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Ligand Steric Effects on the Photophysics of Bis- and Tris(2,2′-bipyridine) Complexes of Rhodium(III)

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The effects of 3,3′-dimethyl steric interactions on the luminescence of 2,2′-bipyridine complexes of rhodium(III) have been investigated. The tris complex, $Rh(dmbpy)_3^{3+}$, is found is display both metal-centered and ligand-centered emissions. The metal-centered emission is the dominant luminescence feature at 77 K, but the ligand-centered emission is enhanced relative to the metal-centered luminescence in fluid solutions. The bis complex, $Rh(dmbpy)_2Cl_2^+$, displays a dominant ligand field emission under all conditions that were studied. Reinvestigation of the luminescence of the tris(1,10-phenanthroline) and tris(2,2′-bipyridine) complexes of Rh(III) in fluid solutions indicates that these species emit only from ligand-centered excited states. Comparison of the 3,3′-dimethyl-2,2′-bipyridine and unsubstituted 2,2′-bipyridine complexes of Rh(III) indicates that both ligand-centered and metal-centered excited states have lower energies for the methyl-substituted complexes but the effect is larger for the metal-centered states.

Introduction

In recent years a number of workers have demonstrated the use of ligand substituents to modify the energies of transition-metal-complex excited states. The use of ligand substituents to alter absorption and emission properties in this manner has been termed "tuning", and such molecular engineering has proved especially successful in modifying the photochemical properties of various pyridyl, polypyridyl, and similar nitrogen aromatic heterocycle transition-metal complexes.[2] In most of these cases the substituent role is largely confined to electronic effects on the σ- and π-donor and -acceptor properties of the heterocyclic ligands. Steric effects of ligand substituents might also be expected to play a role in photoreaction properties but as yet have been exploited only modestly. One such substituent steric effect is that shown by 3,3′-dimethyl-2,2′-bipyridine (dmbpy), which can form chelated metal complexes such as $Rh(dmbpy)_3^{3+}$ (I).[3] Unlike the complexes of the unsubstituted 2,2′-bipyridine, such as $Ru(bpy)_3^{2+}$,[4] the two pyridine rings of coordinated dmbpy are not coplanar when coordinated, owing to the steric repulsion between the two methyl groups.[3] The structure[3d] determined for I shows the dihedral angle between the two pyridine planes of individual dmbpy ligands to be about 30°. As a consequence, one might expect the energies of excited states involving π-symmetry ligand orbitals to be affected owing to decreased delocalization between the rings.[5] In this context we have measured the emission properties of $Rh(dmbpy)_3^{3+}$ and of $Rh(dmbpy)_2Cl_2^+$ (III) in order to compare these photophysical properties to those of the analogous complexes of bipyridine, $Rh(bpy)_3^{3+}$ (II) and $Rh(bpy)_2Cl_2^+$ (IV), and of 1,10-phenanthroline, $Rh(phen)_3^{3+}$ (V),[6a] which we have reinvestigated. There has been considerable recent interest in the spectral properties of tris chelate Rh(III) complexes and in their potential as electron-transfer agents in the storage of radiant energy.[6b-d] The present study extends current information regarding the low-energy excited states of these complexes.

Experimental Section

Syntheses. $[Rh(dmbpy)_3](ClO_4)_3$. A mixture of $RhCl_3{\cdot}3H_2O$ (0.26 g in 20 mL of H_2O), dmbpy[3] (0.66 g in 10 mL of ethanol), and a catalytic amount of 85% hydrazine hydrate (~0.01 g) was heated at reflux for 30 min. The resulting pale yellow solution was filtered, a small quantity of 70% $HClO_4$ (0.1 mL) was added, and this solution was allowed to stand at room temperature for 1 h. The fine white crystals that precipitated were removed by filtration, then washed with water, ethanol, and ether sequentially, and air-dried. The resulting product was recrystallized from hot water, and attempts were made to purify the product further by column chromatography on Sephadex LH-20 using acetonitrile for elution. These attempts proved to be unsuccessful due to apparent decomposition of the product on the column to give an unknown yellow material. However, the product could be successfully purified prior to emission measurements by cation-exchange chromatography on a column composed of CM-Sephadex. The resin was first converted to the Na^+ form by treatment with aqueous NaCl. A column of this resin was prepared and then washed repeatedly with water to remove excess Na^+. After application to the column, samples were eluted with successive aliquots of 5×10^{-4}, 5×10^{-2}, and 5×10^{-1} M $NaHCO_3$ solutions. An uncharged impurity was removed in the first aliquot, and the purified $Rh(dmbpy)_3^{3+}$ cation was found in the aliquot eluted with 0.5 M $NaHCO_3$. Anal. Calcd for $C_{36}H_{36}N_6Cl_3O_{12}Rh$: C, 45.33; H, 3.68; N, 8.81. Found: C, 45.29; H, 3.75; N, 8.92.

$[Rh(dmbpy)_2Cl_2](ClO_4){\cdot}0.25H_2O$. A mixture of $RhCl_3{\cdot}3H_2O$ (0.26 g in 20 mL of H_2O), dmbpy (0.45 g in 10 mL of ethanol), and a catalytic amount of 85% hydrazine hydrate (~0.01 g) was heated at boiling for 5 min. The resulting yellow solution was filtered; then a small quantity of 70% $HClO_4$ (0.1 mL) was added, and the solution was allowed to stand at room temperature for 20 min. The yellow crystals that appeared were removed by filtration and washed sequentially with hot water (80 °C), ethanol, and ether. Anal. Calcd for $C_{24}H_{24}N_4Cl_3O_4Rh{\cdot}0.25H_2O$: C, 44.63; H, 3.82; N, 8.67. Found: C, 44.98; H, 4.23; N, 9.02.

$[Rh(bpy)_3](ClO_4)_3$ and $[Rh(phen)_3](ClO_4)_3$. These two complexes were both prepared according to published procedures.[7] The emission of $Rh(bpy)_3^{3+}$ in fluid acetonitrile at ambient temperatures initially showed a broad band in the red, similar to that reported for $Rh(phen)_3^{3+}$.[6a] However, purification by column chromatography on Sephadex LH-20 followed by repeated recrystallizations from water–methanol solutions gave samples of both $Rh(bpy)_3^{3+}$ and $Rh(phen)_3^{3+}$ which showed no red emission in fluid acetonitrile. Constancy of the emission spectrum and luminescence lifetime in 77 K methanol–water glasses (4:1 v/v) following the final stages of recrystallization was judged to be a valid test for purity.

Luminescence Procedures. Time-Integrated Emission Spectra. Two sets of apparatus were used in the measurement of time-integrated emission spectra. Corrected emission spectra of the free ligands and of the $Rh(bpy)_3^{3+}$ and $Rh(phen)_3^{3+}$ complex ions in the range 400–700

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Table I. Spectral Data for 2,2′-Bipyridine- and 3,3′-Dimethyl-2,2′-bipyridine-Rhodium(III) Complexes

	absorption data (293 K)		emission data (77 K)	
complex[a]	ν, μm^{-1}	$10^{-4}\epsilon$, M^{-1} cm^{-1}	ν, μm^{-1}	lifetime, ms
$[Rh(bpy)_3](ClO_4)_3 \cdot 3H_2O$	3.14	4.33	2.22[b,c]	2.19 ± 0.05[d]
	3.28	3.95		
	4.13	3.95		
$[Rh(dmbpy)_3](ClO_4)_3$	3.03	2.61	1.64	0.0754 ± 0.0013[e]
	3.12	2.69	2.07[c]	3.75 ± 0.50
	4.27	5.12		
$[RhCl_2(bpy)_2]ClO_4$	2.63 sh	0.0101	1.42[b]	0.0272 ± 0.0011[d]
	3.21	2.87		
	3.33 sh	2.37		
	4.00	2.31		
$[RhCl_2(dmbpy)_2]ClO_4$	2.53 sh	0.0175	1.44	0.0642 ± 0.0007
	3.11	1.68		
	4.26 sh	3.50		

[a] dmbpy denotes 3,3′-dimethyl-2,2′-bipyridine; bpy denotes 2,2′-bipyridine. [b] See ref 12. [c] Highest energy maximum in vibrational progression. [d] See ref 10. [e] Two emissions with different lifetimes are seen (see text).

nm were determined with a Hitachi Perkin-Elmer MPF-3 spectrophotometer equipped with a Hamamatsu Type 106 photomultiplier. A second apparatus, described previously,[8] with enhanced red sensitivity to 1100 nm was utilized for determination of the emission spectra of the remaining complex ions. For the purposes of this study, excitation was achieved at 366 nm, and a dry-ice-cooled RCA 7102 photomultiplier was used to detect the emission. The spectral response of the photomultiplier was calibrated with an NBS standard quartz tungsten-halogen lamp, and corrected emission spectra were computed with correction factors generated in the calibration procedure.

Time-Resolved Emission Spectra. A PAR Model 162 boxcar averager with a Model 163 gated integrator was used in the determination of time-resolved emission spectra. Two different sets of pulsed excitation sources and optical components were used in conjunction with this gated detection system. One set utilized pulses from the third harmonic of a Quanta-Ray DCR-1 Nd/YAG laser for excitation and a Spex Spectramate double-grating monochromator with an EMI 9808 or an RCA 8852 photomultiplier for detection. The second set utilized fundamental pulses (337 nm) from an AVCO C950 pulsed nitrogen laser and a Fastie Ebert 0.5-m scanning monochromator equipped with an EMI 9558 QA photomultiplier for detection. Both sets of apparatus could be successfully applied to the measurement of time-resolved spectra of samples at 77 K. However, photodecomposition of samples at 231 K was observed during the time required for determination of time-resolved spectra when excitation was carried out with the Nd/YAG laser.

Luminescence Lifetime Determinations. Both the Nd/YAG and nitrogen laser systems and the associated optics described above were used in determination of luminescence lifetimes.[9] The boxcar averager was replaced by either a Tektronix Model 7904 oscilloscope or a Tektronix 7912 AD transient digitizer to facilitate determination of lifetimes upon application of a single pulse from the laser system.

Results

Emission spectra and lifetimes of compounds I–V were investigated both in low-temperature (77 K) glasses and in fluid solutions between 231 and 295 K. Absorption spectra were recorded with a Cary 118 spectrometer only in ambient-temperature fluid solutions.

The Free Ligands. The phosphorescence spectra of bpy and dmbpy appear at similar energies although the vibrational structure is different in the two spectra (Figure 1). These results suggest that, in the absence of coordination to a metal center, the two ligands assume comparable conformations.

$Rh(dmbpy)_2Cl_2^+$ and $Rh(bpy)_2Cl_2^+$. The absorption spectra in aqueous solutions and emission spectra in 77 K glasses (Figure 2) are qualitatively similar for these two ions. The absorption spectrum of each shows an intense intraligand

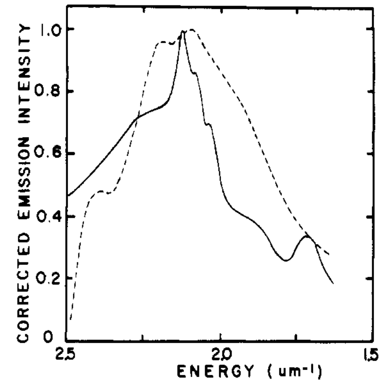

Figure 1. Phosphorescence spectra of 2,2′-bipyridine (---) and 3,3′-dimethyl-2,2′-bipyridine (—) in methanol–water glass (4:1 by volume) at 77 K.

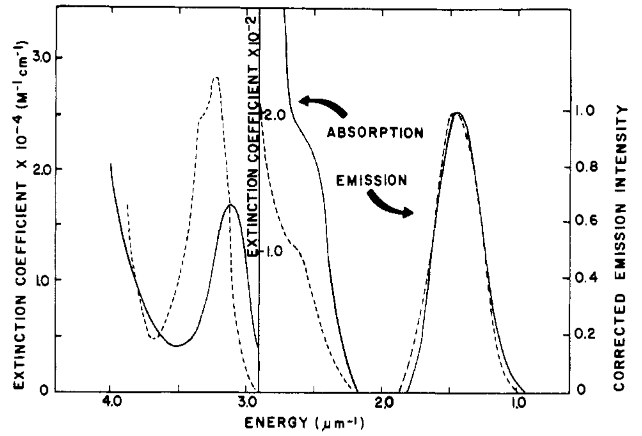

Figure 2. Absorption and emission spectra of *cis*-dichlorobis(2,2′-bipyridine)rhodium(III) perchlorate (---) and *cis*-dichlorobis(3,3′-dimethyl-2,2′-bipyridine)rhodium(III) perchlorate (—). Absorption spectra were taken at 293 K in aqueous solution; emission spectra, at 77 K in methanol–water glass (4:1 by volume).

transition in the ultraviolet region (3.22 μm^{-1} for III, 3.11 μm^{-1} for IV) as well as a much lower intensity, longer wavelength shoulder, which suggests a LF absorption. The emission spectra of III and IV each show broad Gaussian bands with maxima at about 1.4 μm^{-1} (Table I). Lifetime measurements gave exponential decays with relatively short lifetimes of 27.2 and 64.2 μs, respectively, at 77 K (Table I). The spectral properties found for IV agree with those reported previously,[10] and these characteristics are consistent with the assignment

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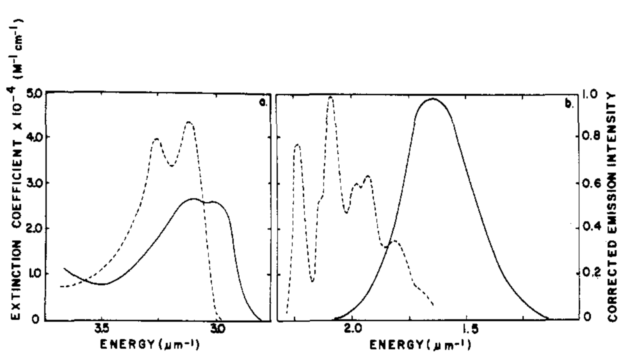

Figure 3. (a) Absorption spectra of tris(2,2′-bipyridine)rhodium(III) perchlorate (---) and tris(3,3′-dimethyl-2,2′-bipyridine)rhodium(III) perchlorate (—) at 293 K in aqueous solution. (b) Emission spectra of tris(2,2′-bipyridine)rhodium(III) perchlorate (---) and tris(3,3′-dimethyl-2,2′-bipyridine)rhodium(III) perchlorate (—) in methanol–water glass (4:1 by volume) at 77 K.

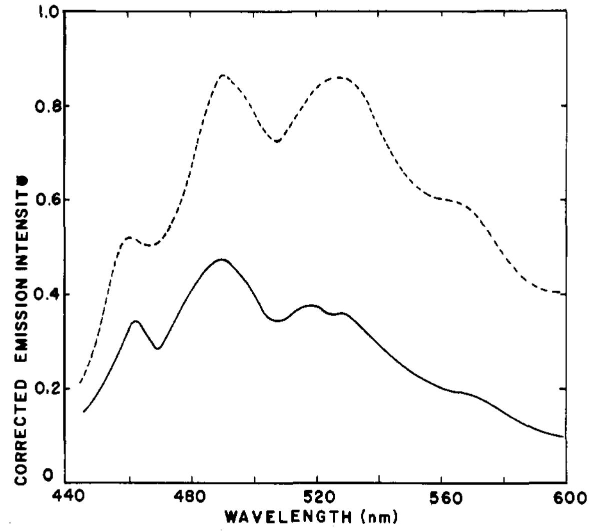

Figure 4. Emission spectra of tris(2,2′-bipyridine)rhodium(III) perchlorate in acetonitrile at 263 K (---) and at 297 K (—).

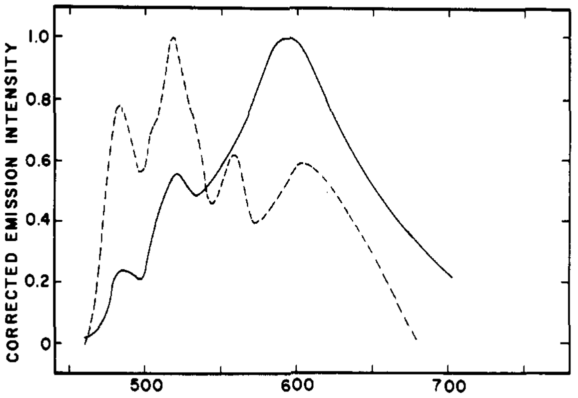

Figure 5. Time-resolved emission spectra of tris(3,3′-dimethyl-2,2′-bipyridine)rhodium(III) perchlorate in methanol–water glass (4:1 by volume) at 77 K: (—) spectrum measured 0.5 ms after pulsed excitation; (---) spectrum measured 2.0 ms after pulsed excitation.

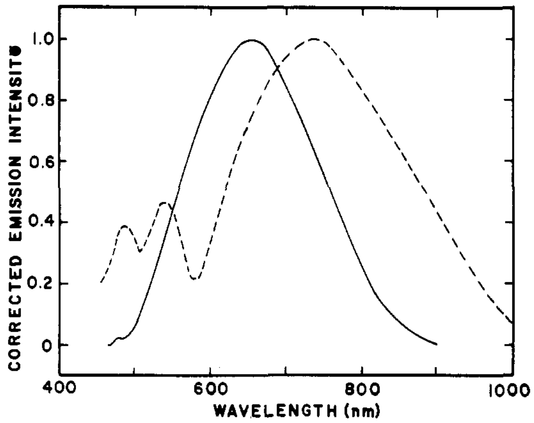

Figure 6. Emission spectra of tris(3,3′-dimethyl-2,2′-bipyridine)rhodium(III) perchlorate in acetonitrile at 212 K (—) and at 232 K (---).

of the emitting states as ligand field triplets, as made previously for IV.[10] Analysis of the emission bands according to a Gaussian band shape[8,11] gives estimated values of 1.88 and 1.86 μm^{-1} for the 0–0 triplet excited-state energies of III and IV, respectively.

Rh(dmbpy)$_3^{3+}$ and Rh(bpy)$_3^{3+}$. In contrast to the results seen for the dichloro bis(ligand) complexes, the photophysical properties of the two tris(ligand) complexes, I and II, are dramatically different. In low-temperature glasses, the Rh(bpy)$_3^{3+}$ ion displays a long-lived (2.2 ms) structured emission with the 0–0 transition identified at 2.22 μm^{-1} (Figure 3). The combination of long lifetime and structured emission for this complex has led to an intraligand π–π^* assignment for its emission.[10,12] In fluid acetonitrile solutions the same emission spectrum, slightly red-shifted (0–0 energy 2.20 μm^{-1}) and having much weaker intensity, was observed at 263 and 297 K (Figure 4). Attempts to measure the luminescence lifetime at these temperatures in fluid acetonitrile showed the lifetime to be shorter than the pulses from either of the two lasers used for excitation (<15 ns).

A different emission spectrum was found for Rh(dmbpy)$_3^{3+}$ in the 77 K glass (Figure 3). The predominant characteristic is an intense, broad band centered at 1.66 μm^{-1}. Calculation of the 0–0 energy according to the method used for the dichloro complexes above gives a value of 2.15 μm^{-1}. The high-energy edge of this emission spectrum shows a second, very weak structured emission. The lifetime of the intense, broad emission, monitored at the 1.66-μm^{-1} maximum, is 75 μs. Examination of the weak, structured emission using the boxcar averager with a time delay of 2 ms shows this structured emission more clearly, with maxima at 2.07, 1.93, and 1.78 μm^{-1} (Figure 5). Lifetime measurements yield a value of 3.75 ms for this emission.

The same types of emission are in evidence at higher temperatures; however, there is a dramatic dependence of the emissions on the phase of the solvent medium. Figure 6 illustrates the emission spectrum of Rh(dmbpy)$_3^{3+}$ in acetonitrile at 212 K, a temperature at which this solvent is still crystalline. Under these conditions, the corrected emission is dominated by the broad Gaussian band, now with a maximum intensity at ~1.5 μm^{-1}. The structured emission remains barely discernible on the high-energy shoulder of this band. Luminescence decay curves were distinctly nonexponential at 212 K, and a range of lifetimes between 2 and 18 μs resulted from analysis in various portions of the decay. However, at 231 K, the melting point of acetonitrile, the emission is markedly different (Figure 6). The broad band is much weaker and broader than noted in crystalline solvent, while the structured emission, though weaker than that at 77 K, now has an integrated intensity comparable to that of the broad emission. Moreover, as the temperature is raised further, the structured-to-broad emission intensity ratio increases. Lifetimes

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(11) This analysis estimates the 0–0 energy as the energy at which the emission intensity drops to 1% of the intensity at the band maximum on the high-energy side of the band. This point is given by $\nu_{1\%} = \nu_{\max} + 1.29\Delta\nu_{1/2}$, where $\Delta\nu_{1/2}$ is the bandwidth at half-height for a Gaussian band shape.

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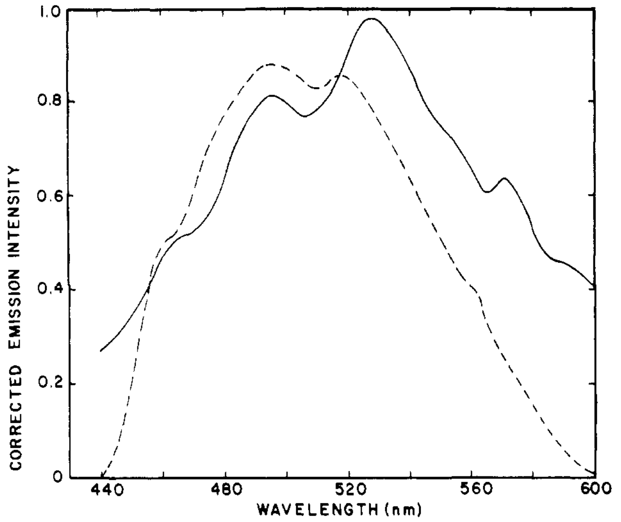

Figure 7. Emission spectra of tris(1,10-phenanthroline)rhodium(III) perchlorate in acetonitrile at 268 K (—) and at 297 K (- - -).

in the fluid solutions were again shorter than the laser pulses used to excite the complex (<15 ns).

Rh(phen)$_3^{3+}$. The emission spectrum of Rh(phen)$_3^{3+}$ in a methanol–ethanol glass at 77 K was identical with that reported previously,[10] a structured progression of bands at 2.22, 2.08, 1.94, and 1.80 μ^{-1}. The luminescence lifetime under these conditions was quite long (47.1 ms), consistent with previous reports. Careful examination of the emission spectrum in fluid acetonitrile solution at 268 and 297 K (Figure 7) showed a very similar spectrum with the bands slightly red-shifted (2.15, 2.02, 1.91, and 1.75 μm^{-1} at 268 K) and a considerably shortened lifetime (18.7 ns at 297 K, Figure 7). In rigorously purified samples, there was no evidence of the Gaussian band reported previously and assigned as a LF emission.[6a] Since several of the Rh(phen)$_3^{3+}$ samples did show the latter emission properties prior to column chromatography, the likely explanation of the discrepancy is emission from an impurity ubiquitous to samples of these complex ions.

Discussion

The emission data described above will be discussed in terms of two key features: first, the qualitative similarity of the emission spectra of the dichloro bis(ligand) complexes III and IV, and second, the marked differences in excited-state luminescence properties of the tris(ligand) complexes.

As noted above, the broad Gaussian emission and relatively short excited-state lifetime of Rh(bpy)$_2$Cl$_2^+$ (27 μs at 77 K) led to the assignment of the lowest energy, emitting excited state of this complex as a triplet ligand field state.[10] On the basis of the similar Gaussian band shape and short lifetime of the Rh(dmbpy)$_2$Cl$_2^+$ emission, the analogous excited-state assignment in this case would be appropriate. Although initial 336–366-nm excitation is into π–π^* intraligand absorption bands, it has been well established in the case of II that internal conversion/intersystem crossing to the lowest excited state is very rapid.[13]

The electronic effect of methyl substitution on the aromatic ring should be an increase in the σ-donor strength of the bipyridine ligand; however, a counteracting decrease in π-acceptor strength has also been proposed[14] for Rh(III) complexes such as RhCl$_4$L$^-$ where L is a substituted 1,10-phenanthroline. The net electronic result of methyl substitution on the LF emission is small. The steric effect of the methyl groups forcing the pyridine rings 30° out of coplanarity might be more dramatic. Qualitatively, one might expect that the twisting of the bipyridine would reduce the π-acceptor ability of the rings as well as reduce the overlap between the pyridyl nitrogen σ orbitals and metal orbitals of the same symmetry. In this context it was thus somewhat surprising to find that the LF emission bands of Rh(bpy)$_2$Cl$_2^{2+}$ and Rh(dmbpy)$_2$Cl$_2^+$ have nearly identical ν_{max} values ($\sim$1.43 μm^{-1}) and calculated ν_{00} values (1.86 and 1.88 μm^{-1}, respectively). One possible explanation can be drawn from viewing these complexes in terms of holohedral D_{4h} symmetry where the xy plane is defined as that which includes the two Rh–Cl bonds. Given that Cl$^-$ is the weaker field ligand, the lowest excited state would likely be the "A$_2$" state with the one-electron orbital population $(d_{xy})^1(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^1(d_{z^2})^0$. The energies of the respective $d_{x^2-y^2}$ and d_{xy} orbitals of the two complexes may be sufficiently dominated in these cases by electronic effects from the two Cl's that modest differences in the nature of the nitrogen ligands in the xy plane have little influence on the emission energies. Notably, the emission spectra of both *cis*-Rh(phen)$_2$Cl$_2^+$ and *cis*-Rh(NH$_3$)$_4$Cl$_2^+$ have ν_{max} values (1.42 μm^{-1})[2,15] close to those of III and IV, consistent with this argument.

When the tris(bipyridine) type complexes are considered, a greater response by the ligand field state energies to the differences in the nitrogen donor ligands should logically be expected. Such an argument may explain the differences in the spectral properties of Rh(bpy)$_3^{3+}$ and Rh(dmbpy)$_3^{3+}$. The distortion noted above should indeed have the effect of lowering the LF state energies of dmpy complexes relative to those of the bpy analogues. The low-temperature spectra of I and V suggest that the measurable emissions from Rh(bpy)$_3^{3+}$ and Rh(phen)$_3^{3+}$ are π^*–π intraligand transitions characteristic of the lowest energy excited states of these complexes. A different situation is the case for the Rh(dmpby)$_3^{3+}$ ion. At 77 K two independent emissions are observed; the broad Gaussian band centered at 1.66 μm^{-1} has the shape and lifetime (75 μs) characteristic of a LF emission while the emission appearing as a high-energy shoulder on the LF band has the structure and longer lifetime (3.75 ms) expected for an independent π^*–π emission.[16] Since repeated purification of this compound did not change the relative importance of the two emissions, we conclude that both emissions are indeed characteristic of the Rh(dmbpy)$_3^{3+}$ complex. The coexistence of two independent emissions from similar complex ions at low temperature where the two have different orbital parentages has been described previously.[17] At higher temperatures in fluid solutions both emissions are very short, suggesting that the two states thermally equilibrate under these conditions. The nonexponential decay observed at 212 K in crystalline acetonitrile suggests that the two states remain nonequilibrated below the melting point of the solvent, although environmental inhomogeneities[18] may also contribute to the complex decay curves.

The 0–0 energies of the two low-temperature transitions seen for Rh(dmbpy)$_3^{3+}$ can be estimated for the π^*–π transition from the position of the highest energy peak in the vibrational progression (Figure 3) as 2.07 μm^{-1} and for the LF emission according to the Gaussian analysis[11] as 2.15 μm^{-1}. Uncertainties in these analysis methods are sufficiently large to place in doubt the exact ordering of these two states. However, the primary point is that the two states are quite close in energy.

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The observation that both emissions apparently occur with the same lifetime at $T > 231$ K is consistent with thermal equilibration of the two close-lying states in fluid solutions. The failures of the two states to interconvert efficiently at lower temperatures may represent significant differences in the geometries of the two states and in the structures of the associated solvation spheres. This can result in large, viscosity-dependent activation barriers[19] for the nonradiative transitions between these states. Thus, once the LF and $\pi^*-\pi$ excited states are populated by competing internal-conversion/intersystem crossing/vibrational relaxation pathways from the upper states formed by initial excitation, the rates of internal conversion between them are slower than the independent deactivation processess to the ground state. At higher temperatures and lower viscosities, solvent reorganizational barriers are reduced, and the thermal energy of the system becomes sufficient to overcome the remaining activation barriers.

Observation of both $\pi^*-\pi$ and LF emission under the higher temperature conditions where the two are equilibrated has a further connotation. Given that the radiative rate constant from the $\pi^*-\pi$ state is likely to be much smaller than that from the LF excited state,[16] this implies that the ligand-centered excited state has the greater population and is therefore lower in energy, in agreement with the estimates above. The marked intensity enhancement of the $\pi^*-\pi$ emission relative to the LF emission upon the phase change to the liquid acetonitrile medium at 231 K is consistent with equilibration of the two states, which, according to the present analysis, should result in a substantial increase in population of the lower energy $\pi^*-\pi$ state. Similar perturbations of the emission properties upon the solvent phase change from solid to liquid have been observed for several complexes of Ir(III),[17] which also display several nonequilibrated emissions below the solvent melting point. In addition, several complexes of Re(I) are known to undergo large changes in their emission band energies at the solvent melting point, and the term "rigidochromic" effect has been coined for this phemonenon.[20]

An especially interesting comparison can be made between the $Rh(dmbpy)_3^{3+}$ ion and the $Ir(5,6\text{-Mephen})_2Cl_2^+$ ion studied previously[17] (5,6-Mephen = 5,6-dimethyl-1,10-phenanthroline). In both cases $\pi^*-\pi$ and LF excited states are close in energy. In the latter case excitation in nonequilibrated glasses results in predominant emission from the $\pi^*-\pi$ state whereas the LF emission is enhanced relative to the ligand-centered emission upon melting the solvent. This behavior was attributed[17] to solvent-induced barriers[19] for conversion of the $\pi^*-\pi$ state to the LF state, presumably due to motions of the bulky Mephen ligands required for this radiationless transition. These barriers are reduced in fluid solvents where rapid equilibration occurs. The situation in $Rh(dmbpy)_3^{3+}$ is reversed since the LF emission predominates in nonequilibrated rigid media and the $\pi^*-\pi$ emission is relatively enhanced in fluid media. This result suggests that formation of the $\pi^*-\pi$ state requires a geometry change that is particularly strongly influenced by interactions with the rigid solvent cage. Some required twisting about the bridging bond between the pyridine rings could, for example, lead to large solvent-induced barriers to formation of the $\pi^*-\pi$ state. Since the ground-state structure indicates substantial twisting about this bond can indeed occur, it is not unreasonable that formation of the $\pi^*-\pi$ excited state might result in significant changes in the dihedral angle between the methyl-substituted pyridine rings. The sweeping motion of these large rings through the solvent should be particularly sensitive to viscosity considerations.

Lastly, one might ask why the emission properties of the two tris complexes, $Rh(dmbpy)_3^{3+}$ and $Rh(bpy)_3^{3+}$, are so different. In the former case, it is clear that the methyl groups substituted in the positions ortho to the C–C bond linking to two pyridine rings have served to lower the energies of both the LF and $\pi^*-\pi$ triplet excited states. Relative to $Rh(bpy)_3^{3+}$, the energy of the metal-centered state is apparently the more greatly affected by methyl substitution since LF emission is not seen in the parent ion but is the major contributor for the methyl-substituted ion. This lowering of the LF state energies can be rationalized in terms of the ligand out-of-plane distortion causing decreased overlap between metal and ligand σ orbitals. The result is the decrease in the effective ligand field strengths of the distorted ligands. That the lowest LF excited state of $Rh(dmbpy)_3^{3+}$ is indeed lower in energy than the analogous LF excited state of $Rh(bpy)_3^{3+}$ is evidenced by the fact that the emitting $\pi^*-\pi$ state of the latter ion has a 0–0 energy of 2.21 μm^{-1}, which is higher than the 2.15 μm^{-1} value estimated for the LF excited state 0–0 energy of the former ion. Although measurable emission is not seen from the LF excited state of $Rh(bpy)_3^{3+}$, two observations point to this state being reasonably close to the lowest $\pi^*-\pi$ state energetically. First, emission lifetimes drop precipitously as the temperature is raised above the melting point of the solvent medium, suggesting the presence of a thermally accessible excited state from which nonradiative deactivation is very rapid. Second, irradiation of $Rh(bpy)_3^{3+}$ and $Rh(dmbpy)_3^{3+}$ in acidic aqueous solution have shown both of these complexes to be fairly photoactive (quantum yields for disappearance of starting material are ~0.1 mol/einstein) toward ligand labilization.[21] Given that ligand labilization is a commonly observed reaction of the LF excited state of d^6 metal complexes,[2] it is likely that the photoreactivity can be attributed to such states populated thermally from the lowest energy $\pi^*-\pi$ excited state.

In summary, we conclude that the orderings of the lower energy excited states of the $Rh(bpy)_3^{3+}$ and $Rh(dmbpy)_3^{3+}$ ions are qualitatively similar in the sense that triplet $\pi^*-\pi$ intraligand states are the lowest energy excited states in each case and that a LF excited state lies somewhat above this lowest excited state. These two states are energetically close enough in $Rh(dmbpy)_3^{3+}$ to have sufficient populations for each to emit in equilibrated fluid solvents. In rigid media, viscosity barriers to formation of the $\pi^*-\pi$ excited state lead to a nonequilibrated emission dominated by the LF state. In addition, we conclude that while both the LF and $\pi^*-\pi$ excited states have lower 0–0 energies as the result of the electronic and steric effects of the methyl groups in the 3 and 3′ positions, the LF states are the more greatly affected. The result is a smaller LF/$\pi^*-\pi$ excited state separation for the $Rh(dmbpy)_3^{3+}$ complex ion.

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Registry No. $[Rh(bpy)_3](ClO_4)_3$, 28018-83-9; $[Rh(dmbpy)_3](ClO_4)_3$, 89955-34-0; *cis*-$[RhCl_2(bpy)_2]ClO_4$, 49727-33-5; *cis*-$[RhCl_2(dmbpy)_2]ClO_4$, 89909-14-8; $[Rh(phen)_3](ClO_4)_3$, 23907-76-8.

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