

reaction with hydrogen ions or impurities and/or the diffusion away of them from the ITO electrode. Research is currently in progress to improve the efficiencies by fixing $[\text{Ru}(\text{bpz})_3]^{2+}$ and other chemicals in a Nafion membrane.

Acknowledgment. This work was supported in part by a Grant-in-Aid (63790220) from the Ministry of Education, Science and Culture of Japan. S.N. gratefully acknowledges financial support from the Japan Society for the Promotion of Science.

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Photoselection Studies of Mixed-Ligand Ruthenium(II) Complexes: $[\text{RuL}_2\text{L}']^{2+}$ Multiple-State Emission

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Received May 15, 1989

Comparison of photoselection spectra for tris $[\text{RuL}_3]^{2+}$ and mixed-ligand $[\text{RuL}_2\text{L}']^{2+}$ complexes as a function of temperature, solvent, excitation, and detection wavelength indicates that the large oscillations in the steady-state excitation polarization (SSEXP) and steady-state emission polarization (SSEMP) spectra result from multiple-state emission of these materials. A type of heterogeneous solvation of the individual ligand chromophores creates the oscillating pattern and does result in the variation of the magnitude and wavelength of P_{max} with detection wavelength. A rough estimate of the magnitude of this heterogeneous solvation energy is obtained by comparison of tris and mixed-ligand complexes. The invariance with solvent of the P_{max} magnitude as well as earlier results verifies that the solvent heterogeneity effect is not the origin of the single ring charge localization.

Introduction

The photoselection spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) and other tris chelate ruthenium species have been important in the assignment of the lowest excited manifold of this series as spatially isolated localized orbital states, similar to those charge-transfer excited states of monomeric species such as $[\text{Ru}(\text{bpy})(\text{py})_4]^{2+}$ (py = pyridine).¹ Results obtained for mono chelate, tris chelate, and cis-configuration bis chelate complexes have been reported^{1,2} with a variety of different solvents, ligands, and counterions.

The interchromophoric coupling (ICC) model presented, which rationalized the polarization results obtained for the complexes, is based upon the spin-orbit coupling (SOC) interactions of the lowest triplet state with a single manifold of mixed character. The model demonstrated that the complexes possess levels of both localized and delocalized spatial extent. The results of this analysis compared well with the experimental steady-state photoselection spectra.

In the work that led to the development of the interchromophoric coupling model, only complexes that were nearly exact mono, bis, or tris complexes were used. However, the model is also valid for molecules which do not fit this description. That is, the limiting values obtained for bis and tris complexes should not be found when the degeneracy of the ligand-localized states is lifted to some degree as in $[\text{RuL}_2\text{L}']^{2+}$, where L and L' are bidentate diimine complexes. By use of the optical energies and electrochemical redox patterns of the parent $[\text{RuL}_3]^{2+}$ and $[\text{RuL}'_3]^{2+}$ complexes, predictions of the degeneracy or lack of degeneracy for mixed-ligand complexes as $[\text{RuL}_2\text{L}']^{2+}$ can be made.

This paper focuses upon details of both photoselection and luminescence spectra for these Ru(II) complexes synthesized with ligands that contain small perturbations in their π^* energy levels due to incorporation of substituent groups into the ligand. For example, the steady-state emission photoselection (SSEMP) of $[\text{Ru}(\text{bpy})_2(\text{pphen})](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine; pphen = 4,7-diphenyl-9,10-phenanthroline) was done with excitation at P_{max} , while measuring the emission polarization as a function of emission wavelength gave large oscillations of P . Data for true tris complexes such as $[\text{Ru}(\text{bpy})_3]^{2+}$ typically display such oscillations as

well, though of much smaller magnitude than found in these mixed-ligand complexes. Thus, a similarity exists between the structure found in the emission photoselection of mixed-ligand species with near-degenerate chromophoric units and true tris complexes, though the effect is exaggerated in the former by the lack of any formal degeneracy. Therefore, this paper focuses upon the relationship between emitting oscillators in tris and mixed-ligand complexes that contain orbital π^* near-degeneracies. This is described in terms of the ICC model and indicates the extent of heterogeneous solvation found for tris complexes, a factor frequently cited by some to explain localization in dilute, disordered media.

Experimental Section

$[\text{Ru}(\text{pphen})(\text{mphen})_2](\text{PF}_6)_2$ (pphen = 4,7-diphenyl-1,10-phenanthroline; mphen = 4,7-dimethyl-1,10-phenanthroline), $[\text{Ru}(\text{bpy})_2(\text{pphen})](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine), and $[\text{Ru}(\text{bpy})(\text{mphen})_2](\text{PF}_6)_2$ were prepared by R.L.B. and were available from previous studies.² $[\text{Ru}(\text{tmbpy})_3](\text{ClO}_4)_2$ (tmbpy = 4,4',5,5'-tetramethyl-2,2'-bipyridine), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $[\text{Ru}(\text{bpy})_2(\text{pbpy})](\text{PF}_6)_2$, and $[\text{Ru}(\text{pbpy})_3](\text{PF}_6)_2$ (pbpy = 4,4'-diphenylbipyridine) were available from previous studies. Purity was determined by the excitation independence of the emission energy and band shape.

Plastic samples were prepared by dissolving the complex in methyl methacrylate monomer. Addition of 2,2'-azobis[2-methylpropionitrile], an initiation agent, followed by evacuation and sealing of the samples in 7 mm o.d. glass cells and incubation at 60 °C for 1-5 days, produced hard clear plastic materials with minimal surface defects. The samples contracted during polymerization in a manner qualitatively similar to that found when alcoholic glasses are formed. Samples were brightly luminescent even at room temperature under interior fluorescent lighting. Samples were removed from the glass cells by cracking the cell.

Plastics were processed as follows. For only room-temperature studies, the sample was left untreated and was immersed in *m*-xylene for study. The primary reason for this was to ensure that mechanical working of the plastics did not affect the polarization properties of the guest materials. The liquid *m*-xylene was used, as it does not easily dissolve the plastics and possesses a refractive index close to that of the plastics themselves. Thus, a clear system was produced, with little indication of any surface scatter effects from the imperfect polymer. A second procedure utilized carborundum powder to polish the samples by using first a coarse grit for rough grinding, then a fine grit for a smooth finish.

(1) Myrick, M. L.; Blakley, R. L.; De Armond, M. K.; Arthur, M. J. *Am. Chem. Soc.* 1988, 110, 1325.

(2) Blakley, R. L.; Myrick, M. L.; De Armond, M. K. To be submitted for publication.

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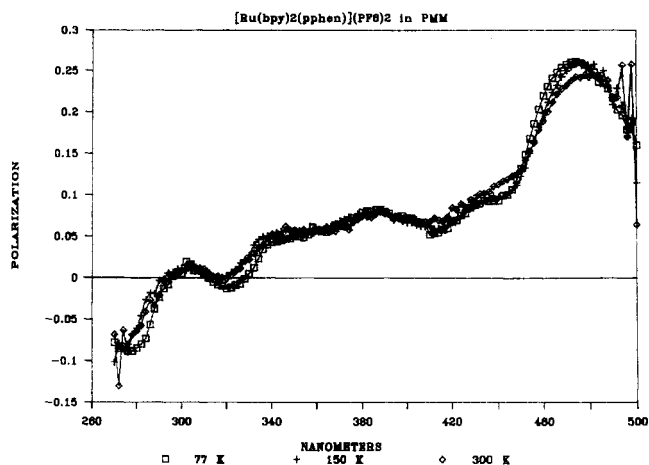


Figure 1. Temperature effect upon SSEXP of $[\text{Ru}(\text{bpy})_2(\text{pphen})]^{2+}$. Polarization values obtained from SSEXP experiments at 77, 150, and 300 K for $[\text{Ru}(\text{bpy})_2(\text{pphen})](\text{PF}_6)_2$ in PMM are shown as a function of detection wavelength. Detection is at the wavelength of the emission maximum at each temperature.

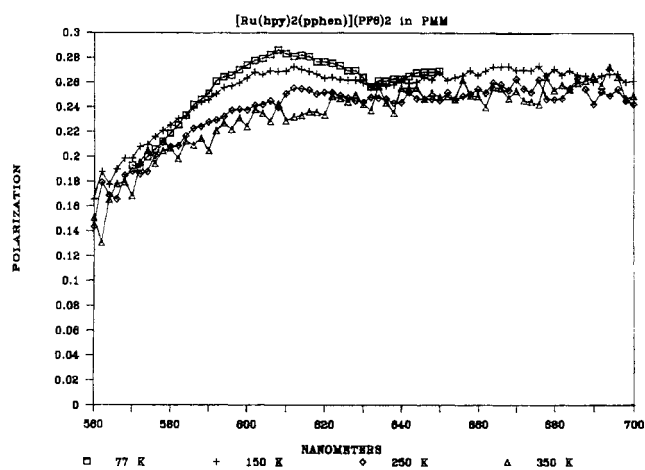


Figure 2. Temperature effect upon emission photoselection of $[\text{Ru}(\text{bpy})_2(\text{pphen})]^{2+}$. Emission photoselections of the complexes are presented for 77, 150, 250, and 350 K in poly(methyl methacrylate). Excitation is at the wavelength of P_{max} .

Upon completion, the sample was blackened on half of its surface with a marker to prevent reflection of excitation light and inserted into the sample compartment of an Air Products Cryotip for study. No luminescence was obtained from the dyes in the marker. Crycon grease was used to provide thermal contact between the sample and copper holder.

A calibrated gold/chromel thermocouple indicated that, with liquid-nitrogen coolant, a minimum temperature of 79 K was attainable. Temperatures other than 77 K and room temperature were obtained by an Air Products Model K temperature indicator/controller.

Normal steady-state excitation polarization spectra (SSEXP) were obtained by detection of the luminescence at the emission maximum, using an instrument previously reported.^{3,4} Normal SSEmP was performed with excitation at the wavelength of P_{max} , using the same instrument. The error limits for the P measurement were ± 0.005 .

Luminescence studies were performed on this instrument by removal of the rotating polarizer. Emission spectra reported are uncorrected for polarization effects and detector response.

Electronic absorption spectra were measured on a Cary 14 spectrometer interfaced to a Zenith Z-100 computer by On-Line Instrument Systems software. Room-temperature measurements of solutions were performed in quartz cuvettes to obtain spectra in the near-UV region. The 77 K measurements of solutions were performed in polystyrene cuvettes by using an Oxford Instruments DN-1704 $\text{N}_2(\text{l})$ cryogenic cell, adapted for the Cary 14 spectrometer. Measurements of plastic samples were made by forming large cylindrical samples in evacuated test tubes.

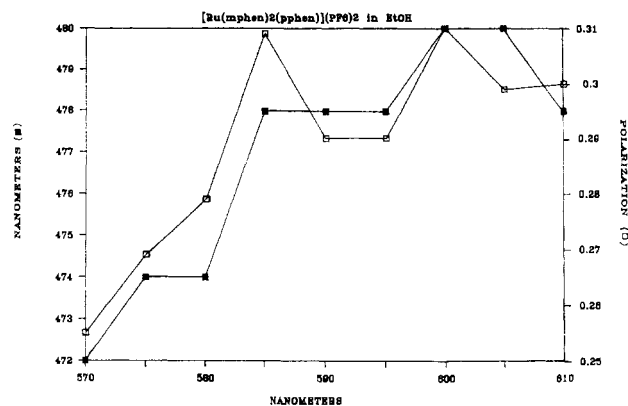


Figure 3. Variation of P_{max} and $\lambda(P_{\text{max}})$. Variation of the value of P_{max} (\square) and the wavelength at which it occurred (\blacksquare) with the detection wavelength is shown for $[\text{Ru}(\text{mphen})_2(\text{pphen})]^{2+}$ in EtOH.

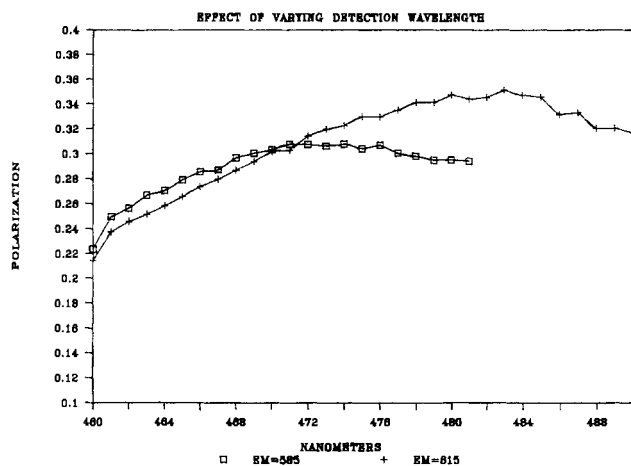


Figure 4. Data showing variation of P_{max} and $\lambda(P_{\text{max}})$ with detection wavelength. An example of raw data for $[\text{Ru}(\text{bpy})_2(\text{pphen})]^{2+}$ in PMM is shown: (\square) detection wavelength at 585 nm; ($+$) detection wavelength at 615 nm. All measurements were made at 77 K.

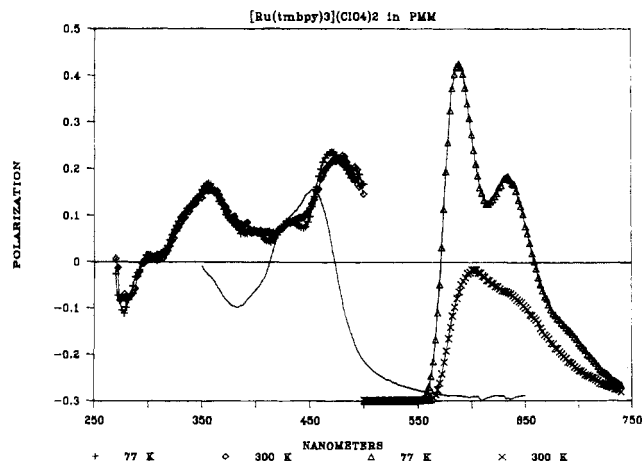


Figure 5. Temperature effect upon spectra of $[\text{Ru}(\text{tmby})_3]^{2+}$. On the right, the emission spectra of the complex in PMM are shown, at both 77 and 300 K. On the left, the SSEXP, at 77 and 300 K, is plotted across the absorbance spectra (absorbance was measured in PMM at 300 K).

These cylindrical samples were filed flat on two opposing surfaces and then polished to a smooth finish. All spectra are corrected for base-line errors, though no reference was used for the plastics.

Results

Table I lists the P_{max} values for the various complexes as a function of temperature and solvent. Also tabulated are values for the energy and wavelength of the emission maximum.

The SSEXP of $[\text{Ru}(\text{bpy})_2(\text{pphen})](\text{PF}_6)_2$ in PMM is presented in Figure 1 as a function of temperature, and SSEmP for this

(3) Carlin, C. M. Ph.D. Thesis, North Carolina State University, 1983.

(4) Carlin, C. M.; Hanck, K. W.; De Armond, M. K. *Rev. Sci. Instrum.* **1981**, *52*, 137.

Table I. Data for Complexes with Near-Degeneracies

complex	solvent/temp, K	abs max ^a	emission max ^a	photoselection max/wavelength
[Ru(bpy) ₂ (pphen)](PF ₆) ₂	PMM/77		596 (16.8)	0.26/474 (21.1)
	PMM/150		596 (16.8)	0.26/476 (21.0)
	PMM/250		598 (16.7)	0.24/478 (20.0)
	PMM/300	453 (22.1)	604 (16.6)	0.25/478 (20.9)
[Ru(mphen) ₂ (pphen)](PF ₆) ₂	EtOH/77		604 (16.6)	0.34/480 (20.8)
	MeCl ₂ /Et ₂ O/77		604 (16.6)	0.34/478 (20.9)
	<i>b</i> PMM/77		604 (16.6)	0.23/478 (20.9)
	<i>b</i> PMM/300	435 (23.0)	610 (16.4)	0.24/482 (20.7)
[Ru(pphen) ₃](PF ₆) ₂	MeCl ₂ /Et ₂ O/77		594 (16.8)	0.20/480 (20.8)
	<i>b</i> PMM/77		606 (16.5)	0.12/486 (20.6)
	<i>b</i> PMM/300	438 (22.8)	608 (16.4)	0.15/492 (20.3)
[Ru(mphen) ₂ (bpy)](PF ₆) ₂	<i>b</i> PMM/77		586 (17.1)	0.19/466 (21.5)
	<i>b</i> PoMM/300		598 (16.7)	0.20/476 (21.0)
[Ru(bpy) ₂ (pbpy)](PF ₆) ₂	EtOH/77	466 (21.5)	602 (16.6)	0.34/478 (20.9)
	<i>b</i> PMM/77		598 (16.7)	0.20/476 (21.0)
	<i>b</i> PMM/300		608 (16.4)	0.21/484 (20.7)
[Ru(pbpy) ₃](PF ₆) ₂	EtOH/77	480 (20.8)	614 (16.3)	0.19/492 (20.3)
	<i>b</i> PMM/77		614 (16.3)	0.20/490 (20.4)
	<i>b</i> PMM/300	475 (21.1)	622 (16.1)	0.17/498 (20.1)
[Ru(tmbpy) ₃](ClO ₄) ₂	EtOH/77	457 (21.9)	574 (17.4)	0.21/466 (21.5)
	<i>b</i> PMM/77		588 (17.0)	0.24/470 (21.3)
	<i>b</i> PMM/300	453	602 (16.6)	0.23/480 (20.8)

^a Wavelengths are given in nanometers; energies, in cm⁻¹ × 10³. ^b Polarization reduced by optical activity.

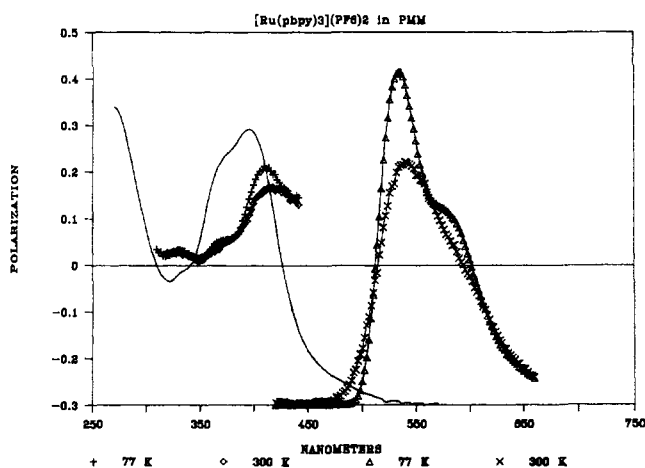


Figure 6. Temperature effect upon spectra of [Ru(pbpy)₃]²⁺. On the right, the emission spectra at 77 and 300 K are shown. To the left, the SSEXP for the complex is plotted against the absorbance (absorbance was measured at 300 K; both absorbance and emission were measured on samples in PMM).

complex vs temperature is presented in Figure 2. It was found that the value of P_{\max} and the wavelength at which it occurred for this complex varied systematically with the detection wavelength. This variation is plotted in Figure 3 at 77 K. Raw data for the [Ru(bpy)₂(pphen)]²⁺ complex are given in Figure 4.

For [Ru(tmbpy)₃](ClO₄)₂, Figure 5 illustrates the change in SSEXP with temperature, as well as the change in emission. Figure 6 presents the same data for [Ru(pbpy)₃](PF₆)₂. The variation in wavelength of P_{\max} for the [Ru(tmbpy)₃](ClO₄)₂ complexes is shown in Figure 7 as a function of detection wavelength. Data for the [Ru(bpy)₃]²⁺ complex are similar.

Discussion

The complexes presented in this paper are examples of complexes with orbital degeneracies or near-degeneracies in the π^* systems of the ligands. This leads to the observation of MLCT states of localized character in the materials that are closely spaced. For true tris complexes, such as [Ru(bpy)₃]²⁺, [Ru(tmbpy)₃]²⁺, [Ru(pphen)₃]²⁺, and [Ru(pbpy)₃]²⁺, these states are exactly degenerate except for differences due to solvation effects. In mixed-ligand species such as [Ru(bpy)₂(pphen)]²⁺, [Ru(mphen)₂(pphen)]²⁺, [Ru(mphen)₂(bpy)]²⁺, and [Ru(bpy)₂(pbpy)]²⁺, a small but real displacement exists between the MLCT states originating on different ligand species due to the unequal energies

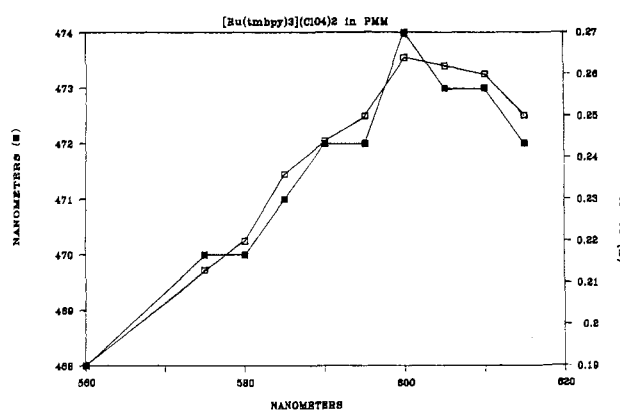


Figure 7. Variation of P_{\max} and $\lambda(P_{\max})$. Variation of P_{\max} (\square) and the wavelength at which it occurred (\bullet) is plotted as a function of detection wavelength. Data shown are for [Ru(tmbpy)₃](ClO₄)₂ in PMM at 77 K.

of the π^* orbitals of the different types of diimines. This causes the photoselection values of these mixed-ligand species to attain maxima intermediate between and distinct from those predicted by the ICC model.¹ The principal reason for this is that the coupling between localized MLCT states is reduced when the MLCT states diverge in energy. Thus, in complexes of the sort [Ru(bpy)₂(bpz)]²⁺, in which the MLCT states are well separated, coupling is reduced to a negligible amount so that this material can be used as an example of a monomeric complex.

Relative Energies of π^* Orbitals. The absolute energy difference between the π^* orbitals on the different ligands is difficult to obtain exactly, as the energy of the MLCT states is determined by the energy difference between these ligand-localized orbitals and the $d\pi$ orbitals of the metal; the energy of the $d\pi$ orbitals has been shown previously to vary with ligand substituent. Qualitatively, the energy of the simple chelate ligand, such as bpy or phen, is lowered by phenyl substitution due to the electron-withdrawing nature of the substituent. Methyl substitution serves to increase the energy of the π^* orbital by electron donation. In both instances, the energy perturbation is small in magnitude.

In general, the energy distribution of the emitting level of a typical chromophore may be pictured as in Figure 8a, where an average energy of the chromophore exists, but solvation effects alter the exact value. Assuming that the probability of a level possessing a specific energy drops in a statistical fashion with increasing separation from the average, an approximately Gaussian (normal) distribution of energies should occur. The exact value

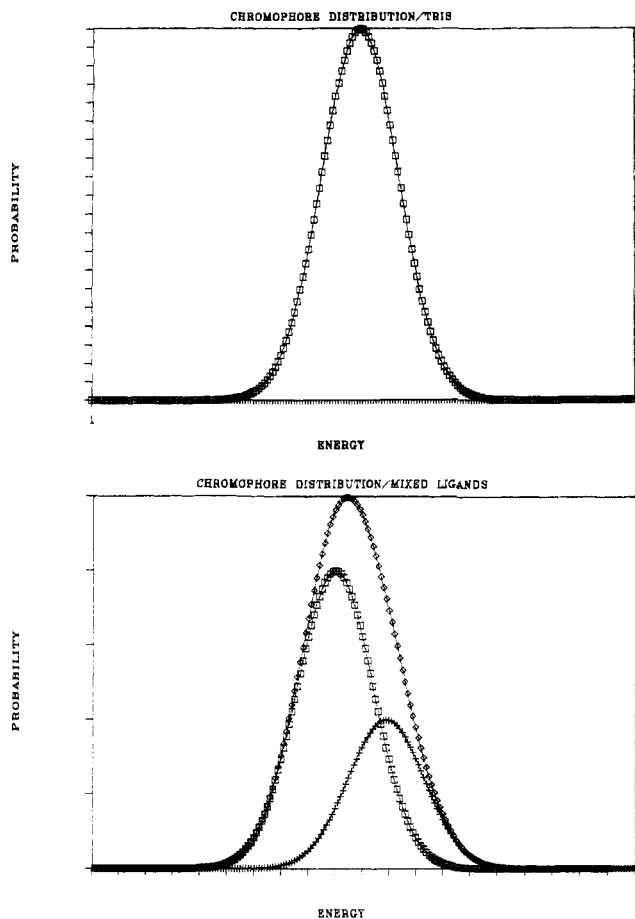


Figure 8. Energy distributions of chromophore. In (a, top), the energy distribution of the emitting level of a typical chromophore is shown for a tris complex. In (b, bottom), the same is shown for mixed-ligand species of two different chromophores.

of the standard deviation of this distribution would depend upon the average magnitude of solvent-solute interactions. Obviously, this qualitative treatment does not account for specific interactions but only for general heterogeneity effects that should exist in solutions due to the lack of microscopic order in such media.

When three identical ligands exist in a tris complex, the total distribution of chromophore energies remains the same and possesses the same value of σ . However, when ligands of different types are attached to the metal, the distribution of chromophores consists of the summation of two (or more) Gaussian curves offset by a difference of average values and not necessarily possessing the same values for σ . To illustrate this situation, Figure 8b shows the situation for mixed-ligand species of two different chromophores, assuming the same value of σ for each chromophore. As shown, the distribution for complexes with a single lowest lying chromophore is relatively "top heavy". For complexes with two lowest lying chromophores, the distribution is "bottom heavy".

This general observation, coupled with the conclusions of the ICC model, provides the explanation for many of the specific polarization properties of the complexes examined here. In short, the magnitude of the maximum value of the SSEXP varies for the mixed-ligand species because the values of the ratio K/B (ratio of that of the roughly localized singlet to that of the delocalized singlet in the ICC model) in the description of the mixed-polarization emission oscillator of the emitting triplet state deviate from those of tris and bis complexes.

Typically, luminescence is dominated by the lowest lying chromophore. When the chromophore energy distribution dictates that the intersection of monomeric potential energy surfaces (PES) occurs at a higher energy relative to the lowest level than in a true tris or bis complex, K_m (K_m is the constant for the monomer surface) is increased at the expense of B , since K_m derives from the localized portion of the excited singlet state and thus is a

measure of the relative size of that region. This topic is covered in a separate publication² and will not be discussed here.

In this discussion, the focus is upon some specific properties of the emitting states of these complexes. In particular, we wish to investigate the oscillations observed in the emission photoselection (SSEmP) of these species, the detection-wavelength dependence of the magnitude of P_{\max} , the detection-wavelength dependence of the excitation wavelength at which P_{\max} occurs, and the possibility of observing exciton motion at elevated temperatures. As will be discussed below, the photoselection technique may be utilized to obtain rough estimates of the actual energy separation of the chromophores in these complexes, as well as information on solvent heterogeneity effects in true tris complexes.

Oscillations of Emission Photoselection. Generally, in tris complexes and bis complexes, a small detection-wavelength dependence is found for P .^{1,3,5} In the parent complex $[\text{Ru}(\text{bpy})_3]^{2+}$, the variation of P for excitation at P_{\max} is relatively small. Other results^{1,5} show this oscillation to be approximately 0.02 polarization unit across most of the MLCT emission, but becoming as large as 0.04 unit on the high-energy edge of the luminescence. Even at this high-energy edge, polarization significantly exceeds the 0.14 value required to demonstrate localization. For this reason, the previous work did not perform an exhaustive analysis of the SSEmP of the series of complexes.

However, the recent results of Myrick and Blakley¹ indicated that another tris complex, $[\text{Ru}(\text{bpz})_3]^{2+}$, while exhibiting the P_{\max} value of 0.23 characteristic of most tris chelates when detection is at the emission maximum, exhibits a larger oscillation of P ($\Delta P = 0.06$) across the emission band. Indeed, the high-energy edge of the luminescence gave rise to a photoselection value of approximately 0.19 and was sloping steeply down toward higher energy, necessitating an analysis to explain the phenomenon.

Curiously, in both of the tris complexes above, as well as in the molecules presented here in the figures, the maximum SSEmP does not occur at the energy of the emission maximum. At this point, P is generally rising toward lower energy. The maximum P is attained between the two maxima found in the Ru-dimine luminescence. The oscillatory pattern in the SSEmP clearly repeats the emission pattern, since the energy separation between maxima in SSEmP approximates that of the emission, with polarization maxima associated with each distinct transition of the luminescence. The variation of P across the emission presents the appearance of the overlap of two or more distinct emissions, slightly displaced in energy, with the higher lying spectrum having a lower photoselection value; the oscillation results from the varying contributions of each emission are a function of emission wavelength.

In the case of the tris complexes, at least two possible origins of the "multiple emissions" above exist. The first is that, as indicated in the ICC model, two spin sublevels of the emitting triplet possess radiative moment. Possibly the vibronic components of the emissions deriving from the two are different, resulting in different intensity distributions. However, two points argue against this interpretation. First, the ICC model indicates that the second component of the triplet state acquires intensity from mostly the same singlet levels as the z -polarized level does; this would result in identical vibronic components. Presumably, since only a small portion of the excited singlet state is localized and capable of coupling with only the z -polarized sublevel, this effect would dominate. Second, the fact that large experimental differences occur among the tris complexes (Table I) makes difficult an explanation based upon the existence of different vibronic components. In particular, this would be true when the basic π system is little altered, as is the case for the ligands bpy and tmbpy.

A second process that could affect polarization can be obtained from the ICC analysis. Notably, all complexes that exhibit any fluctuation in P across the emission band have lower values of P_{\max} at high energy. From an inspection of Figure 8, which shows the distribution of chromophoric energy levels in a heterogeneous solution, it is apparent that luminescent units which have emission

(5) Blakley, R. L. Ph.D. Thesis, North Carolina State University, 1987.

Table II. Spread in Emission Photoselection Values for Several Complexes

complex	solvent	SSEmP _{max} /wavelength ^a	SSEmP _{min} /wavelength ^{a,c}	ΔP
[Ru(bpy) ₂ (pphen)](PF ₆) ₂	PMM	0.29/608 (1.64)	0.19/572 (17.5)	0.10
[Ru(tmbpy) ₃](ClO ₄) ₂	PMM	0.26/602 (16.6)	0.18/560 (17.9)	0.08
[Ru(mphen) ₂ (pphen)](PF ₆) ₂	EtOH	0.35/616 (16.2)	0.23/570 (17.5)	0.12
[Ru(bpy) ₂ (pphen)](PPf ₆) ₂	EtOH	0.27/620 (16.1)	0.13/565 (17.7)	0.14
[Ru(bpy) ₃] ²⁺ ^b	EtOH	0.24/586 (17.1)	0.20/562 (17.8)	0.04
[Ru(bpz) ₃] ²⁺ ^b	EtOH	0.25/586 (17.1)	0.19/558 (17.9)	0.06

^aWavelength given in nanometers, energies in cm⁻¹ × 10³. ^bReproduced by permission from R.L.B. ^cLimited by sensitivity of instrument.

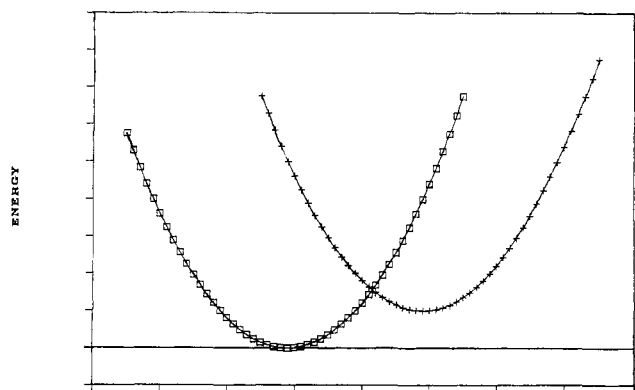


Figure 9. PES for states displaced from one another. Potential energy surfaces derived from weak exciton interactions of monomer units of slightly different energies are shown. For the higher energy unit, the region in which localization can occur is significantly smaller than the same region in the unit of lower energy. Q is a generalized coordinate.

maxima at relatively high energy are above the average energy of the chromophores in solution. In tris complexes, the two additional chromophores, associated with the same central metal, as the emitter unit, will probably occur at lower energy. The result of this is illustrated in Figure 9. A key feature here is that the energy spacing between the lowest levels of the high-energy-emitting chromophore and the barrier of the PES is reduced. The ICC model postulates that the relative "size" of the localized and delocalized regions of the excited emitting chromophore dictate the polarization of the luminescence. (In fact, this is a simplification, as the actual "size" is not the important parameter, but rather the convolution of size, SOC efficiency between the singlet levels and triplet emitting states, and details of exciton coupling in the singlet manifold. However, the simplified description is sufficient to demonstrate that a high-energy chromophore, having a small localized region and enlarged delocalized region, will give rise to a K/B ratio smaller than that of the average chromophore, resulting in lower P .)

Further, molecules that have a greater σ or, in other words, molecules with a greater energy variation as a function of solvent orientation should exhibit larger oscillations of P across the emission band. For this reason, the tris complex of bpz shows more oscillation than that of bpy, since bipyrazine has functionalities (aromatic nitrogens) exposed to the solvent environment and capable of accepting hydrogen bonds in protic solvents. Unfortunately, this complex was insoluble in MeCl₂/Et₂O (methylene chloride/ether), an aprotic solvent frequently utilized in this laboratory as a glassy medium, and this hypothesis could not be directly tested. Support does, however, come from [Ru(bpy)₂(CN)₂], a relatively solvent-sensitive complex. Despite the relatively large polarization of bis complexes and the typically smaller fluctuations of SSEmP found for bis chelates, this complex in EtOH displays a variation of 0.06. Other complexes expected to display enhanced variations in SSEmP across the emission would be those with phenyl groups of other functionalities, especially when these groups are directed away from the center of the complex into the solvation sphere.

The present mixed-ligand cases, however, offer the opportunity of observing the effects of variable-energy-emitting states without

the vicissitude of solvation heterogeneity. In these mixed-ligand species, the major energy variation in the emitting energy derives from the average displacement of the MLCT states resulting from different ligands.

Table II gives the variation of P , ΔP , across the emission band for several complexes at 77 K. This ΔP value was determined from the maximum value attained on the immediate low-energy edge of the emission maximum minus the value found as far to the blue edge of the emission as possible, being limited by detector sensitivity. In addition, the energy at which the P_{\max} occurs in the SSEmP spectrum is tabulated. Some complexes are not listed in this table due to unusual specific solvation effects present in poly(methyl methacrylate), the only solvent in which SSEmP was investigated for these materials.

As shown in Table II, the mixed-ligand molecules presented possess significantly larger oscillations in the SSEmP than the tris analogues. Among the six complexes listed, the tris complex of bpy has by far the smallest degree of oscillation. The bpz ligand, with exposed functionalities, has a somewhat larger oscillation in the tris complex, as does the tetramethylbipyridine complex. However, the mixed-ligand species all exceed the values of the tris complexes, even those with functionalities.

The largest oscillation is found for [Ru(bpy)₂(pphen)]²⁺ in EtOH. Interestingly, though the excitation photoselection of this molecule is virtually identical in EtOH and PMM, the SSEmP is different: In EtOH the emission polarization of this complex only reaches 0.27 as a maximum but has significantly lower values on the blue edge of the emission (an oscillation of 0.141). In PMM, however, the value reaches as high as 0.29, though the total oscillation is lower ($\Delta P \approx 0.10$). This indicates that different solvents may affect this oscillation without significantly disturbing the SSEmP.

Barton and co-workers⁶ have shown that [Ru(bpy)₂(pphen)]²⁺ has emitting states on both bpy and pphen, though the distribution favors the pphen ligand due to the lower energy of that chromophore. For this molecule, the lower energy of the pphen chromophore means that the distribution of chromophores is of the "top heavy" type shown in Figure 8b. When the Ru-bpy luminophore of the complex emits, the Ru-phen chromophore of the molecule will be at lower energy than the emitting chromophore. This reduces the "size" of the localized portion of the singlet manifold of the bpy unit, causing P to be lower for this luminescence. When the pphen chromophore is excited, the likelihood is that the remaining chromophores will be at higher energy, resulting in larger localized coupling for this chromophore, thus higher P . Since the Ru-bpy units should emit at higher energy, P should be lower at the high-energy edge of the luminescence and should rise across the emission maximum as the emission bands overlap.

We may now summarize the factors that influence the oscillations of SSEmP for tris and mixed-ligand complexes. A significant fluctuation of P across the emission band occurs when chromophores are at different energies and when the luminescence derives from all these chromophores. Thus, the [Ru(bpy)₂(pphen)]²⁺ molecule is a good example of this. [Ru(mphen)₂(pphen)]²⁺ should have chromophores at even more disparate energies² but actually has a slightly lower oscillation of P , since little luminescence originates in the mphen chromophore because

(6) Kumar, C.; Barton, J.; Gould, I.; Turro, N.; Van Houten, J. *Inorg. Chem.* 1988, 27, 648.

it occurs at much higher energy than the Ru–bpy chromophore. This may be carried to an extreme, of course, as in $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$, in which the chromophores are very widely separated in energy as described previously. The oscillation of P across the emission band for this complex (not listed in the table) is virtually zero because no luminescence derives from the Ru–bpy unit in this complex.^{1,5}

In tris complexes the chromophores are not exactly degenerate due to heterogeneous solvation effects, giving rise to a distribution of chromophore energies. For chromophores near the top of the energy distribution, luminescence will be shifted to the blue edge of the total emission spectrum. These emitting species experience reduced localized coupling and therefore decreased polarization values. For those species occurring at lower energy than the average, the remaining chromophores will occur at higher energy, increasing the amount of localized coupling occurring and increasing P . For those chromophores possessing the average chromophore energy, the likelihood that the remaining chromophores of the metal ion will have energies above this will exactly equal the probability that they will have energies below this. We thus expect these to exhibit values of P near the true value for a hypothetical system with homogeneous solvation.

This should give rise to oscillations of P in the emission photoselection simply due to "heterogeneity". Thus, the magnitude of the variations may indeed be dependent upon the particular solvent. Still, the magnitude of P at the emission maximum (assuming that the bulk of chromophores with energies near the center of the energy distribution have emission maxima that coincide with the bulk emission maximum) should be relatively insensitive to the solvent. "Heterogeneity" is defined here as heterogeneous solvation energies of localized excited states, rather than a symmetry-reducing effect. If the latter were occurring, the bulk of chromophores with average energies in the distribution (and emission coincident with the emission maximum) would be of high symmetry (delocalized). That this is not occurring is evident by the fact that P_{max} for tris complexes is much greater than the value of 0.14 expected for the delocalized emitter.

Chromophores that have stronger interactions with the solvation sphere should possess larger magnitudes of "heterogeneity" and as such should give rise to larger oscillations in P_{max} . Hence, $[\text{Ru}(\text{bpy})_3]^{2+}$ gives rise to small variations in P , while $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}(\text{tmbpy})_3]^{2+}$ give rise to significantly larger wave patterns.

The Variation of $\lambda(P_{\text{max}})$ with Detection Energy. These differences in energy of emitting chromophores should be reflected in a variation of the position of P_{max} in the excitation photoselection spectra as a function of detection energy. To determine whether this was the case, a series of photoselection spectra were obtained for several complexes, changing the detection wavelength in 5-nm increments over the high-energy portion of the emission (Figure 4). Data for six complexes were obtained (Figures 3 and 6 show examples). Shown are the wavelength at which P_{max} occurs and the value of P_{max} , both versus detection wavelength. Errors in the value of P_{max} appear to be smaller than those of the wavelength at which it occurs. As shown, a significant dependence of P_{max} upon detection wavelength is obtained. This in itself is not surprising, since the similarity of this plot to the SSEmP spectra of the various complexes is not coincidental—they, in fact, should be very similar. However, the surprising observation is that the wavelength at which P_{max} occurs is also a strong function of detection wavelength.

This latter fact indicates that the emitting chromophore has variable absorption energy, depending upon the detection wavelength. This proves that the luminescence in these solutions is not due to a single emission spectrum broadened solely by homogeneous processes but represents the overlapping of the emission spectra from localized chromophores in a variety of different environments.

Furthermore, this "heterogeneity" of the emitting chromophores is significantly larger in the mixed-ligand species. If an energy spread is defined as the difference between the highest and lowest energies of $\lambda(P_{\text{max}})$ recorded for each complex, we find that the two true tris complexes listed have an energy spread of less than

300 cm^{-1} . The value for $[\text{Ru}(\text{pphen})_3]^{2+}$ is not reported because the region of flat P in that complex is so broad that good wavelength values are difficult to obtain. However, a tentative value for that complex in EtOH appears to be between 200 and 300 cm^{-1} also. In contrast, the three mixed-ligand species have an energy spread of greater than 300 cm^{-1} , reaching as high as 460 cm^{-1} for $[\text{Ru}(\text{mphen})_2(\text{bpy})]^{2+}$.

Difficulty in interpretation of these data is encountered primarily because detector sensitivity prevents recording of photoselection spectra when the intensity of emission is small, so that the very highest energy portion of the spectrum is absent. Even so, these data indicate that such information is useful in classifying complexes and obtaining qualitative estimates of the "heterogeneity" of dilute disordered solid solutions.

Our other data have indicated that the emitting chromophores of the bpy/pphen mixed-ligand complexes are separated by approximately 200–300 cm^{-1} , those of the mphen/pphen series by approximately 600 cm^{-1} and those of the mphen/bpy series by approximately 300–400 cm^{-1} , on the basis of luminescence, absorption, and photoselection data of the mixed-ligand species.

For the bpy/pphen series, the estimate is certainly reasonable, given the results of Barton and Turro,⁶ who found significant population of localized states of each chromophore in this complex. The energy spread for this mixed-ligand complex is significantly larger than those for the tris complexes. This datum implies that we are observing significant radiation from molecules with chromophores that are separated by more than the usual heterogeneous solvation energies of tris complexes, probably nearly twice that energy.

The situation for $[\text{Ru}(\text{mphen})_2(\text{bpy})]^{2+}$ is very similar. Likely, we are also observing a dual luminescence in this case, with chromophores separated by approximately 300 cm^{-1} in addition to the solvation heterogeneity.

However, the $[\text{Ru}(\text{mphen})_2(\text{pphen})]^{2+}$ complex gives rise to an energy spread, obtained from the experimental variation of $\lambda(P_{\text{max}})$ with detection energy, significantly smaller than those of the previous two complexes. The SSExP values are larger than those of a true tris complex, even larger than those of the mixed-ligand complexes with which we are comparing it. This implies that the chromophores must be separated by a greater energy gap. The smaller energy spread then is due to the near-negligible contribution that the Ru–mphen chromophore is making to the luminescence. Apparently (excited-state resonance Raman could confirm this supposition) the 600- cm^{-1} energy separation between chromophores² is sufficient to result in localization mostly in the pphen chromophore. Thus, the energy spread between P_{max} determined with high-energy and low-energy detection is reduced to near the "heterogeneity"-only value. This is reflected in a smaller variation in P_{max} for detection at different wavelengths.

As an example, the mono emitting complexes $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{pq})]^{2+}$ ($\text{pq} = 2,2'$ -pyridylquinoline) were shown by us¹ to have negligible oscillation in the SSEmP. This now appears to be due to the absence of any significant change in the ICC localized/delocalized coupling as a function of the energy of the emitting chromophore. The mixed-ligand complexes presented here, in which low-lying chromophores exist that may participate in the luminescence processes, do possess a significant variation of the ICC localized/delocalized coupling as a function of the energy of the emitting state.

To summarize, luminescence originating from a Ru–diimine chromophore in dilute disordered solid solution results from "heterogeneously" solvated localized chromophores. When SSExP may be utilized to estimate the relative energy of the absorbing chromophores, all molecules should display this solvent effect as a variation of the absorbing-state energy for P_{max} as a function of detection energy. This variation of P_{max} excitation energy will increase when the distribution of emitting chromophores deviates from a simple Gaussian pattern, as in near-degenerate mixed-ligand complexes. When, in such species, the higher lying chromophore is displaced by such an energy gap that luminescence originates from only a single type of chromophore, the Gaussian distribution of emitting states is recovered. Thus, the distribution

of emitting states is given by the product of the actual distribution of chromophores and a function that describes the relative probability of excitation residing on higher lying chromophores. Though the precise formulation of this function is unknown, qualitatively it must go to zero as the energy of the secondary emitting state increases.

From the data of Figures 3 and 6 and those for the other four complexes, a first approximation can be made of the dependence of the energy of the emitting chromophore upon solvation heterogeneity. Despite being unable to measure P all the way to the origin of the luminescence, a comparison of the values of energy spread for the mixed-ligand complexes and true tris complexes is possible. For instance, for [Ru(bpy)₂(pphen)]²⁺, the value of the energy separation between chromophores is 300 cm⁻¹.² The comparison between the energy spread for tris complexes with that of this material leads to the conclusion that solvation heterogeneity leads to average energy displacements of the order of 200–300 cm⁻¹. This is, of course, only a crude measure, obtained by assuming the energy spread for the mixed-ligand derives from both the 300-cm⁻¹ energy gap and the effects of heterogeneity, while that of tris species derives from only heterogeneity.

Temperature Dependence of Emission and Photoselection Spectra. A question that arises for the mixed-ligand complex [Ru(bpy)₂(pphen)]²⁺ (and all mixed-ligand complexes) is whether the localized chromophores of this complex are in thermal equilibrium with one another. For the tris complexes such as [Ru(bpy)₃]²⁺, the question of thermal equilibrium between the localized states is easily answered: thermal motion of the exciton between localized states is not possible, since this would reduce the expected value of P below 0.14; the randomization of the exciton in the $D_3(x,y)$ plane would result in a pseudoplanar oscillator, and the high value of 0.23 should not occur. For the mixed-ligand species, the nondegeneracy of the emitting chromophores would permit larger values of P even if thermal "hopping" of the excitation energy occurs between ligand-localized states. However, the presence of a significant population of states 300 cm⁻¹ above the lowest emitting state, as in [Ru(bpy)₂(pphen)]²⁺ at 77 K (53 cm⁻¹ of thermal energy), indicates that these states are not in thermal equilibrium with one another at this temperature.

Another question raised is whether such motion could occur in tris complexes on the time scale of the luminescence if the temperature were increased from the 77 K at which photoselection phenomena are typically measured. Data for reduced [Ru(bpy)₃]⁺ indicate that the process may be rapid at room temperature,⁷ but early attempts to measure such a process for the excited-state species were difficult to distinguish from solvent melting and true rotational depolarization.⁸ To investigate this question, studies were done of true tris and mixed-ligand species at high temperatures in clear poly(methyl methacrylate) plastic.

Emission spectroscopy of various complexes in PMM indicates, in general, that the bathochromic shift is measured upon warming to room temperature. This may be ascribed to some reorientation of the surrounding plastic during the lifetime of the excited state.

Figure 10 displays the temperature-dependent emission maximum for [Ru(bpy)₂(pphen)]²⁺. As shown, the emission is little affected by the increase of T between 77 and 200 K. At 250 K, some small relaxation of the emitting state is indicated by a very small shift to lower energy. Concurrently, the luminescence begins to broaden and become less well resolved. The increase in wavelength for the emission maximum is at 300 and 350 K, at which temperature the luminescence is greatly broadened and

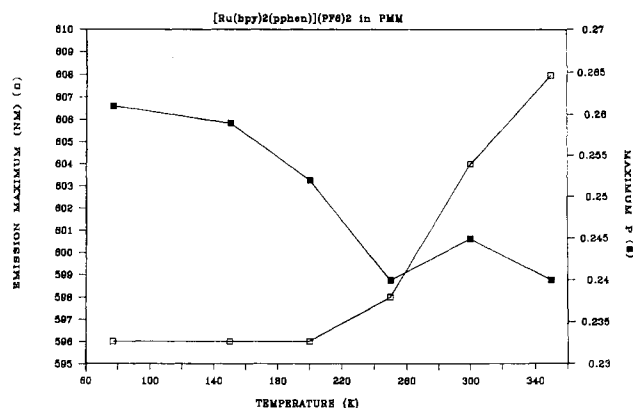


Figure 10. Temperature dependence for spectra of [Ru(bpy)₂(pphen)]²⁺. Variation in the wavelength at which the emission maximum occurred (□) and that of P_{\max} (●) are shown, each as a function of temperature.

much weaker due to an increase in the rate of nonradiative relaxation of the excited state.

The largest red shift between 77 and 300 K is found for molecules with bipyridine luminophores. Chromophores that contain pphen and mphen appear less temperature sensitive, as shown in Table II.

The luminescence of the mixed-ligand chelates presented here confirms that the emitting states of the chromophores are not in thermal equilibrium with one another. If equilibration were occurring on the time scale of the luminescence, we would expect that the proportion of emission deriving from the Ru-bpy unit of [Ru(bpy)₂(pphen)]²⁺ would increase with temperature so that the emission would undergo a hypsochromic shift (higher energy) as the luminescence of the higher lying bpy chromophore were turned on, at least until the emission began to broaden at 200 K.

As was indicated above, on the basis of the variation of $\lambda(P_{\max})$ with detection energy, the proportion of Ru-bpy luminescence in the two mixed-ligand species [Ru(bpy)₂(pphen)]²⁺ and [Ru(mphen)₂(bpy)]²⁺ should be comparable (approximately 0.5, from the data of ref 6 and the comparison of the spectral properties of the two materials). This appears to be true as the temperature dependences of the emission maxima for these two complexes are very similar, the former displaying an 8-nm shift and the latter a 10-nm shift upon warming from 77 to 300 K. By contrast, the [Ru(tmbpy)₃]²⁺ species exhibits a shift of 16 nm with the same temperature variation.

On the basis of the variable-temperature luminescence results, the ligand-localized states of different near-degenerate chromophores are not in a rapid equilibrium even at room temperature.

Upon analysis of the temperature dependence of the SSEmP (Table II), the establishment of a thermal equilibrium at any temperature should reduce the value of P for the complex under study. This results from the recognition that any randomization process such as exciton hopping will inevitably result in the loss of "information" contained in the localized absorption, much as the process of emission by a planar or spherical oscillator does. As a result, if hopping does occur and is a thermally activated process, we should observe the presence of some temperature, T_{hop} , at which the maximum polarization value of any complex drops in a nearly step-type function. This would occur when the rate of thermal motion equals that of luminescence; an Arrhenius-type process should increase in rate rapidly with temperature, and thus the transition would be relatively sharp.

Inspection of Figure 10, showing the maximum polarization of [Ru(bpy)₂(pphen)]²⁺ as a function of T , indicates that a step-type drop in P does occur at approximately 200 K. However, this drop is rather small, $\Delta P \approx 0.02$, and occurs concurrently with the beginning of the increase in the emission energy of the complex. Hence, this is assigned as due to a small amount of motion of the complex induced by the thermally activated motion of the polymer matrix. The fact that the polarization then remains constant even to 350 K indicates that no thermal scrambling of P is occurring, and no change in the ratio of the population of Ru-bpy units to

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Ru-pphen units is occurring: these units are not in equilibrium even at high temperature.

A possible exception to the observation of no hopping at increased T may occur for $[\text{Ru}(\text{pbpy})_3]^{2+}$. This complex demonstrates a significantly larger decrease in P with temperature than the previous two examples. Indeed, the full photoselection spectrum for this complex shown in Figure 5 is nearly invariant between 77 and 300 K with the exception that the region near P_{max} seems "clipped", as though some limiting P were being encountered at approximately $P = 0.16$. This reduced value of P is tantalizingly close to $P = 0.143$, which may be taken as evidence that hopping is beginning to compete efficiently with luminescence.

The smaller change in the energy of emission for this complex indicates that the effect of the solvent environment on this chromophore is smaller than some of the other complexes. Thus, the decrease in P_{max} by approximately 0.045 may in reality reflect the beginning of energy transfer in this molecule at 300 K.

To summarize, we must conclude that the multiple emitting chromophores of the tris complexes and the mixed-ligand species with near-degenerate ligand-localized states are not in a dynamic equilibrium at 77 K or even at significantly higher temperatures, though some evidence for the initiation of this process is found for $[\text{Ru}(\text{pbpy})_3]^{2+}$ at room temperature.

Conclusion

The detailed photoselection study of molecules with near-orbital degeneracies has indicated that the oscillating pattern seen in the SSEmP spectroscopy of Ru-diimine tris complexes, which correlates with the emission spectrum, derives from the effects of a type of "heterogeneous" solvation of the chromophores. The ICC model indicates that this causes the localized emitting triplet state to couple in different degrees of localized and delocalized portions of the excited singlet manifold.

Related to this is the variation of the wavelength at which P_{max} occurs in the SSEmP spectroscopy of the complexes as a function of detection wavelength. This indicates that luminescence in tris complexes does in fact derive from chromophores that are "heterogeneously" solvated. In mixed-ligand species, the observation of the same result but of larger magnitude due to the nonidentical nature of the chromophores supports the same conclusion. A rough estimate of the magnitude of heterogeneous solvation of $200\text{--}300\text{ cm}^{-1}$ was obtained by comparison of the mixed-ligand species with tris complexes. In no case is evidence available relating this solvation heterogeneity to the mechanism of the localization. Both the solvent independence of $P_{\text{max}}^{1,2}$ and the time-dependent P_{max} data implicate an intrinsic mechanism as the source of the localization.

An increase in temperature has the effect of red-shifting the luminescence of most complexes dissolved in PMM plastic. However, this effect is apparently inconsistent with thermal equilibration between localized emitting states in complexes with multiple nondegenerate chromophores. Thus, the presence of a dynamic exciton hopping process in the excited state of these species appears unlikely, at least on the time scale of the luminescence (approximately $5\ \mu\text{s}$). This conclusion was supported by temperature-dependent photoselection data that indicated that P was relatively unaffected for the mixed-ligand complexes by an increase in temperature, other than the effects of a slight loosening of the solvent with increased T .

Finally, the study of mixed-ligand complexes has provided some insight into the nature of localization in Ru-diimine species, as well as the nature of the luminescence process in this series of materials.

Acknowledgment. Support of this research by the Army Research Office (RTP) is gratefully acknowledged.

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MLCT Excited States. Role of the Hydrido Ligand in Hydrido Polypyridyl Complexes of Osmium(II) and Ruthenium(II)

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Received October 12, 1988

The photochemical and photophysical properties of the complexes $[\text{M}(\text{bpy})_2(\text{CO})\text{X}]\text{PF}_6$ ($\text{bpy} = 2,2'$ -bipyridine; $\text{M} = \text{Os}$, $\text{X} = \text{H}$, D , Cl ; $\text{M} = \text{Ru}$, $\text{X} = \text{H}$, D) are reported in 4:1 ethanol/methanol solution from 90 to 300 K. Metal to ligand charge-transfer (MLCT) excitation fails to induce metal hydride photochemistry, but oxidative or reductive quenching of $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}]^{++}$ does induce a net redox chemistry. There is no evidence for significant contributions to the emission spectrum nor to nonradiative decay by the $\nu(\text{Os}-\text{H})$ mode. For the analogous complex of Ru, there is a significant $\nu(\text{Ru}-\text{H})$ $k_{\text{H}}/k_{\text{D}}$ kinetic isotope effect for nonradiative decay.

Introduction

There is an extensive chemistry of transition-metal hydrido complexes, and such complexes play an important role in many metal-catalyzed reactions.¹ An extensive photochemistry has also been reported, but it has generally been based only on product and quantum yield studies.² There is little insight in this area

into excited-state dynamics, detailed photochemical mechanisms, or the nature of the excited state or states responsible for the photochemistry. In general, the complexes that have been studied do not absorb appreciably in the visible region, they require ultraviolet excitation, and they lack a clearly defined or well-established chromophoric base.

In contrast, the photochemical and photophysical properties of the metal to ligand charge-transfer (MLCT) excited states of

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