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Emission Photoselection Studies of Transition-Metal Complexes. 1. Bis(diimine) Complexes

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The technique of emission photoselection spectroscopy utilized with organic systems to determine nonradiative selection rules and orbital relaxation pathways has seldom been used with transition-metal systems. The ability of the technique to acquire polarization data for randomly oriented samples can be useful in clarifying some of the unique excited-state relaxation pathways (multiple-state emission) observed for these inorganic complexes. Therefore, a polarization spectrometer designed and assembled in this laboratory has been used to acquire emission and excitation polarization spectra for the three $[IrL_2Cl_2]^+$ complexes (where L is 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 5,6-dimethyl-1,10-phenanthroline (5,6-Mephen)), $[Ga(phen)_2Cl_2]^+$, and the three free ligands. The magnitude of the polarization, P, obtained for the three C_2 Ir(III) complexes and the free ligands indicates that these emission chromophores all behave as linear oscillators. The slope of the emission polarization found for the three Ir(III) complexes indicates the presence of two emitting states, consistent with an earlier suggestion of a charge transfer and dd* emission from these complexes. The polarization spectra for the three Ir(III) are similar; however, this result cannot alone be used to distinguish between assignment of the emission origin as either $d\pi^*$ (charge transfer) or $\pi\pi^*$ (ligand localized). The photoselection spectra of the Ga complex is depolarized, implying an intramolecular hopping of the localized excited state from ligand to ligand. The dominant intensity mechanism for the phosphorescence of the free ligands apparently is a second-order vibronic scheme involving an out-of-plane vibration while, as expected, a first-order spin–orbit mechanism is utilized with the transition-metal complexes.

Introduction

Typically, the relaxation of excited states for complex organic molecules has been rationalized from a combination of emission and absorption spectra, decay times, and quantum yields.[1,2] A substantial body of such experimental data accumulated for aromatic hydrocarbon and heterocyclic molecules has permitted generation of detailed and sophisticated theories[3,4] describing the nonradiative processes in these systems by emphasizing the role of molecular vibrations in these deactivation processes. A successful subsidiary effort for light-atom organic systems has utilized the emission photoselection technique[5] to determine nonradiative selection rules[6,7] and orbital relaxation pathways[8] for aromatics and heteroaromatics.

From these data and theories, some simple and useful generalizations concerning relaxation of excited states of organic aromatics have been elaborated. (1) Fluorescence (spin-allowed emission) typically occurs from the vibrationless state of the lowest excited singlet level (and only this state) irregardless of the excitation energy. (2) A single phosphorescence (spin-forbidden emission) typically occurs from the lowest vibrational state of the lowest excited triplet state. (3) Intersystem crossing (singlet to triplet nonradiative processes) typically occurs only from the lowest singlet electronic state, since vibrational relaxation from higher excited singlets called "internal conversion" is extremely rapid. As a consequence, emission quantum yields are typically wavelength independent. (4) Molecular vibrations of the emitter can function as either acceptors or activators in the nonradiative deactivation of excited states.[3,8]

Construction of an appropriate detailed theory of the excited state for transition-metal complexes necessitates accumulating sufficient emission data for a large number of structurally related complexes. Only two metal ion configurations, d^3 and d^6, are found to luminescence in a number of complexes.[9,10] For the d^3 Cr^{3+} systems, a weak luminescence occurs from dd* states, most commonly a line like phosphorescence from the excited ^2E state.

For the d^6 configuration, complexes of Ru^{2+}, Os^{2+}, Rh^{3+}, and Ir^{3+} provide examples of not only dd* type emission but also emission from ligand localized $\pi\pi^*$ and charge-transfer states,[11] metal to ligand type. Here the different types of emitting states and the range of spin–orbital coupling schemes exceed that for either the d^3 configuration or the organic emitters; consequently unusual behavior becomes more common. For example, the intense "phosphorescent" emission of a number of diimine complexes of Ru^{2+} and Ir^{3+} is measurable at room temperature. Moreover the temperature variation of the intensity and lifetime of the $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes varies in a manner indicating that a manifold of close-lying thermally equilibrated states of common orbital origin produces the emission.[12,13] Further, wavelength-dependent quantum yields[14] and laser rise-time experiments[15] imply that upper level intersystem crossing occurs. Such phenomena imply (1) that upper level intersystem crossing can compete with internal conversions for these ma-

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terials and (2) that coupling (spin–orbit, vibronic spin–orbit) between states of distinct orbital origin may be of magnitudes different from that between states of comparable origin. Perhaps most unique among the phenomena observed for d^6 complexes are the numerous, mostly recent examples of multiple emission.[16-21] These range from emissions described in single ring localized exciton emission[16] (a $\pi\pi^*$ state localized on the phen and a $\pi\pi^*$ state localized on the bpy rings) from complexes as $[Rh(bpy)_2phen]^{3+}$ to multiple emission having distinct orbital origin as the charge transfer and dd* emission apparently observed[17,18] for the $[Ir(phen)_2Cl_2]^+$ and $[Ir(5,6\text{-}Mephen)_2Cl_2]^+$ complexes.

The magnitude and range of the spin–orbit coupling possible for the different types of emitting states is obviously responsible for some large part of the unique results obtained. In particular, the observation of room-temperature "phosphorescence" and the unique thermally equilibrated emission from the $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ can be related to the breakdown of the Russell–Saunders spin–orbit model; i.e., S is not a good quantum number. The most obvious evidence for this is the large radiative rate constant and the large intensity of the so-called spin-forbidden absorption band. A model emphasizing the large spin–orbit coupling has been developed to attempt to quantitatively rationalize these data for the Ru^{2+} complexes.[22] Semiquantitative spin–orbit models[14,23] based upon McClure's simple spin–orbit model[24] have been utilized to rationalize the quantum yields and lifetimes for a number of the Ir(III) systems.

Somewhat neglected thus far, but likely of comparable significance to electronic relaxation factors in these systems, are the vibrational factors. Certainly the $\pi\pi^*$ transitions of these complexes and organic systems are sufficiently comparable that vibrational coupling involving these states should not differ; however, the presence of the heavy metal ion may alter the electronic coupling in the complex via an external spin–orbit coupling. Likewise $n\pi^*$ (organic) and $d\pi^*$ (metal complexes) states and the transitions involving them might be expected to be similar. But, the addition of dd* states (metal complex) within the available spectroscopic energy region (no comparable state exists at low energies in organic systems) necessarily provides new spin–orbit and vibrational coupling. Robbins and Thomson[25] have adopted the light-atom theory of the vibrational factor to the elaboration of Cr(III) emission while we have attempted to correlate nonradiative relaxation with[10,14,26,27] weak and strong vibronic coupling limits proposed by Jortner[28] and Rice.[29] However, the limited amount of experimentation directed toward elaboration of vibrational effects upon the systems necessarily limits the value of such attempts.

The emission photoselection technique elaborated by Albrecht[5] in which polarization (eq 1, where I_{vv} and I_{vh} are the

$$P = \frac{I_{vv} - I_{vh}}{I_{vv} + I_{vh}} \tag{1}$$

measured emission intensities with the analyzers vertical (v) and horizontal (h), respectively; the excitation source is polarized vertically (v)) is determined as a function of emission or excitation wavelength has been uniquely successful in providing details of the electronic and vibrational excited-state relaxation for organic emitter systems. For example, El Sayed has utilized emission and magnetic resonance photoselection techniques to postulate nonradiative selection rules[6,7] between $n\pi^*$ and $\pi\pi^*$ excited states and to define spin–orbit mechanisms for aromatics containing heavy halogen atoms.[30,31] Lim and co-workers have utilized the techniques to define the vibronic spin–orbit perturbation[8] and to assign the multiple emission of 1-indanone[32,33] Further Lim has succeeded with the method and selective deuteration techniques in identifying out-of-plane vibrations significant to the nonradiative relaxation of diazines.[8,34]

The one published example of the use of the technique for a d^6 transition-metal complex involves a point by point measurement method to obtain excitation polarization for the D_3 symmetry $[Ru(bpy)_3]^{2+}$ complex.[35] These data have been used to assign the emission as from a planar oscillator (i.e., E-type state). Earlier, Russian workers[36] utilized a point-by-point fluorescence polarization method to verify a planar oscillator for the D_{4h} zinc porphyrin system. Most recently, we have utilized a point-by-point method for a near-IR emission to verify a multiple emission for Rh(III) and Ir(III) sulfur chelate complexes.[21]

Quite obviously the photoselection technique should prove advantageous in answering many questions related to the unique phenomena observed for transition-metal complexes, since appropriate dilute single crystal samples, necessary for polarized data, are difficult to acquire and to manipulate for many transition-metal complexes. Nevertheless, the inability to obtain a direct spectral display of the corrected P function (eq 2, where I_{hv} and I_{hh} are the measured emission intensities

$$P = \frac{I_{vv} - CI_{vh}}{I_{vv} + CI_{vh}} \qquad C = \frac{I_{hv}}{I_{hh}} \tag{2}$$

vertical and horizontal, respectively, with the excitation source oriented horizontally (h)) has likely inhibited application of the technique. Further sensitivity limitations imposed by introduction of the polarizing elements into the optics limit use of the method for medium- and weak-intensity emitters. Although a number of designs[37-41] have been utilized to acquire data, no sensitive recording commercial instrumentation has been available until recently.[42] Consequently we did design, construct, and utilize such an instrument to measure photoselection spectra.

We report here the emission and excitation polarization spectra for a series of bis(diimine) complexes of Ir^{3+}, $[Ga(phen)_2Cl_2]^+$, and the free diimine ligands. The purposes of this research were (1) to demonstrate the functioning of our instrument, (2) to determine if these C_2 symmetry complexes produce polarization values consistent with expectation for a so-called linear oscillator system, (3) to clarify the multiple emission reported for these materials, (4) to attempt to distinguish between emission of distinct orbital origin (i.e., $\pi\pi^*$, $d\pi^*$, or dd*), and (5) to determine, where possible, details of the radiative and nonradiative excited-state relaxation mechanism (i.e., pure spin–orbit, vibronic spin–orbit, second-order vibronic spin–orbit). This paper emphasizes the latter four points with the instrument aspects of this work to be reported elsewhere. The next paper in the series deals with higher symmetry D_3 complexes.[43]

Experimental Section

Solvents. Low-temperature absorption and emission spectra were obtained in an ethanol–methanol mixture (4:1 by volume). Ethanol was purified by the method of Halper,[44] and Spectranalyzed methanol from Fisher Scientific Co. was used as received.

Free Ligands. 2,2′-Bipyridine (bpy) and 1,10-phenanthroline (phen) were purchased from Fisher Scientific Co., and 5,6-dimethyl-1,10-phenanthroline (5,6-Mephen) was supplied by G. Frederick Smith Chemical Co. All were recrystallized from H_2O/MeOH before use.

Protonated Ligands. bpy·HCl was prepared by bubbling HCl(g) through a solution of bpy in ether. The white precipitate was filtered, dried, and recrystallized from MeOH/ether before use. phen·HCl and 5,6-Mephen·HCl were prepared by analogous procedures.

Metal Complexes. $[Ga(phen)_2Cl_2]Cl\cdot 1^1/_2H_2O$ was prepared by a modified method of Carty and Dymock.[45] Ga metal was dissolved in warm HCl (12 M) and evaporated to near dryness. A 20-mL sample of HCl (5 M) was added, and the $GaCl_3$ was extracted with ether. phen·H_2O (6.34 g) was dissolved in 100 mL of MeOH/ether and added to the $GaCl_3$/ether solution. The white precipitate was filtered, dried, and recrystallized several times from MeOH/ether.

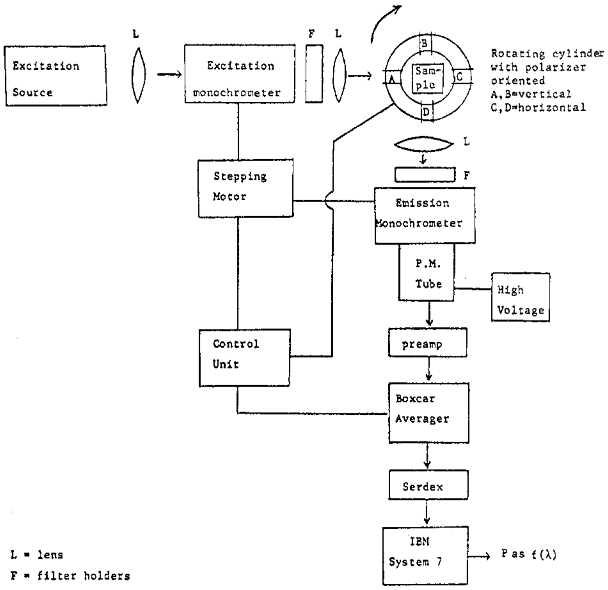

Figure 1. Block diagram of the high-resolution polarizing spectrophotometer.

Anal. Calcd for $[Ga(phen)_2Cl_2 \cdot 1^1/_2H_2O$: C, 51.18; H, 3.40; N, 9.94; Cl, 18.88. Found: C, 51.13; H, 3.41; N, 9.92; Cl, 18.79.

$[Ir(phen)_2Cl_2]Cl \cdot 3H_2O$ was prepared by the method of Broomhead and Grumley[46] and was purified by repeated recrystallization from MeOH. Purity was checked by the method of Ballardini et al.[47]

$[Ir(5,6\text{-}Mephen)_2Cl_2]Cl \cdot 3H_2O$ was synthesized according to Watts[48] and purified by repeated recrystallization from MeOH. Purity was again checked by the method of Ballardini.[47]

$[Ir(bpy)_2Cl_2]Cl \cdot 2H_2O$ was prepared by the method of Gillard and Heaton[49] and was purified by chromatography on a column of Sephadex LH-20. Anal. Calcd for $[Ir(bpy)_2Cl_2]Cl \cdot 2H_2O$: C, 37.13; H, 3.12; N, 8.66; Cl, 16.43. Found: C, 37.12; H, 3.13; N, 8.66; Cl, 16.32.

Instrumentation. Low-temperature (83 K) absorption measurements were done with a Cary 14 spectrophotometer. Samples were cooled in a copper block cryostat.

Low-temperature (77 K) emission spectra in EtOH/MeOH mixtures were obtained with an Aminco-Bowman spectrophotofluorometer (SPF). A Hanovia 200-W Hg–Xe lamp and a Hamamatsu R136 photomultiplier tube provided line excitation and emission detection.

Emission photoselection measurements of long-lived species (ligands, protonated ligands, and the Ga chelate) were obtained with the Aminco-Bowman SPF after fitting with Glan-Thompson polarizing prisms. Excitation sources were the Hanovia 200-W Hg–Xe lamp for emission polarization and a Hanovia 200-W Xe lamp for excitation polarization. The photoselection measurements of the Ir chelates were made with a high-resolution polarizing spectrometer which was designed and constructed in this laboratory (Figure 1). Either a 450-W Osram xenon arc lamp (for excitation polarization) or a 1000-W Hanovia Hg–Xe lamp (for emission polarization) served as the light source. Two 0.25-m Jarrell-Ash monochromators and a Model 82-462 Jarrell-Ash Omni Drive stepping motor were used in the system. A mechanical rotating shutter that supported vertically and horizontally oriented Polaroid sheets (HNP'B polarizers) were driven by the synchronous motor of a PAR Model 125 light chopper. The emission was detected by a Hamamatsu R955 photomultiplier tube, and the signal was amplified and measured by a PAR Model 162-164 boxcar averager equipped with a digital voltmeter (DVM) to permit repetitive signal averaging. The control unit contained the circuitry necessary to synchronize the rotating shutter, monochromator advance mechanism, and boxcar averager. Data processing was done with IBM System 7 and 360-175 computers which were interfaced with the DVM through a Serdex data aquisition system.

Measurement Technique. The degree of polarization is defined in eq 1. The failure of the spectrometer to transmit vertically (v) and horizontally (h) polarized light equally is considered in eq 2.

Polarization spectra obtained with the Aminco-Bowman SPF were determined according to Azumi and McGlynn.[52] With the high-resolution polarizing spectrometer, the four intensity combinations (I_{hh}, I_{hv}, I_{vv}, and I_{vh}) necessary for the calculation of P at a particular wavelength were determined in one period of the rotating shutter (~30 ms). The ability to collect these data rapidly permitted the use of the boxcar averager to increase S/N and digitize the signals. The digital information was sent through the System 7 to the 360-175 where polarization spectra were calculated, smoothed, and filed for plotting. The average of two or three spectra was graphed on a Cal Comp x-y plotter. The smoothed spectra were determined from data at 2-nm intervals. The error in P was estimated to be less than ±0.02 and ±0.003 polarization units with the Aminco-Bowman and high-resolution polarizing spectrometer, respectively. Emission spectra and lifetime as a function of concentration indicate that the Ga complex dissociates to produce free ligand. Consequently polarization spectra were determined at concentrations sufficient to minimize dissociation ($>10^{-4}$ M) but small enough ($<10^{-3}$ M) to preclude intermolecular energy transfer at 77 K.

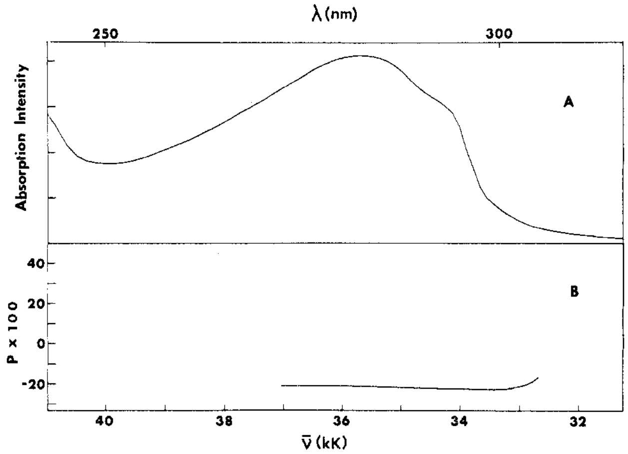

Figure 2. Absorption and excitation polarization spectra of bpy·HCl: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (433-nm emission).

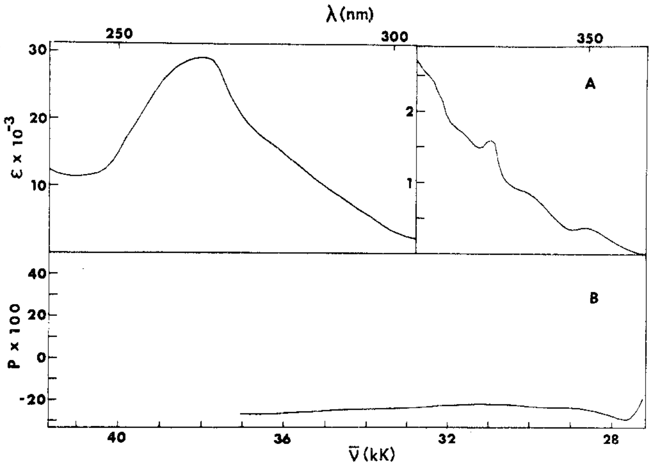

Figure 3. Absorption and excitation polarization spectra of phen·HCl: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (460-nm emission).

Results

Absorption (83 K) spectra for the protonated bpy and phen ligands, the three iridium complexes and the gallium–phen complex are seen in the top halves of Figures 2–7. The emission spectra for the $bpy \cdot H^+$ ligand, $[Ir(bpy)_2Cl_2]^+$, and $[Ga(bpy)_2Cl_2]^+$ are presented in the top halves of Figures 8–10. The bottom halves of Figures 2–7 give excitation polarization spectra and the bottom halves of Figures 8–10 give emission polarization spectra.

The absorption spectra for the protonated ligands and the Ga complex are comparable and can be used to locate spin-allowed ligand-localized π–π^* transitions. Weak n–π^* transitions expected for the free ligands may be covered by the intense π–π^* transitions. The Ir(III) complexes show bands

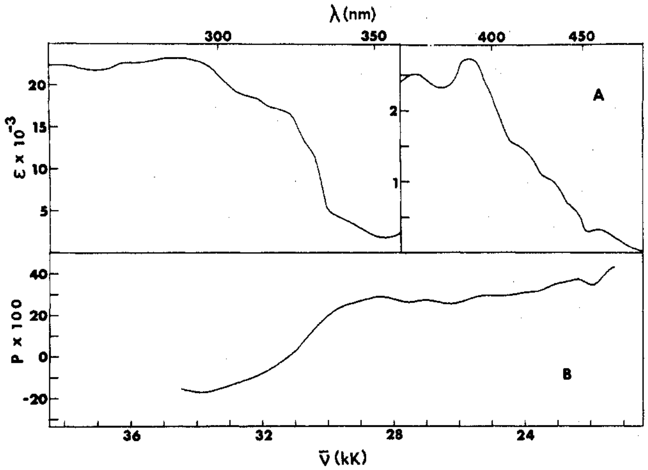

Figure 4. Absorption and excitation polarization spectra of [Ir(bpy)$_2$Cl$_2$]$^+$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 502-nm emission).

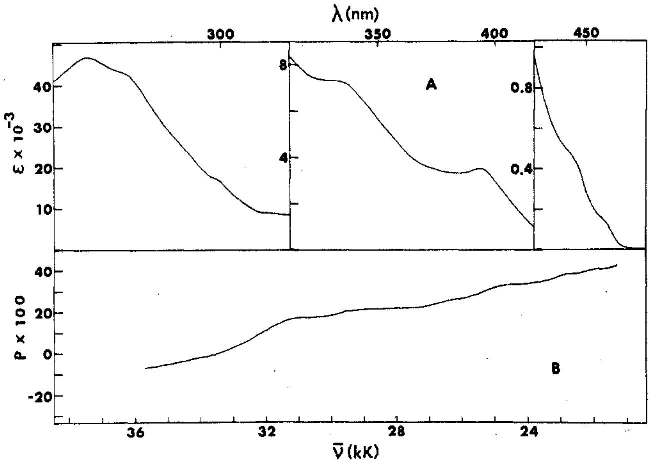

Figure 5. Absorption and excitation polarization spectra of [Ir(phen)$_2$Cl$_2$]$^+$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 474-nm emission).

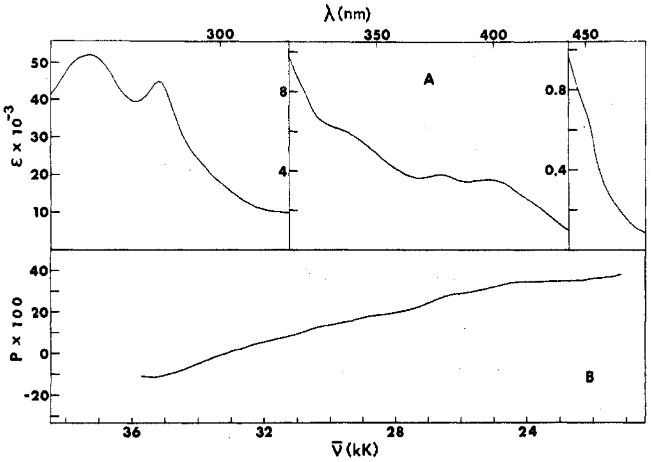

Figure 6. Absorption and excitation polarization spectra of [Ir(5,6-Mephen)$_2$Cl$_2$]$^+$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 488-nm emission).

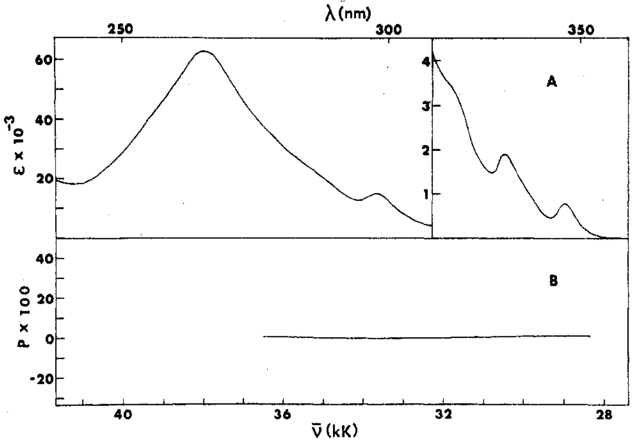

Figure 7. Absorption and excitation polarization spectra of [Ga(phen)$_2$Cl$_2$]$^+$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 485-nm emission).

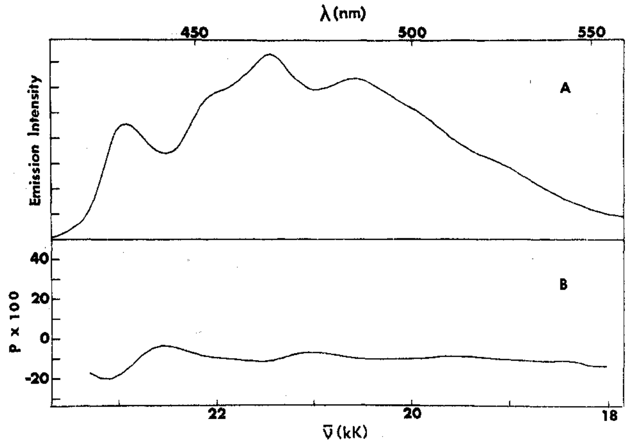

Figure 8. Emission and emission polarization spectra of bpyH$^+$ (77 K): (A) emission spectrum (313-nm excitation); (B) emission polarization spectrum (313-nm excitation).

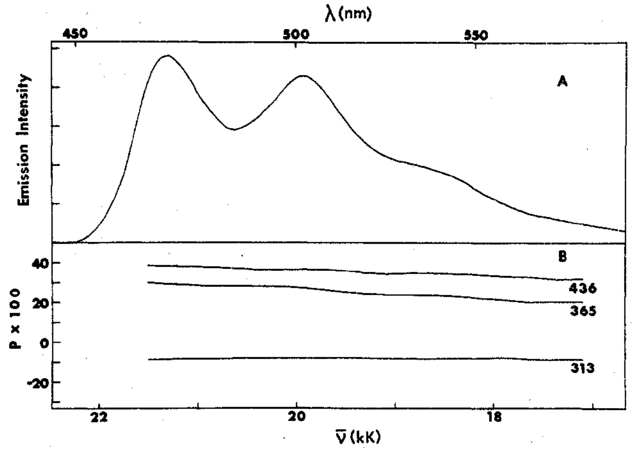

Figure 9. Emission and emission polarization spectra of [Ir(bpy)$_2$Cl$_2$]$^+$ (77 K): (A) emission spectrum: (B) emission polarization spectra (313-, 365-, and 436-nm excitation).

in the 320–200-nm region that are likely the π–π^* bands and, in addition, exhibit intermediate-intensity ($\sim 10^4$–10^3) bands at lower energy thought to be charge-transfer bands. At lowest energies (350–470 nm), almost overlapping with the emission, the Ir(III) complexes exhibit structured bands of low intensity ($\epsilon \sim 10^2$–10^1) that may contain nominal spin-forbidden bands of all three orbital origins (i.e., ligand-localized $\pi \rightarrow \pi^*$, charge-transfer d → π^*, and possibly localized d → d transitions). Analogous absorption bands are not observed for the Ga(III) compound although medium-intensity structure is seen in the 315–350-nm region.

Excitation polarization spectra for the three Ir(III) complexes indicate a gross similarity beginning at $\sim 36 \times 10^3$ cm^{-1}. The 5,6-Mephen complex does not show the sharp inflection at 32×10^3 cm^{-1} observed for the other two complexes. Further, the spacing of the polarization of the bpy complex in the

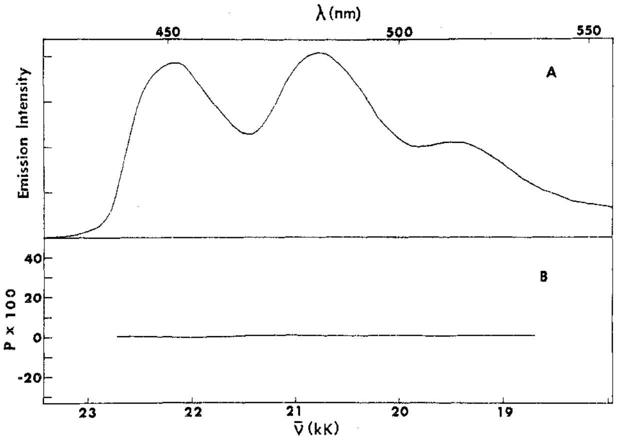

Figure 10. Emission and emission polarization spectra of [Ga(phen)$_2$Cl$_2$]$^+$ (77 K): (A) emission spectrum (313-nm excitation); (B) emission polarization spectrum (313-nm excitation).

394–470-nm region suggests that one or more vibronic progressions is present here. For all three complexes the excitation polarization at the lowest energy wavelength is above 40%. Excitation polarization for the protonated phen and 5,6-Me-phen ligands are similar to each other but different from the complexes in two respects. First, the polarization is negative and approaching −30% at ~32 × 10^3 cm^{-1}. Second, the polarization in the ~27 × 10^3 cm^{-1} region dips negative and then goes positive unlike the polarization of the complexes. The bpyH$^+$ polarization also inflects positive at ~33 × 10^3 cm^{-1}. Such a variation for the ligands may result from low-lying n–π* transitions not present in the metal complexes. The excitation spectra measured for the Ga(III) complex is unique with the curve flat and ca. zero through the (39–28) × 10^3 cm^{-1} region, substantially depolarized from the limiting value (−33%) of the C_2 species and different from that observed for the free ligands.

Emission polarization spectra divide into three types with that of the three transition-metal complexes almost flat but with a small and reproducible decreasing slope initiating in the vicinity of 530 nm. The Ga(III) complex emission polarization by contrast is flat throughout the entire region of the emission. The phosphorescence excitation spectra for the protonated ligands all exhibit large vibrational oscillations within the emission polarization spectra.

Discussion

Polarization spectra measured for most organic systems have been those typical of a linear emitting oscillator since most do not have a rotation axis of order greater than 2; consequently large positive polarization values (0.5) are possible. Reports of planar oscillators[36] are rare with the first being a phosphorescence from a metal porphyrin for which the maximum positive polarization is 0.14 and the maximum negative is −0.33. Various combinations of absorption and emission oscillators with the resultant polarizations are listed in Table I.

None of the ligands and complexes examined belong to point groups containing degenerate species; consequently, the limits pertaining to planar oscillators will not be pertinent here, and the polarization limits are 0.5 and −0.33. The origins of small depolarization to give values slightly less than these limits are unclear but may derive from overlapping bands of different polarization or microscopic rotational depolarization.[50]

The phosphorescence polarization of the phen ligand has previously been determined and our polarization curves are consistent with those reported.[51] The negative polarization values obtained for the 0–0′ band for all excitation wavelengths are consistent with an out-of-plane polarization for the emission as expected for the π–π* phosphorescence which acquires intensity via a spin–orbit mechanism likely involving coupling with an n–π* singlet. The emission polarization of the protonated phen is similar to that of free phen showing an oscillation corresponding to the ~1500-cm^{-1} vibrational progression observed in the emission spectrum. A comparable vibrational progression (1608 cm^{-1}) of a$_1$ symmetry has been observed by Azumi and McGlynn[52] for phenanthrene. The 400-cm^{-1} vibration observed for the nonprotonated phen ligand is also observed for phenanthrene and is ascribed to an a$_1$ mode. A vibration of approximately 800 cm^{-1} in the free phen ligand (830 cm^{-1}) also occurs in the phenanthrene ligand and is either an a$_2$ or a b$_1$ mode. The polarization spectra observed for the free and the protonated bpy verify assignment of the ~1500-cm^{-1} vibration as an a$_1$ mode. A mode of approximately 900 cm^{-1} observed in the emission of the free bpy and the monoprotonated bpy emission is likely the analogue to the 800-cm^{-1} vibration of phen. The more positive polarization (Figure 8) beyond the 0–0 band may result from the presence of this underlying vibrational progression of positive polarization, i.e., the a$_2$ or b$_1$ mode previously discussed.

Table I. Limiting Polarization Values

absorption oscillator	emission oscillator	polarization, P
linear (z)	linear (z)	$+^1/_2$
linear (z)	linear (x)	$-^1/_3$
linear (z)	planar (z, x)	$+^1/_7$
linear (z)	planar (x, y)	$-^1/_3$
planar (x, y)	linear (z)	$-^1/_3$
planar (x, y)	planar (x, y)	$+^1/_7$

Lim and co-workers[34] have utilized polarization measurements for partially deuterated polycyclic azines to characterize the second-order vibronic spin–orbit coupling mechanism responsible for the π–π* phosphorescence in these materials. For dibenzo[*f*,*h*]quinoxaline a vibration of ~850 cm^{-1} corresponding to an out-of-plane hydrogen wagging vibration of CH adjacent to the nitrogen atoms is identified as the mode responsible for the coupling of nπ* and ππ* modes. The appearance of the ~800-cm^{-1} vibration in the emission for all three diimine ligands and the appearance of in-plane polarized bands at spacings consistent with the 800-cm^{-1} vibration suggest that nπ* states participate here as intermediate states to permit dipole-allowed phosphorescence. Emission and polarization spectra for partially deuterated ligands could verify this conjecture.

The emission of the [Ga(phen)$_2$Cl$_2$]$^+$ complex (Figure 10) is, as the phenH$^+$ phosphorescence, dominated by the 1500-cm^{-1} (a$_1$) emission. The excitation polarization spectrum (Figure 7) is considerably depolarized. Only a$_1$ modes can be determined in the emission spectrum, as for the protonated phen, and the flat depolarized emission polarization spectrum contrasts that of the protonated phen ligand. The excitation polarization spectrum is also flat, contrasting that of the free ligand and Ir(III) complexes. Comparable depolarization of emission has been reported[53] and verified[43] for [Zn(bpy)$_3$]$^{2+}$ and for [Zn(phen)$_2$(H$_2$O)$_2$]$^{2+}$. Japanese workers[53] have suggested that the origin of the depolarization is the small splitting (~70 cm^{-1}) of the E and A$_2$ states in the tris complexes thus resulting in emission from the E and A$_2$ components at 77 K. Such an interpretation is contradicted by Mason's circular dichroism spectra and calculations for tris(diimine) complexes where a much larger splitting of E and A is predicted.[54,55] Additionally, the ESR spectra of the phosphorescent state for the analogous [Zn(phen)$_3$]$^{2+}$ complex[56] suggest that the phosphorescent triplet is localized on a single ligand and that the emission is depolarized by intramolecular energy transfer. This is the explanation that we favor for the Ga(III) complex depolarization.

The emission vibronic pattern of the three Ir(III) complexes is qualitatively similar to that of the Ga(III) complex and the protonated ligand spectra with only the $\sim$1400-cm^{-1} a_1 symmetry vibration visible in the complex spectra. However, the 0–0′ band of the three complexes is most intense and differs from that of the Ga(III) complex and the protonated ligand implying that the Franck–Condon factors differ. Such a difference could conceivably reflect a difference in the orbital origin of the dπ* and $\pi\pi$* excited states and might also imply comparable orbital origin for all three Ir(III) complexes in contrast to the assignments of Crosby and co-workers[48] for these three compounds. Crosby's assignment of the emission of the 5,6-Mephen complex as $\pi\pi$* in nature is based primarily upon absence of an emission solvent shift and the magnitude of the lifetime observed for the phen and bpy complexes.

Excitation polarization spectra of the phen and 5,6-Mephen complexes are qualitatively similar with the high-energy ($\pi\pi$*) polarization beginning at ca. −12% increasing until at $\sim$460 nm the polarization is $\sim$40%, approaching the 50% limit expected for a linear absorber–linear emitter case. The bpy complex indicates a negative polarization in the region (300 nm) of the $\pi\pi$* absorption but then does increase rapidly to positive values in the 320-nm region where the charge-transfer bands begin. Further the structures observed in the emission and in the polarization spectra are similar, suggesting that the lowest energy absorption band at $\sim$23 000 cm^{-1} is an essentially pure 0–0′ absorption transition with a vibronic progression initiating from here. The emission polarization spectra for 436 and 365 nm excitations for all three complexes exhibit a small negative slope toward lower energy distinct from the zero slope observed for the Ga(III) complex.

The similarity of the excitation and emission polarization can be used to argue that orbital characters of all three Ir(III) complexes are similar. However, the possibility exists that the lowest $\pi\pi$* and dπ* excited states are the same symmetry or that borrowing of intensity from singlets produces similar polarization spectra. In any case, no difference in the spectra of the two phen compounds can be ascertained; therefore no final judgment as to the orbital origin of the three complexes can be made.

The negative slope for all three Ir(III) complexes can be interpreted to indicate an underlying state of different symmetry. This result is consistent with the photochemical results of Balzani and co-workers[57] that were interpreted to indicate existence of a low-lying dd* state. More recently, Watts and co-workers[19,58] have demonstrated the existence of a long-wavelength structureless emission that dominates at room temperature. This has been interpreted as a dd* emission and our polarization results are consistent with this conclusion. Limitations of the polarizer wavelength response, the necessity for a rigid isotropic solvent medium, and sensitivity limitations have thus far prevented measurement of excitation polarization spectra in regions and at temperatures where the dd* emission dominates. Modification of the instrument and use of solvent media should soon permit such measurements.

The absence of any evidence for vibronic perturbation for the three Ir(III) chelates contrasts with that of the free ligands and the protonated ligands and is indicative of the contrasting mechanisms for the triplet emission intensity. For these transition-metal chelates, the presence of a heavy atom with a large spin–orbit mixing coefficient implies that pure first-order spin–orbit interaction involving states having a heavy-metal contribution must dominate any first-order vibronic or second-order vibronic mechanisms occurring.[59] The use of other solvent systems may permit identification of other intensity mechanisms. The large first-order spin–orbit coupling necessary for intersystem crossing also rationalizes the absence of fluorescence for these Ir complexes. Such behavior is quite comparable to that observed for the porphyrin complexes of Rh(III)[60] and Pd(III)[61] which exhibit strong phosphorescence and weak fluorescence ($\phi \sim 10^{-4}$). Presumably the dd* transitions for ruthenium(III) and palladium(II) porphyrins are at sufficiently higher energy[60] that they do not perturb, as here, the basic emission pattern.

Conclusions

Polarization spectra can be measured for three Ir(III) chelates and the free and protonated ligands and for the [Ga(phen)$_2$Cl$_2$]$^+$ complex. For all species except the Ga complex, the chromophores behave as linear oscillators with positive polarizations approaching the 0.50 limit. The Ga complex exhibits a unique depolarization suggesting a hopping of the localized excited state from ligand to ligand. The polarization spectra observed for the three transition-metal complexes are similar; however, this result cannot be used to justify assignment of the orbital origin of all three complexes as either dπ* or $\pi\pi$*. All three Ir(III) complexes have a negative slope of the emission polarization toward the red, apparently indicating the presence of two emitting states, the second of which is apparently a dd* emission. The dominant intensity mechanism for the free ligands apparently is a second-order vibronic mechanism involving an out-of-plane mode while a first-order spin–orbit mechanism, as expected, dominates for the transition-metal complexes.

Obviously ESR and photoselection ESR of the phosphorescent excited state would be useful in characterizing the nature of these emitting states (as for the [Zn(phen)$_3$]$^{2+}$); however, earlier attempts to measure the ESR of the long-lived excited states of the two Rh(III) were unsuccessful, apparently because there is complicating radical photolysis[62] ($S = {}^1/_2$) for the [Rh(phen)$_3$]$^{3+}$ and also because a very small percentage of Rh(III) d orbital increases the zero field splitting beyond the range of the ESR quantum quanta ($\sim$0.3–3 cm^{-1}).[44] A variety of experiments might prove useful here including polarization of stretched polymer samples to obtain absolute polarization assignments and enhanced polarization spectrometer sensitivity to obtain polarization values in the long-wavelength region where minimal band overlap can occur.

Registry No. [Ir(bpy)$_2$Cl$_2$]$^+$, 47514-19-2; [Ir(phen)$_2$Cl$_2$]$^+$, 17992-95-9; [Ir(5,6-Mephen)$_2$Cl$_2$]$^+$, 17992-95-9; [Ga(phen)$_2$Cl$_2$]$^+$, 47667-88-9; bpy·HCl, 65520-13-0; phen·HCl, 3829-86-5.

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Stereochemistry and Quantum Yields for the Ligand Field Photolysis of Rhodium(III) Complexes. 2.[1] *cis*- and *trans*-Rh(en)$_2$XBr^{n+}

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Ligand field excitations of *cis*- and *trans*-Rh(en)$_2$XBr^{n+} complexes (X = Br, H$_2$O, NH$_3$), in all cases but one, lead exclusively to the formation of *trans*-Rh(en)$_2$(H$_2$O)Br^{2+} as the photoproduct. The exception is the *cis*-Rh(en)$_2$(NH$_3$)Br^{2+} complex, where irradiation leads to the formation of both *cis*-Rh(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ and *trans*-Rh(en)$_2$(H$_2$O)Br^{2+}. The stereochemistry of all of the photochemical products has been examined in relation to the Vanquickenborne–Ceulemans mechanism, where thermal equilibrium takes place between triplet, five-coordinate, square-based-pyramid isomers generated by loss of a ligand from the six-coordinate ligand field excited state. Experimentally, the rearrangement of the [Rh(en)$_2$Y]* fragments depends on the nature of Y. For Y = Br, an energetic preference for Y in the apical position leads solely to trans products. For Y = NH$_3$, the absence of rearrangement is interpreted as a barrier for isomerization which is too large to compete with nonradiative deactivation of the triplet, five-coordinate fragment. The three separate reaction channels observed for the photolysis of the spectroscopically similar *trans*- and *cis*-Rh(en)$_2$(NH$_3$)Br^{2+} complex ions (loss of NH$_3$ trans to Br$^-$ for the former and loss of Br$^-$ or the NH$_3$ cis to Br$^-$ for the latter) have been interpreted as a strong preference for the Rh(III) metal center not to break a Rh(III)–en bond in a ligand field excited state.

Introduction

Ligand field photolysis of rhodium(III) amine complexes in aqueous solution customarily leads to the photoaquation of one ligand from the complex,[2] resulting in a monoaquo complex as the photolysis product. Subsequent ligand photosubstitution reactions are not observed spectroscopically since further reactions are usually limited to aquo ligand exchange.[3]

The thermal substitution reactions[4] of cis and trans tetraamine complexes in aqueous solution are stereoretentive, as are the photosubstitution reactions of the trans tetraamine complexes (eq 1). However, the photoaquation of cis tetraamine–Rh(III) complexes does lead, in some instances, to trans-substituted products (eq 2).

$$\textit{trans}\text{-RhA}_4\text{XY}^{n+} \xrightarrow[\text{H}_2\text{O}]{h\nu,\ \text{LF}} \textit{trans}\text{-RhA}_4(\text{H}_2\text{O})\text{X}^{(n-1)+} + \text{Y}^- \tag{1}$$

X = Y = Cl; A$_4$ = (NH$_3$)$_4$,[5,6] (en)$_2$,[1,5,6] (cyclam)[5]
X = Y = Br; A$_4$ = (NH$_3$)$_4$,[7] (en)$_2$[6]
X = Y = I; A$_4$ = (NH$_3$)$_4$,[8] (en)$_2$[6]
X = NH$_3$; Y = Cl; A$_4$ = (NH$_3$)$_4$,[6,8] (en)$_2$[1]

$$\textit{cis}\text{-RhA}_4\text{XY}^{n+} \xrightarrow[\text{H}_2\text{O}]{h\nu,\ \text{LF}} \textit{trans}\text{-RhA}_4(\text{H}_2\text{O})\text{X}^{m+} + \text{Y}^{(m-n)-} \tag{2}$$

X = Y = Cl; A$_4$ = (NH$_3$)$_4$,[9] (en)$_2$[1,6]
X = Cl; Y = H$_2$O; A$_4$ = (NH$_3$)$_4$,[9] (en)$_2$[10]
A$_4$ = (NH$_3$)$_4$; (X = Y = H$_2$O),[9] (X = Y = Br),[7]
(X = Br, Y = H$_2$O)[7]

The geometric difference in products obtained from the thermal and photochemical aquation reactions of the cis tetraamine complexes suggests that the photoaquation process occurs from an electronic excited state, rather than a highly excited vibrational level in the ground electronic state. In fact, Ford and co-workers[11] have proven conclusively that aquation does occur from the ligand field excited state in halopentaamminerhodium(III) complexes.

Vanquickenborne and Ceulemans[12] have used an "additive point ligand model" to explain the stereochemical changes

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