

Temperature Dependent Emission Properties of Rhenium(I) Tricarbonyl Complexes Containing Alkyl- and Aryl-Substituted Phenanthrolines as Ligands

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The results of the temperature dependence in fluid solution of the emission behavior of a series of $[\text{Re}(\text{L-L})(\text{CO})_3\text{py}]^+$ complexes (L-L = 3,4,7,8-Me₄phen, 4,7-Ph₂phen, 2,9-Me₂-4,7-Ph₂phen, 4',7-Me₂phen, 5,6-Me₂phen, 5-Phphen, 2,9-Me₂phen, and phen) are presented along with an interpretation which assigns the lowest excited state as ³MLCT, with a contribution from a higher-energy, shorter-lived state of unknown character. The emission lifetime of $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$ actually increases with temperature, reaches a maximum at approximately 230 K, and then decreases in the usual manner. This behavior is attributed to population of the lowest ³LC state, which in this complex lies just above the ³MLCT emitting state and below the upper state.

Introduction

Previously we reported emission properties of a series of complexes $\text{Re}(\text{L-L})(\text{CO})_3\text{py}^+$, where L-L was a phenanthroline derivative with methyl or phenyl substituents located in various ring positions and py was pyridine.¹ Emission from these species was assigned principally to a ³MLCT (metal-to-ligand charge-transfer) state, but some ³LC (ligand-centered) character was also evident to a greater or lesser degree, depending on the substituents and their location on the phenanthroline ligand. The contribution from the ³LC state was most evident in the emission lifetimes and time-resolved spectra of the complexes at 77 K. However, it was also necessary to postulate the presence of another emitting state to account for some of the room temperature observations, such as trends involved in emission maxima and lifetimes. On the basis of the 77 K results, this was thought to be the ³LC state.

Since the ³MLCT and ³LC energies were affected differently by a given substitution pattern on the phenanthroline ring, it was not possible to predict how the energy gap between the states was affected by substitution, although this was thought to be important in determining the overall character of the luminescence. We now present the results of studies on the temperature dependence of the emission lifetimes, which have provided new insight into the nature of the room temperature luminescence and its dependence on the energy gaps within the emitting manifold.

Experimental Section

Complexes $\text{Re}(\text{L-L})(\text{CO})_3\text{py}^+$ (L-L = 3,4,7,8-Me₄phen, 4,7-Me₂phen, 5,6-Me₂phen, 2,9-Me₂phen, phen, 5-Phphen, 4,7-Ph₂phen, 2,9-Me₂-4,7-Ph₂phen) were prepared as their triflate salts as described earlier.¹ Absolute ethanol and methanol were spectroscopic grade. Samples were prepared by dissolving the complex in ethanol/methanol (4:1 v/v) to provide an optical density of ca. 0.1 at 355 nm, which was the excitation wavelength for all experiments. The solutions were purged with argon for 15 min., then freeze–pump–thaw degassed at least four times prior to being vacuum sealed. We found it was necessary to bubble the solutions with argon prior to the usual freeze–pump–thaw

procedure, as samples which had not been treated in this way showed considerable quenching due to incomplete removal of oxygen, even after four freeze–pump–thaw cycles. Prepared samples were stored in the dark at all times other than during experiments.

For emission lifetime measurements, samples were excited using a Photochemical Research Associates (PRA) Model LN1000/pulsed N₂ laser, fitted with a PRA LN102 dye laser. Data were collected with a LeCroy TR8828C transient digitizer interfaced to an IBM PS/2 Model 60 computer. The samples for emission lifetime measurements and emission spectra were contained in a Cryo Industries Model NVT variable temperature dewar, which was cooled with liquid N₂, and the sample temperature was controlled by a Lakeshore Cryotronics 805 controller. Sample temperatures, determined using a thermocouple sealed inside a sample tube filled with epoxy, were accurate to ± 1.6 K over the range 90–290 K with an exchange gas (He) pressure of 200 mTorr. For emission lifetimes determined over the 290–315 K range, temperatures were controlled by immersing the samples in a Fisher Scientific Model 9100 circulating bath. The temperature of the brass sample holder was regulated by the same circulating bath. Emission spectra were recorded on a Spex Fluorolog 212 spectrometer.

The observed rates of emission decay for a given compound were plotted as a function of the absolute temperature and a basic three step strategy was used to fit the experimental data to the equations. Initial values for the variables were obtained using the program "FLEXFIT"² which utilizes a simplex algorithm to determine approximate first "guesses" for each variable. Once the initial values were determined, the matrix routine in the "FLEXFIT" program was used to further improve the initial guesses. However, the program routine only allows weighting "y" values. Therefore, once the improved initial values were obtained, a weighted nonlinear least-squares dedicated program was used to further improve the values for each of the variables. The algorithm used in this program utilized a set of normal equations as prescribed by Wentworth,³ which allowed for weighting of both x and y values, using the standard deviations of x and y. Values for the variables were calculated until the weighted sum of the squares of the residuals was minimized.

Results and Discussion

Theoretical Model. Examination of the temperature dependence of emission lifetime has frequently been helpful in elucidating the energy levels and decay pathways involved in deactivation of excited-state species.^{4–12} The general model

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suggested by Watts^{4,5} and developed further by the groups of Meyer⁶⁻⁸ and Balzani⁹⁻¹² is based on the following expression (eq 1).

$$k_{\text{obs}} = k_0 + \sum k_i \quad (1)$$

In eq 1, k_{obs} is the observed decay rate measured at temperature T , k_0 is a temperature independent term, and the k_i terms correspond to the rate constants of the various temperature-dependent processes which contribute to the deactivation of the emitting state.⁹⁻¹² The rate constants k_i are usually expressed in Arrhenius form (eq 2) since the population of the upper-lying states requires overcoming a barrier E_i . The frequency factor for the i th process is given by A_i .

$$k_i = A_i \exp(-E_i/RT) \quad (2)$$

From previous studies, it has been shown that temperature dependent emission lifetimes could be fitted to eq 3,¹³ where

$$k_{\text{obs}} = [k_0 + \sum_i k_i \exp(-E_i/RT)] / [1 + \sum_i \exp(-E_i/RT)] \quad (3)$$

the denominator corrects for electronic distribution between close lying states ($E_i < 3kT$). For most complexes in the present work, a two-level model was adequate to describe the temperature dependence, which corresponds to $i = 1$ (eq 4). For [Re-

$$k_{\text{obs}} = \frac{[k_0 + k_1 \exp(-E_1/RT)]}{1 + \exp(-E_1/RT)} \quad (4)$$

(3,4,7,8-Me₄phen)(CO)₃py]⁺, a three-level model was necessary to provide a good fit to the experimental data ($i = 1, 2$; eq 5),

$$k_{\text{obs}} = \frac{[k_0 + k_1 \exp(-E_1/RT) + 3k_2 \exp(-E_2/RT)]}{1 + \exp(-E_1/RT) + 3 \exp(-E_2/RT)} \quad (5)$$

with the third level ($i = 2$) being assigned a degeneracy of 3. This was accounted for by multiplying the terms involving the third state by three.^{13a} We found it was not possible to model the U-shaped trend in the experimental data unless the third state had a degeneracy of greater than one and was positioned between the other two levels.

In both of these models the lowest ³MLCT state is treated as a single level. This is because the energy gaps within the ³MLCT manifold are expected to be very small ($< 60 \text{ cm}^{-1}$),^{13d} so that by 150 K the luminescence can be considered to be from the uppermost level only.

Attempts were made to fit the data over the whole temperature region by appending an empirical term to eq 4, which has been used to model the temperature dependence of the observed emission lifetimes over the glass-to-fluid transition.¹⁰⁻¹² This

approach, however, was unsuccessful due to the occurrence of multiple emission in the glassy matrix (see below).

Emission Lifetimes. At 77 K in ethanol-methanol, the decay profiles of all the complexes in the present study were non-single exponential. In four cases (L-L = phen, 2,9-Me₂-phen, 2,9-Me₂-4,7-Ph₂phen, 4,7-Ph₂phen), the decays were close to single exponential. These complexes were called group A in earlier work. The other four complexes, L-L = 3,4,7,8-Me₄-phen, 4,7-Me₂phen, 5,6-Me₂phen, and 5-Phphen, called group B in earlier work, showed structure similar to that observed in the emission spectra of the corresponding free ligand and biexponential decay. Decay of luminescence like that found in the present cases has by now been reported for many different transition metal complexes,¹⁴⁻²¹ and different explanations for the phenomenon have been put forward. Most commonly, it is believed that the glassy matrix in which many photophysical experiments are performed is not homogeneous,²⁰⁻²² so that where the emissions are environment-sensitive (such as CT), a range of emitting states can be produced. In the present case, where Re(I) complexes have low-lying ³MLCT and ³LC emitting states, the effect is particularly dramatic. Recent work²³ has shown that in a low temperature glass, the emission from [Re(4,7-Me₂phen)(CO)₃py]⁺ is derived from a ³LC state which is perturbed by the nearby ³MLCT state. In the inhomogeneous glass matrix a range of ³LC/³MLCT energy gaps are found, and therefore the degree of perturbation is variable, causing a range of lifetimes throughout the sample. It is thought that a similar effect operates for all of the Re(I) complexes in the present study, in the low temperature rigid glass.

In room temperature fluid solution, all complexes display single exponential decay profiles and broad, unstructured luminescence spectra, characteristic of ³MLCT emission. The change in the nature of the emission between fluid and rigid solutions is caused by the difference in the solvent environment in the two cases. The charge-transfer process produces a considerable change in the dipole moment of the complex, so that the equilibrium solvent environment is different for ground- and excited-state species. In contrast, ligand-centered transitions tend to display much less dependence on the external environment since there is usually a much smaller change in dipole moment in forming the excited state. In a fluid medium, the solvent molecules can reorientate in response to the charge redistribution, so that the lowest ³MLCT emitting state is

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equilibrated with its current solvent environment. When the solution is frozen the $^3\text{MLCT}$ excited state is not fully equilibrated, since the solvent cage remains in the ideal ground-state situation. Thus the lowest $^3\text{MLCT}$ state lies at higher energy in the rigid matrix and in some cases can be higher than the lowest ^3LC state. The luminescence is then derived from the lowest ^3LC state, as occurs for $[\text{Re}(4,7\text{-Me}_2\text{phen})(\text{CO})_3\text{py}]^+$.²³

The temperature dependent studies showed that the decays remained multiexponential for all of the complexes up to 110 K. Then, over the glass-to-fluid transition region (115–145 K), a dramatic reduction in decay rates occurred. Over the same range, a rise time could clearly be discerned in the initial portion of the decay profiles. The amplitude of the rise was dependent on the observation wavelength; generally it became more pronounced at longer wavelengths. The occurrence of a rise time in the decay profiles indicates that the principal emitting state is gaining intensity on a timescale comparable with the emission lifetime. A recent report on similar Re(I) complexes also noted the occurrence of a rise time in the decay profiles over the glass-to-fluid transition, but only in the presence of quenchers.^{20c}

The onset of the "rise" behavior occurs at temperatures immediately after multiexponential behavior ceases, which was around 115 K for most of the complexes. Thus, as soon as the matrix becomes fluid and the solvate molecules become mobile, those excited-state species which are in higher energy configurations can relax to lower-energy configurations, causing a build-up of luminescence intensity at longer wavelengths. This accounts for the wavelength dependence of the relative intensity of the rise time. Solvent reorientation is a recognized cause of this phenomenon in the measurement of emission lifetimes.²⁴

In fluid solution (above 150 K) the decay profiles of the complexes were single exponential at all temperatures. Under these conditions each excited-state species can be expected to have an approximately equilibrated solvent environment, since outer-shell reorientation rates are fast compared with the lifetime of the luminescence.

Temperature Dependence of Emission Lifetimes in Fluid Solution. Plots of observed decay rates (k_{obs}) vs temperature are displayed in Figure 1 a–h. Most of the complexes behave similarly, showing a steady increase in k_{obs} with temperature. At no point over the temperature range of the experiment did we encounter a strongly temperature-activated region, such as occurs for many ruthenium(II) polypyridyl²⁵ and platinum²⁶ complexes, where k_{obs} increases much more sharply near room temperature. The decay amplitudes also increased steadily with temperature, indicating that the increase in observed decay rates is due to thermal population of a more allowed state, rather than being caused by an increase in the nonradiative decay rate. One complex, $\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}^+$ (Figure 1a), displayed quite different and unusual behavior. Between 150 and 230 K, k_{obs} decreased steadily, then increased over the rest of the temperature range (230–315 K), resulting in a U-shaped curve.

The U-shaped behavior of $\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}^+$ was fitted by equation 5, whereas the temperature dependent emission lifetime behavior of the other complexes was fitted by eq 4. The parameters in Table 1 result in the fits illustrated

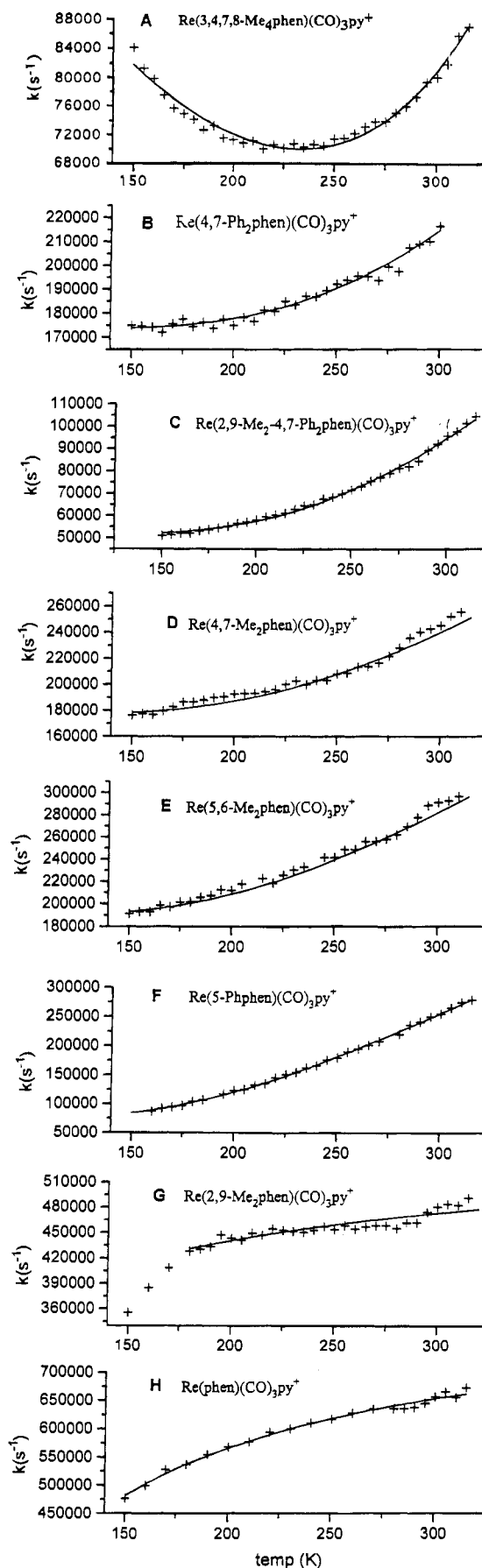


Figure 1. Temperature dependence of emission lifetimes: (A) $\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}^+$; (B) $\text{Re}(4,7\text{-Ph}_2\text{phen})(\text{CO})_3\text{py}^+$; (C) $\text{Re}(2,9\text{-Me}_2\text{-}4,7\text{-Ph}_2\text{phen})(\text{CO})_3\text{py}^+$; (D) $\text{Re}(4,7\text{-Me}_2\text{phen})(\text{CO})_3\text{py}^+$; (E) $\text{Re}(5,6\text{-Me}_2\text{phen})(\text{CO})_3\text{py}^+$; (F) $\text{Re}(5\text{-Phphen})(\text{CO})_3\text{py}^+$; (G) $\text{Re}(2,9\text{-Me}_2\text{phen})(\text{CO})_3\text{py}^+$; (H) $\text{Re}(\text{phen})(\text{CO})_3\text{py}^+$ in ethanol–methanol (4:1) over the 85–315 K range.

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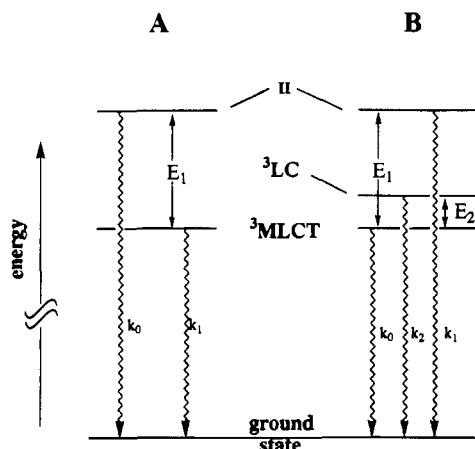
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Table 1. Results of Emission Lifetime Temperature Dependence for $\text{Re}(\text{L-L})(\text{CO})_3\text{py}^+$ Complexes^a

L-L	k_0 (s ⁻¹) ^b	k_2 (s ⁻¹)	k_1 (s ⁻¹)	E_2 (cm ⁻¹)	E_1 (cm ⁻¹)
3,4,7,8-Me ₄ phen	1.46×10^5	9×10^4	5×10^7	130	1430
4,7-Ph ₂ phen	$(1.73 \pm 0.01) \times 10^5$		$(1.94 \pm 0.6) \times 10^6$		960 ± 80
2,9-Me ₂ -4,7-Ph ₂ phen	$(5.15 \pm 0.05) \times 10^4$		$(1.2 \pm 0.1) \times 10^6$		830 ± 20
4,7-Me ₂ phen	$(1.77 \pm 0.01) \times 10^5$		$(1.5 \pm 0.2) \times 10^6$		760 ± 50
5,6-Me ₂ phen	$(1.89 \pm 0.02) \times 10^5$		$(1.5 \pm 0.1) \times 10^6$		680 ± 30
5-Phphen	$(7.2 \pm 0.2) \times 10^4$		$(1.87 \pm 0.07) \times 10^6$		600 ± 10
2,9-Me ₂ phen	$(3 \pm 3) \times 10^5$		$(6 \pm 1) \times 10^5$		200 ± 300
phen	$(2 \pm 40) \times 10^5$		$(1.2 \pm 0.1) \times 10^6$		120 ± 60

^a 4:1 ethanol-methanol, $T > 150$ K. ^b k_0 represents the extrapolated rate constant of the "solution" at zero degrees.

**Figure 2.** Model representing the excited state behavior in the rhenium(I) complexes.

in Figure 1. The data in Table 1 are arranged sequentially from the complex with the highest E_1 value, $\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}^+$, to the one with the lowest, $\text{Re}(\text{phen})(\text{CO})_3\text{py}^+$.

A number of similarities were evident upon comparison of the results in Table 1. The values of k_0 tended to be unaffected by substituents on the phenanthroline ring, being evaluated between 1×10^5 s⁻¹ and 3×10^5 s⁻¹ for six of the eight complexes (L-L = 3,4,7,8-Me₄phen, 4,7-Ph₂phen, 4,7-Me₂phen, 5,6-Me₂phen, 2,9-Me₂phen, phen). The other two (L-L = 2,9-Me₂-4,7-Ph₂phen, 5-Phphen) had lower values of 5×10^4 s⁻¹ and 7×10^4 s⁻¹, respectively. The k_1 values ranged from 1.2×10^6 s⁻¹ to 1.9×10^6 s⁻¹. The two exceptions, L-L = 3,4,7,8-Me₄phen and 2,9-Me₂phen, had values of 5×10^7 s⁻¹ and 6×10^5 s⁻¹, respectively. The main difference occurred in the E_1 values which ranged from 1432 to 120 cm⁻¹. The tetramethyl-substituted derivative, L-L = 3,4,7,8-Me₄phen, produced the largest E_1 value, five had E_1 values that ranged from 600 to 980 cm⁻¹ (L-L = 5-Phphen, 5,6-Me₂phen, 4,7-Me₂phen, 2,9-Me₂-4,7-Ph₂phen, 4,7-Ph₂phen), and two had lower values, 200 cm⁻¹ for L-L = 2,9-Me₂phen and 120 cm⁻¹ for L-L = phen. The only other information in Table 1 to be noted are the two additional listings for $\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}^+$ which are related to another temperature dependent step. A k_2 value of 9×10^4 s⁻¹ and an E_2 value of 127 cm⁻¹ were deduced for this additional process.

The Model. The model that accounts for the temperature dependence of the emission lifetime of most of the complexes is illustrated in Figure 2A. A different model, shown in Figure 2B, is used to interpret the unusual behavior of $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$.

In the general case, we attribute the gradual increase in the observed decay rate to the thermal population of a higher-energy state (called II here) which has a shorter lifetime than the principal emitting ³MLCT state. With a larger energy gap (E_1) between these states (> 800 cm⁻¹), a stronger temperature dependence is found over the high temperature range (> 230 K). An intermediate E_1 (≈ 400 – 800 cm⁻¹) results in a steadier

increase over the entire fluid temperature range, whereas a small E_1 (< 300 cm⁻¹) gives a strong initial dependence (< 200 K) which levels off as a "steady-state" population of the two levels is reached.

We can speculate as to the nature of the higher-lying state II. As the decay rate is faster than that of the ³MLCT state, it is unlikely that II is the ³LC state, although the ³LC is known to be quite close in energy to the ³MLCT in rigid media. Other possibilities include ¹MLCT or a ligand field (dd) state, but it is not possible to make a distinction between the alternatives based on the present data.

The variation in the energy gap E_1 can account for the trend in room-temperature lifetimes amongst the seven complexes, as shown in Table 1. A smaller E_1 corresponds to a shorter lifetime, and those complexes with larger E_1 values are longer-lived. It was previously speculated that the ³MLCT/³LC energy gap was the chief factor governing the lifetime differences.¹ The present data imply that at room temperature the ³LC state does not contribute significantly to the luminescence in most cases, the lifetime instead being determined by the energy gap between the ³MLCT and another higher-lying state. This in turn requires that the ³LC state generally lies higher in energy than state II in fluid solution.

The two-level model outlined above could not be used to account for the temperature dependence of the lifetime of $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$. Instead, a three-level model described by eq 5 and illustrated in Figure 2B was used. In this scheme, the extra level lies between the ³MLCT and state II, and has a slower decay rate than either of them. We assign this as the ³LC level, for several reasons. In the 3,4,7,8-Me₄phen complex, the ³LC state is expected to be much closer to the ³MLCT state than in any of the other complexes, based on comparison of spectroscopic data¹ for $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$ with that for $[\text{Re}(4,7\text{-Me}_2\text{phen})(\text{CO})_3\text{py}]^+$ reported previously. The structured luminescence spectra of these two complexes occur at very similar energies (464 and 463 nm respectively at 77 K). This implies that the energy of the ³LC state is approximately the same in either case. However, the room temperature ³MLCT emission band of $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$ is considerably higher in energy than that of $[\text{Re}(4,7\text{-Me}_2\text{phen})(\text{CO})_3\text{py}]^+$ (by ≈ 800 cm⁻¹ in CH₃CN). The ³MLCT/³LC gap is then expected to be much smaller for $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$, assuming that the ³LC energy is approximately the same in fluid or rigid solvent. Since the middle level in model 3B has a longer lifetime than the ³MLCT state, it seems reasonable to assign this to the ³LC state.

Other observations also indicate that the ³LC state contributes to the luminescence of $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$ at room temperature. The room temperature lifetime (13 μ s in CH₂-Cl₂)¹ is rather long for a ³MLCT emitting state of this type and is affected very little by changing the solvent. This is in contrast to the other complexes in the series which display a decrease in lifetime in more polar solvents,¹ a common occurrence for ³MLCT emitters. In addition, a high-energy shoulder appears

in the luminescence band of $[\text{Re}(\text{3,4,7,8-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$ at 298 K while the other complexes show no trace of structure at all.

Thus the U-shaped behavior can be rationalized as follows: at 150 K the luminescence occurs primarily from the $^3\text{MLCT}$ state with a small proportion of ^3LC emission. Raising the temperature to 230 K increases the thermal population of the ^3LC state and hence increases the amount of ^3LC character in the spectrum. This is reflected in the longer lifetimes of the complex. Further increasing the temperature causes thermal population of state II, thus reducing the observed luminescence lifetime over the range 230–290 K.

Conclusions

The photophysical behavior of the $\text{Re}(\text{L-L})(\text{CO})_3\text{py}^+$ complexes is very complex due to contributions from multiple emitting states. In a glass, which gives an inhomogeneous environment, dual exponential decay of the emission occurs since a range of species, with varying $^3\text{MLCT}/^3\text{LC}$ separations, exists in the matrix. At temperatures just above the glass-to-fluid transition of EM, a wavelength-dependent rise time is observed in the decay of all complexes, which is probably

caused by reorientation of the solvent cage during the lifetimes of the excited state.

In fluid solution, the emission is derived from thermally-equilibrated excited states. In the general case, the decrease in emission lifetime with temperature is attributed to thermal population of a higher energy state which has a faster decay rate than the lowest-energy $^3\text{MLCT}$ state. The nature of the upper state is not clear, but it seems unlikely to be the ^3LC state. A larger energy gap between the $^3\text{MLCT}$ state and state II results in a longer lifetime at room temperature. For $[\text{Re}(\text{3,4,7,8-Me}_4\text{phen})(\text{CO})_3\text{py}]^+$, the $^3\text{MLCT}/^3\text{LC}$ energy gap is much smaller than for any of the other complexes, so that ^3LC state does constitute part of the luminescent manifold of states. A three-level model is required to account for the observed temperature dependence, with the ^3LC state lying between the lowest $^3\text{MLCT}$ state and the upper state II. Thermal population of the ^3LC state increases the lifetime of the luminescence, which then decreases as the population of state II ensues.

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