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THE EMISSION OF PYRIDINE AND POLYPYRIDINECHROMIUM(III) COMPLEXES IN RIGID AND FLUID MEDIA

by

Abdulatif Mohammad Ghaith

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1987
As members of the Final Examination Committee, we certify that we have read
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SIGNED: \textit{Abdulatif Shaikh}
To the memory of my mother,
Norah Ibrahim Al-Mudiamigh
ACKNOWLEDGMENTS

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ABSTRACT

The excited state emissions and lifetimes of $[\text{Cr(bipy)}_3]^3+$, cis-$[\text{Cr(bipy)}_2\text{Cl}_2]^+$, trans-$[\text{Cr(py)}_4\text{FBr}]^+$, cis-$[\text{Cr(phen)}_2\text{F}_2]^+$, and trans-$[\text{Cr(py)}_4\text{F}_2]^+$ were studied in hydroxylic and nonhydroxylic solvents at 77 K and as a function of temperature. The emission characteristics are determined by the relative disposition of $^2E$ and one component of $^2T_1$. The energy of these two levels is influenced by intramolecular and environmental factors, and solvent-induced level inversion occurs in cis-$[\text{Cr(phen)}_2\text{F}_2]^+$. The influence of temperature and solvent viscosity were studied in several glasses with variable melting ranges. The emission of all of the complexes, except $[\text{Cr(bipy)}_3]^3+$, were found to be influenced by solvent viscosity. This influence is large when $^2E$ and the component of $^2T_1$ are close in energy, and level inversion upon melting of the solvent occurs in cis-$[\text{Cr(phen)}_2\text{F}_2]^+$. The decay of the emission of Cr(III) complexes normally shows small temperature dependence at lower temperatures and large temperature dependence at higher temperatures. The threshold for the appearance of strong temperature dependence depends on intramolecular and environmental factors. The decays of all the complexes except $[\text{Cr(bipy)}_3]^3+$ show strong discontinuities in the
rigid-fluid transition regions of the solvent glasses which are accompanied by risetimes in the decay profiles when the emission intensity is monitored at long wavelengths. This is attributed to solvent relaxation during the excited state lifetime.
CHAPTER 1

BACKGROUND

Chromium(III) complexes are well known for their luminescence from their lowest excited state after light absorption especially at low temperatures [1, 2, 3, 4]. In most cases the emission is due to the $^2E \rightarrow ^4A$ transition. Excitation in the d-d, charge transfer or interligand bands leads to the rapid population of this state through internal conversion and intersystem crossing radiationless processes [5, 6]. Such processes are very rapid and the rise of the $^2E$ emission has been estimated from the fluorescence lifetime of the $^4T_2$ to be in the range of 1 ps [7]. Figure 1.1 shows the primary processes that populate and depopulate the $^2E$ state. At low temperatures, where photochemical reactions and back intersystem crossing are unimportant, the decay rate constant reaches a limiting value made up of the sum of the radiative ($k_5$) and nonradiative ($k_6$) decay rate constants.

1.1 State Ordering in Quadrate Fields

A quadrate field is a field in which the axial differs from the equatorial field. This definition applies also to cis complexes if holohedrized symmetry is employed. In holohydrized symmetry the ligand field strength on each
Figure 1.1. Radiative (→) and nonradiative (↔) primary processes in Cr(III) complexes.
axis is taken to be equal to the average of those of the two ligands on that axis.

In most Cr(III) complexes, the cubic $^2T_1$ state or its components in the lower symmetry quadrate field is usually found at energies greater than 200 cm$^{-1}$ above the $^2E$ state and consequently plays no role in the emission [8, 9]. The energies of the $^2E$ components are largely insensitive to quadrate fields, while the $^2EQ$ component of $^2T_1$ is stabilized through configuration interaction with the higher energy $^2EQ$ component of $^2T_2$ [10, 11]. In complexes with large enough quadrate fields, $^2EQ$ can fall below the components of the cubic $^2E$ state [10, 11, 12] hence becoming the emitting state [12, 13, 14, 15]. For brevity the ground state and the quadrate components of the cubic $^2E$ state will be referred to by their octahedral symmetry labels, while the spin-orbit components of the quadrate $^2E$ state will be referred to as $^2EQ$.

The stabilization of the $^2EQ$ state is a quadratic function of the quadrate splitting of the $t_2$ orbitals [10, 11, 13]:

$$\Delta E = -\frac{[\Delta(t_2)]^2}{6B + 2C}$$

1.1

where $\Delta(t_2)$ is the quadrate splitting of the $t_2$ orbitals, B and C are the Racah electronic repulsion parameters. In the Additive Angular Overlap Model, $\Delta(t_2)$ is a function of the difference between the $\pi$-bonding parameters of the axial and equatorial ligands [16, 17]. These parameters are a measure
of the π-bonding strength between the ligands and the chromium metal center.

The components of the cubic \(2^E\) state remain nearly unchanged in energy in quadrate fields \([10, 11]\). Consequently, the separation between them and the \(2^E_Q\) state is largely a function of \(\Delta(t_2)\) (Fig. 1.2). For small values of \(\Delta(t_2)\), the \(2^E\) components are the lowest excited states while \(2^E_Q\) is the lowest for large values of \(\Delta(t_2)\). For intermediate \(\Delta(t_2)\) values where these states are very close in energy, vibronic and spin-orbit mixing between them is expected \([18, 19, 20]\).

1.2 Emission in Quadrate Fields

The photophysics of the \(2^E \rightarrow 4^A\) emission has been studied extensively \([5, 21, 22]\). It is characterized by sharp and solvent independent emission spectra \([23, 24, 28]\). The decay of the emitted intensity is normally exponential in solutions and dilute crystals \([25, 27]\).

A number of complexes have been identified in which \(2^E_Q\) is the lowest excited state. The resulting \(2^E_Q \rightarrow 4^A_2\) emissions are broad \([13]\) and, in cases where single crystal emissions were measured, the spectra showed extensive vibrational structure at low temperatures \([12, 14, 15]\). This is taken as evidence of significant differences in nuclear geometries of the ground and excited states \([12, 13, 14]\).
Figure 1.2. Schematic energy level diagram of $d^3$ complexes in quadratic fields.
Forster et al. have studied the luminescence of a large number of quadrate chromium(III) ammine and ethylenediamine complexes in rigid hydroxylic glasses. Complexes with narrow emission spectra were classified as $^2E$ emitters, while those with broad emission spectra were classified as $^2E_Q$ emitters. The emission assignment of intermediate cases, however, was problematical [26, 27]. The emissions of the $^2E_Q$ emitters were later found to have a large solvent dependence in rigid media at 77 K. The emissions of the intermediate cases, such as cis-$[\text{Cr(NH}_3)_4(\text{OH})_2]^+$ were found to be narrow in hydroxylic solvents and broad in nonhydroxylic solvents such as DMF or DMSO [28]. On this basis, the complexes were classified as mixed emitters. The emission of the latter complexes showed a large delay time dependence in mixed solvent environments such as DMF/H$_2$O, indicating the existence of a large number of species with differing emission spectra and lifetimes. Moreover, all the mixed emitters identified so far have the potential for hydrogen binding to hydroxylic solvents. Since the emission is sharp in such solvents and broad in nonhydroxylic solvents, solvent-solute hydrogen bonding was thought to play a role in the $^2E$-$^2E_Q$ ordering.

1.3 Systems Studied

Glerup et al. analyzed the absorption spectra of a number of quadrate pyridinechromium(III) complexes in terms
of the Angular Overlap Model and found significant variation of the $\Delta(t_2)$ values [17]. Consequently, the $^2E-^2EQ$ disposition in these complexes must vary considerably. These complexes, in addition to the closely related polypyridine chromium(III) complexes such as cis-$[\text{Cr(phen)}_2\text{F}_2]^+$, constitute an ideal group for comparing the solvent, temperature and viscosity effects on the emission of complexes with varying $^2E-^2EQ$ energy gaps. This may provide an insight into the nature of the solvent-solute interactions that influence this energy gap and the effect of this energy gap on the luminescence characteristics of rigid and fluid solutions.
CHAPTER 2

EXPERIMENTAL

In this work the time resolved emission spectra and decay rates of the complexes under study were measured in different solvents as a function of temperature and, in the case of the decay rates, as a function of the monitoring wavelength.

2.1 Lifetime and Emission Spectral Measurements

The experimental setup for the measurement of lifetimes and time resolved emission spectra consisted of an excitation source and a detection system placed perpendicular to the exciting beam. The signal from the detection system was then channeled to signal averaging instruments. The averaged signal was sent to the computer for lifetime calculations or to a chart recorder in the case of emission spectral measurements. All of the measurements were done in subdued light. A block diagram of the experimental setup is shown in Figure 2.1.

2.1.1 Excitation Source

An AVCO Model C950 nitrogen gas laser was used as the exciting light source in most of this work. It had an
Figure 2.1. Block diagram for time-resolved emission and lifetime measurements. -- C = Computer; D = Quartz dewar; F = Glass filter; L1 = Quartz lens; L2 = Glass lens; LR = Linear recorder; M = Monochromator; NL = N2 laser; PM = Photomultiplier; S = Sample; SF = Solution filter; SA1 = Box-car signal averager; SA2 = Fabri-Tek signal averager; T = Trigger; and WR = Biomation waveform recorder.
excitation wavelength of 337 nm which was focused onto the sample using a quartz lens. The pulse width was 10 ns. The pulse rate could be varied between 1 and 100 Hz, but 30 Hz was used unless otherwise indicated. The laser was operated at 14.5 kV except where photodecomposition was a problem. Then the voltage was reduced to 11 kV. In some of the experiments 545 nm excitation generated by pumping a fluorescein disodium solution with the nitrogen laser.

2.1.2 Sample Setup and Temperature Control

The samples were placed in long 10 mm diameter borosilicate glass tubes. The tube containing the samples was cooled by immersion into a quartz glass Dewar flask containing liquid nitrogen. Three mm diameter tubes were used when very rapid cooling was needed to facilitate glass formation at liquid nitrogen temperature. Temperatures above 77 K were achieved by bubbling nitrogen gas through liquid nitrogen and into the sample Dewar. The temperature was controlled by varying the nitrogen gas flow and monitored inside and outside the sample by copper-constantan thermocouples and Omega digital thermometers. Agreement of the two thermocouples within 1 degree was taken as indication of temperature uniformity within the sample. In temperature regions where lifetimes were strongly temperature dependent, the temperature was maintained for at least 5 minutes before any measurements were done.
2.1.3 The Detection System

The components of the detection system, which was placed perpendicular to the excitation beam were:

a. A glass lens to focus the emitted light onto the entrance slit of the monochromator.

b. A 2-60 Corning Glass filter, in addition to 5 cm of saturated $K_2Cr_2O_7$, solution to remove scattered light.

c. A 0.25 meter Jarrell-Ash monochromator equipped with an 1180 lines/mm grating blazed for 660 nm. 1 mm slits provided a band width of 4.4 nm. A scanning rate of 25 nm per minute was normally used except when it was necessary to employ minimal number of laser pulses to generate a spectrum; then a scanning rate of 125 nm/min was used.

d. An RCA C31034 photomultiplier tube was connected to the exit split of the monochromator. The sensitivity of this photomultiplier tube extended to 900 nm, where it dropped sharply. For detection of emission beyond 900 nm, a red sensitive (S-1 response) photomultiplier tube used. This latter tube was cooled using dry ice. A 3000 $\Omega$ load resistor was used, except when a response faster than 1 $\mu$s was needed, then a 300 $\Omega$ load resistor was used. The applied voltage to the photomultiplier could be varied from
500 to 1500 V using a Fluka 415B high-voltage power supply.

2.1.4 Lifetime Measurements

After pulsed excitation, the photomultiplier output was sampled and digitized using a Biomation Model 805 waveform recorder that has an 8-bit A/D converter. To maximize precision in the A/D output, the signal was adjusted to full scale in the Biomation by varying sample concentration, voltage to the photomultiplier, and by adjusting the baseline using the offset circuit on the Biomation. The sampling intervals were varied from 0.2-100 μs per channel as required by the lifetime being measured. The risetime for the photomultiplier and waveform recorder combination with 3000 Ω load resistor was less than 1 μs. For signal to noise enhancement, 1024 digitized decay traces were added and stored in Fabretek Model 1074 signal averager. The resultant decay profile was then transferred to a Nova 3 computer, which fitted the data to a first-order exponential decay equation using a linear least-squares fitting program. The first 70 channels were reserved for baseline recording. The sampling interval on the Biomation was chosen so the signal intensity at channel 500 has fallen to about 10% of its value at channel 100. The data contained in channels 70 to 100 were not included in the curve fitting since they were usually influenced by scattering light, data beyond channel
500 were also not included in the fit due to baseline fluctuation influence.

2.1.5 Criteria for Decay Exponentiality

Since exponentiality or lack of it was of great importance to this work, a criterion had to be developed for judging the exponentiality of the decay. This criterion consisted of dividing the decay curve into four equal segments and fitting each segment to the single exponential decay equation. For exponentially decaying complexes, such as ruby, the lifetimes extracted from the different intervals usually had a difference of about 5% or less between the shortest and longest lifetimes. A ratio larger than 1.05 between the lifetime extracted from the final interval of the decay profile ($\tau_f$) and that extracted from the initial one ($\tau_i$) was usually taken as evidence of nonexponentiality.

2.1.6 Emission Spectral Measurements

The time-resolved emission spectra were taken with Princeton Applied Research Box-Car Integrator Model 160 signal averager. The synchronization between the exciting pulse and the signal averager was achieved through a trigger coming from the laser. The aperture time, which was the sample measuring time, was 0.5 $\mu$s. Three emission spectra were normally taken of each material under study. One was usually taken at short delay time where greater than 90% of
the emitters contributed. The other two were usually taken where 60% and 30% of the emitters still remained. Most of the emission spectra were taken with a scanning rate which corresponded to about 72 laser pulses per nm scanned. However, in cases where photodecomposition was evident, a faster scanning rate combined with 3 pps pulsing rate on the laser resulted in about 1.4 pulses per nm scanned. This and lower laser power resulted in the elimination of any interference from photoproduct emission with that of the original complex. Furthermore, the emissions of the photoproducts encountered were well separated from those of the original complexes.

2.2 Chemicals

2.2.1 Starting Materials

1,10-phenanthroline was obtained from J. T. Baker Chemical Co.; 2,9-dimethyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline were obtained from G. Fredrick Chemical Co.; 4,7-dimethoxy-1,10-phenanthroline was synthesized by Dr. John Rund. 2-Methoxyethanol was obtained from Aldrich Chemicals and was distilled under reduced pressure after treatment with CaO before use in any of the preparations.
2.2.2 Preparation of the Compounds

The following compounds were prepared or obtained from other workers in the field:

a. \( \text{Trans-}[\text{Cr(py)}_4\text{F}_2]\text{NO}_3 \) and \( \text{cis-}[\text{Cr(phen)}_2\text{F}_2]\text{ClO}_4 \): were prepared according to the method described by Glerup et al. [29]. Each was recrystallized three times before emission or lifetime measurements were taken. The absorption spectra agreed with those reported in the literature.

b. \( \text{Trans-}[\text{Cr(py)}_4\text{FBr}]\text{ClO}_4 \): was a gift from J. Glerup, \( \text{cis-}[\text{Cr(bipy)}_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O} \) was a gift from J. Josephson and \( [\text{Cr(bipy)}_3]\text{ClO}_4)_3 \) was prepared by Y. Kang.

c. Substituted Phenanthroline Complexes: By an extension of Glerup's method for the preparation of \( \text{cis-}[\text{Cr(phen)}_2\text{F}_2]\text{ClO}_4 \), the following substituted phenanthroline complexes were prepared:

1. \( \text{Cis-}[\text{Cr(4,7-dimethoxy-1,10-phenanthroline)}_2\text{F}_2]\text{ClO}_4 \). The elemental analysis, after 3 recrystallizations from 0.01 M HClO_4, gave H: 3.65, N: 8.46, C: 49.75. Calculations for C_{28}H_{24}N_{4}O_{8}F_{2}Cl gave H: 3.62, N: 8.46, C: 49.75.

2. \( \text{Cis-}[\text{Cr(2,9-dimethyl-1,10-phenanthroline)}_2\text{F}_2]\text{ClO}_4 \). The reaction, which took about 3 hours to complete, produced a green solid with a yield of 30%. This solid was then recrystallized from
0.01 M HClO₄. Elemental analysis gave H: 4.25, N: 8.96, C: 54.64. Calculations for C₂₈H₂₄N₄F₂ClO₄·H₂O gave H: 4.21, N: 8.99, C: 53.94.

3. **Cis-**[Cr(3,4,7,8-tetramethyl-1,10-phenanthroline)₂F₂]ClO₄. This complex was prepared in a similar manner to the ones above; however, due to the extreme insolubility of the 3,4,7,8-tetramethyl-1,10-phenanthroline complex in water, it was recrystallized from dichloromethane. It was not sent for elemental analysis, but its visible as well as its emission spectra were very close to the parent compound and to the other analogues, which confirms its similar structure.

### 2.2.3 Mixed Solvent Glasses

The following mixed solvents were employed:

a. **Ethylene glycol/Water**: This solvent was made up of 2:1 ethylene glycol to water by volume (Xₜ₂ₒ = 0.61). It formed a clear cracked glass when immersed in liquid nitrogen and started to soften at about 160 K.

b. **Glycerol/Water**: This was made up of 9 parts glycerol to 1 part water by volume (Xₜ₂ₒ = 0.31). This mixed solvent forms a clear cracked glass at liquid nitrogen temperature and begins to soften at about 190 K.
c. N,N-dimethylformamide/Water: The formation of a glass by dried or slightly wet DMF is influenced by the rate of cooling and by the nature of the solute and its concentration. With certain complexes, such as cis-[Cr(phen)₂F₂]ClO₄, when the solution is placed in 12 mm tubes and then plunged into liquid nitrogen, a finely divided clear glass with many opaque centers forms. However, when such a mixture is placed in 3 mm tubes for faster cooling when placed into liquid nitrogen, a clear glass usually forms. The mixture does not, however, continue to be a glass at all temperatures but turns into an opaque solid in the annealing region of the glass. Addition of water to DMF enhances its ability to form glasses. Mixtures that are between 10% to 50% water by volume form glasses regardless of rate of cooling and maintain normal glass behavior at all temperatures.

d. Tetrahydro-2-methylfuran/2-Methoxyethanol: A solution made up of 2.5 parts of tetrahydro-2-methylfuran to 1 part 2-M.E. forms a clear glass that starts to soften at about 120 K.
CHAPTER 3

SOLVENT EFFECTS ON THE EMISSION OF PYRIDINE AND POLYPYRIDINECHROMIUM(III) COMPLEXES IN RIGID MEDIA

3.1 Introduction

This study is directed toward understanding the photophysical properties of quadrate pyridine and polypyrinechromium(III) complexes in rigid media at 77 K in a variety of solvent environments. Such an understanding will be a helpful starting point in interpreting the effects of temperature and solvent relaxation on the emission and decay rates of these complexes, which will be explored in the next chapter. The points that need to be explored include:

1. The $2^E-2^EQ$ state order and their approximate energy separation (Fig. 1.2).

2. The nature of the solvent-solute interactions that play a role in determining the emitting state in complexes with proximate $2^E$ and $2^EQ$ levels.

3. The effect of the microenvironmental heterogeneity and the relation of these effects to the nature of the emitting state.

4. The importance of state mixing on the emission.

5. The effect of substituents on the polypyrine ring on $\Delta(t_2)$ and the nonradiative rates.

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3.2 Results

Time-resolved emission spectra of the complexes were taken at 77 K in hydroxylic, nonhydroxylic, as well as in mixed solvents made up of varying proportions of both. The lifetimes were measured as a function of the emission wavelength.

3.2.1 [Cr(bipy)$_3$](ClO$_4$)$_3$

The emission spectrum was sharp and independent of delay time in all solvents. Figure 3.1 shows the emission spectrum in Eg/W at 2 ms delay time. The decay was exponential with a lifetime of 5.2 ± 1 ms in all solvents except DMF. In neat DMF the lifetime was only 3 ms and the decay was exponential. There was evidence for photoreaction in this solvent at 77 K, which might have contributed to the decrease in the lifetime. The photoreaction resulted in blackening of the region of illumination by the laser light, leading to a rapid fall in the emission intensity. No photoproduct emission was observed.

3.2.2 Cis-[Cr(bipy)$_2$Cl$_2$]Cl·2H$_2$O

The emission in Eg/W was sharp, with a maximum at 758 nm. It showed very small time dependence. It broadened and shifted to the red by about 9 nm (Fig. 3.2) in DMF. Fast cooling of DMF did not result in a clear glass, but time dependence in such samples was slightly less than in slowly
Figure 3.1. 77 K emission spectrum of $[\text{Cr(bipy)}_3](\text{ClO}_4)_3$ in $\text{Eg/W}$ at 2 ms delay time.
Figure 3.2. 77 K emission spectra of cis-[Cr(bipy)$_2$Cl$_2$]Cl$_2$$\cdot$2H$_2$O in different solvents at 25 μs delay time.
cooled samples. In either case, the time dependence was not much larger than that in Eg/W. Addition of a small amount of water to DMF resulted in an emission that was almost identical in width, position and time dependence to that found in Eg/W. Increasing the amount of water in DMF did not result in further changes. As in [Cr(bipy)$_3$]$^{3+}$, there was evidence for photoreaction, although to a much lesser extent.

The crystalline solid emission was sharp, with a maximum between those in Eg/W and DMF (Fig. 3.3). The lifetimes showed a small wavelength dependence in Eg/W and DMF; they were nonexponential in the latter. Addition of water to DMF resulted in somewhat longer lifetimes than found in Eg/W and DMF (Table 3.1).

3.2.3 Trans-[Cr(py)$_4$FBr]ClO$_4$

**Emission Spectra.** The emission in Eg/W was somewhat broader than that of cis-[Cr(bipy)$_2$Cl$_2$]$^+$ in the same solvent and showed very small time dependence. In DMF the emission maximum shifted to the red by about 22 nm with respect to that in Eg/W, but time dependence remained very small (Fig. 3.4).

Addition of water to DMF ($X_{H2O} = 0.5$) resulted in the appearance of a shoulder whose position was close to the Eg/W maximum. This shoulder gained intensity at longer delay time. Increasing the water level to $X_{H2O} = 0.65$ resulted in further increase in the intensity of the peak to the blue.
Figure 3.3. 77 K emission spectrum of crystalline solid cis-
Cr(bipy)$_2$Cl$_2$Cl·2H$_2$O at 50 µs delay time.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Monitoring Wavelength (nm)</th>
<th>(μs)</th>
<th>$\tau_f/\tau_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eg/W</td>
<td>755</td>
<td>1060</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>900</td>
<td>1.06</td>
</tr>
<tr>
<td>DMF</td>
<td>760</td>
<td>1080</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>790</td>
<td>800</td>
<td>1.32</td>
</tr>
<tr>
<td>DMF/W</td>
<td>(X H₂O = 0.04)</td>
<td>760</td>
<td>1210</td>
</tr>
<tr>
<td></td>
<td>790</td>
<td>990</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>H H₂O = 0.30</td>
<td>758</td>
<td>1320</td>
</tr>
<tr>
<td></td>
<td>H H₂O = 0.65</td>
<td>758</td>
<td>1310</td>
</tr>
</tbody>
</table>
Figure 3.4. 77 K emission spectra of trans-$\text{[Cr(py)$_4$FBr]}\text{ClO}_4$ inEG/W and DMF at 50 $\mu$s delay time.
The emission at $X_{H2O} = 0.80$ was very similar to that in Eg/W (Fig. 3.5).

In the mixed solvent glass 2-M.E./MTHF, the emission was double peaked with the short wavelength peak close to the maximum in Eg/W, while the long wavelength peak close in position to the maximum in DMF (Fig. 3.6). The short wavelength peak intensity increased at long delay times (Fig. 3.7).

In 2-M.E., the emission was double peaked at short delay times. At long delay time the emission shifted to the blue and became similar in shape to that in DMF/W at $X_{H2O} = 0.65$ (Fig. 3.8).

**Lifetimes.** Table 3.2 shows the lifetime of trans-\([Cr(py)4FBr]^+\) measured in different solvents and emission wavelengths. The lifetime is exponential in Eg/W and shows a small wavelength dependence. It is somewhat shorter in DMF and less exponential. Addition of water to DMF increases the lifetime, reaching a maximum at around $X_{H2O} = 0.65$. At $X_{H2O} = 0.80$ the lifetime is close to that in Eg/W.

3.2.4 **Cis-\([Cr(phen)2F2]ClO4\)**

**Emission Spectra.** In Eg/W, Gly/W and DMF/W ($X_{H2O} = 0.80$), the emission spectra were narrow and approximately at the same position (Fig. 3.9). They were also independent of the excitation wavelength. The pattern of time dependence was the same in the tree glasses. In neat DMF the emission
Figure 3.5. 77 K emission spectra of trans-[Cr(py)$_4$FBr]ClO$_4$ as a function of water mole fractions in DMF at 25 μs delay time.
Figure 3.6. 77 K emission spectra of trans-[Cr(py)$_4$FBr]ClO$_4$ in Eg/W, DMF and 2-M.E./MTHF at 50 μs delay time.
Figure 3.7. 77 K emission spectra of trans-[Cr(py)$_4$FBr]ClO$_4$ in Eg/W, DMF and 2-M.E./MTHF at long delay times.
Figure 3.8. 77 K emission spectra of trans-[Cr(py)$_4$FBr]ClO$_4$ in 2-M.E. as a function of delay time.
Table 3.2. Lifetimes of trans-[Cr(py)$_4$FBr]ClO$_4$ at 77 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Monitoring Wavelength (nm)</th>
<th>$\tau_f/\tau_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eg/W</td>
<td>743 (max) 780</td>
<td>1.06 1.09</td>
</tr>
<tr>
<td>DMF/W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X_{H2O} = 0$</td>
<td>763 (max) 800</td>
<td>1.21 1.26</td>
</tr>
<tr>
<td>$X_{H2O} = 0.3$</td>
<td>745 800</td>
<td>1.07 1.15</td>
</tr>
<tr>
<td>$X_{H2O} = 0.50$</td>
<td>760 800</td>
<td>1.01 1.17</td>
</tr>
<tr>
<td>$X_{H2O} = 0.63$</td>
<td>745 780</td>
<td>1.06 1.12</td>
</tr>
<tr>
<td>$X_{H2O} = 0.80$</td>
<td>743 780</td>
<td>1.03 1.06</td>
</tr>
<tr>
<td>2-M.E./MTHF</td>
<td>740 860</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Figure 3.9. 77 K emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in different environments as a function of delay time.
shifted to the red and broadened considerably, it also had much larger time dependence than found in the previous solvents. The crystalline solid emission was broad, with very little time dependence and was significantly shifted to the red relative to that in DMF (Fig. 3.9).

Slow cooling of the DMF solution or warming of the DMF glass from 77 to 158 K resulted in the formation of an opaque solid, which gave an emission spectrum that was very similar in shape and delay time to that in neat DMF but was shifted to the blue by about 280 cm⁻¹.

The emission spectra in 2-M.E. and DMF/W (XH₂O = 0.65) were identical in terms of position and time dependence and were slightly shifted to the red and much more time dependent than in Eg/W, Gly/W (Figs. 3.10, 3.11). Increasing DMF mole fraction resulted in gradually increased redshift and broadening (Figs. 3.12 and 3.13).

Lifetimes. The lifetimes showed varying degrees of emission wavelength dependence in all solvents. The least level of wavelength dependence, although still significant, was found in Eg/W and the most was found in DMF. In all the solvents the lifetime got progressively shorter with increasing wavelength (Table 3.3). The lifetime of the crystalline solid, although nonexponential, was independent of the monitoring wavelength.
Figure 3.10. 77 K emission spectra of \textit{cis-}[\text{Cr(phen)}_2\text{F}_2]\text{ClO}_4 in 2-M.E. as a function of delay time.
Figure 3.11. 77 K emission of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in DMF/W ($X_{H_2O} = 0.65$) as a function of delay time.
Figure 3.12. 77 K emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ as a function of water mole fractions in DMF at 25 μs delay time. That in Eg/W is included for comparison.
Figure 3.13. 77 K emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ as a function of water mole fractions in DMF at 1200 µs delay time. -- That in Eg/W is included for comparison.
Table 3.3. Lifetimes of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ at 77 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Monitoring Wavelength (nm)</th>
<th>(μs)</th>
<th>$\tau_f/\tau_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eg/W</td>
<td>720</td>
<td>1640</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>733</td>
<td>1240</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td>900</td>
<td>1.25</td>
</tr>
<tr>
<td>Gly/W</td>
<td>720</td>
<td>1760</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>732</td>
<td>1290</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td>900</td>
<td>1.36</td>
</tr>
<tr>
<td>2-M.E.</td>
<td>730</td>
<td>1210</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>770</td>
<td>650</td>
<td>1.35</td>
</tr>
<tr>
<td>DMF</td>
<td>750</td>
<td>970</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>767</td>
<td>580</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>290</td>
<td>1.35</td>
</tr>
<tr>
<td>DMF/W</td>
<td>$X_{H2O} = 0.3$</td>
<td>740</td>
<td>980</td>
</tr>
<tr>
<td></td>
<td></td>
<td>760</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td></td>
<td>820</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>$X_{H2O} = 0.65$</td>
<td>730</td>
<td>1230</td>
</tr>
<tr>
<td></td>
<td>$X_{H2O} = 0.81$</td>
<td>720</td>
<td>1625</td>
</tr>
<tr>
<td></td>
<td></td>
<td>730</td>
<td>1250</td>
</tr>
<tr>
<td>Solid</td>
<td>820</td>
<td>110</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>123</td>
<td>1.17</td>
</tr>
</tbody>
</table>
3.2.5 Ring Substituted Analogues of Cis-[Cr(phen)₂F₂]ClO₄

To explore the effects of ring substituents on the emission and lifetimes of the analogues of cis-[Cr(phen)₂F₂]⁺, the lifetimes and emission spectra of cis-[Cr(4,7-dimethoxyphen)₂F₂]⁺, cis-[Cr(3,4,7,8-Me₄phen)₂F₂]⁺ and cis-[Cr(2,9-Me₂phen)₂F₂]⁺ were measured in DMSO/W and 2-M.E. The DMSO/W was chosen over Et₂O due to the insolubility of some of the complexes in the latter.

Emission Spectra. In DMSO/W, the emission maximum of all the complexes including the parent complex were within 10 nm of each other (Figs. 3.14, 3.15, 3.16, 3.17). The emission of the parent complex showed the largest delay time dependence. The emission of 2,9-dimethyl substituted one was almost as broad as the parent complex while those of the other two were somewhat sharper. The emissions of all these complexes shifted to the red somewhat on going from DMSO/W to 2-M.E. (Figs. 3.10, 3.16, 3.17, 3.18). The time dependence also increased for all of them except for cis-[Cr(2,9-Me₂phen)₂F₂]⁺, which maintained the same small level of time dependence as was found in DMSO/W. As in the parent compound, the emission of cis-[Cr(2,9-Me₂phen)₂F₂]⁺ in DMF glass broadened and shifted considerably to the red relative to that in DMSO/W, and again its delay time dependence was much less than that found in the parent compound in the same
Figure 3.14. 77 K emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in DMSO/W as a function of delay time.
Figure 3.15. 77 K emission spectra of cis-[Cr(4,7-dimethoxyphen)2F2]ClO4 in DMSO/W as a function of delay time.
Figure 3.16. 77 K emission spectra of cis-[Cr(3,4,7,8-tetramethylphenyl)\textsubscript{2}F\textsubscript{2}]Cl\textsubscript{4} in DMSO/W and in 2-M.E. as a function of delay time.
Figure 3.17. Emission spectra of cis-[Cr(2,9-Me2phen)2F2]ClO4 in different solvents as a function of delay time.
Figure 3.18. 77 K emission spectra of cis-[Cr(4,7-dimethoxyphen)$_2$F$_2$]ClO$_4$ in 2-M.E. as a function of delay time.
solvent (Fig. 3.17). Also, as in the parent complex, the emission shifted to the blue in opaque DMF relative to that in glassy DMF. The emissions of the other analogues were not measured in DMF.

**Lifetimes.** The lifetimes, as measured at the maximum in DMSO/W, did not differ greatly from that of the parent complex (Table 3.4). They all showed some measure of wavelength dependence.

3.2.6 **Trans-**[Cr(py)₄F₂]NO₃

**Emission Spectra.** Figure 3.19 shows the emission spectra of **trans-**[Cr(py)₄F₂]⁺ in Eg/W, DMF as well as that of the crystalline solid. The DMF emission was taken using a red sensitive photomultiplier tube, so as to follow the emission intensity beyond 900 nm. And except for the redshift, it was similar in shape to that in Eg/W. The crystalline solid emission had extensive vibronic structure. The emission spectrum in Gly/W was essentially at the same position as in Eg/W but peak ratios changed somewhat (Fig. 3.20). In 2-M.E., the emission overlapped extensively with those in Eg/W and DMF. There was also a significant loss of intensity on the blue side of the emission (Fig. 3.21). Addition of water to DMF solution of the complex resulted in gradual shifting of the emission to the blue relative to that in DMF, with increasing water content (Fig. 3.22). At the $X_{H₂O} = 0.80$, the emission was similar to that in Gly/W.
Table 3.4. Lifetimes of ring substituted analogues of $\text{cis-[Cr(phen)$_2$F$_2$]}^+$ in DMSO/W.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Monitoring Wavelength (nm)</th>
<th>$\tau_f/\tau_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{cis-[Cr(phen)$_2$F$_2$]}^+$</td>
<td>736</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td></td>
</tr>
<tr>
<td>$\text{cis-[Cr(4,7-dimethoxyphen)$_2$F$_2$]}^+$</td>
<td>729</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td></td>
</tr>
<tr>
<td>$\text{cis-[Cr(3,4,7,8-Me$_4$phen)$_2$F$_2$]}^+$</td>
<td>734</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td></td>
</tr>
<tr>
<td>$\text{cis-[Cr(2,9-Me$_2$phen)$_2$F$_2$]}^+$</td>
<td>731</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.19. 77 K emission spectra of $\text{trans-}[\text{Cr(py)}_4\text{F}_2]\text{NO}_3$ in different environments. -- Spectrum in DMF was taken using a red-sensitive photomultiplier tube.
Figure 3.20. 77 K emission spectra of $\text{trans-}[\text{Cr(py)}_4\text{F}_2]\text{NO}_3$ in Gly/W as a function of delay time.
Figure 3.21. 77 K emission spectra trans-[Cr(py)$_4$F$_2$]NO$_3$ in 2-M.E. as a function of delay time.
trans-[Cr(py)$_4$F$_2$]NO$_3$

DMF/W

Figure 3.22. 77 K emission spectra of trans-[Cr(py)$_4$F$_2$]NO$_3$ as a function of water mole fractions in DMF at 25 μs delay time.
while that at $X_{H2O} = 0.65$, was indistinguishable from that in 2-M.E. (Figs. 3.22 and 3.23). The time dependence in all of the emission spectra, except that of the crystalline solid, which showed no time dependence, was about the same in Eg/W.

**Lifetimes.** Table 3.5 shows the lifetimes of trans-[Cr(py)$_4$F$_2$]NO$_3$ in different solvents and as a function of the monitoring wavelength. The lifetime showed some dependence on the monitoring wavelength. In DMF, the lifetime was about half of its value in Eg/W. In DMF/W solutions, the lifetime decreased as the mole fractions of DMF increased. At $X_{H2O} = 0.65$, the lifetimes were nearly equal to those in 2-M.E.

3.3 **Discussion**

The $^2E \rightarrow ^4A_2$ emission spectra are generally sharp with only a small number of vibrational bands being excited. Moreover, most of the luminescence intensity is concentrated within a few hundred cm$^{-1}$ of the origin [5, 30, 33]. This is because the nuclear geometries of these two states are very similar since they are drawn from the same d-electron configuration in cubic and quadrate fields (Fig. 1.2). The single crystal spectra are highly resolved at low temperatures, and are of two types. In centrosymmetric complexes such as [Cr(NH$_3$)$_6$]$^{3+}$ [31] and [Cr(CN)$_6$]$^{3+}$ [32], the 0-0 band is weak and most of the intensity is contained within the vibronic bands [5, 33]. In noncentrosymmetric complexes, the 0-0 band is the most intense [34]. In both types of
Figure 3.23. 77 K emission spectra of trans-[Cr(py)$_4$F$_2$]NO$_3$ in DMF ($x_{H_2O} = 0.65$) as a function of delay time.
Table 3.5. Lifetimes of $\text{trans-}[\text{Cr(py)}_4\text{F}_2]\text{NO}_3$ at 77 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Monitoring Wavelength (nm)</th>
<th>$\tau_f/\tau_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG/W</td>
<td>780</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>810</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>170</td>
</tr>
<tr>
<td>Gly/W</td>
<td>780</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>810</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>163</td>
</tr>
<tr>
<td>2-M.E.</td>
<td>780</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>810</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>148</td>
</tr>
<tr>
<td>DMF/W</td>
<td>$X_{H_2O} = 0.81$</td>
<td>780</td>
</tr>
<tr>
<td></td>
<td></td>
<td>810</td>
</tr>
<tr>
<td></td>
<td>$X_{H_2O} = 0.65$</td>
<td>780</td>
</tr>
<tr>
<td></td>
<td></td>
<td>810</td>
</tr>
<tr>
<td></td>
<td></td>
<td>840</td>
</tr>
<tr>
<td></td>
<td>$X_{H_2O} = 0$</td>
<td>830</td>
</tr>
<tr>
<td></td>
<td></td>
<td>865</td>
</tr>
<tr>
<td>Crystalline solid</td>
<td>867</td>
<td>94</td>
</tr>
</tbody>
</table>
emission, the resolution of the vibrational structure is reduced in glassy matrices [23, 28]. Furthermore, the spectral positions are not sensitive to the environment in either crystalline or glassy media [25, 28].

The $2E \rightarrow 2A_2$ emission involves the excitation of a large number of vibronic bands whose relative intensities are determined by the Frank-Condon vibrational overlap factors, and the $0-0$ band is no longer dominant even in a noncentrosymmetric complex. This is strong evidence for dissimilar nuclear geometries in the two states [12, 15], which are drawn from different electronic configurations in quadrate fields (Fig. 1.2) [13]. The emissions of single crystals of $[\text{Cr(NH}_3)_5\text{(OH)}](\text{ClO}_4)_2$ [15] and trans-$[\text{Cr(en)}_2\text{F}_2]\text{ClO}_4$ [12] exemplify this type of emission. In glassy matrices, the vibronic bands are unresolved, resulting in broad and featureless spectra, which show large solvent dependence [26, 28].

The model that will be used as a guide in analyzing the emission and lifetime data at 77 K is based on the idea that these properties are greatly influenced by the relative disposition of $^2E$ and $^2E^\prime$ states (Fig. 1.2) [28].

The emission of $[\text{Cr(bipy)}_3]^{3+}$ is very sharp and independent of the solvent environment (Fig. 3.1). Its decay is exponential, consistent with an emission originating from a $^2E$ state that is far below the $^2E^\prime$ state (Fig. 3.24).
Figure 3.24. The approximate position of each of the complexes with respect to $^{2}E-^{2}E^Q$ disposition.
At the other extreme, the emission of \( \text{trans-[Cr(py)\(_4\)F\(_2\)]\(^+} \) is very broad in all solvents (Figs. 3.19, 3.20). It shifts to the red by about 1000 cm\(^{-1} \) in going from Eg/W to DMF, with little change in spectral shape, while in 2-M.E. it lies in between (Fig. 3.21). These characteristics are consistent with \( ^2\text{E}_\text{EQ} \rightarrow ^4\text{A}_2 \) emission where the \( ^2\text{E}_\text{EQ} \) state is far below the \( ^2\text{E} \) state (Fig. 3.24). The emission of a single crystal has been assigned by Flint et al. as originating from the \( ^2\text{E}_\text{EQ} \) state, based on the vibrational analysis of its luminescence spectrum at 5 K [14].

The following characteristics of \( \text{cis-[Cr(phen)\(_2\)F\(_2\)]\(^+} \) emission are significant.

1. In Eg/W the emission is narrow and shows some time dependence (Fig. 3.9).
2. In 2-M.E. and DMF, the emissions are much broader and shifted far to the red in the latter (Figs. 3.9 and 3.13).
3. The emission of the crystalline solid is broad and shifted to the red the most (Fig. 3.9).

The characteristics of the emission in Eg/W are consistent with \( ^2\text{E} \rightarrow ^4\text{A}_2 \) transitions, while those in DMF and the crystalline solid are consistent with \( ^2\text{E}_\text{EQ} \rightarrow ^4\text{A}_2 \) transitions. This points to an emitting state inversion in going from hydroxylic solvents to nonhydroxylic solvents and to the \( \Delta(t_2) \) values in Eg/W and DMF bracketing the \( ^2\text{E}-^2\text{E}_\text{EQ} \)
intersection, with the solid value being even lower (Fig. 3.24). In 2-M.E. Δ(t₂) appears to be somewhere in between those for Eg/W and DMF.

The emission of trans-[Cr(py)₄FBr]⁺ in hydroxylic solvents, although somewhat broader than in most ²E emitters, is still too narrow to originate from the ²EQ level. In DMF the emission shifts to the red by about 400 cm⁻¹, but does not broaden significantly, which indicates no emitting state inversion (Fig. 3.4). Probably the emitting level in both solvents is primarily the ²E level. However, in DMF the ²EQ level is reduced in energy, thus becoming closer to the ²E level than in Eg/W. This may then lead to greater mixing between ²EQ and ²E in DMF than in Eg/W, causing the energy of the ²E level to drop. Vibronic mixing, while negligible between the ²E and ²T₁ states in octahedral fields, becomes allowed when the symmetry is reduced [20]. The absence of state inversion suggests that the increase in Δ(t₂) in going from Eg/W to DMF is not large enough to cause the energy of the ²EQ state to drop below that for ²E in the latter solvent. It appears also that Δ(t₂) in both solvents is smaller than that of cis-[Cr(phen)₂F₂]⁺ in Eg/W (Fig. 3.24).

The same argument can be advanced to explain the solvent-dependent behavior of the narrow emission of cis-[Cr(bipy)₂Cl₂]⁺ (Fig. 3.2). Its narrower emission, however,
suggests a somewhat smaller \( t_2 \) value than that for trans-
[Cr(py)\(_4\)FBr\(_+\)]\(^+\) (Fig. 3.24).

The crystalline solid emission of cis-
[Cr(bipy)\(_2\)Cl\(_2\)]Cl\(\cdot\)2H\(_2\)O is sharp, with the 0-0 vibrational band
the most intense (Fig. 3.3), a strong indication that the
emission is due to \(^2E \rightarrow ^4A_2\) transition.

3.3.1 Multiple Solvates in Low
Temperature Glasses

Upon the formation of a rigid glassy solution, a
variety of solvent environments are frozen around the solute
molecules [35, 36]. The solute, together with a particular
arrangement of solvent molecules in the second coordination
sphere, will be referred to as a "solvate." The rigidity of
the solvent prevents interconversion between the solvates
during the lifetime of the excited state. When the emission
of a complex is sensitive to microenvironmental hetero-
geneity, the solvates will differ widely in their emission
spectra and lifetimes. The total emission is then a
superposition of the emissions of the individual solvates,
and the decay kinetics will no longer be represented by a
single exponential term but rather by a sum of exponentials.

\[
\frac{I}{I_0} = \sum_i a_i \exp\left[-(t/\tau_i)\right]
\]
The most significant aspect of emission time
dependence in Eg/W, 2-M.E. and DMF of the complexes under
consideration are:

1. The emission of [Cr(bipy)$_3$]$^{3+}$ is independent of time,
   and its decay is exponential.

2. The emission spectra of cis-[Cr(bipy)$_2$Cl$_2$]$^+$ and
   trans-[Cr(py)$_4$FBr]$^+$ show small time dependence.
   Their decays also show a small measure of nonexpo­
nentiality and wavelength dependence (Tables 3.1 and
   3.2).

3. The time dependence of the broad emission of trans­
   [Cr(py)$_4$F$_2$]$^+$ is also small (Fig. 3.19), its decay
   shows a small measure of nonexponentiality and
   wavelength dependence (Table 3.5).

4. Significant time dependence is found in the emission
   of cis-[Cr(phen)$_2$F$_2$]$^+$ in all solvents. Its extent,
   however, varies with the solvent, being relatively
   small in Eg/W and large in 2-M.E. and DMF (Figs. 3.9,
   and 3.10). Decay nonexponentiality and wavelength
   dependence are also large (Table 3.3).

The sharp and time-independent [Cr(bipy)$_3$]$^{3+}$ emission
resembles that of complexes in which $^2$E level is far below
the $^2$E$^Q$ level [23, 26, 28]. As these two levels get closer
together, microenvironmental heterogeneity begins to affect
the emission. This effect is small in cis-[Cr(bipy)$_2$Cl$_2$]$^+$
and trans-[Cr(py)₄F₂]+ where ²E-²EQ are still far apart. It is also small in complexes where ²EQ is far below ²E, as seen in the small time-dependence of trans-[Cr(py)₄F₂]+ (Fig. 3.19) and as reported by Fucaloro et al. in the case of trans-[Cr(NH₃)₄F₂]+, which emits from its ²EQ levels [28].

Microenvironmental heterogeneity has its largest effects on the emission of complexes, such as cis-[Cr(phen)₂F₂]+, that lie near the crossing region of the ²E-²EQ states. Two mechanisms can be envisioned as the source of this effect. One is that small differences in the solvent environment affect the vibronic and spin-orbit mixing of the two states in the quadrate field [18, 19, 20]. Different solvates will then emit from states with varying amounts of ²E-²EQ mixing. These will have slightly different emission spectra and lifetimes, which lead to emission time-dependence, decay wavelength dependence and nonexponentiality. The other is that the emission is a superposition of the emission from the two states because the upper one is close enough to be thermally populated. Time dependence is then caused by the variable ²E-²EQ energy gap in the different solvates. These two mechanisms are not mutually exclusive, and can operate simultaneously.

The time-dependence of the emission of cis-[Cr(phen)₂F₂]+ increases markedly in going from Eg/W to 2-M.E. (Figs. 3.9 and 3.10). The emission in the latter glass
is narrow at long delay times, but broadens gradually with decreasing delay, until it becomes very broad at short delay times. This indicates that the few solvates, whose emission is sampled at a long delay time, are emitting from the $^2E$ state. As the delay time is decreased, increasing numbers of solvates that are emitting from the $^2E_Q$ state are sampled. This leads to the conclusion that in 2-M.E., the $^2E$ and $^2E_Q$ states in cis-[Cr(phen)$_2$F$_2$]$^+$ are close enough for small variation in the solvent environment to affect the mixing and the energy gap between them. This also indicates that $\Delta(t_2)$ of cis-[Cr(phen)$_2$F$_2$]$^+$ in 2-M.E is somewhat larger than that in Eg/W (Fig. 3.24). Although the broad, redshifted emission in DMF narrows at long delay times, it remains too broad to originate from $^2E$. A likely explanation for this narrowing is that in the species sampled at long delay times, the $^2E$-$^2E_Q$ energy gap is small enough for the two states to mix, thus introducing some of the characteristic narrowness of $^2E$ emission into that of $^2E_Q$.

3.3.2 The Angular Overlap Model

To understand the effect of ligand and solvent environments on the $^2E$-$^2E_Q$ ordering in the quadrate complexes under study, a brief description of the angular overlap treatment of the parameters affecting the $^2E_Q$ energy will be given [16, 17].
In the Angular Overlap Model, \( \Delta(t_2) \) for a **trans** complex such as Cr\( \text{N}_4\text{AB} \), is expressed as [16, 17]

\[
\Delta(t_2) = -\frac{1}{4} [ \Delta_{\pi A} + \Delta_{\pi B} ] + \frac{1}{2} \Delta_{\pi N} \quad 3.1
\]

where \( \Delta_{\pi A} \) and \( \Delta_{\pi B} \) are the \( \pi \)-bonding parameters of the axial ligands and \( \Delta_{\pi N} \) is the \( \pi \)-bonding parameter of the equatorial ligand.

In hologedrized symmetry, where the \( \pi \)-parameters along a particular axis are taken to be the average of the \( \pi \)-parameters along that axis, the splitting of the \( t_2 \) orbitals can be expressed as

\[
\Delta(t_2) = -\frac{1}{2} [ \Delta_{\pi AB} - \Delta_{\pi N} ] \quad 3.2
\]

For a **cis** complex, the splitting is

\[
\Delta(t_2) = \frac{1}{4} [ \Delta_{\pi AB} - \Delta_{\pi N} ] \quad 3.3
\]

The sign of a \( \pi \)-bonding parameter is related to the electron donor and acceptor function of the particular ligand with respect to the metal center. Positive values indicate ligand \( \pi \)-donors, while negative values indicate ligand \( \pi \)-acceptors.

The quadratic dependence of the splitting of \( 2T_1 \) on \( \Delta(t_2) \) (Eq. 3.1) makes the energy of the \( 2E_Q \) state very sensitive to any changes in \( \Delta(t_2) \).
3.3.3 Effect of Ligands on $2E^0$ Energy

Two predictions follow from Eqs. 3.2 and 3.3:

1. $\Delta(t_2)$ is twice as large in a trans-$\text{CrN}_4X_2$ complex than in the cis-analogue.

2. $\Delta(t_2)$ can be altered through substitution in the axial positions.

The $2E$ and $2E^0$ are very close in cis-$\text{Cr}($phen$)_2F_2^+$ as opposed to being distant in trans-$\text{Cr}($py$)_4F_2^+$, which is in line with the first prediction. Glerup et al. [17] have shown that the halide ligands act as $\pi$-donors to the chromium metal center in a series tetrapyridine dihalide complexes. Moreover, the fluoride ligand was shown to have the largest $\pi$-donation parameter. The facts that $2E^0$ in cis-$\text{Cr}($phen$)_2F_2^+$ is lower in energy than in cis-$\text{Cr}($bipy$)_2Cl_2^+$ and that $2E^0$ is below $2E$ in trans-$\text{Cr}($py$)_4F_2^+$, while the opposite prevails in trans-$\text{Cr}($py$)_4FBr^+$, are in line with the second prediction of the Angular Overlap Model.

3.3.4 Effects of Solvent on $2E^0$ Energy

The properties of the emission spectra discussed so far appear to be determined by the $2E$-$2E^0$ energy gap. The solvent influence on the emission of the complexes under study will be analyzed in terms of the effect of solvent-solute interactions on this energy gap. These include
solvent-solute hydrogen bonding and electrostatic interactions such as ion-dipole and dipole-dipole interactions.

The energy of the $^{2}E_{Q}$ state in cis-[Cr(phen)$_{2}$F$_{2}$]$^{+}$ and in trans-[Cr(py)$_{4}$F$_{2}$]$^{+}$ is reduced in going from a hydrogen bonding solvent such as Eg/W to a nonhydrogen bonding solvent such as DMF (Figs. 3.9 and 3.19), while 2-M.E, which is intermediate in H-bonding, is also intermediate in producing a redshift (Fig. 3.10).

The quadratic dependence of the $^{2}E_{Q}$ energy on $\Delta(t_{2})$ makes it very sensitive to any changes in the $\pi$-donation by F$^{-}$ (Eq. 3.3). $\pi$-donation and $\Delta(t_{2})$ are reduced by H-bonding with the solvent [37]. A correlation between the $^{2}E_{Q}$ energy and hydrogen bonding of the solvent to the axial ligands is then to be expected. In complexes with close $^{2}E$ and $^{2}E_{Q}$ levels, a reduction in $\Delta(t_{2})$ through hydrogen bonding of the axial ligands may lead to enough destabilization of the $^{2}E_{Q}$ state for $^{2}E$ to be the emitting state. This appears to be the case in cis-[Cr(phen)$_{2}$F$_{2}$]$^{+}$, cis-[Cr(NH$_{3}$)$_{4}$(OH)$_{2}$]$^{+}$ and cis-[Cr(en)$_{2}$(OH)$_{2}$]$^{+}$ [28]. When $^{2}E_{Q}$ is far below $^{2}E$, hydrogen bonding leads only to a blue shift as seen in trans-[Cr(py)$_{4}$F$_{2}$]$^{+}$ and trans-[Cr(NH$_{3}$)$_{4}$F$_{2}$]$^{+}$ [28].

In both trans-[Cr(py)$_{4}$FBr]$^{+}$ and cis-[Cr(bipy)$_{2}$Cl$_{2}$]$^{+}$ the emitting state is largely $^{2}E$, but the $^{2}E$-$^{2}E_{Q}$ gap is not too large and the two state mix somewhat. H-bonding of the fluoride ligand in the first complex destabilizes the $^{2}E_{Q}$
state, reduces state mixing, leading to the observed blue-shift of the emission in \( \text{Eg} / \text{W} \) relative to that in DMF. The hydrogen bonding ability of the chloride ligand is less than that of the fluoride, yet the emission of the second complex shifts to the blue in going from DMF to \( \text{Eg} / \text{W} \). The \( 2\text{E}^\text{Q} \) energy appears to be sensitive to the resulting small change in dipolar interactions. The existence of a broad range of solvates in DMF solutions of \( \text{cis-[Cr(phen)\textsubscript{2}F\textsubscript{2}]}^+ \) with differing emission spectra indicate the \( 2\text{E}^\text{Q} \) energy of \( \text{cis-}[\text{Cr(phen)\textsubscript{2}F\textsubscript{2}]^+} \) is affected by small changes in solvent-solute dipolar interaction from one solvate to the other.

3.3.5 Emission in Mixed Solvent Glasses

The emission spectra of \( \text{trans-[Cr(py)\textsubscript{4}FBr]}^+ \) in mixed DMF/H\textsubscript{2}O glasses consist of two peaks that depend differently on delay time (Fig. 3.5). This suggests that the emission is made up of a superposition of the emission of two types of species. The narrowness of the two peaks also suggests that the emission of each type of species depends little on microenvironmental heterogeneity. Since the two peaks correspond in position to those found in \( \text{Eg} / \text{W} \) and DMF, and since the emissions in the latter two solvents are narrow and insensitive to solvent heterogeneity, it seems reasonable to assume that the emission is made up of a superposition of the emissions of hydrogen bonded and nonhydrogen bonded species. The two species model can also be applied to the emission of
this complex in 2-M.E./MTHF (Figs. 3.6 and 3.7). In both solvent systems, the presence of one solvent does not seem to alter the interaction of the complex with the other. The emission of this complex in neat 2-M.E. is also made up of two peaks that depend differently on time (Fig. 3.8), which suggests that 2-M.E. offers two types of environments to the solute.

The introduction of a small amount of water \((X_{H2O} = 0.041)\) in a DMF solution of cis-[Cr(bipy)\(_2\)Cl\(_2\)]\(^+\) resulted in an emission spectrum that resembles that in Eg/W (Fig. 3.2). Increasing the water content resulted in no further changes. This may indicate that the water preferentially bonds to the complex (water to complex molar ratio is roughly 200:1). However, since the introduction of a small amount of water in the solution resulted in the formation of a glass instead of the opaque solid in neat DMF, the glass structure may have something to do with the blueshift, not just specific interactions.

The emission of trans-[Cr(py)\(_4\)F\(_2\)]\(^+\) in mixed DMF/W glasses is difficult to interpret. It is broad at all water levels with peaks and shoulders that correspond in positions to those in Eg/W and DMF (Fig. 3.22). This suggests that the emission might be a superposition of two broad emission spectra of hydrogen bonded and nonhydrogen bonded species. However, the emission time dependence was small at all water
levels, and in contrast to \( \text{trans-}[\text{Cr(py)}_4\text{FBr}]^+ \), the emissions of hydrogen bonded and nonhydrogen bonded species could not be separated.

In contrast to \( \text{trans-}[\text{Cr(py)}_4\text{FBr}]^+ \), the spectra of \( \text{cis-}[\text{Cr(phen)}_2\text{F}_2]^+ \) in any of the DMF/W glasses do not appear as a superposition of the emissions of only two species, but narrow gradually with increasing delay time. The blueshift that takes place between \( X_{\text{H}_2\text{O}} = 0 \) and 0.3 is not accompanied by narrowing of the emission, and no peak or shoulder appears on the blue side to indicate H-bonded species (Figs. 3.12 and 3.13). As the water content is increased from \( X_{\text{H}_2\text{O}} = 0.30 \), the continuous blueshift is accompanied by gradual narrowing of the emission, until at \( X_{\text{H}_2\text{O}} = 0.81 \), the emission resembles that in \( \text{Eg/W} \) in terms of position, narrowness and time dependence. It appears that the energy of the \( ^2\text{E}_{\text{g}} \) state increases gradually with increasing water content of the solution. Furthermore, the lack of spectral shape changes between \( X_{\text{H}_2\text{O}} = 0 \) to 0.3, suggests that the mixing between the two states is unaffected in this range. At higher water levels, the mixing of the two states increases gradually and eventually leads to complete state inversion at high enough water levels. It appears then that there is a continuous change in the solvent-solute interaction as a function of solvent composition, and that the interaction of the complex with one of the solvents is influenced by the presence of the
<table>
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<th>Complex</th>
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<th>Monitoring Wavelength (nm)</th>
<th>$(S^{-1}) \times 10^{-4}$</th>
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</thead>
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<tr>
<td>Cr(bipy)$_3^{3+}$</td>
<td>Eg/W</td>
<td>730</td>
<td>0.019</td>
</tr>
<tr>
<td>trans-[Cr(py)$_4F_2]^+$</td>
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</tr>
<tr>
<td>trans-[Cr(py)$_4FBr]^+$</td>
<td>Eg/W</td>
<td>743</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>763</td>
<td>0.18</td>
</tr>
<tr>
<td>cis-[Cr(phen)$_2F_2]^+$</td>
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<td>0.081</td>
</tr>
<tr>
<td></td>
<td>2-M.E.</td>
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<td></td>
<td></td>
<td>770</td>
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</tr>
<tr>
<td></td>
<td>DMF</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>840</td>
<td>0.34</td>
</tr>
</tbody>
</table>
other. The unique behavior of this complex may be related to its polarity, H-bonding ability and the closeness of its $^2E$ and $^2EQ$ levels. Moreover the fact that cis-$[\text{Cr}(2,9-$Me$_2$phen)$_2F_2]^+$, which behaves in a similar manner to the parent complex with respect to solvent dependence, shows much less delay time dependence in all solvents suggests that the phenanthroline structure may be playing a role in determining whether the multiple solvates have similar or different emission spectra (Fig. 3.17).

3.3.6 Nonradiative Decay Rates and Structure

The following points concerning the limiting decay rate constant ($\tau^{-1}$) of the complexes under consideration (Table 3.6) merit attention:

1. The decay rate of $[\text{Cr}(\text{bipy})_3]^3+$ is smaller than the rest of the complexes.

2. The decay rate of trans-$[\text{Cr}(\text{py})_4F_2]^+$ in Eg/W is larger than that of trans-$[\text{Cr}(\text{py})_4FBr]^+$ in the same solvent. Both increase in going from Eg/W to DMF.

3. The decay rate of cis-$[\text{Cr}(\text{phen})_2F_2]^+$ depends significantly on the monitoring wavelength in any of the solvents tried. The greatest dependence, however, is found in 2-M.E. and in DMF.

At low temperatures the limiting decay rate ($\tau^{-1}$) is equal to the sum of the radiative rate ($k_5$) and the
nonradiative decay rates ($k_6$). Theoretical treatments of radiationless transitions in large molecules predict that in the weak coupling limit, the nonradiative rate constant is dependent on several factors that include [38, 39, 40]:

1. Presence of effective accepting vibrations.
2. The energy gap between the states involved in the transition.
3. The horizontal shift between the surfaces involved in the transition along the accepting vibrational coordinate.
4. The magnitude of the perturbations that couple the two states.

The radiative rate in Cr(III) complexes is between 100 and 300 s$^{-1}$ [5, 30, 25]. The limiting decay rate of [Cr(bipy)$_3$]$^{3+}$ is 190 s$^{-1}$, which indicates that the nonradiative decay rate is small in this complex. High-energy vibrations such as O-H, N-H and C-H are thought to be the most effective accepting modes [22, 30, 41, 42]. The small value of $k_6$ in [Cr(bipy)$_3$]$^{3+}$ indicates that the good accepting C-H vibrations on the bipyridine ring do not interact effectively with the d-electron density on the metal, which suggests weak π-interaction between the metal and the pyridine ring.

The nonradiative decay rate ($k_6$) significantly contributes to the limiting decay rate of trans-
[Cr(py)$_4$FBr]$^+$, while the decay is mostly nonradiative in \textit{trans}-[Cr(py)$_4$F$_2$]$^+$. The larger increase in \( k_6 \) is probably due to the smaller energy gap and greater horizontal shift between the ground and \( 2E_Q \) energy surfaces in the latter [23, 27, 38]. Moreover, greater \( \pi \)-interaction between the ring system and the metal center may have contributed to the lowering of the \( 2E_Q \) energy in \textit{trans}-[Cr(py)$_4$F$_2$]$^+$ compared to that in \textit{trans}-[Cr(py)$_4$FBr]$^+$. This then leads to more effective coupling of the good accepting C-H vibrations to the metal center in \textit{trans}-[Cr(py)$_4$F$_2$]$^+$ and contributes to the enhancement of its nonradiative rate.

The time-resolved emission spectra of \textit{cis}-[Cr(phen)$_2$F$_2$]$^+$ show that the shorter-lived species have broader and redshifted emissions relative to those of the longer-lived species. The larger nonradiative rates of the redshifted species may be due in part to the smaller energy gap and greater horizontal shift between the surfaces involved in the transition.

3.3.7 Effects of Substituents on the Phenanthroline Skeleton on the Emission of \textit{Cis}-[Cr(R$_x$phen)$_2$F$_2$]ClO$_4$

Introducing substituents on the skeleton of the phenanthroline ring did not markedly change the lifetime from that of the parent compound. Equally small changes were found in the transition energy. This is in marked contrast to the findings of DeArmond and Forster, which showed that in
Cr(III) complexes of β-diketones where metal d-electron delocalization onto the acac π-system is important, substitution onto the acac skeleton affected both the lifetime and emission maximum significantly [43, 44]. The d-electron delocalization in the β-diketone complexes increase the coupling between the d-election density and the good accepting C-H vibrational modes. Such coupling is weak in the phen complexes, as evidenced by their relatively long lifetimes and the small effect of the reduction of the number C-H ring vibrations through substitution.

In contrast to the small effect of substituents on the lifetime and emission maximum, emission time dependence was affected significantly. Emission time dependence was reduced by substitution. This may indicate that the presence of substituents on the phen ring reduces the effect of microenvironmental heterogeneity (Figs. 3.13-3.18).

3.3.8 Summary and Conclusions

In quadrat fields, chromium(III) complexes can be classified as 2E, 2EQ, or mixed emitters (Fig. 3.24). [Cr(bipy)₃]³⁺ is a 2E emitter, while trans-[Cr(py)₄F₂]⁺ is a 2EQ emitter. In 2E emitters, the 2E state is below the 2EQ state in all solvents, while in 2EQ emitters the 2EQ state is below the 2E in all solvents. The energy of the 2E -> 4A₂ transition is insensitive to the solvent environment, while that of 2EQ -> 4A₂ is. In mixed emitters 2E and 2EQ are
close enough for the solvent environment to affect their emission significantly. In \textit{cis}-[Cr(phen)$_2$F$_2$]$^+$ the emitting state is changed from $^2E$ in hydroxylic solvents to $^2EQ$ in nonhydroxylic solvents, while in \textit{cis}-[Cr(bipy)$_2$Cl$_2$]$^+$ and \textit{trans}-[Cr(py)$_4$FBr]$^+$ this results in a small emission redshift with emitting state remaining largely $^2E$ in character, as seen from the relative narrowness of their emission in all media.

The solvent-solute interactions that affect the energy of the $^2EQ$ state include H-bonding between the solvent molecules and the fluoride ligands, which decrease $\Delta(t_2)$, and consequently increase the $^2EQ$ energy. This is seen in the shifting of the $^2EQ \rightarrow ^4A_2$ emission of \textit{trans}-[Cr(py)$_4$F$_2$]$^+$ to the red in going from hydrogen bonding to nonhydrogen bonding solvent and in the raising of the $^2EQ$ level upon $^2E$ in \textit{cis}-[Cr(phen)$_2$F$_2$]$^+$ in going from nonhydrogen bonding to hydrogen bonding solvents. Dipolar interactions may also affect the $^2EQ$ energy, as seen from the shift of the emission of some of the solvates of \textit{cis}-[Cr(phen)$_2$F$_2$]$^+$ in DMF to the blue.

Microenvironmental heterogeneity has minimal effects on $^2E$ emission, as evidenced by the delay time independence of such emissions and the exponentiality of their decay. When $^2EQ$ is far below $^2E$, as in \textit{trans}-[Cr(py)$_4$F$_2$]$^+$, microenvironmental heterogeneity leads to small delay time dependence of the emission and to some nonexponentiality.
The greatest effect of microenvironmental heterogeneity is observed in mixed emitters when \(^2\text{E}\) and \(^2\text{E}Q\) are nearly equi-energetic. In this case the \(^2\text{E} - ^2\text{E}Q\) energy gap and mixing are very sensitive to the solvate structure. This leads to large delay time dependence of the emission spectra and large nonexponentiality and monitoring wavelength dependence of the decay. This is exemplified by the behavior of the \textit{cis-}\[\text{Cr(phen)}_2\text{F}_2\]^+ in 2-M.E. and in DMF.

The emission spectra of \textit{trans-}\[\text{Cr(py)}_4\text{FBr}\]^+ in DMF/W solution indicate the presence of two types of solvates, one hydrogen bonded and the other nonhydrogen bonded. On the other hand, the emission spectra of \textit{cis-}\[\text{Cr(phen)}_2\text{F}_2\]^+ shift continuously with changes in the DMF/W composition, which indicates that the character of the multiple solvates varies continuously with solvent composition.

Substituents on the skeleton of the phenanthroline ring in \textit{cis-}\[\text{Cr(phen)}_2\text{F}_2\]^+ do not significantly affect the position of the emission maxima in DMSO/W or the decay rate. This is taken to mean that \(\pi\)-delocalization of the metal d-electrons in the phenanthroline ring is small.
CHAPTER 4

TEMPERATURE AND VISCOSITY EFFECTS ON EMISSION SPECTRA AND LIFETIMES

4.1 Introduction

Numerous temperature dependence studies of the luminescence behavior of transition metal complexes in solution have been carried out [36, 45, 46, 47, 48]. When the temperature range of these studies spans a rigid-fluid transition of the solvents, an emission redshift may occur with increasing fluidity [36, 47, 48, 49]. This has been referred to by Wrighton as luminescence rigidochromism [49]. Changes in spectral emission begin to appear when the solvent relaxation times are approximately equal to the excited state lifetimes [48, 50, 51, 52]. In alcohol/H_2O glasses, the viscosity varies by four orders of magnitude within 20 degrees [53]. Here the emission spectra generally show some time dependence and the lifetimes become nonexponential [51, 52, 54].

Most temperature dependence studies of Cr(III) emission spectra and lifetimes have been carried out on complexes in which ^2E is the lowest excited state [9, 21, 55, 56, 57]. Emission spectral changes are normally confined to some thermal broadening and to emission from higher
vibrational levels of the excited state. The temperature
dependence of the lifetimes can, generally, be divided into
two stages. At low temperatures the lifetimes show little or
no temperature dependence, but at high temperatures they
decrease strongly [45, 56, 57]. The threshold of the second
stage varies widely and depends on intramolecular and solvent
environmental factors [21, 45, 56, 57, 58, 59, 60]. For
cis-[Cr(NH₃)₂(H₂O)₄]³⁺ and fac-[Cr(NH₃)₃(H₂O)₃]³⁺ it
coincides with the rigid-fluid transition region of the Eg/W
glass [21]. For [Cr(NH₃)₆]³⁺ it comes at a higher tempera­
ture than the rigid-fluid transition regions of any of the
glasses used [21, 57].

Very little is known about the dependence on tempera­
ture and solvent viscosity of the lifetimes and emission
spectra of quadrate Cr(III) complexes with proximate ²E and
²EQ levels or where ²EQ is lower. In this work we have found
that they undergo changes in the transition region of the
solvent which resemble those found in the previous chapter
accompanying the change from hydroxylic to nonhydroxylic
glasses. They also experience a lifetime drop that coincides
with solvent melting.

4.2 Results

The dependence of the emission and lifetimes on
temperature were studied in a number of solvent glasses. Two
changes in spectra are of interest. One is the position
shift, which is referred to as "overall shift," and the other is a shift with delay time at any particular temperature, which is referred to as "delay-time shift." Of particular interest are changes in emission and lifetimes brought about by the melting of the solvent glasses. Except for \([\text{Cr(bipy)}_3]^{3+}\), the lifetimes were not affected by the presence of oxygen, and unless indicated otherwise, the solutions were air saturated.

4.2.1 Trans-[Cr(py)\(_4\)F\(_2\)]NO\(_3\)

This complex has a low temperature emission that is solvent dependent and arises from the \(2E^Q \rightarrow 4A^2\) transition (Chapter 3). The temperature effects on its lifetime and emission were examined in the crystalline solid and in \(\text{Eg/W, Gly/W}\) and DMF glasses.

**Emission Spectra.** In \(\text{Eg/W}\) no overall shift of the spectrum was observed between 77 and 158 K (Fig. 4.1). Between 161 and 167 K, the spectrum began to shift to the red and a long delay time redshift appeared, which could still be detected at 184 K (Fig. 4.2). Above 192 K, the delay time dependence disappeared and the overall spectral position no longer changed with temperature (Fig. 4.1). In \(\text{Gly/W}\) no overall shift was observed between 77 and 185 K. A small overall redshift was observed at 192 K, which became more pronounced between 211 and 227 K. No overall shift or time
Figure 4.1. Emission spectra of \( \text{trans-}[\text{Cr(py)}_4\text{F}_2]\text{NO}_3 \) in \( \text{Eg/W} \) as a function of temperature at 50 \( \mu \text{s} \) delay time.
Figure 4.2. 184 K emission spectra of trans-\([\text{Cr(py)}_4\text{F}_2]\)\text{NO}_3 in \text{Eg/W} as a functions of delay time.
dependence was observed at temperatures higher than 227 K (Fig. 4.3).

Upon melting, a DMF solution of this complex gave no redshift of the emission maximum (Fig. 4.4).

In the crystalline solid, no overall shift of the emission was observed from 77 to 227 K, but a blue tail developed. The facts that the development of the tail was reversible and that it showed no time dependence at any temperature ruled out photoreaction as the source of the spectral change (Fig. 4.5).

**Lifetimes.** The temperature dependence of the lifetimes in Gly/W and Eg/W glasses are compared in Figure 4.6. They showed only small temperature dependence at all monitoring wavelengths when the glasses were rigid. Between 160 and 180 K in Eg/W and 190 and 210 K in Gly/W, they developed very strong temperature dependencies. In these temperature ranges, the solvents experienced rapid change in viscosity. Monitored on the blue side of the maximum in Eg/W between 166 and 178 K, the lifetimes were shorter than those obtained by monitoring on the red side. A hint of risetime in the decay profile can also be seen at long wavelengths (Fig. 4.7). Between 140 and 210 K, the lifetimes became independent of temperature and monitoring wavelength. Strong temperature dependence reappeared at temperatures greater than 220 K. Monitored on the blue side of the maximum in
Figure 4.3. Emission spectra of trans-[Cr(py)₂F₂]NO₃ in Gly/W as a function of temperature at 50 μs delay time.
Figure 4.4. Emission spectra of trans-[Cr(py)$_4$F$_2$]NO$_3$ in rigid and fluid DMF at 50 μs delay time.
Figure 4.5. Emission spectra of crystalline solid trans-[Cr(py)$_4$F$_2$]NO$_3$ as a function of temperature at 50 µs delay time.
Figure 4.6. Lifetimes of trans-[Cr(py)$_4$F$_2$]NO$_3$ in Eg/W and Gly/W as a function of temperature at different monitoring wavelengths.
Figure 4.7. Decay profiles of the emission intensity of \( \text{trans-}[\text{Cr(py})_4\text{F}_2]\text{NO}_3 \) in \( \text{Eg/W} \) at 177 K.
Gly/W between 205 and 215 K, the lifetimes were shorter than those obtained by monitoring on the red side, but no risetime was detected. The rate at which the lifetime decreased as the temperature was raised was slightly reduce between 220 and 230 K.

The lifetime of the crystalline solid was exponential and independent of monitoring wavelength at all temperatures. It showed little temperature dependence between 77 and 230 K, but beyond this range strong temperature dependence occurred (Fig. 4.8).

4.2.2 Cis-[Cr(phen)$_2$F$_2$]ClO$_4$

The low temperature results show that the $^2$E and $^2$EQ states are proximate in this complex. Which of these two states is the emitting state is determined by the solvent environment. In hydroxylic solvents such as Gly/W and Eg/W, the emitting state is the $^2$E state, as shown by its sharp emission. In DMF and in the crystalline solid, $^2$EQ is the emitting state, as shown by its broad emission. In 2.M.E., a wide range of solvates exists. A minority of these solvates has sharp emission spectra, indicative of $^2$E as the emitting state. Most of the species, however, have broad enough emission to indicate some contribution of the $^2$EQ state to the emission. The thermal effects on the emission and lifetimes of this complex were examined in Gly/W, Eg/W,
Figure 4.8. Lifetimes of crystalline solid trans-\([\text{Cr(py)}_4\text{F}_2]\text{NO}_3\) as a function of temperature.
2. M. E. and DMF. The effects on the crystalline solid were also explored:

A. Gly/W, Eg/W and 2. M. E.:

Emission Spectra. The most significant emission spectral changes in Gly/W, Eg/W and 2. M. E. are:

1. The long delay time emission gradually broadened with increasing temperature in the rigid regions of all three glasses (Figs. 4.9, 4.10, 4.11). The broadening of the short delay time emission was much less pronounced in the same regions.

2. Overall shifts began at 199 K in Gly/W, 162 K in Eg/W, and at 144 K in 2. M. E. (Figs. 4.9, 4.10, 4.11). The emission time dependence diminished at these temperatures in each of the glasses. The emissions still shifted to the blue at long times, however (Figs. 4.12, 4.13, 4.14). Also at these temperatures the glasses annealed, as indicated by reduced cracking.

3. The overall shifts became more pronounced between 199 and 224 K in Gly/W (Fig. 4.9), between 162 and 145 K in Eg/W (Fig. 4.10), and between 144 and 160 K in 2. M. E. (Fig. 4.11).
Figure 4.9. Emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in Gly/W as a function of temperature and delay time.
Figure 4.10. Emission spectra of cis-\([\text{Cr(phen)}_2\text{F}_2\text{]}\text{ClO}_4\) in Eg/W as a function of temperature.
Figure 4.11. Emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in 2-M.E. as a function of temperature and delay time.
Figure 4.12. 199 K emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in Gly/W as a function of delay time.
Figure 4.13. 161 emission of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in Eg/W as a function of delay time.
Figure 4.14. 144 K emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in 2-M.E. as a function of delay time.
4. Long delay-time redshift was present between 207 and 220 K in Gly/W, 166 and 184 in Eg/W, and between 147 and 160 K in 2.M.E. (Figs. 4.15, 4.16).

5. The high temperature limits, where the emissions became time and temperature independent, was reached at 232 K in Gly/W, 195 K in Eg/W and at 185 K in 2.M.E. (Figs. 4.9, 4.10, 4.11).

6. Irradiation of Gly/W solutions at 183 K and above resulted in photoreaction (Fig. 4.17), but not at lower temperatures. In Eg/W, photoreaction took place at 162 K and above. In both cases, the photoproduct had blue shifted emission relative to the parent compound (Figs. 4.17 and 4.10). Irradiation of fluid 2.M.E. also resulted in photoreaction. The photoproduct in this case had broad, redshifted emission at 77 K relative to the parent compound (Fig. 4.18).

**Lifetimes.** The most significant features of temperature dependence of the lifetime in Gly/W, Eg/W and 2.M.E. are:

1. The lifetimes showed a large dependence on the monitoring wavelength at temperatures where the glasses were rigid and in the rigid-fluid transition region (Figs. 4.9, 4.20, 4.21). The decays were nonexponential in these regions and could not be fitted even
Figure 4.15. 173 K emission spectra cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in Eg/W as a function of delay time.
Figure 4.16. 154 K emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in 2-M.E. as a function of delay time.
Figure 4.17. 122 K emission spectra of in Gly/W cis-[Cr(phen)$_2$F$_2$]ClO$_4$. --- Irradiated at 183 K for 1/2 hour, --- minimal irradiation.
Figure 4.18. 77 K emission spectrum of decomposition product of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in 2-M.E.
Figure 4.19. Lifetimes of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in Gly/W as a function of temperature at different monitoring wavelengths.
Figure 4.20. Lifetimes of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in Eg/W as a function of temperature at different monitoring wavelengths.
Figure 4.21. Lifetimes of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in 2-M.E. as a function of temperature at different monitoring wavelengths.
to double exponentials. The lifetimes plotted in Figs. 4.19, 20 and 21 were obtained by fitting the data to single exponentials. The error bars represent the range of $\tau_i$ and $\tau_f$ (Chapter II).

2. At $T \geq 193$ K and 167 K where, Eg/W and 2-M.E. were fluid respectively, the lifetimes became exponential and independent of the monitoring wavelength.

3. Where the glasses were rigid, the lifetimes, monitored at short wavelengths, showed large temperature dependence compared with the other complexes. The temperature dependence was largest in 2.M.E. It was nearly absent in all three glasses at long monitoring wavelengths (Figs. 4.19, 4.20, 4.21).

4. The lifetimes at all wavelengths began to fall precipitously with increasing temperature at around 185 K in Gly/W, 155 K in Eg/W and 140 K in 2.M.E. All three glasses showed evidence of mobility at these temperatures, as indicated by annealing of cracks. At about 10 degrees above these temperatures, the glasses became mobile enough for the thermocouple embedded in them to be moved.

5. A risetime could be detected at 170 K in Eg/W when the emission is monitored at $> 790$ nm. and in 2.M.E. at 146 K at $> 815$ nm. The effect of the risetime is largest at 175 K in Eg/W and at 155 K in 2.M.E. No
risetime was detected in Gly/W. Figure 4.22, which was taken in Eg/W at 177 K, shows typical decay profiles as a function of the monitoring wavelength in the rigid-fluid transition region of the glasses.

6. In contrast to trans-[Cr(py)$_4$F$_2$]$^+$, no plateaus occurred in the lifetime temperature plots in any of the glasses.

B. DMF:

Emission Spectra. The 77 K emission, at short delay times (max. 790 nm), was a broad asymmetric peak, which upon warming to 149 K gave a slight red shift (Fig. 4.23). At long delay time the 77 K emission was a narrow asymmetric emission (max. = 760 nm). Upon warming to 136 K, it broadened and shifted slightly to the red (Fig. 4.24). From there to 149 K, a pronounced redshift accompanied by large broadening was observed. Between 77 and 136 K, increased delay times produced narrowing and a blueshift in the emission, and thereafter, a redshift accompanied by broadening. The cracks in the glass were seen to anneal near 136 K. At 149 K, the glass was fluid enough for the thermocouple to be moved. At a slightly higher temperature, DMF turned into an opaque solid, the emission shifted to the blue of the 77 K emission in DMF glass, but had a similar time dependence. Further increase in the temperature of the opaque solid resulted in
Figure 4.22. Decay profiles of the emission intensity of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in Eg/W at 175 K.
Figure 4.23. Emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ as a function of temperature at 10 μs delay time.
Figure 4.24. Emission spectra of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in DMF as a function of temperature and delay time.
similar changes as those in glassy DMF, but at 25 degrees higher.

**Lifetimes.** Figure 4.25 shows the temperature dependence of the lifetimes in opaque DMF (all of which are highly nonexponential) for different monitoring wavelengths. Observed at 740 nm, lifetimes showed a strong decrease from 77 K to 145 K. Monitored at 840 nm, emission lifetimes were much shorter and temperature independent in the same region. Thereafter, the lifetimes, measured at short and long wavelengths, began to decline. This decline was not associated with melting of the solvent. A small risetime can also be detected when monitoring at 840 nm.

**C. Crystalline Solid:**

**Emission Spectra.** The maximum of the $2E_Q \rightarrow 4A_2$ emission in solid cis-[Cr(phen)$_2$F$_2$]ClO$_4$ was unaffected by temperature. The emission broadened, however, with increasing temperature. The extent of the broadening to the red could not be ascertained, however, due to the sharp drop in detector sensitivity beyond 900 nm (Fig. 4.26).

**Lifetimes.** The lifetimes of the crystalline solid decrease gradually with increasing temperature. A break in the temperature dependence profile was observed at about 210 K, after which the lifetime temperature dependence increased somewhat (Fig. 4.27). In contrast to trans-[Cr(py)$_4$F$_2$]NO$_3$,
Figure 4.25. Lifetimes of cis-[Cr(phen)$_2$F$_2$]ClO$_4$ in DMF as a function of temperature at different monitoring wavelengths.
Figure 4.26. Emission spectra of crystalline solid cis-
\([\text{Cr(phen)}_2\text{F}_2]\text{ClO}_4\) as a function of temperature.
Figure 4.27. Lifetimes of crystalline solid cis-
[Cr(phen)$_2$F$_2$]ClO$_4$ as a function of temperature.
where the lifetime of the crystalline solid was very exponential at all temperatures, the lifetimes of the crystalline solid of this complex were highly nonexponential, although they were independent of the monitoring wavelength.

4.2.3 **Trans-**-[Cr(py)$_4$FBr]ClO$_4$

The thermal effects on the emission and lifetimes of this complex were followed in Eg/W and 2.M.E./MTHF glasses.

**Emission Spectra.** Figure 4.28 shows the temperature dependence of the emission in Eg/W. Time dependence was very small and remained so even after the emission had slightly shifted to the red at 161 K. Long delay time redshift developed at 173 K (Fig. 4.29). The glass was fairly fluid at this temperature. The emission became time and temperature independent at 187 K.

Figure 4.30 shows the temperature dependence of the emission in 2.M.E./MTHF. By 137 K, the peak at 757 nm shifted to 764 nm, while the peak at 740 nm disappeared altogether. At 132 K, the peak at 740 nm could be seen at short delay times, but disappeared at long delay times (Fig. 4.31). The glass was fairly fluid at this temperature.

**Lifetimes.** The temperature dependence of the lifetimes in the two glasses are compared in Figure 4.32. The lifetimes, regardless of the monitoring wavelength, began to decrease sharply with the temperature at the beginning of the rigid fluid transition regions of each of these glasses.
Figure 4.28. Emission spectra of trans-[Cr(py)$_4$FBr]ClO$_4$ in £g/W as a function of temperature.
Figure 4.29. 173 K emission spectra of trans-
trans-[Cr(py)$_4$FBr]ClO$_4$ in Eg/W as a function of delay 
time.
Figure 4.30. Emission spectra of trans-$[\text{Cr}\,(\text{py})_4\text{Br}]\text{ClO}_4$ in 2-M.E./MTHF as a function of temperature.
Figure 4.31. 132 K emission spectra of trans-[Cr(py)$_4$FBr]ClO$_4$ in 2-M.E./MTHF as a function of delay time.
Figure 4.32. Lifetimes of trans-[Cr(p-y)4FBr]ClO4 in Eg/W and 2-M.E./MTHF as a function of temperature at different monitoring wavelengths.
Monitor on the blue side of the emission, the lifetimes became very nonexponential in the rigid-fluid transition regions of the glasses but more so in 2.M.E./MTHF, especially at short wavelengths. Monitored at long wavelengths, a risetime in the decay profile was evident in Eg/W between 169 and 180 K and in 2.M.E./MTHF between 126 and 131 K. A concomitant sharp initial decay was present at short wavelengths. A plateau developed in the temperature dependence of the lifetime in 2.M.E./MTHF between 140 and 160 K, after which it dropped again. No plateau developed in Eg/W. This is similar to the behavior of trans-[Cr(py)4F2]NO3 in Gly/W and Eg/W.

4.2.4 Cis-[Cr(bipy)2Cl2]Cl·2H2O

The thermal effects on the emission and lifetimes were followed in Eg/W.

Emission Spectra. The narrow 77 K emission (Fig. 4.33) broadened with increasing temperature until 188 K, where the emission became time and temperature independent. Before 161 K, the emission narrowed slightly at long delay times. At 161 K emission, time dependence diminished while at higher temperatures the emission shifted to the red at long delay times (Fig. 4.34). Evidence for photoreaction could be seen after prolonged irradiation at 161 K (Fig. 4.35), but not at lower temperatures.
Figure 4.33. Emission spectra of \textit{cis-}[Cr(bipy)$_2$Cl$_2$]Cl$\cdot$2H$_2$O in Eg/W as a function of temperature and delay time.
Figure 4.34. 166 K emission spectra of cis-[Cr(bipy)$_2$Cl$_2$]Cl·2H$_2$O in Eg/W as a function of delay time.
Figure 4.35. Emission spectrum of the photoproduct of cis-[Cr(bipy)$_2$Cl$_2$]Cl·H$_2$O in Eg/W.
Lifetimes. Figure 4.36 shows the temperature dependence of the lifetimes. As in trans-[Cr(py)$_4$F$_2$]$^+$ and trans-[Cr(py)$_4$FBr]$^+$ it had a small wavelength dependence in the rigid region of the glass. The lifetimes were slightly nonexponential in this region, especially at longer wavelength. It began to decrease with temperature, regardless of the monitoring wavelength, at the beginning of the rigid-fluid transition region of the glass. There were risetimes and sharp initial decays at long and short monitoring wavelengths respectively in the rigid-fluid transition regions of both Eg/W and 2-M.E./MTHF.

4.2.5 [Cr(bipy)$_3$](ClO$_4$)$_3$

Emission Spectra. The thermal effects on the emission and lifetimes were done in Gly/W and Eg/W. In contrast to the other complexes, the change in the sharp $2E \rightarrow ^4A_2$ emission spectrum was confined to some thermal broadening (Fig. 4.37).

Lifetimes. The decay was exponential at all temperatures. Figure 4.38 shows the temperature dependence profiles in Eg/W and Gly/W. The strong decrease in the lifetime with increasing temperature started well after the rigid-fluid transition regions of both solvents. In O$_2$ saturated Eg/W solutions the onset of large temperature dependence occurred at about 100 lower than in deoxygenated
Figure 4.36. Lifetimes of cis-\([\text{Cr(bipy)}_2\text{Cl}_2]\)Cl\(\cdot\)2H\(_2\)O as a function of temperature at different monitoring wavelengths.
Figure 4.37. Emission spectra of [Cr(bipy)$_3$](ClO$_4$)$_3$ in Eg/W as a function of temperature.
Figure 4.38. Lifetimes of \([\text{Cr(bipy)}_3](\text{ClO}_4)_3\) in oxygenated and deoxygenated \(\text{Eg/W}\) and \(\text{Gly/W}\) as a function of temperature.
solutions. No oxygen effect was found in the more viscous Gly/W at any temperature.

4.3 Discussion

The spectral characteristics of the compounds under study depend on their position in Figure 3.24, which shows schematically the relationship between the angular overlap parameter $\Delta(t_2)$ and the energies of $2E$ and $2EQ$ states. Complexes such as $[Cr(bipy)_3]^{3+}$, where $2E$ is far below $2EQ$, have sharp spectra and show no solvent dependence; however, the emission spectra of complexes such as trans-$[Cr(py)_4F_2]^+$, where $2EQ$ lies far below $2E$, are broad and solvent sensitive. The most striking effect of solvents is found in complexes that lie close to the crossing region of those two states. In this case the level ordering is sensitive to the solvent.

4.3.1 Emission Spectra in Rigid and Fluid Media

The emission spectrum of $[Cr(bipy)_3]^{3+}$ is unaffected by solvent melting (Fig. 4.37). This is consistent with the insensitivity of $2E$ emission to changes in solvent viscosity. In contrast, the $2EQ$ emission of trans-$[Cr(py)_4F_2]^+$ shifts to the red significantly upon melting of hydroxylic solvents (Figs. 4.1, 4.3).

These observations suggest that the spectral changes that accompany the rigid-fluid transitions of the solvents occur because the energy of the $2EQ$ state is reduced by
increased solvent mobility while that of the $^2E$ state remains unchanged.

Further evidence for this contention is provided by the response of the emission spectra of cis-[Cr(phen)$_2$F$_2$]$^+$ to rigid-fluid transition of hydroxylic solvents. This complex lies in the crossing region of $^2E$ and $^2EQ$ energy (Fig. 3.24), and the order of these states is sensitive to the solvent environment (see Chapter 3). In rigid hydroxylic solvents, such as Eg/W, the $^2E$ state is the lower excited state in this complex, as evidenced by its emission. Melting of these glasses results in broad, redshifted emission, which is characteristic of $^2EQ$ emission (Figs. 4.9, 4.10, 4.11). Going from a rigid to a fluid hydroxylic solvent results in enough reduction in the $^2EQ$ energy for it to be the lowest excited state. This emitting state inversion is parallel to that achieved in the same compound at 77 K when a hydrogen bonding solvent is substituted by a nonhydrogen bonding solvent.

In rigid DMF glass, the emitting state in cis-[Cr(phen)$_2$F$_2$]$^+$ is the $^2EQ$ state. Melting of this glass results in an emission redshift (Fig. 4.24). This lends further support to the contention that the energy of the $^2EQ$ state is reduced by solvent melting.

The emission spectra of cis-[Cr(bipy)Cl$_2$]$^+$ are sharp enough in rigid Eg/W and DMF for it to be classified as a
largely $^2E$-emitter in all media (Fig. 3.2.). Yet, the emission is shifted to the red and broadened as a result of melting of $E_g/W$ (Fig. 4.33). However, in contrast to cis-[Cr(phen)$_2$F$_2$]$^+$, the broadening and redshifting are not large enough to indicate emitting state inversion. Since the $\pi$-donation for Cl$^-$ is smaller than that for F$^-$ [17], $\Delta(t_2)$ is larger in cis-[Cr(phen)$_2$F$_2$]$^+$ than in cis-[Cr(bipy)$_2$Cl$_2$]$^+$ (Eq. 3.3), which results in a larger $^2E$-$^2E^Q$ energy gap in the latter. The absence of level inversion in cis-[Cr(bipy)$_2$Cl$_2$]$^+$ when $E_g/W$ melts is then plausible. We suggest that the emission in all environments is due $^2E \rightarrow ^4A_2$, but the reduction in the energy of the $^2E^Q$ level induced by melting leads to smaller separation between the latter and the $^2E$ state. This results in increased vibronic mixing between them and/or enhancement of the thermal population of the $^2E^Q$ state. The emission spectrum in the fluid then takes on some of the characteristic broadness of $^2E^Q$ emission.

Trans-[Cr(py)$_4$FBr]$^+$ (Fig. 4.28) behaves in a similar way to cis-[Cr(bipy)$_2$Cl$_2$]$^+$ when $E_g/W$ melts, except that the redshift and broadening is somewhat greater, and the same explanation is applicable to it as well.

4.3.2 Correlation of Spectral and Lifetime Changes with Increased Solvent Motions

The emission spectra and lifetimes of the complexes under study, except [Cr(bipy)$_3$]$^{3+}$, undergo profound changes
in the rigid-fluid transition regions of the glasses used. By rigid-fluid transition is not meant the thermodynamic transition point of the glass, but rather, a temperature region much above it where the viscosity of the glass changes rapidly with temperature. Phenomenologically, at the beginning of the region the thermocouple embedded in the sample cannot be moved at all, and at the end of it, the thermocouple can be moved with ease.

The emission spectra and lifetimes of all the complexes, except [Cr(bipy)$_3$]$^{3+}$, exhibit large changes in the rigid-fluid transition region of Eg/W (Figs. 4.1, 4.10, 4.28, 4.33, 4.6, 4.20, 4.32, 4.36). When some of these complexes are studied in glasses whose rigid-fluid transition regions lie above and below that for Eg/W respectively, the same emission and lifetime changes take place in the rigid-fluid transition regions of those glasses (Figs. 4.3, 4.9, 4.11, 4.30, 4.6, 4.19, 4.21, 4.32).

In a complex such as [Cr(bipy)$_3$]$^{3+}$, whose emission does not shift above solvent melting, the sharp decrease in the lifetime with increased temperature comes well after the rigid-fluid transition region of the glasses used (Fig. 4.38). These observations indicate that the redshift of the emission spectra are associated with increased solvent motions.
4.3.3 Solvent Relaxation Dynamics
and Spectral Changes

Two important points concerning the emission time
dependence and the lifetime decay profiles in the rigid-
fluid transition region merit attention:

1. The emission spectra undergo a delay time dependence
reversal at some point in the rigid-fluid transition
region, i.e., the emission begins to shift to the red
at long delay time instead of the usual blueshift at
long delay time encountered in rigid media
(Figs. 4.2, 4.15, 4.16, 4.34).

2. The decay profile of the excited state shows a
risetime when the emission is monitored far enough to
the red and declines sharply when the emission is
monitored on the blue. The decay profiles of cis-
[Cr(phen)$_2$F$_2$]$^+$ in E$_g$/W is typical (Fig. 4.22).

The simplest model that can be advanced to account
for these changes consists of two interconverting excited
species A$^*$ and B$^*$, whose interconversion rate is dependent on
solvent viscosity. The kinetic scheme is then:
where $k_1$ and $k_3$ stand for the decay rate of each species in the absence of interconversion. In rigid media, viscosity dependent potential barriers prevent the interconversion between the two species [36, 61, 62]. However, when these barriers are removed through the rapid decrease in solvent viscosity in the rigid-fluid transition region, several possibilities arise, depending on the initial conditions and the magnitude of $k_2$. If all the rates are comparable and the emissions of the two species are well separated, then the emission intensity of $A^*$, if monitored alone, will decay according to a double exponential while the decay of $B^*$, if its initial population is negligible, may show a risetime [63].

The observation of a risetime is definitive evidence for a process involving the excited state, in contrast to processes in which two ground state species, A and B, are exited [50, 51].

The following systems exhibit risetime in the rigid-fluid transition region when their emission is monitored far enough to the red and concomitant sharp initial drop when the emission is monitored on the blue (Figure 4.22 shows typical decay profiles in this region):

a. Cis-$[\text{Cr(phen)}_2\text{F}_2]^+$ in Eg/W and 2-M.E.

b. Trans-$[\text{Cr(py)}_4\text{FBr}]^+$ in Eg/W and 2-M.E./MTHF

c. Cis-$[\text{Cr(bipy)}_2\text{Cl}_2]^+$ in Eg/W
These observations indicate the presence of an excited state process that converts the species first formed into other species of lower energy. The fast initial drop in the intensity of short wavelength emission demonstrates the contribution of this conversion process to the depopulation of the unrelaxed species.

Only a hint of a risetime was detected in the decay profile of trans-[Cr(py)4F2]⁺ in Eg/W at 875 nm. Monitoring at longer wavelengths was prevented by the sharp drop in the detector sensitivity at 900 nm. As in the previous systems, the intensity still showed sharp initial decay when monitored to the blue (Fig. 4.7).

A model involving only two interconverting excited-state species is too simple to describe the situation, however, for the following reasons:

1. The decay profiles cannot be fitted to double exponential decay as would be required by that model.
2. The time-dependent emission in the rigid-fluid transition regions do not show two separate peaks for relaxed and unrelaxed species, but shift gradually to the red with increasing delay time.
3. The emission of cis-[Cr(phen)2F2]⁺ shows large time dependence even in rigid glasses, which is indicative of the presence of a large number of species. These
will respond slightly differently to increased solvent mobility.

A more realistic model is the one advanced by Bakshiev in a treatment of the emission characteristics of a model system that experiences an emission redshift caused by solvent relaxation in the excited state [64, 65]. In the temperature region where the rates of solvent motions are of the same magnitude as those of the excited state, the total emission should be a superposition of the emission spectra of a continuum of species at different stages of relaxation. The emission maximum should shift to the red with increasing delay time. When monitored far enough to the red, the decay profiles show risetimes. This model can be applied to the present systems, treated as having a large number of interconverting semi-relaxed states between A*, the initial excited state, and B*, the solvent relaxed excited state.

All complexes except [Cr(bipy)3]3+ exhibited long delay time redshifts in the rigid-fluid transition regions of all the glasses used, in contrast with the usual long delay time blueshifts encountered in rigid regions. No risetime was detected in the decay profiles of cis-[Cr(phen)2F2]+ and trans-[Cr(py)4F2]+ in Gly/W despite the presence of such risetime in Eg/W. The conditions for observation of a
risetime have been shown to be more stringent than those for long delay time redshift [50].

In summary risetimes and long delay-time redshifts observed in the rigid-fluid transition regions, fit a model in which the solvent around the initially excited species starts to relax to lower energy arrangements. They are observed when the rates of solvent relaxation is comparable to the excited state decay rate.

4.3.4 Factors Leading to Lower $^2E_Q$ Energy in Fluid Media

A solvated excited state molecule produced through δ-function excitation is created in the geometry and solvent cage orientations of the ground state. This Frank-Condon state starts immediately to relax toward its equilibrium solvent-solute orientations [66, 67, 68, 69]. Relaxation processes involving rotational and translational motions of the solvent can take a wide range of values depending on the solvent viscosity [68]. When solvent motions are fast on the excited state time scale, the emission takes place from a fully solvent relaxed excited state, and it is shifted to the red relative to that in rigid solutions, where the solvent relaxation is slow on the excited state time scale. Many examples of redshifts in emission induced by solvent melting are known. In most of the reported cases, this shift occurs in polar solvents when the dipole moment direction of the
solute is different in the ground and excited states [48, 54]. There is no change in dipole moment direction in metal-centered transitions. Consequently, this mechanism does not apply to the complexes under consideration.

Changes in H-bonding ability and/or dipole moment upon excitation will result in the Frank-Condon excited state having greater energy than the solvent relaxed state [66, 67]. This will also result if the ground and excited states are of different geometries. The difference between the rigid and fluid $^{2\text{EQ}} \rightarrow ^{4\text{A}_2}$ emissions of trans-[Cr(py)$_4$F$_2$]$^+$ in Eg/W resembles those found at 77K in going from a hydrogen bonding to a nonhydrogen bonding solvent. This is suggestive of weaker hydrogen bonding in the $^{2\text{EQ}}$ state.

The melting of the polar solvent DMF results in a redshift of the $^{2\text{EQ}} \rightarrow ^{4\text{A}_2}$ emission of the polar cis-[Cr(phen)$_2$F$_2$]$^+$ but not in that of the nonpolar complex trans-[Cr(py)$_4$F$_2$]$^+$. This suggests that dipolar interaction may also differ in the ground and $^{2\text{EQ}}$ states of polar molecules. The geometry and electronic distribution differ in $^{4\text{A}_2}$ and $^{2\text{EQ}}$ states, as shown by the fact that the Cr-F bond in trans-[Cr(py)$_4$F$_2$]NO$_3$ is 0.1 Å shorter in the $^{2\text{EQ}}$ state than in the ground state, and the electronic density is removed from around the z-axis to the xy-plane [12, 14]. If the emitting state in a rigid solvent is $^{2\text{EQ}}$, as is the case in trans-[Cr(py)$_4$F$_2$]$^+$, the above factors will lead to a reduction in
the $^{2}\text{E}Q$ energy and the observed emission redshift upon increased solvent motions.

In the case of cis-[Cr(phen)$_2$F$_2$]$^+$, cis-[Cr(bipy)$_2$Cl$_2$]$^+$ and trans-[Cr(py)$_4$FBr]$^+$, where the emitting-state geometry and electronic distribution are essentially the same as the ground state, it is not obvious why increased solvent mobility results in redshift and broadening of the emission of these complexes.

A unifying approach that may aid in understanding the redshifts and broadening induced by increased solvent motions, is to look at a schematic representation of the energies of the ground, $^2\text{E}$ and $^2\text{EQ}$ states as a function of $Q(\text{solv})$ (Fig. 4.39). $Q(\text{solv})$ is taken to symbolize the different solvent arrangements. The energies of the ground and $^2\text{E}$ states depend only weakly and in the same direction on $Q(\text{solv})$, while the $^2\text{EQ}$ dependence on it is stronger. The rate with which a system moves along $Q(\text{solv})$ is slow in rigid media but is increased in the fluid. Figure 4.39a shows the case where $^2\text{E}$ is much lower than $^2\text{EQ}$. Some of the solvent arrangements accessible in the fluid have lower $^2\text{EQ}$ energies than the rest of the solvent arrangements, but due to the large energy gap between $^2\text{E}$ and $^2\text{EQ}$, the $^2\text{E}$ emission is not affected by the lowering of the $^2\text{EQ}$ energy. Such systems are exemplified by [Cr(bipy)$_3$]$^{3+}$, whose emission is not affected by increased solvent motions. In cases where $^2\text{E}-^2\text{EQ}$ is not
Figure 4.39. Schematic diagram for the dependence of the energies of $^{4\text{A}_2}$, $^2E$, and $^2\text{E}^Q$ on the solvate coordinate.
large, increased solvent motions lower the energy of the $2E$ state because it has some $2E_Q$ character. The energy of $2E_Q$ has already been shown to decrease as the state moves along $Q(solv)$. This seems to be the case in complexes such as trans-Cr(py)$_4$FBr$^+$ and cis-[Cr(bipy)$_2$Cl$_2$]$^+$. Figure 4.39b shows the situation where $2E$ and $2E_Q$ states are close enough to cross. In the rigid region $2E$ is the lowest excited state; however, when the solvent motions increase in the fluid, $Q(solv)$, in which $2E_Q$ is the lowest excited state, becomes accessible. Its lower energy constitutes a driving force for emitting state inversion. This situation is exemplified by cis-[Cr(phen)$_2$F$_2$]$^+$ in hydroxylic solvents. Figure 4.39c shows the situation where $2E_Q$ state is the lowest excited state in both rigid and fluid solvents. In this case, the emission is broad in both media but is shifted to the red as solvent motion increase in going from rigid to fluid media, due to the formation of a solvent relaxed state, or what is commonly referred to as a "thexi" state [24, 70, 71].

4.3.5 Solvent Relaxation and Excited State Decay

The temperature dependence of the decay rate constant of Cr(III) complexes has been described by Targos and Forster [72] as a sum of three terms

$$\tau^{-1} = k_{lim} + k_a + k_b$$
The first term, $k_{1im}$, is temperature independent and refers to the limiting decay rate constant reached by most Cr(III) complexes at low temperatures. This term is made up of the sum of the radiative ($k_5$) and nonradiative decay rates ($k_6$) (Fig. 1.1). $k_a$ reflects the temperature dependence of the total decay rate at low temperature which includes the radiative and nonradiative decay rates. The third term, $k_b$, which dominates at relatively high temperatures, describes the emergence of a thermally activated decay channel with a higher activation energy.

The following points concerning the appearance of strong temperature dependence of the decay rate of $[\text{Cr(bipy)}_3]^{3+}$ merit attention:

1. It appears well above the rigid-fluid transition regions of Eg/W and Gly/W glasses.
2. Its onset is still dependent on increased solvent viscosity, as indicated by its occurrence at higher temperatures in Gly/W and Eg/W (Fig. 4.38)
3. It appears at slightly lower temperatures in $O_2$ saturated Eg/W and descends more steeply (Fig. 4.38).

The appearance of strong temperature dependence of the decay rate is not likely to be due to changes in the radiative decay rate since $k_5$ for Cr(III) complexes does not show strong dependence on temperature and solvent viscosity changes [25]. Several models have been proposed to account
for the appearance of the strongly temperature dependent
decay channel [4, 46, 57, 72, 73]. These include:

1. Thermally activated photophysical process that
   enhances $k_6$ and back-intersystem crossing to $^4T_2$.
2. Photochemical reaction originating from the doublet
   state.
3. Solvent mediated intersystem crossing to the ground
   state.

The large $^2E$-$^4T_2$ gap rules out back-intersystem
crossing as the deactivation pathway in fluid solutions [4].
Although the onset of strong temperature dependence does not
coincide with the rigid-fluid transition regions of Eg/W and
Gly/W, it still requires their melting. This supports a role
for the solvent in mediating the depopulation of the $^2E$
state.

The emission of [Cr(bipy)$_3$]$^{3+}$ is quenched by O$_2$ in
low-viscosity solutions [74]. Consequently the effect of
oxygen quenching becomes noticeable when the oxygen can
diffuse to the complex. This takes place in the rigid-fluid
transition region of the Eg/W glass. The contribution of
oxygen quenching makes the descent of the lifetime steeper
(Fig. 4.38). For trans-[Cr(py)$_4$F$_2$]$^+$ and trans-[Cr(py)$_4$FBr]$^+$,
several points about their temperature dependence are
significant:
1. Their lifetimes decrease rapidly in the rigid-fluid transition region, \( \text{trans} - [\text{Cr(py)}_4\text{F}_2]^+ \) develops a plateau in Eg/W followed by the second region of strong temperature dependence, but in the higher melting Gly/W only a small interval separates the two regions (Fig. 4.6). For \( \text{trans} - [\text{Cr(py)}_4\text{FBr}]^+ \), there is no plateau in Eg/W, but a plateau appears in the lower melting 2.M.E./MTHF (Fig. 4.32).

2. In the rigid-fluid transition regions, the decay profiles of both complexes show a risetime when monitored to the red and a sharp initial drop when monitored to the blue of the emission.

The above observations indicate that the first discontinuity in the temperature dependence of the lifetimes of \( \text{trans} - [\text{Cr(py)}_4\text{F}_2]^+ \) in Eg/W and Gly/W and that of \( \text{trans} - [\text{Cr(py)}_4\text{FBr}]^+ \) in 2.M.E./MTHF is due to the solvent relaxation of the excited state. The appearance of risetime in the decay profiles of \( \text{trans} - [\text{Cr(py)}_4\text{F}_2]^+ \) in Eg/W and \( \text{trans} - [\text{Cr(py)}_4\text{FBr}]^+ \) in 2.M.E./MTHF when the emission intensity is monitored to the red indicates that the rates of formation and decay of the solvent relaxed state are comparable. The fast initial decay when monitoring to the blue is a result of the contribution of solvent relaxation to the decay rate of the species in the process of solvent relaxation. Once
solvent relaxation becomes fast relative to the excited state lifetime, temperature dependence of the latter disappears.

Since the second region of strong temperature dependence appears well after the rigid-fluid transition regions of the Eg/W and 2.M.E./MTHF glasses, the two causes of discontinuity in the temperature dependence of these two complexes have been separated. One is due to the solvent relaxation of the initially prepared excited state and coincides with rigid-fluid transition region of the glass, and the other is due to a thermally activated channel commonly observed in the temperature dependence profiles of the decay rates of transition metal complexes [4, 46, 57].

Comparison of the lifetimes of trans-[Cr(py)_4F_2]^+ just before and just after the melting of Eg/W and that of trans-[Cr(py)_4FBr]^+ just before and just after the melting of 2-M.E./MTHF shows that solvent relaxation has caused an almost 2-fold increase in the limiting decay rate. This increase is almost entirely due to an increase in the nonradiative rate (k_6) since the radiative rate (k_5) is small and depends little on temperature and viscosity [24]. Two factors may be responsible for k_6 enhancement in these two complexes:

1. Solvent melting causes increased anharmonicity in the ground state accepting modes [48, 75, 76], which may enhance the nonradiationless crossing to the ground
state. This mechanism has been invoked to explain small discontinuities encountered in the temperature dependence profiles of some Cr(III) ammine complexes in the melting regions of the glasses used [76]. These discontinuities were not accompanied by spectral shifts. The fact that the lifetimes in trans-[Cr(py)₄F₂]⁺ and trans-[Cr(py)₄FBr]⁺ start to fall slightly before any spectral shifts are detected suggests a contribution from this factor.

2. Nonradiative rates increase with decreasing energy gap between the states involved in the transition [23, 24], and the lower energy of the solvent relaxed state in both complexes leads to k₆ enhancement.

The following points about the onset of the thermally activated decay channel of trans-[Cr(py)₄F₂]⁺ and trans-[Cr(py)₄FBr]⁺ are significant:

1. In trans-[Cr(py)₄F₂]⁺, it starts at approximately the same temperature in Eg/W, Gly/W and in the crystalline solid (Figs. 4.6 and 4.8).

2. The onset of the thermally activated decay channel in the temperature dependence profile of trans-[Cr(py)₄FBr]⁺ in 2.M.E./MTHF comes in the temperature region of the rigid-fluid transition region of Eg/W (Fig. 4.32).
The onset of the thermally activated channel in \textit{trans}-[Cr(py)$_4$F$_2$]$^+$ at nearly the same temperature regardless of the solvent medium suggests that the appearance of this decay channel is due to an intramolecular process and that the solvent plays no role in it. Thermally activated delayed $^4T_2 \rightarrow ^4A_2$ emission is definitive evidence for back-intersystem crossing as a decay channel [73]. Such emission has not been observed in \textit{trans}-[Cr(py)$_4$F$_2$]$^+$ [77]. Photochemical decomposition or thermally activated enhancement of $k_6$ may be the source of the appearance this decay channel.

A combination of solvent relaxation and a thermally activated channel causes the strong temperature dependence of the decay rate of \textit{trans}-[Cr(py)$_4$FBr]$^+$ upon the melting of Eg/W. This is evidenced by the presence of risetimes, the absence of a plateau beyond the rigid-fluid transition region, and the appearance of the thermally activated channel in 2.M.E./MTHF in this temperature region as well. The lifetime of \textit{cis}-[Cr(phen)$_2$F$_2$]$^+$ in 2.M.E., Eg/W and Gly/W begins to decrease precipitously at the start of the rigid-fluid transition regions of the three glasses (Figs. 4.19, 4.20 and 4.21). The presence of risetime and/or spectral redshifts in the rigid-fluid transition regions with 2-M.E., Eg/W and Gly/W (Figs. 4.22) and the fact that the temperature dependence does not develop a plateau past the melting region indicate that, as in \textit{trans}-[Cr(py)$_4$FBr]$^+$ in Eg/W, the strong
temperature dependence of the decay rate is due to a combination of solvent relaxation of the excited state and a thermally activated decay channel. Irradiation of the complex in the rigid-fluid transition regions of Eg/W and Gly/W results in a photoreaction whose product emits to the blue of the parent complex. The photoproduct in 2-M.E. emits to the red of the parent complex (Figs. 4.10, 4.17 and 4.18). This implicates a photochemical pathway as a contribution to the thermally activated channel. The fact that the photochemical changes coincide with the start of glass melting suggests a role for the solvent in the reaction.

As in cis-[Cr(phen)\(_2\)F\(_2\)]\(^+\) complex, the lifetime of cis-[Cr(bipy)\(_2\)Cl\(_2\)]\(^+\) shows strong temperature dependence in the melting region of Eg/W coupled with risetime at long wavelengths (Fig. 4.36), and evidence for photoreaction on the blue side of the emission (Fig. 4.35). No plateau develops past the rigid-fluid transition region. So as in cis-[Cr(phen)\(_2\)F\(_2\)]\(^+\), the strong temperature dependence of the decay rate is due to solvent melting and the opening of a thermally activated decay channel. Photoreaction is, at least in part, responsible for this channel.

4.3.6 Summary and Conclusions

The energy of the \(^2\)E state relative to that of the ground state is the same in rigid and fluid solvents. This is illustrated by the insensitivity of the energy of the \(^2\)E
$\rightarrow ^4A_2$ transition to solvent melting. On the other hand, the energy of the $^2E_Q$ state may be lower in fluid than in rigid media. The $^2E_Q$ emission of trans-$\text{Cr(py)}_4F_2]^+$ is shifted to the red in fluid versus rigid hydroxylic solvents. In mixed emitters, where $^2E$ and $^2E_Q$ levels are proximate, an emitting state reversal may result from going from rigid to fluid hydroxylic solvents. This is exemplified by the behavior of cis-$\text{Cr(phen)}_2F_2]^+$ when the emission shifts to the red and broadens upon the melting of hydroxylic solvents, which indicates that the $^2E_Q$ level which was above the $^2E$ level in rigid media has decreased enough in energy to fall below the $^2E$ state and become the emitting state in the fluid.

Increased solvent motions are necessary for the processes of emission redshift to begin, as indicated by the correlation of the onset of the redshift with the rigid-fluid transition regions of each of the solvent glasses. The presence in these regions of risetimes in the decay profiles at long monitoring wavelengths, and long delay time redshifts is indicative of a process involving the excited state as opposed to one involving the ground state. This process may involve solvent rearrangements to produce solvates with decreased $^2E_Q$ energies. The lower $^2E_Q$ energies may be due to lower solvent-solute hydrogen bonding in the newly formed solvates, which leads to larger $\Delta(t_2)$ and lower $^2E_Q$ energy.
Two processes responsible for discontinuities in the temperature dependence profiles of mixed and $^{2}$E$_{Q}$ emitters have been identified. One is due to solvent relaxation during the excited state lifetime, and the other is due to the more common thermally activated decay related to the opening up of photochemical and photophysical decay channels. In trans-[Cr(py)$_4$F$_2$]$^+$ in Eg/W and Gly/W and in trans-[Cr(py)$_4$FBr]$^+$ in 2-M.E./MTHF, these two processes have been separated, but in the case of the latter, in Eg/W the two processes occur together once the solvent starts to melt. These processes occur together in the case of cis-[Cr(phen)$_2$F$_2$]$^+$ in all solvents and in the case of cis-[Cr(bipy)$_2$Cl$_2$]$^+$ in Eg/W. Moreover, there is clear evidence for photoreaction in the case of the latter two compounds once the solvent glasses start to soften.
REFERENCES


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