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Photophysical investigations of rhenium(I)Cl(CO)$_3$(phenanthroline) complexes

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Contents

Abstract

The electronic states of three complexes with the generic formula Re(I)Cl(CO)$_3$(s-phen) [s-phen = 4,7-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline] have been characterized by absorption and luminescence

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spectroscopy and the T-dependence of the decay times in rigid glasses in the range 4–77 K. Methyl substitution leads to composite phosphorescence bands that arise from ^{3}MLCT and $^3\pi\pi^*$ terms that are separated by Franck–Condon barriers. Evidence is also presented for the existence of FC barriers in singlet manifolds. Criteria are defined for the occurrence of FC barriers and slow rates of radiationless transitions between terms arising from disparate electronic configurations. The energy splittings and the decay constants of the individual sublevels of the ^{3}MLCT manifolds have been determined.

Keywords: Rhenium(I) complexes; Luminescence; Excited states; Radiationless transitions; Barriers; Orbital configurations

1. Introduction

Enormous progress has been made during the last 30 years in the understanding of the excited states of metal complexes. For those with $(nd)^6$ metal ions [Ru(II), Ir(III), Rh(III), Re(I)] and α,α'-diimine ligands the effort has been especially intense since these substances display a variety of excited states that can be tuned in energy by subtle changes in the structures; in some cases, inversion of the lowest configurations can be achieved [1]. Within a few thousand wavenumbers of the lowest (emitting) excited configuration all coordination compounds containing a chelated 1,10-phenanthroline and one of the $(nd)^6$ metal ions in the group listed above possess $^3\pi\pi^*$, ^{3}dd (LF), and $^3d\pi^*$ (MLCT) excited terms that can be reached indirectly by radiationless decay from higher lying singlet states upon UV photoexcitation. By routine luminescence measurements at 77 K the orbital nature of the lowest excited manifold can be confidently assigned. For [tris(1,10-phenanthroline)Ru(II)]$^{2+}$ the lowest excited term is a ^{3}MLCT manifold [2,3]; for [tris(1,10-phenanthroline)Rh(III)]$^{3+}$ the emitting term is clearly $^3\pi\pi^*$ [4]; for [bis(1,10-phenanthroline)Cl$_2$Ir(III)]$^+$, it is $^3d\pi^*$ [1]. Detailed photophysical studies have been published on these and analogous species and the characteristics of the emitting terms are well documented [5].

Among the less studied $(nd)^6$ complexes containing a phenanthroline ligand are those of rhenium(I), particularly those with the generic formula [Re(I)Cl(CO)$_3$(s-phen)] where s-phen represents a 1,10-phenanthroline ligand with methyl groups at various positions on the rings. These species are thermally stable and many of them display emission in fluid solution from a ^{3}MLCT excited term; thus they are candidates for effecting energy transfer and/or electron transfer. In glasses at 77 K some of the species display emission from a single configuration, while others show phosphorescence bands that are clearly composites. Few low-temperature investigations on rigid glasses of these materials have been reported [6–14], and virtually no quantitative studies have been made on their photoluminescence properties in the range 77–4 K. In the current work we report low-temperature optical investigations on three Re(I)Cl(CO)$_3$(s-phen) complexes that display two emission bands, nonexponential decays, and significant sensitivity of the photoluminescence to solvent polarity. Our intent is to assign the orbital and spin labels for the low-lying levels, to quantify the emitting manifolds, and to elucidate the factors controlling the radiative and radiationless processes in this class of photoluminescent molecules.

2. Experimental

2.1. Materials

$Re(CO)_5Cl$ was obtained from Pressure Chemical or Aldrich Chemical. The 5,6-dimethyl-1,10-phenanthroline ligand (5,6-Me_2phen) was purchased from GFS Chemicals. Both 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen) and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) were purchased from Aldrich. The *fac*-Re[(I)(Cl)$(CO)_3$(s-phen)] complexes were prepared by heating equimolar mixtures of the pentacarbonyl chloride with the s-phen ligand in toluene under reflux for 1 h [15]. After the solutions cooled, the products were collected. Purification was achieved by silica gel chromatography. Methylene chloride eluted unreacted material, and a 5% methanol in methylene chloride solvent eluted the product. Upon slow evaporation of the eluent high yields of microcrystalline products were recovered.

2.2. Spectroscopy

All spectroscopic measurements were conducted on 10^{-5}–10^{-4} M solutions of the substances in a variety of rigid glasses: 5:5:2 diethylether–3-methylpentane–ethanol (EPA), 2-methyl-tetrahydrofuran (2-MeTHF), 4:1 ethanol–methanol (EtOH–MeOH), EtOH, and 1:4:1 ethanol–methanol–water (EtOH–MeOH/H_2O). For measurements below 77 K the sample was introduced into a rod equipped with optical fibers that was inserted directly into a liquid helium storage Dewar flask [16]. The sample temperature was controlled by raising or lowering the fiber rod relative to the surface of the liquid helium or by means of a heater controlled by a Lakeshore Cryotronics DRC-80C temperature controller. The temperature was monitored by recording the voltage drop across a cryodiode sensor or calibrated resistor (Cryo Cal).

Emission excitation spectra at 77 K were obtained with a Hitachi MPF-2A spectrofluorimeter corrected for monochromator efficiency and fluctuations in lamp intensity. Broad band excitation (365 nm) was achieved by passing the light from an Osram 150-W high-pressure Xe lamp through 5 cm of saturated $CuSO_4$ and a Corning 7-60 glass UV filter. The emitted light was filtered through 33 M aqueous KNO_2, passed through a Spex Minimate or Spex Doublemate monochromator, and detected by a thermoelectrically cooled RCA C31034 PM tube. The signal was fed to a Keithley 610-CR electrometer; the analog signal was processed by a computer-driven data acquisition system. For decay-time and time-resolved measurements the excitation source was replaced by a Molectron UV22 N_2 laser (10 ns FWHM), and the resultant signal was fed to a Princeton Applied Research 162 Boxcar averager fitted with a 164 gated integrator.

All the complexes exhibited nonexponential decay at all temperatures investigated. To isolate ligand phosphorescence decays the emissions were monitored at 480 nm and only data obtained after the decay of the short-lived component were included in the analyses. The ^{3}MLCT emission decays were obtained after the laser pulse by monitoring the emission at 600 nm. ^{3}MLCT decay data were fit to a biexponential function in which the ligand phosphorescence decay constant obtained previously was held constant. A nonlinear least-squares simplex program was employed [17].

The detailed characteristics of the ^{3}MLCT manifolds were obtained by monitoring the decay times of the short-lived components of the phosphorescences as a function of temperature. The sublevel splittings and rate constants were obtained by the procedure described previously [2,18].

3. Results

3.1. Spectral data

Emission and excitation spectra are presented in Figs. 1–4. In Fig. 1 the steady-state emissions of the complexes at 4 K are displayed. Structure appears on the high-energy side of each band, in stark contrast to the broad band ^{3}MLCT emission characteristic of the parent (unsubstituted) Re(I)Cl(CO)$_3$(phen) complex [18]. The relative amount of structure in the spectrum depends on the α,α′-diimine in the complex: 5,6-Me$_2$phen > Me$_4$phen > 4,7-Me$_2$phen, but the energy of the first band maximum decreases along the series: 4,7-Me$_2$phen (464 nm) > Me$_4$phen (473

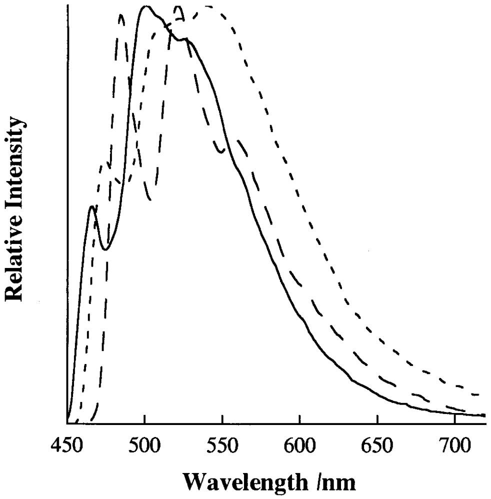

Fig. 1. Luminescence spectra of Re(I)Cl(CO)$_3$(s-phen) complexes in EtOH–MeOH at 4.15 K under 365 nm broad-band excitation. (—) 4,7-Me$_2$phen; (- - - - - -) Me$_4$phen; (— — —) 5,6-Me$_2$phen.

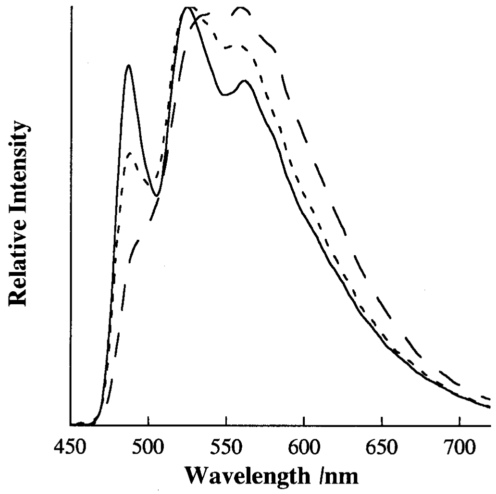

Fig. 2. Temperature dependence of the luminescence of Re(I)Cl$(CO)_3$(5,6-Me_2phen) in EtOH–MeOH. (—) 4.17 K; (- - - - - -) 42.8 K; (— — —) 82.5 K. 365-nm broad-band excitation was employed.

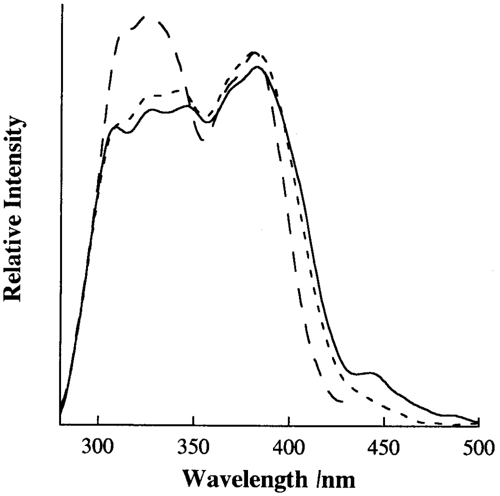

Fig. 3. Excitation spectra of Re(I)Cl$(CO)_3$(5,6-Me_2phen) in EtOH–MeOH monitored at various wavelengths of the emission. (—) 600 nm; (- - - - - -) 535 nm; (— — —) 480 nm.

nm) > 5,6-Me_2phen (484 nm). The emission of Re(I)Cl$(CO)_3$(5,6-Me_2phen) in EtOH–MeOH at various temperatures is plotted in Fig. 2. As the sample cools from 82.5 to 4.17 K, the resolution of the structure improves considerably.

Excitation spectra of Re(I)Cl$(CO)_3$(5,6-Me_2phen) at 77 K are shown in Fig. 3. Both the features of the spectra and the relative intensities of the bands change as the monitoring wavelength varies. In Fig. 4 the emission and excitation spectra of

Re(I)Cl(CO)$_3$(5,6-Me$_2$phen) at 77 K are plotted as a function of solvent. As the solvent polarity increases the relative intensity of the structured part of the emission increases. The features of the excitation band, produced by monitoring at a fixed wavelength (535 nm), are also a function of the rigid glass environment. In the steady state emission the first band maximum is invariant to the matrix; however, the changes of the excitation spectra shown in Fig. 4, due to variations of solvent polarity, are not unlike those produced when the monitoring wavelength is varied as shown in Fig. 3. The red edge of the excitation spectrum is lost when the polarity of the solvent is increased and also when the emission is monitored at progressively shorter wavelengths.

The behavior of the band envelopes with change in temperature is of special interest for our subsequent analysis. As shown in Fig. 2, the relative importance of the diffuse component with respect to the structured component increases dramatically with increasing temperature. This observed envelope change is evidently the result of two opposite trends; population of the state(s) giving rise to the broad band increasing with temperature, while the opposite is occurring for those giving rise to the diffuse component.

3.2. Results of kinetic measurements

At the temperatures employed all the systems exhibited complex biexponential decays. The existence of two emitting configurations is confirmed by the time-resolved spectrum of Re(I)Cl(CO)$_3$(Me$_4$phen) at 62 K shown in Fig. 5. The structure of the long-lived component is almost identical to the $^3\pi\pi^*$ emission characteristic

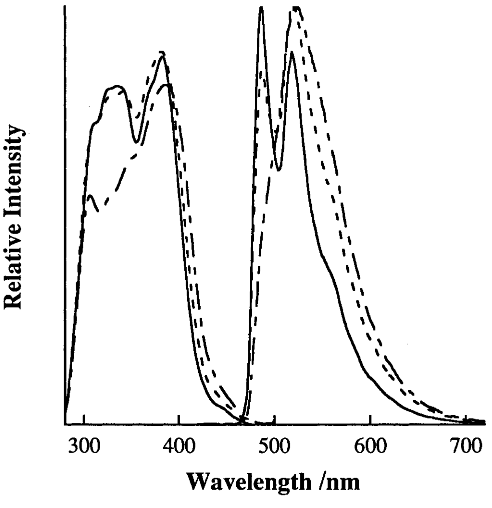

Fig. 4. Excitation and emission spectra at 77 K of Re(I)Cl(CO)$_3$(5,6-Me$_2$phen) in various solvents. (— – —) EPA; (- - - - -) EtOH–MeOH; (—) EtOH–MeOH–H$_2$O. Luminescence was stimulated by 365-nm broad-band light. Excitation spectra were obtained by monitoring the emission at 535 nm.

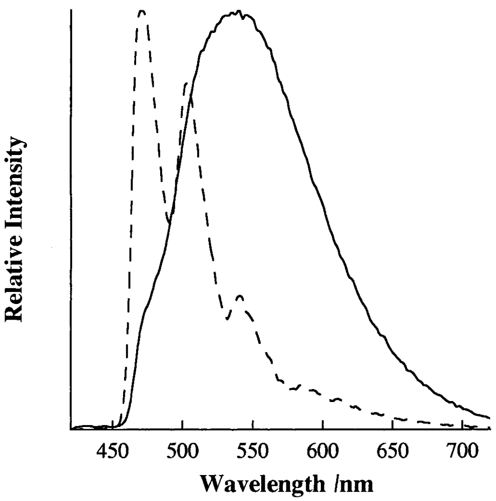

Fig. 5. Time-resolved phosphorescence spectra of Re(I)Cl(CO)$_3$(Me$_4$phen) in EtOH–MeOH at 62.5 K monitored at (—) 300 ns and (– – –) 600 μs after excitation by the 337-nm pulse of a N_2 laser.

Table 1
Measured decay times of the emitting terms of Re(I)Cl(CO)$_3$(s-phen) complexes at 77 K in EtOH–MeOH

Ligand	τ (μs)	
	$^3\pi\pi^*$	^{3}MLCT
4,7-Me$_2$phen	135	12.8
Me$_4$phen	175	13.2
5,6-Me$_2$phen	279	9.1

of the uncoordinated ligand and also of the corresponding $^3\pi\pi^*$ band observed from Rh(s-phen)$_3^{3+}$ species containing these same substituted phenanthroline ligands [4]. The long-lived component of the observed decay is temperature invariant, while the fast component of the lifetime is highly temperature dependent, increasing by an order of magnitude as the temperature decreases to 4 K. Enhancement of the slow component amplitude in the decay kinetics can be achieved by monitoring on the high-energy side of the emission whereas the short component is enhanced by monitoring on the red side. The results of such kinetic studies are presented in Tables 1 and 2. The fast component of the lifetime is invariant to the solvent used and does not substantially change with the ligand used either. The slow component of the decay depends on both the polarity of the matrix and the nature of the polypyridyl ligand. There is also a direct correlation between the slow decay rate and the amount of structure appearing in the steady-state emissions; the longer the lifetime of the slower decaying component, the more structured the spectrum.

The results of the T-dependence measurements on the ^{3}MLCT manifolds for Re(I)Cl(CO)$_3$(phen) and Re(I)Cl(CO)$_3$(5,6-Me$_2$phen) are included in Fig. 6. Best-fit parameters for the level manifolds are included in Table 3.

Table 2
Measured decay times of the emitting terms of Re(I)Cl(CO)$_3$(5,6-Me$_2$phen) at 77 K in a variety of glasses

Solvent	τ (μs)	
	$^3\pi\pi$*	^{3}MLCT
2-MeTHF	130	9.1
EPA	140	9.2
EtOH	260	8.8
EtOH–MeOH	280	9.1
EtOH–MeOH/H$_2$O	360	9

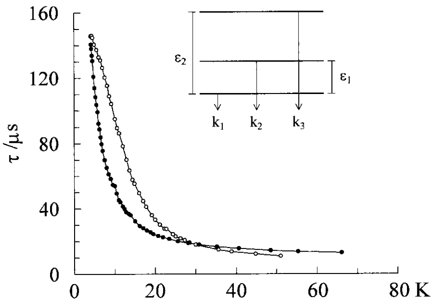

Fig. 6. Decay times of the ^{3}MLCT manifolds of Re(I)Cl(CO)$_3$(s-phen) complexes as a function of temperature. (○ ○ ○) Re(I)Cl(CO)$_3$(phen) (from Ref. [18]); (• • •) Re(I)Cl(CO)$_3$(4,7-Me$_2$phen); (—) 'best-fit' computer generated curves for parameters defined in insert and reported in Table 3.

Table 3
^{3}MLCT parameters of Re(I)Cl(CO)$_3$(s-phen) complexes derived from the T-dependence of the phosphorescence[a]

Complex	ε_1 (cm^{-1})	ε_2 (cm^{-1})	k_1 (μs^{-1})	k_2 (μs^{-1})	k_3 (μs^{-1})
phen (in EPA)[b]	14.0	42.1	0.0067	0.029	0.52
4,7-Me$_2$phen (in EPA)[c]	8.3	27.3	0.0042	0.055	0.24
Me$_4$phen (in EtOH–MeOH)[c]	11.0	27.6	0.011	0.065	0.20
5,6-Me$_2$phen (in EtOH–MeOH)[c]	10.4	40.0	0.0095	0.028	0.47

[a] 337-nm pulsed excitation.

[b] Single exponential decay.

[c] Parameters obtained from fast component of biexponential decay.

4. Discussion

4.1. Assignment of the emitting configurations

The low-temperature spectroscopic results from this series of complexes confirm the existence of two emitting manifolds in rigid glasses, each with vastly different characteristics. The structured, long-lived phosphorescence observed from all the molecules we assign to a $^3\pi\pi^* \rightarrow$ g.s. transition on the basis of three criteria: (a) the band structures and energy maxima closely resemble the $^3\pi\pi^*$ phosphorescences of the corresponding uncoordinated ligands and lie very near in energy to the $^3\pi\pi^*$ bands observed from the analogous tris(s-phen)rhodium(III) complexes [4]; (b) the positions of the band maxima are insensitive to changes of solvent; and (c) the lifetimes are temperature independent in the range 4–77 K. The triplet, however, cannot be 'pure' because these $^3\pi\pi^*$ decay times are four orders of magnitude shorter than those of the protonated ligands. They are also significantly shorter than those of the corresponding rhodium(III) species that are mixed with other triplets and singlets through spin–orbit coupling [19].

The diffuse, short-lived component of the phosphorescence band of each molecule clearly arises from a ^{3}MLCT configuration. Its unstructured band envelope, the strong temperature dependence of the observed lifetime, and the close resemblance of all its features to the ^{3}MLCT band of the parent unsubstituted Re(I)Cl$(CO)_3$(phen) complex, (Fig. 6, Table 3), clearly label it as a $^3\mathrm{MLCT} \rightarrow$ g.s. transition.

The disparate nature of the two components in the observed phosphorescences are also revealed by the behavior of the decay times with changes in temperature. As the temperature increases from 4 K, the decay rates of ^{3}MLCT manifolds are known to increase [2,18]; whereas the decay of $^3\pi\pi^*$ phosphorescence remains essentially constant. This behavior is exhibited by all the reported complexes.

4.2. Effect of methyl substitution

The effect on the energy of the $^3\pi\pi^*$ configuration induced by placing methyl groups at different sites on the phenanthroline rings is not large. An approximate measure of the $^3\pi\pi^*$ energy is the location of the first peak maximum of the structured component of each phosphorescence. This occurs at 464 (459) nm for the complex containing 4,7-Me_2phen, at 473 (461) nm for the Me_4phen complex, and at 484 (488) nm for Re(I)Cl$(CO)_3$(5,6-Me_2phen). Thus, the total shift of the $^3\pi\pi^*$ configuration spans only ~ 900 cm^{-1}. The values in parentheses are for the corresponding tris-rhodium(III) complexes of the same ligands, measured in glycerol matrices at 77 K. For the $Rh(phen)_3^{3+}$ parent complex the $^3\pi\pi^*$ is located at 450 nm (22 200 cm^{-1}), and we infer that its position is the same in the parent Re(I)Cl$(CO)_3$(phen), although this latter molecule emits only from a ^{3}MLCT configuration and no direct measurement can be made. From these data we draw the following conclusion: the (unobserved) $^3\pi\pi^*$ configuration in the parent Re(I)Cl$(CO)_3$(phen) complex lies > 1000 cm^{-1} above the center of gravity, 21 100 cm^{-1}, of the $^3\pi\pi^*$ configuration in the methyl substituted complexes.

The effect of methyl substitution on the ^{3}MLCT energy is impossible to measure directly, since the ^{3}MLCT component is very diffuse and its origin cannot be precisely located. Nevertheless, from a comparison of excitation and emission spectra (e.g. Fig. 4) of this series of complexes it appears that the ^{3}MLCT manifold energy is relatively constant in all complexes, both parent and substituted, and lies at ~ 475 nm (21 000 cm^{-1}), a value that should be compared with the $^3\pi\pi^*$ center of gravity calculated above. We thus arrive at the following conclusions for this set of rhenium molecules. When two triplets of disparate orbital parentages are separated by > 1000 cm^{-1}, only the lowest triplet is emissive under broad band excitation at 77 K; when their separation is < 1000 cm^{-1}, both can emit, and the relative amount emanating from each is a function of the excitation wavelength. The data also imply a radiationless transition rule for complexes with quasi-degenerate configurations of different orbital parentages: $^1\pi\pi^*$ states decay to $^3\pi\pi^*$ levels and ^{1}MLCT states decay preferentially to ^{3}MLCT manifolds. Invoking this radiationless decay rule adequately accounts for the change in the excitation spectra as a function of the monitoring wavelength. The data for the Re(I)Cl$(CO)_3$(5,6-Me_2phen) complex shown in Fig. 3 are typical. When the emission is monitored at long wavelengths where the ^{3}MLCT component dominates, the low-energy singlet MLCT absorption band is clearly visible in the excitation spectrum; when the emission is monitored on the blue edge, this band disappears. Thus, monitoring the emission where $^3\pi\pi^*$ emission is dominant yields an excitation contour that discriminates against ^{1}MLCT absorption, whereas monitoring in the region where ^{3}MLCT emission dominates accentuates the ^{1}MLCT component(s) in the absorption envelope.

4.3. Incidence of Franck–Condon barriers

The experimental generalizations enunciated above are most easily accommodated in an electronic model that assumes the existence of FC barriers in this structurally related set of Re(I)Cl$(CO)_3$(s-phen) molecules. Thus, we assert that a FC barrier separates the lowest $^3\pi\pi^*$ level from the lowest ^{3}MLCT manifold, and that this barrier is not surmounted in the temperature range of this experiment. This assertion accounts for the invariance of the $^3\pi\pi^*$ decay time with temperature. However, a barrier separating triplet terms does not account for the variation of the intensity changes that occur with changes in temperature. As revealed in Fig. 2 the $^3\pi\pi^*$ component of the spectrum decreases as the temperature increases, but there is no corresponding decrease in its decay time. The intensity of the ^{3}MLCT emission increases dramatically, much more than expected from measurements on this manifold in the analogous unsubstituted phen complex. Thus, the relative loading of the two emitting terms changes with temperature and we attribute this behavior to the occurrence of a FC barrier separating the lowest $\pi\pi^*$ and MLCT singlets that is surmountable in the range 4–77 K. The existence of such a barrier, in conjunction with the preferential decay rule stated above for intraconfigurational radiationless processes, explains all our observations. Moreover, the absorption and excitation spectra show a near coincidence of $^1\pi\pi^*$ and ^{1}MLCT terms, satisfying the energy gap criterion for the incidence of intraconfigurational barriers (vide infra).

4.4. Role of singlet states in controlling the emission process

Although the measurements in this laboratory on a series of both rhenium(I) and rhodium(III) (nd)^6 complexes of these same ligands clearly confirm that the energy of the lowest ligand $^3\pi\pi^*$ level is relatively insensitive to the metal ion, the metal in the system clearly affects the lifetime of the $^3\pi\pi^*$ manifold. For the analogous Rh(III) complexes the lifetimes are shortened from seconds for the protonated and uncoordinated ligands to milliseconds in a complex, and the effect of Re(I) is to reduce the $^3\pi\pi^*$ lifetime by an additional factor of ten (Table 1). In addition, the long-lived decay ascribed to the $^3\pi\pi^*$ term is sensitive to the solvent. As the polarity of the glass increases the decay of the $^3\pi\pi^*$ term also increases (Table 2). With the increasing polarity of the glass the lowest ^{1}MLCT band shifts to higher energy as expected for singlet CT states of complexes with large dipole moments [20], whereas the $^1\pi\pi^*$ terms are expected to red-shift slightly as recorded for most unsaturated hydrocarbons. We conclude that the lifetime of the $^3\pi\pi^*$ term is controlled by mixing with the lowest ^{1}MLCT state and the degree of mixing is modulated by solvent polarity through changes in the energy gap between the two interacting states. Reducing the polarity of the glass increases the mixing and shortens the $^3\pi\pi^*$ lifetime; increasing the polarity increases the $^3\pi\pi^*$ lifetime by increasing the ^{1}MLCT–$^3\pi\pi^*$ energy gap.

This intensity borrowing model can also be used to rationalize the differences in the $^3\pi\pi^*$ lifetimes observed for the three rhenium(I) complexes in the same solvent. If the ^{1}MLCT states are insensitive to methyl substitution (as we have assumed for the ^{3}MLCT manifolds), then the energy gap between the interacting ^{1}MLCT state and the emitting $^3\pi\pi^*$ term depends primarily on the energy of the latter. Since methyl substitution lowers the energy of the $^3\pi\pi^*$ term in the order 4,7-Me$_2$phen > Me$_4$phen > 5,6-Me$_2$phen, one expects the lifetime of the $^3\pi\pi^*$ term to increase as its energy decreases, exactly what Table 1 shows.

4.5. Consequences of broad-band excitation of overlapping states

^{1}MLCT bands are intrinsically broad and diffuse. Absorption to $^1\pi\pi^*$ states also leads to broad bands, but with some structure. The near-UV spectra of these Re(I)Cl(CO)$_3$(s-phen) complexes are obviously composites of several overlapping bands of both types. Excitation by a broad-band source populates both types of singlet states, and the relative population of each type is a function of the intrinsic disposition of the states, the polarity of the solvent, and the degree of heterogeneity of the sites in the glass. Excitation spectra (see Fig. 4) clearly show that one can change the relative weights of each component in the emission envelope, but we have been unable to separate the two components completely, except by employing time resolution (Fig. 5).

4.6. Relation to previous work on interconfigurational conversion

The energy criterion enunciated above for the occurrence of a composite band was stated clearly by Watts and co-workers [21,22] as a criterion for the incidence of slow radiationless interconversion among closely lying triplet states in metal complexes. From a series of studies on hetero tris complexes of rhodium(III) hindered energy conversion between $^3\pi\pi^*$ levels on different ligands coordinated to the same metal ion was shown to arise when the separation of the two configurations lay in the range 100–400 cm^{-1}. This range compares quite favorably with our range for slow interconversion between $\pi\pi^*$ and MLCT terms deduced from data on these rhenium(I) molecules. Watts et al. also stressed the concept of disparate orbital parentages as a necessary condition for the incidence of slow interconversion among configurations. Our assignment of the two levels responsible for the composite bands observed from these three complexes of rhenium(I) to $^3\pi\pi$ and ^{3}MLCT terms also corroborates this necessary condition of disparate orbital parentages for slow rates of radiationless interconversion. Our investigations also display the counter case. The parent Re(I)Cl(CO)$_3$(phen) complex only displays ^{3}MLCT emission and the gap between this term and the higher-lying $^3\pi\pi^*$ level exceeds 1000 cm^{-1}, well outside the narrow energy range requisite for hindered interconfigurational conversion in rigid glasses. Inversion of quasi-degenerate excited states in analogous Re(I) complexes by subtle modification of the ligands was reported by Demas and co-workers who also correctly identified the ^{3}MLTC and $^3\pi\pi^*$ emitting manifolds [11–13].

5. Summary and conclusions

The present study confirms that the rates of interconfigurational radiationless processes in Re(I)Cl(CO)$_3$(s-phen) complexes can be controlled by adding methyl groups to the phenanthroline rings. The data also support the rule that a small energy gap between excited terms of disparate orbital parentages is a necessary condition for observing slow rates. Our observations also imply the existence of FC barriers within both singlet and triplet manifolds. This study also shows that the position of the lowest $^3\pi\pi^*$ level of a s-phen ligand is relatively insensitive to the nature of the (nd)^6 ion. Thus, it is possible to place this level within a narrow energy range in complexes where it cannot be directly observed. The data also imply that the phosphorescence band envelope observed from the complexes in rigid glasses originates from both a ^{3}MLCT and a $^3\pi\pi^*$ term that are not in thermal communication at 77 K. The lifetime of the $^3\pi\pi^*$ level is a factor of $\sim 10^4$ shorter than that observed for the uncoordinated s-phen ligand and this is attributed to mixing with a ^{1}MLCT state through spin-orbital coupling. Analysis of the T-dependence of the ^{3}MLCT emission leads to sublevel characteristics that are typical for triplet MLCT manifolds of (nd)^6 complexes containing α,α'-diimine ligands.

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