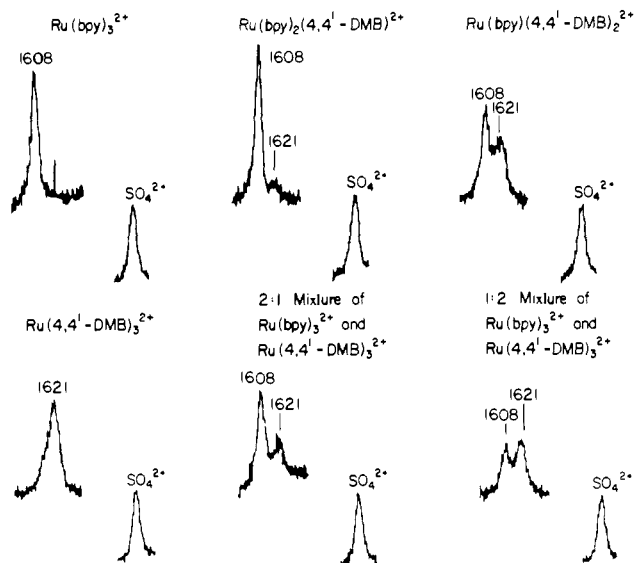


Figure 3. Resonance Raman spectra of  $\text{Ru}(\text{bpy})_3\text{-N}(\text{DMB})_N^{2+}$  complexes ( $N = 0\text{-}3$ ) from 900 to 1700  $\text{cm}^{-1}$  with use of 457.9-nm excitation.

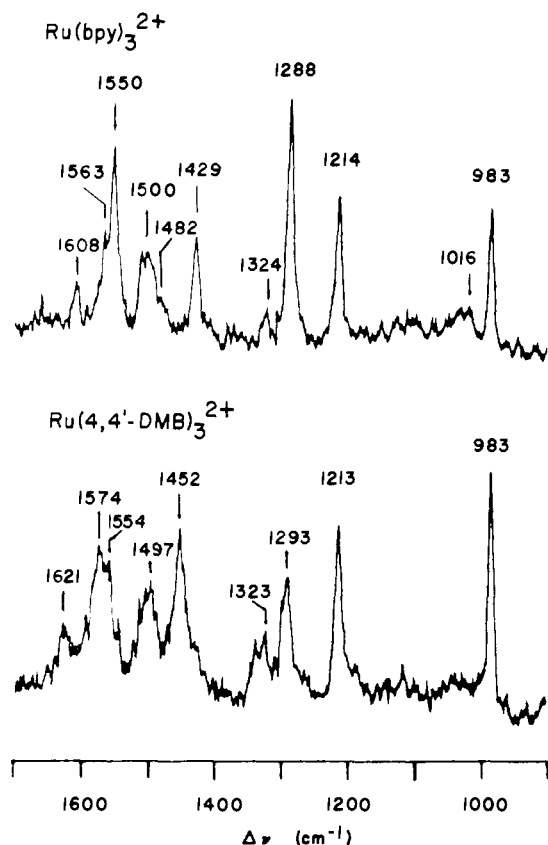
in enhancement of bpy bands as it is now more nearly coincident with the laser excitation line. For the complex  $[\text{Ru}(\text{bpy})(\text{DMB})_2]^{2+}$ , the increase in energy of the d orbitals relative  $[\text{Ru}(\text{bpy})_2(\text{DMB})]^{2+}$  will cause a slight red shift of the MLCT associated with the DMB ligand. This results in an increase in enhancement (79% vs. 35%) of DMB bands relative to  $[\text{Ru}(\text{bpy})_2(\text{DMB})]^{2+}$ .

The data presented above provide support for the interpretation of the electronic absorption spectra of these complexes in terms of ligand-localized MLCT transitions.<sup>26</sup> In fact, it should prove possible to resolve the overlapping electronic transitions via carefully determined excitation profiles of individual ligand bands with the aid of tunable CW dye lasers which could access this region (400–500 nm).

**Excited-State Resonance Raman Spectra.** Figure 5 presents the time-resolved resonance Raman ( $\text{TR}^3$ ) spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{DMB})_3^{2+}$  using the 355-nm third harmonic line of the Nd:YAG laser. This 7-ns pulse serves both to create a saturated population of electronic excited states within the scattering volume and to probe the Raman spectrum of this excited-state population. Thus, these data represent the vibrational spectra of the emissive MLCT excited states. It should be noted, by comparison to the intensity of the 983- $\text{cm}^{-1}$  ( $\text{SO}_4^{2-}$ ) band, that the enhancements of the  $\text{TR}^3$  bands in  $\text{Ru}(\text{bpy})_3^{2+}$  are greater than those of  $\text{Ru}(\text{DMB})_3^{2+}$  even though the solutions are isoabsorbing at  $\lambda_{\text{MLCT}}$ . In fact, such behavior is expected. At 355 nm (the excitation line in these experiments), the *ground-state* absorption by the two tris complexes is essentially identical; however, the *excited-state* ab-



**Figure 4.** Resonance Raman spectra of  $\text{Ru}(\text{bpy})_3\text{-N}(\text{DMB})_N^{2+}$  complexes ( $N = 0-3$ ) and 2:1 and 1:2 mixtures of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{DMB})_3^{2+}$  from 1580 to 1640  $\text{cm}^{-1}$  with use of 457.9-nm excitation. Also included with each scan is the 983- $\text{cm}^{-1}$  peak due to 0.5 M  $\text{Na}_2\text{SO}_4$  internal standard.



**Figure 5.** Excited-state resonance Raman spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{DMB})_3^{2+}$  from 900 to 1700  $\text{cm}^{-1}$  with use of 354.7-nm excitation.

sorption of the bpy anion radical is greater than that of the DMB anion radical by a factor of about 2.<sup>25</sup> As shown previously,<sup>7-9,31</sup> the TR<sup>3</sup> spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$  is interpreted in terms of an excited-state formulated as  $[\text{Ru}^{3+}(\text{bpy})_2(\text{bpy}^{\cdot-})]^{2+}$ , that is, a ligand-localized excited state, during the 7-ns time scale of the experiment. The TR<sup>3</sup> spectrum of the  $\text{Ru}(\text{DMB})_3^{2+}$  complex may also be interpreted in a similar fashion. For example, a 1621- $\text{cm}^{-1}$  band, corresponding to the "neutral" DMB ligand, is observed as is the anion radical band at 1574  $\text{cm}^{-1}$ . In addition, bands associated with the (DMB<sup>·-</sup>) moiety are seen at 1452, 1293, and

1213  $\text{cm}^{-1}$ , whereas other bands due to the  $(\text{Ru}^{\text{III}}\text{-DMB})$  fragment are observed at 1554, 1497, and 1323  $\text{cm}^{-1}$ . Again, although this spectrum closely resembles the excited-state spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$ , significant differences exist such that distinct bands associated with each ligand can be identified.

Figure 6 gives a portion of the TR<sup>3</sup> spectra for the two mixed-ligand complexes as well as the 2:1 and 1:2 mixtures of the "tris" complexes. The symmetric stretch of 0.5 M  $\text{SO}_4^{2-}$  is included as both a frequency and intensity standard. Examination of these spectra reveals that bands associated with the DMB ligand are weaker in intensity than is expected based on the stoichiometric composition of the complexes while those due to the unsubstituted bipyridine are stronger. It is noted that the solutions used to obtain these spectra were identical with those used to record the ground-state RR spectra in Figure 4. Visible spectra taken immediately after performing a TR<sup>3</sup> experiment showed no significant spectral changes.

In Figure 6, the TR<sup>3</sup> spectra were obtained by summing eight different scans of the 1400–1650- $\text{cm}^{-1}$  region, whereas the  $\text{SO}_4^{2-}$  region was scanned only once. Therefore, although the relative intensities of the bands from the metal complexes are exaggerated relative to the  $\text{SO}_4^{2-}$  band, internally consistent ratios of peak heights of the metal complex bands to that of  $\text{SO}_4^{2-}$  (on a per ligand basis) can be calculated and these are also listed in Table IV (excited state). Again, these data represent the intensity of a particular band in the mixed-ligand complexes relative to that expected from 2:1 and 1:2 mixtures of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{DMB})_3^{2+}$ . Error limits on these data are difficult to judge but are probably comparable to the ground-state data.

In contrast to the ground-state data, it is not reasonable to invoke slight shifts in the energies of the resonant transitions in order to explain intensity differences in the TR<sup>3</sup> spectra of the mixed-ligand complexes. Resonance enhancement in the excited state involves  $\pi\text{-}\pi^*$  transitions of the ligands, the  $\pi\text{-}\pi^*$  of the anion radical moieties occurring at  $\sim 350$  nm and that of the "neutral ligand" at  $\sim 280$  nm (i.e., similar to its value in the ground state). These are ligand-localized transitions; their energies are not strongly affected by slight changes in  $d\pi$  orbital energies. Thus, it must be expected that the  $\pi\text{-}\pi^*$  absorption bands (both "neutral ligand" and anion radical) occur at comparable energies and intensities in the excited-state absorption spectra of the mixed-ligand complexes.

Inspection of the data in Table IV (excited state) indicates that for  $[\text{*Ru}(\text{bpy})_2(\text{DMB})^{2+}]$ , the bpy<sup>·-</sup> bands are enhanced to a greater extent (on a per ligand basis) than they are in the TR<sup>3</sup> spectrum of  $[\text{*Ru}(\text{bpy})_3^{2+}]$ , while the "neutral ligand" bands of bpy are enhanced to a lesser extent. Conversely, the DMB<sup>·-</sup> bands are enhanced to a lesser extent than in  $[\text{*Ru}(\text{DMB})_3^{2+}]$ , while the "neutral ligand" bands are enhanced to a greater extent. These spectra then provide an internally consistent set of data which argues that  $[\text{*Ru}(\text{bpy})_2(\text{DMB})^{2+}]$  is most reliably formulated as  $[\text{Ru}^{3+}(\text{bpy})(\text{bpy}^{\cdot-})(\text{DMB})]^{2+}$ . That is, during the 7-ns time scale of the experiment, the optical electron is localized on a bipyridine to a greater degree than on a DMB ligand. The data for  $[\text{*Ru}(\text{bpy})(\text{DMB})_2^{2+}]$  can be interpreted similarly, although the degree of selective formation of the bpy-localized state has apparently decreased somewhat relative to the  $[\text{Ru}(\text{bpy})_2(\text{DMB})]^{2+}$  complex.

**Excited-State Decay Parameters.** We have investigated the excited-state properties and decay characteristics of this series of complexes in an attempt to provide an independent determination of the extent of selective population of excited states implied by the TR<sup>3</sup> experiments. The excited-state decay times for the series of complexes were determined by time-correlated single-photon counting and are listed in Table V along with the measured emission quantum yields ( $\phi_{\text{em}}$ ) and energies of the emission maxima ( $E_{\text{em}}$ ). The measured lifetimes of  $\text{Ru}(\text{bpy})_3^{2+}$  agree well with those reported by Lin et al.<sup>24</sup> However, Nakamaru et al.<sup>39</sup> report an emission quantum yield of 0.26 for  $\text{Ru}(\text{DMB})_3^{2+}$  which is a factor of 2 higher than our value. The reason for this dis-

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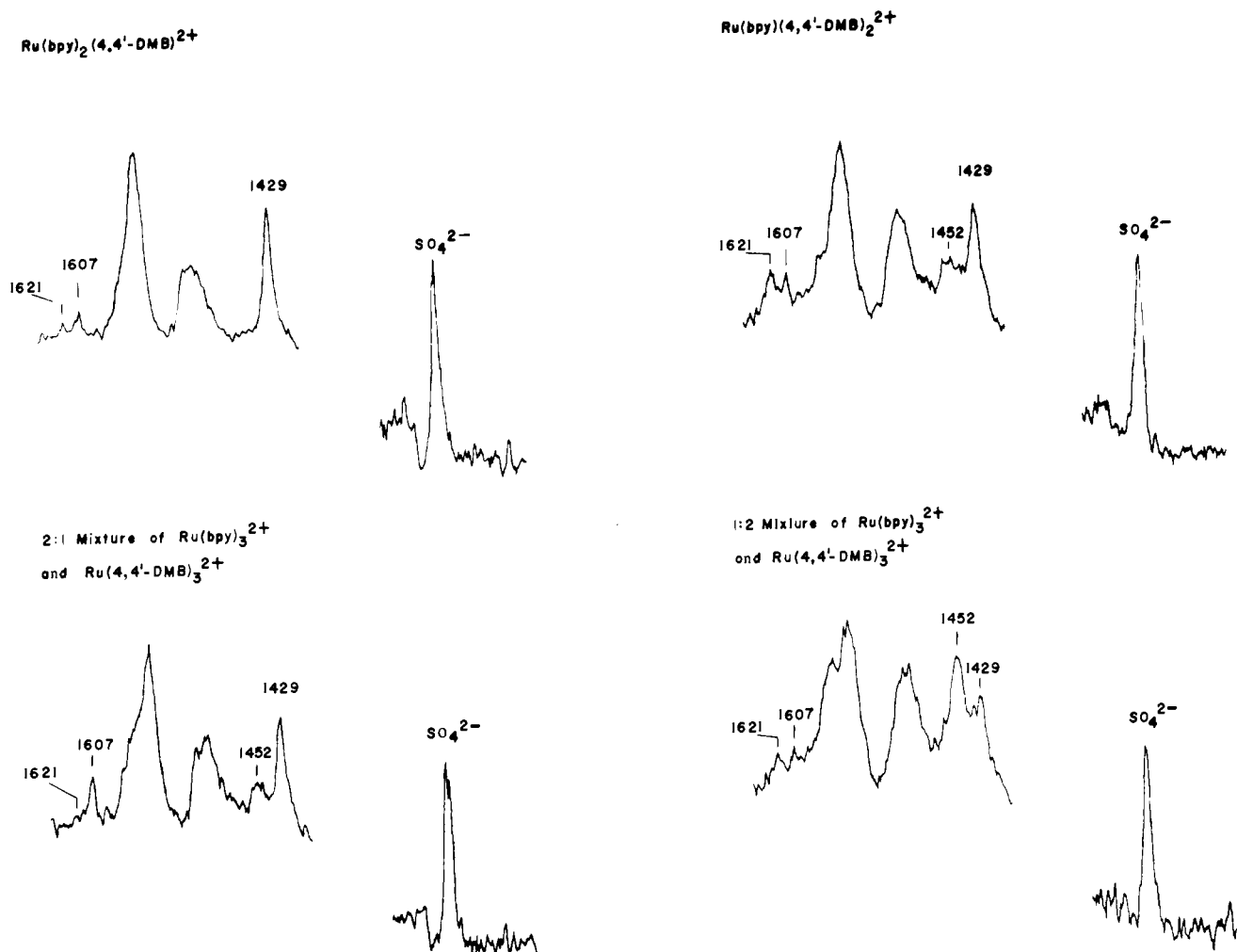


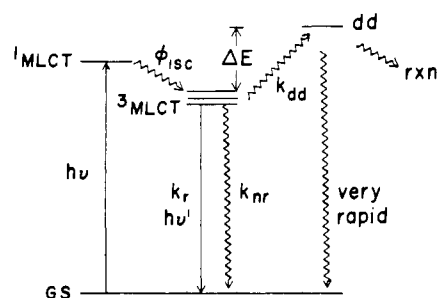
Figure 6. Excited-state resonance Raman spectra of  $\text{Ru}(\text{bpy})_2(\text{DMB})_2^{2+}$  and  $\text{Ru}(\text{bpy})(\text{DMB})_2^{2+}$  relative to 2:1 and 1:2 mixtures of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{DMB})_3^{2+}$  from 1400 to 1650  $\text{cm}^{-1}$  with use of 354.7-nm excitation. Also included in each scan is the 983- $\text{cm}^{-1}$  peak due to 0.5 M  $\text{Na}_2\text{SO}_4$  internal standard.

Table V. Excited-State Parameters for the  $\text{Ru}(\text{bpy})_{3-N}(\text{4,4'-DMB})_N^{2+}$  Complexes in  $\text{H}_2\text{O}$  at Room Temperature

$N$	$\tau$ , ns	$\phi_{\text{em}}$	$E_{\text{em,max}}$ , $\text{cm}^{-1}$	$k_r$ , $10^{-4}$ , $\text{s}^{-1}$	$(K_{\text{nr}} + K_{\text{dd}}) \times 10^{-6}$ , $\text{s}^{-1}$
0	580	0.042	16475	7.24	1.65
1	470	0.025	16130	5.53	2.07
2	385	0.014	15850	3.64	2.56
3	335	0.014	15850	4.18	2.94

crepancy is not obvious, but the data shown in Table V are highly reproducible for different samples of the same complex. In Figure 7 is given a schematic diagram of the relevant photophysical processes for these types of complexes. In this figure, radiative transitions are depicted with solid lines while nonradiative processes are shown with a zig-zag. It is seen that the  $^3\text{MLCT}$  state has three major decay pathways available to it, two of which involve decay directly to the ground state, either by photon emission ( $k_r$ ) or vibrational relaxation ( $k_{\text{nr}}$ ). The third pathway ( $k_{\text{dd}}$ ) which Meyer and co-workers<sup>40</sup> have shown to be important for these types of ruthenium complexes, involves crossover into thermally accessible (energy of  $\Delta E$ ) d-d excited states followed by very rapid decay to the ground state (or in certain situations by ligand ejection). Thus, following Meyer and co-workers,<sup>40</sup> the lifetime of the excited state,  $\tau$ , is given by eq 2 where  $k_r$ ,  $k_{\text{nr}}$ , and  $k_{\text{dd}}$  are

$$\tau^{-1} = k_r + k_{\text{nr}} + k_{\text{dd}} = k_r + k_{\text{nr}} + A \exp(-\Delta E/RT) \quad (2)$$



Photophysical Processes

Figure 7. Schematic diagram of the relevant photophysical processes in  $\text{Ru}(\text{bpy})_3^{2+}$ .

the radiative, nonradiative, and d-d crossover rates, respectively. Now,  $k_r$  is readily available from the expression shown in eq 3 and is listed for each of the complexes in Table V. However,

$$\phi_{\text{em}} = k_r \tau \quad (3)$$

$k_{\text{dd}}$  can only be determined via temperature-dependent lifetime measurements. Thus, only the  $(k_{\text{nr}} + k_{\text{dd}})$  sum can be calculated directly from our data, and this sum is also listed in Table V. Upon inspection of these values, it is seen that  $(k_{\text{nr}} + k_{\text{dd}})$  values are roughly 2 orders of magnitude greater than the  $k_r$  values, thus demonstrating that the lifetimes of these  $^3\text{MLCT}$  states are

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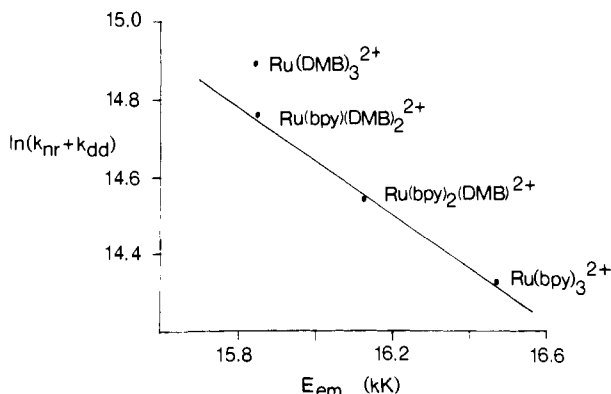


Figure 8. Plot of  $\ln(k_{nr} + k_{dd})$  vs.  $E_{em}$  for  $\text{Ru}(\text{bpy})_{3-N}(\text{DMB})_N^{2+}$  complexes ( $N = 0-3$ ).

principally controlled by these nonradiative processes.

Meyer and co-workers have shown that the excited-state decay characteristics of these types of complexes can be adequately interpreted in terms of the energy gap law formalism,<sup>19,41-45</sup> that is, a plot of  $\ln k_{nr}$  vs. the emission energy is expected to be linear. In fact, these workers have recently reported results for several series of mixed-ligand complexes of Ru(II) containing the ligands 2,2'-bipyridine, 2,2'-bipyrazine (bpyz), and 2,2'-bipyrimidine (bpy). For the series  $\text{Ru}(\text{bpy})_{3-N}(\text{bpyz})_N^{2+}$ , plots of  $\ln k_{nr}$  vs.  $E_{em}$  were linear for  $N = 1, 2$ , and 3, but the point corresponding to  $\text{Ru}(\text{bpy})_3^{2+}$  was well removed from the line. Similar behavior was observed for the bpy/bpy series.<sup>45</sup> As Meyer and co-workers have emphasized, the observation of linearity of such plots depends on the validity of certain underlying assumptions, the most important of which, in the context of the present work, is that the members of the series possess a common lumiphore.<sup>19,41-45</sup> Thus, their results strongly imply that the excited state which dominates the decay properties is centered on a bpyz or bpy rather than a bpy ligand. This is consistent with the fact that the  $\pi^*$  levels of bpyz and bpy are lower than that of bpy. In order to carry

out a comparable analysis for the bpy/DMB series, it would be necessary to determine the values for  $k_{dd}$  via temperature-dependent lifetime measurements. However, provided that the relative contribution of  $k_{dd}$  to the  $(k_{nr} + k_{dd})$  sum varies smoothly through the series, plots of  $\ln(k_{nr} + k_{dd})$  vs.  $E_{em}$  may be expected to exhibit linearity. The expectation that  $k_{dd}$  should vary smoothly through the series (at least for  $\text{Ru}(\text{bpy})_{3-N}(\text{DMB})_N^{2+}$ ; where  $N = 0, 1$ , and 2) is based on the following considerations.

The value of  $k_{dd}$  is expected to decrease as  $\Delta E$  (Figure 7) increases. The energy of the  $d\pi$  orbitals (and presumably also the  $d\sigma^*$ ) have been shown to vary smoothly in other series of mixed-ligand complexes wherein the  $\text{Ru}(3+/2+)$  potentials were measured.<sup>28</sup> In the present series, the energy of  $d\sigma^*$  should thus increase smoothly as bpy is replaced by DMB. On the other hand, the  $\pi^*$  orbitals are ligand-localized and retain their relative energies in the mixed-ligand complexes.<sup>28</sup> In this series, the  $\pi^*$ -(DMB) orbitals are higher in energy than the  $\pi^*$ (bpy) orbitals by  $\sim 800 \text{ cm}^{-1}$  based on the potentials given in Table III ( $1 \text{ eV} = 8065 \text{ cm}^{-1}$ ).

A plot of  $\ln(k_{nr} + k_{dd})$  vs.  $E_{em}$  for the present series of complexes is shown in Figure 8. The observation of linear behavior for the complexes corresponding to  $N = 0, 1$ , and 2 demonstrates that  $k_{dd}$  can be expressed as a constant fraction of  $k_{nr}$  and, most importantly, that these data are consistent with the  $\text{TR}^3$  data inasmuch as a common lumiphore (i.e., the  $(\text{Ru}^{III}(\text{bpy}^-))$  fragment is implicated).

The results presented here indicate that for a series of poly(pyridine) complexes, involving even a relatively mild chemical modification, the mixed-ligand complexes,  $\text{Ru}(\text{bpy})_2(\text{DMB})^{2+}$  and  $\text{Ru}(\text{bpy})(\text{DMB})_2^{2+}$ , possess isolated MLCT excited states with apparently insignificant interligand electronic coupling. The most obvious manifestation of such behavior is the observation of selective population of the lowest lying  $^3\text{MLCT}$  state. Furthermore, it has been shown that  $\text{TR}^3$  spectroscopy provides an especially effective and convenient method for the detection of this selectivity.

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**Registry No.**  $\text{Ru}(\text{bpy})_3^{2+}$ , 15158-62-0;  $\text{Ru}(\text{bpy})_2(4,4'\text{-DMB})^{2+}$ , 70281-18-4;  $\text{Ru}(\text{bpy})(4,4'\text{-DMB})_2^{2+}$ , 97135-47-2;  $\text{Ru}(4,4'\text{-DMB})_3^{2+}$ , 32881-03-1.

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## Infrared Intensities: Cyclohexane. A Molecular Force Field and Dipole Moment Derivatives

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**Abstract:** A force field derived from an ab initio molecular orbital procedure by using the 4-31G basis set was taken as the starting point for a normal coordinate analysis. The calculated F matrix was adjusted to fit the experimental vibrational frequencies and led to a root-mean-square error of  $10 \text{ cm}^{-1}$ . The intensities of the vibrational bands of cyclohexane and cyclohexane- $d_{12}$  were measured and were transformed into dipole moment derivatives. The signs of  $\partial\mu/\partial S$  are discussed in terms of a model we have developed for their interpretation.

Cyclohexane plays a special role in the study of cycloalkanes and related compounds. It is usually taken as the "unstrained"

model against which other compounds are compared, and force constants derived from cyclohexane have been used as the "normal"