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The Effect of Energy Gaps on Multiple Emissions in Heterotriscchelated Rhodium(III) Complexes

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Abstract: Three groups of complexes have been prepared and studied by emission spectroscopy: (A) $[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$; (B) $[\text{Rh}(\text{bpy})_n(5,6\text{-Mephen})_{3-n}]^{3+}$; (C) $[\text{Rh}(\text{phen})_n(5,6\text{-Mephen})_{3-n}]^{3+}$. The nonexponential luminescence decays of the group A complexes ($n = 1, 2$) have been time resolved by boxcar averaging techniques. The group B and C complexes are characterized by exponential luminescence decays. The results are correlated with the energy gaps between the $^3\pi\pi^*$ states of the coordinated ligands. These are found to be $\sim 100 \text{ cm}^{-1}$ for group A and $\sim 1600 \text{ cm}^{-1}$ for groups B and C.

I. Introduction

The occurrence of multiple emissions from polyatomic molecules containing only light atoms is commonplace as evidenced by simultaneous fluorescence and phosphorescence exhibited by numerous organic species. The effect of heavy central metal ions with a variety of electronic configurations on the emissions of organic ligands has been the subject of many studies. For example, systematic studies of metalloporphyrins² have shown that central metal ions with closed shells (groups 2A, 2B, 3A, 4A) form metalloporphyrins which show both fluorescence and phosphorescence;^{2a,c} modification of this behavior by the presence of metal ions with open shells but closed subshells [Rh(III), Ru(II), Pd(IV), Pt(II), Pd(II)] is manifested in enhancement of phosphorescence, although weak fluorescence is still observed.^{2d,e,g} Several cases of multiple fluorescence emissions ($S_2 \rightarrow S_0$, $S_1 \rightarrow S_0$) from metalloporphyrins have also been reported.^{2f,h}

Studies of the emissions of complexes of Rh(III) with the bidentate ligands 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) indicate that the homotriscchelated complexes $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Rh}(\text{phen})_3]^{3+}$ phosphoresce from one thermally equilibrated manifold of ligand localized $\pi\pi^*$ states at 77 K.^{3,4} At lower temperatures (7–9 K), spin-lattice relaxation processes are slowed sufficiently to cause nonexponential decay from the thermally nonequilibrated triplet sublevels.^{4c} The heterotriscchelated complexes, $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ and $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$, display multiple phos-

phorescence emissions at 77 K from $\pi\pi^*$ states localized on phen and on bpy.^{3b,4b} Furthermore, several heterotriscchelated complexes of Ir(III) show multiple emissions from $d\pi^*$ and $\pi\pi^*$ states at low temperatures⁵ (77 K) and the homobiscchelated complex, $[\text{IrCl}_2(\text{phen})_2]^{1+}$, emits from both $d\pi^*$ and dd states at intermediate temperatures ($\sim 230 \text{ K}$).⁶ Recent reports indicate that the *fac*- $\text{ClRe}(\text{CO})_3\text{L}_2$ ($\text{L} = 4\text{-phenylpyridine}$) complex emits from a $\pi\pi^*$ state at 77 K and from a CT state at 298 K,^{7a} suggesting that dual $\pi\pi^*$ and CT emissions are likely at intermediate temperatures, and simultaneous emissions from thermally nonequilibrated $n\pi^*$ and charge-transfer levels in *fac*- $\text{XRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$ at 77 K have been observed.^{7b} Hence, there is mounting evidence that radiationless transitions between excited states of metal complexes are not always efficient.

The factors relevant to radiationless relaxation between electronic excited states have been widely discussed. Intramolecular features which influence spin-orbit coupling, energy gaps between electronic states, and vibrational frequencies are particularly important. Perturbations introduced by viscosity and temperature changes in the environment also make significant contributions to radiationless decay rates.⁸ In order to study the influence of these various factors, it is desirable to vary only one while keeping the others constant. In this paper, we report the effects of varying the energy gap between the lowest two $\pi\pi^*$ triplets of several heterotriscchelated complexes of Rh(III). To a good approximation, other factors

Table I. Luminescence Lifetimes, τ , and Emission Energies, E^0 , of Triscelated Complexes of Rhodium(III) at 77 K in Methanol-Water Glasses

n	$[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$		$[\text{Rh}(\text{bpy})_n(5,6\text{-Mephen})_{3-n}]^{3+}$		$[\text{Rh}(\text{phen})_n(5,6\text{-Mephen})_{3-n}]^{3+}$	
	τ , ms	E^0 , μm^{-1}	τ , ms	E^0 , μm^{-1}	τ , ms	E^0 , μm^{-1}
3	2.2 ^{a,b}	2.22 ^b	2.2 ^{a,b}	2.22 ^b	48.0 ^{a,b}	2.22 ^b
2	2.3 and 37 ^b		49.9	2.06	48.0	2.06
1	2.3 and 36 ^b		48.0	2.06	48.6	2.06
0	48.0 ^{a,b}	2.22 ^b	48.4	2.06	48.4	2.06

^a See ref 2. ^b See ref 3.

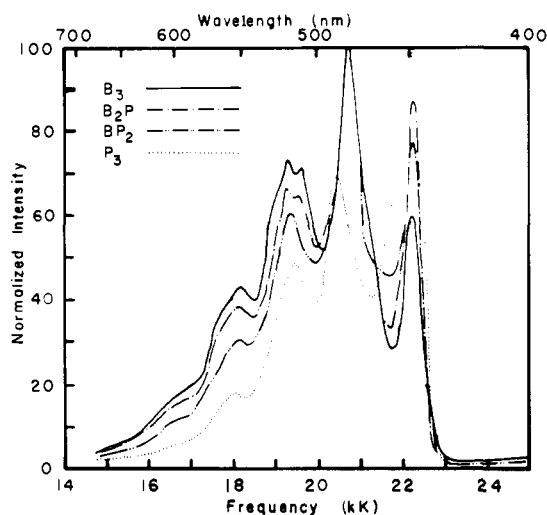


Figure 1. Luminescence of group A complexes in methanol-water at 77 K.

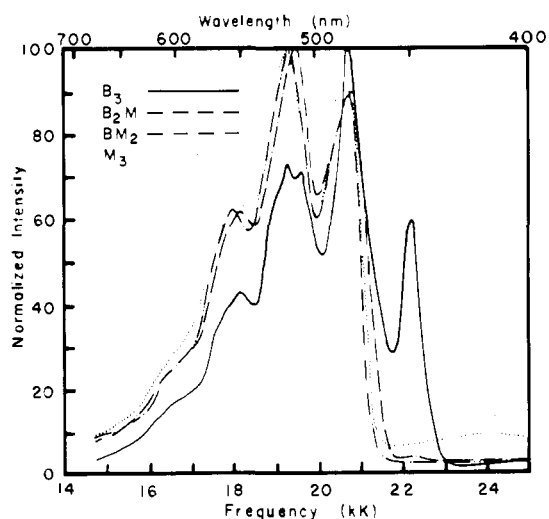


Figure 2. Luminescence of group B complexes in methanol-water at 77 K.

which might influence the radiationless decay rate were held constant.

II. Experimental Section

The homobiscelated complexes $[\text{RhCl}_2(\text{bpy})_2]^+$, $[\text{RhCl}_2(\text{phen})_2]^+$, and $[\text{RhCl}_2(5,6\text{-Mephen})_2]^+$ were prepared from rhodium(III) chloride and the appropriate ligand by the method of Broomhead and Grumley.⁹ The absence of uncomplexed ligand in samples of these complexes was established by emission spectroscopy of glassy solutions of them at 77 K. Conversion to the desired heterotriscelated complex was accomplished by treatment with a stoichiometric amount of the desired ligand by the method of Gillard.^{10,11} Time-integrated emission spectra were recorded with a Perkin-Elmer Hitachi MPF-3A spectrophotofluorimeter. Phosphorescence decay curves and time-resolved phosphorescence spectra were determined with an Avco C-950 pulsed nitrogen laser by techniques previously described.^{5b}

III. Results and Discussion

The results of this study are presented in three groups according to the two bidentate ligands (L, L') bound to Rh(III) in the triscelated complexes, $[\text{Rh}(\text{L})_n(\text{L}')_{3-n}]^{3+}$. Group A consists of the complexes $[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$; group B of the complexes $[\text{Rh}(\text{bpy})_n(5,6\text{-Mephen})_{3-n}]^{3+}$; and group C of the complexes $[\text{Rh}(\text{phen})_n(5,6\text{-Mephen})_{3-n}]^{3+}$. The time-integrated emission spectra of these three groups of complexes are shown in Figures 1-3 and their luminescence lifetimes are tabulated in Table I.

The group A complexes displayed nonexponential luminescence decay curves as reported previously by Halper and DeArmond.⁴ Their analysis of the decay curves of $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ and $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$ indicates that the short component (2.3 ms) in each is due to a localized $^3\pi\pi^*$ emission of the bpy ligand. No significant transfer of energy from bpy to phen occurs during the lifetime of the $^3\pi\pi^*$ state of bpy. The longer component (36-37 ns) is due to a localized

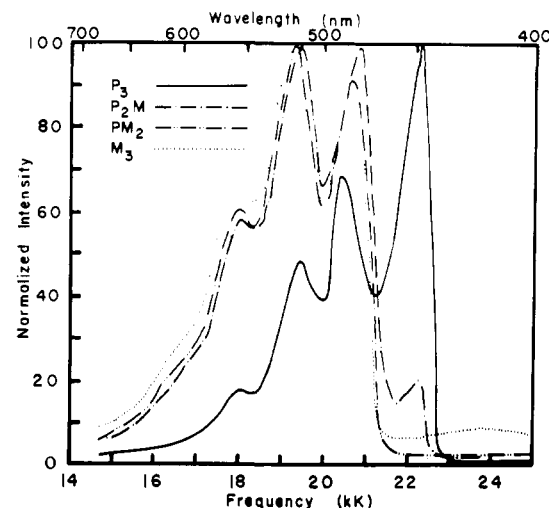


Figure 3. Luminescence of group C complexes in methanol-water at 77 K.

$^3\pi\pi^*$ emission of the phen ligand. The lifetime of this component is somewhat shorter than that of $[\text{Rh}(\text{phen})_3]^{3+}$ (48 ms) indicating some transfer of energy from the $^3\pi\pi^*$ of phen to the $^3\pi\pi^*$ of bpy. The reciprocal rate constants for this interligand transfer are estimated to be 72 and 64 ms for $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ and $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$, respectively.⁴

Although the $^3\pi\pi^*$ emissions of phen and bpy have their origins at nearly the same energies as evidenced by the emissions of $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Rh}(\text{phen})_3]^{3+}$ in Figure 1, the vibrational intensity distribution in the two are quite different. Therefore, time resolution of the nonexponential emissions of $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ and $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$ should reveal intensity variations in the vibrational structure with time.

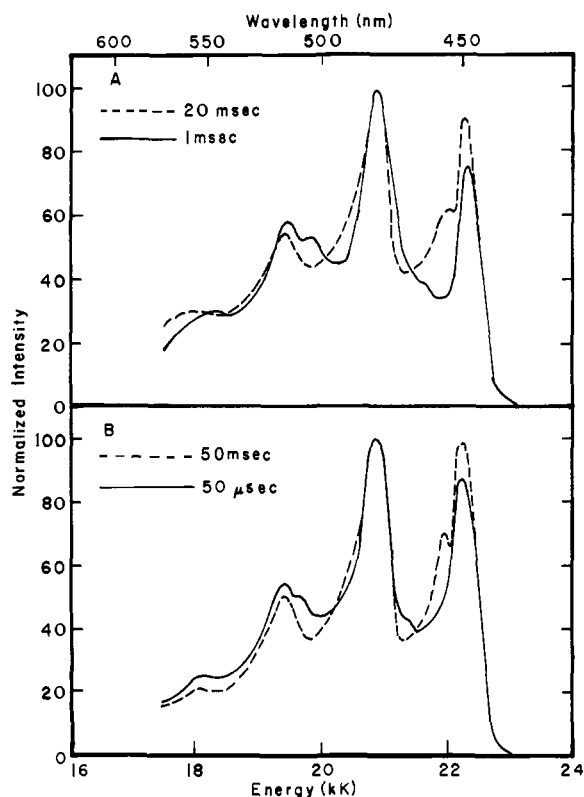


Figure 4. Time-resolved luminescence of $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ (A) and $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$ (B) in methanol-water at 77 K.

Halper and DeArmond were able to observe such variations for $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ via mechanical chopping techniques, but were unable to detect any variations in the $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$ emissions. The results of the present study, obtained by boxcar averaging techniques, are shown in Figure 4. Variation in the vibrational intensity distribution with time is evident in both complexes. Furthermore, the figure shows that the spectra at short times more closely resemble that of $[\text{Rh}(\text{bpy})_3]^{3+}$ while the spectra at longer times resemble that of $[\text{Rh}(\text{phen})_3]^{3+}$. This strongly supports the interpretation of the nonexponential decays as localized $^3\pi\pi^*$ emissions on bpy and on phen.

Although the emissions of $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Rh}(\text{phen})_3]^{3+}$ in Figure 1 have isoenergetic origins, a small shift in the origins of the two emissions of $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ and $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$ are evident in the time-resolved spectra, Figure 4. The emission at short times has its origin at 446 nm while that at longer times shifts to 448 nm. This shift is substantially larger than the resolution of our spectrometer (0.1 nm), and we therefore estimate that the $^3\pi\pi^*$ of phen lies about 100 cm^{-1} below that of bpy in the mixed complexes.

From Figure 2 and Table I it is evident that the $^3\pi\pi^*$ of 5,6-Mephen lies well below that of bpy. In this case the energy gap is estimated to be about 1600 cm^{-1} . We found no evidence for nonexponential decay in the group B complexes. The $[\text{Rh}(\text{bpy})_2(5,6\text{-Mephen})]^{3+}$ and $[\text{Rh}(\text{bpy})(5,6\text{-Mephen})_2]^{3+}$ complexes both showed exponential decays with lifetimes nearly equal to that of $[\text{Rh}(5,6\text{-Mephen})_3]^{3+}$. The emission spectra of both were nearly identical with that of $[\text{Rh}(5,6\text{-Mephen})_3]^{3+}$ also. Hence, we conclude that energy transfer from the $^3\pi\pi^*$ of bpy to the $^3\pi\pi^*$ of 5,6-Mephen occurs on a time scale much shorter than the 2.3-ms lifetime of bpy.

Within the group C complexes we found that the lifetimes of $[\text{Rh}(\text{phen})_3]^{3+}$ and $[\text{Rh}(5,6\text{-Mephen})_3]^{3+}$ are nearly identical. The $^3\pi\pi^*$ emission of the 5,6-Mephen complex lies about 1600 cm^{-1} below that of the phen complex. As a result,

the two emissions are easily resolved in energy, but time resolution is expected to be difficult. One might expect to time resolve two emissions if energy transfer from the higher energy $^3\pi\pi^*$ of phen to the lower energy $^3\pi\pi^*$ of 5,6-Mephen were sufficiently rapid to shorten the lifetime of the phen emission but not so rapid as to reduce the intensity of the emission below the limits of detection. Although a weak shoulder appears at 2.22 μm^{-1} in the emission of $[\text{Rh}(\text{phen})_2(5,6\text{-Mephen})]^{3+}$ in addition to the strong band at 2.06 μm^{-1} , the luminescence lifetime monitored at 2.22 μm^{-1} was found to be identical with that monitored at 2.06 μm^{-1} (48 ms). Furthermore, no evidence for an emission at 2.22 μm^{-1} was found in the case of $[\text{Rh}(\text{phen})(5,6\text{-Mephen})_2]^{3+}$. As a result, we conclude that the shoulder at 2.22 μm^{-1} in $[\text{Rh}(\text{phen})_2(5,6\text{-Mephen})_2]^{3+}$ is due to a small amount of $[\text{Rh}(\text{phen})_3]^{3+}$ impurity, and that energy transfer from phen to 5,6-Mephen is much faster than emission from phen.

Owing to the apparent structural similarities in the group A, B, and C complexes, the spin-orbit coupling effects and fundamental vibrational frequencies of all of these complexes should be roughly equivalent. Hence, the primary factors which are relevant to changes in radiationless transition rates between the two low-lying $^3\pi\pi^*$ states are linked to the energy gap between them. In the case of the group A complexes, we have estimated this gap to be $\sim 100 \text{ cm}^{-1}$, while it is 1600 cm^{-1} for the group B and C complexes. This suggests that there are no appropriate promoting modes available to accept the 100- cm^{-1} energy for the $^3\pi\pi^*(\text{bpy}) \leftrightarrow ^3\pi\pi^*(\text{phen})$ radiationless transition in the group A complexes. Presumably, the only remaining mechanism available for the transition in a rigid glass would be via coupling to the phonon lattice, which may account for the small rate constants (13.9, 15.7 s^{-1}) reported for the transitions.

Since no emission is observable from the higher of the two $^3\pi\pi^*$ states in the group B and C complexes, the radiationless transition from the higher to the lower state must be at least two orders of magnitude faster than the decay rate where the lower state is absent (i.e., the decay rate of the homotriscchelated $\text{Rh}(\text{bpy})_3^{3+}$ or $\text{Rh}(\text{phen})_3^{3+}$ complexes). We therefore estimate the $^3\pi\pi^*(\text{bpy}) \leftrightarrow ^3\pi\pi^*(5,6\text{-mephen})$ rate constant to be $> 45\,000 \text{ s}^{-1}$ and the $^3\pi\pi^*(\text{phen}) \leftrightarrow ^3\pi\pi^*(5,6\text{-mephen})$ rate constant to be $> 2100 \text{ s}^{-1}$. These estimates are several orders of magnitude larger than the rate constants for the group A complexes (vide supra), presumably due to the presence of at least one promoting mode capable of accepting a portion of the 1600- cm^{-1} energy released in the group B and C transitions. Since 1600 cm^{-1} is substantially less than the C-H vibrational frequency, the C-H modes may be eliminated as potential promoting modes. The primary geometrical distortions in the $^3\pi\pi^*$ states of these complexes are probably in the carbon skeletons of the ligands. Since the vibrations of the carbon skeleton are generally within the range of the 1600- cm^{-1} energy gap, it is likely that at least one of these modes acts as a promoting mode.

Comparison of these results with previous measurements of nonexponential decay rates in heterobischelated complexes of $\text{Ir}(\text{III})^4$ suggests that there is a critical energy gap range over which radiationless transitions of transition metal complexes dissolved in rigid glasses may be severely hindered. The previous results along with the present ones suggest that slow radiationless transitions occur when the energy gap between the states lies in the range 100–400 cm^{-1} . At energy gaps of 1600 cm^{-1} the transitions occur rapidly, and rapid transitions at very low energy gaps may be anticipated owing to enhanced coupling with phonon modes of the lattice. Hence, a narrow energy gap region in which radiationless transition between states of molecules in low-temperature glasses are very slow appears to occur.

Factors other than the magnitude of this gap are undoubt-

edly influential in determining radiationless transition rates between states in this region. For example, thermal equilibration between states separated by $\sim 100 \text{ cm}^{-1}$ in the charge-transfer manifold of several Ru(II) complexes illustrates that very rapid transitions may occur in this energy gap region.^{3b,13-16} Since these complexes (Ru(bpy)₃²⁺, for example) are structurally similar to those which we have studied, the small changes in skeletal vibrational factors are unlikely to account for the difference in radiationless decay rates. Rather, geometrical distortions of the relevant excited states are expected to be a key feature. Since the states in the charge-transfer manifold of Ru(II) complexes have similar geometries and the excitation is delocalized over an extensive segment of the metal-ligand framework, a variety of promoting modes appropriate to the transition are likely to occur. On the other hand, the excited states of the heterochelated Rh(III) and Ir(III) complexes we have studied have rather different geometries and a more highly localized excitation energy. As a result, promoting modes are limited to those which involve nuclei located in the region where the transition density changes during the radiationless process. The requirement of geometry changes and/or localized excitation for inhibition of radiationless processes is summarized in the concept of orbital parentage. Thus, states of different orbital parentage are likely to have different geometries, and radiationless transitions between them are likely to be hindered when energy gaps are small enough to prohibit appropriate promoting modes. Previous studies have shown that even when the energy gaps are large, radiationless transitions which preserve orbital parentage are favored over those which alter it.^{5c}

In view of the present study, it is necessary to expand the concept of orbital parentage to include labeling of a ligand π orbital with the name of the particular ligand when several different ligands are present in the coordination sphere of a central metal ion. Thus, a selection rule for a forbidden radiationless process between the phen and bpy ³ $\pi\pi^*$ states of [Rh(bpy)₂(phen)]³⁺ would be stated as $\pi\pi^*(\text{bpy}) \leftrightarrow \pi\pi^*(\text{phen})$, and should be considered an example of a hindered radiationless transition between states of different orbital parentage. From this and previous studies it is quite apparent that the operation of selection rules for radiationless transitions based upon orbital parentage is critically dependent upon other factors such as solvent viscosity,⁶ temperature,⁷ and energy

gaps. Complete determination of the role of each of these factors will require careful studies of the effect of variation of one while the others are held constant.

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