ELSEVIER

Coordination Chemistry Reviews
171 (1998) 43-59

COORDINATION CHEMISTRY REVIEWS

The photophysical behavior of d^6 complexes having nearly isoenergetic MLCT and ligand localized excited states

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Received 7 July 1997; received in revised form 20 August 1997; accepted 19 November 1997

Contents

Abstract

A large number of second- and third-row d^6 transition metal complexes with *N*-heterocyclic ligands have been prepared in which the lowest energy excited state is a metal-to-ligand charge transfer (MLCT) state. In some of these complexes ligand localized (IL) excited states exist which are of the same spin multiplicity as the MLCT state and are energetically accessible

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PII S0010-8545(98)00040-X

from the ^{1}MLCT state. Several complexes have been examined which exhibit luminescence from two states in frozen matrices. In fluid solutions, however, only a few examples exist of complexes having two non-equilibrated triplet excited states. This article provides a brief overview of the experimental methods commonly used in the analysis of triplet excited state formation and relaxation in transition metal complexes having coexisting triplet excited states. In addition, descriptive examples are given of complexes for which both ^{3}IL and ^{3}MLCT states can be populated following excitation into the ^{1}MLCT state.

Keywords: MLCT states; Intraligand; Diimine complexes

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1. Introduction

The photophysical behavior of well over 1000 complexes containing a d^6 transition metal coordinated to one or more aromatic *N*-heterocyclic ligands has been investigated [1–3]. These complexes have been intensively studied because of the potential for various applications such as luminescence-based sensors, electroluminescent displays and dye-sensitized semiconductor-based photoelectrochemical cells [4,5]. The *N*-heterocycles employed span a broad range of structures and the excited states of these ligands vary widely in energy for both singlet and triplet states.

Regardless of symmetry, the d^6 *N*-heterocyclic complexes of second- and third-row transition metals have low spin ground states ($S=0$). The thermally equilibrated excited states of these complexes, observed on nanosecond or longer time scales, are usually assigned as being either metal-to-ligand charge transfer (MLCT) or intraligand ($\pi\rightarrow\pi^*$) states with varying degrees of triplet character. Very often the complexes are luminescent in solution and, in most cases, the observed steady state emission arises exclusively from the lowest energy state in the triplet manifold. In a relatively small number of complexes, particularly as single crystals or in organic matrices at low temperature, luminescence from two triplet excited states is observed. The work of Watts and van Houten in the 1970s provided clear evidence for multiple emission from two different $^3(\pi\rightarrow\pi^*)$ states in complexes of the type $[Rh(bpy)_n(phen)_{3-n}]^{3+}$. They found that internal conversion between the two $^3(\pi\rightarrow\pi^*)$ states was slow relative to relaxation of the states when the energy gap between the states was small [6]. Watts' group also observed simultaneous emission from an $M(d\pi)\rightarrow bpy(\pi^*)$ MLCT state ($M=Rh^{3+}$, Ir^{3+}) and a dd state in $[MCl_2(bpy)_2]^+$ in DMF solutions at temperatures below 298 K [7]. Also in the mid-1970s Wrighton and coworkers showed that Re(I) complexes exist which exhibit emission from an MLCT state in solution at room temperature but have structured ^{3}IL luminescence in glasses at 77 K [8,9]. This was attributed to the fact that formation of the glassy matrix raises the energy of the ^{3}MLCT state while leaving the ^{3}IL state relatively unperturbed. More recently it has been established that, while solution luminescence is generally observed only from a single state, some complexes have ^{3}MLCT and ^{3}IL states which coexist and relax to the ground state with different rate constants. This review will present examples of complexes which have coexistent IL and MLCT states and will explore issues relating to internal conversion of the

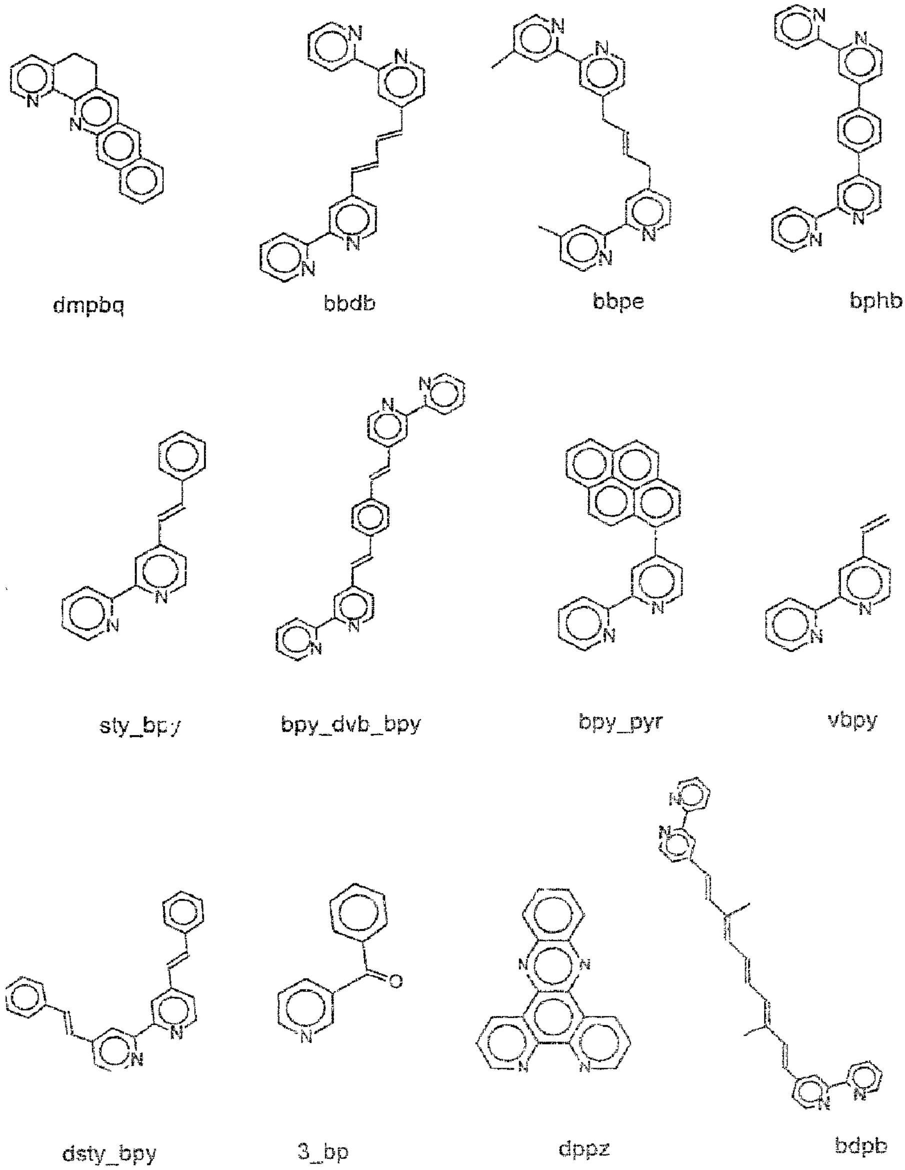

Fig. 1. Structures of ligands known to have observable intraligand excited states when coordinated to d^6 transition metals.

two nominally triplet states. Fig. 1 shows the structures of some *N*-heterocyclic ligands which have been shown to have accessible ^{3}IL states in d^6 metal complexes.

Fig. 2 shows a general state diagram for this class of complexes. Excitation into either ^{1}IL or ^{1}MLCT absorption bands results in rapid intersystem crossing to

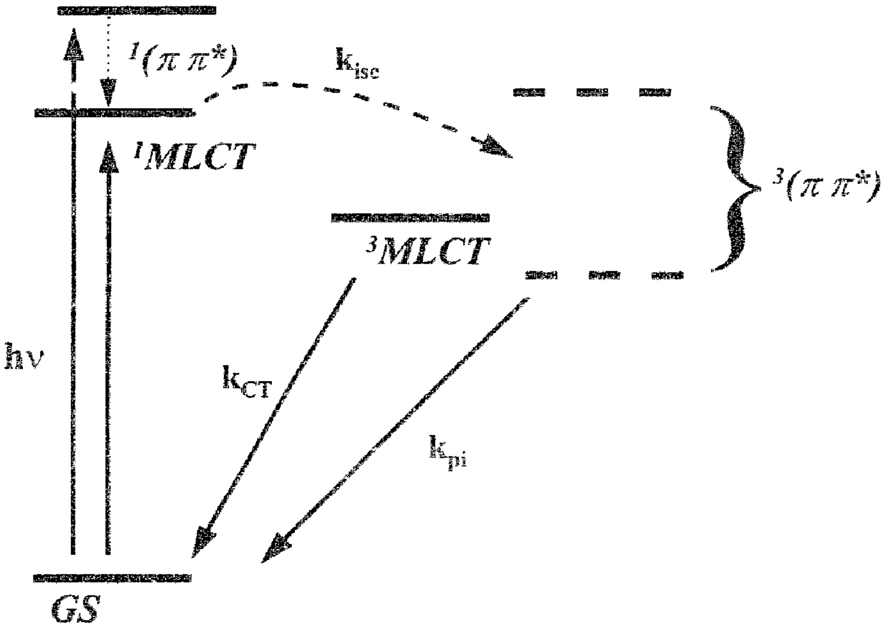

Fig. 2. Relative energy level diagram for complexes having observable ³MLCT and ³IL excited states.

populate accessible triplet states. While limited data is available on the intersystem crossing process, recent sub-picosecond transient absorption measurements on $[Ru(bpy)_3]^{2+}$ suggest the internal conversion to the triplet manifold is complete in less than 1 ps [10]. The singlet can, in principle, partition between the ^{3}MLCT and ^{3}IL states in the intersystem crossing process. Once the triplet(s) are formed, relaxation in the triplet manifold can yield the thermally equilibrated excited state which can then relax to the ground state via radiative and non-radiative paths or react via either unimolecular or bimolecular processes. When the MLCT transition is selectively pumped, the ^{3}IL state can only be populated if it is lower in energy than the ^{1}MLCT state. There are a growing number of complexes for which this condition is true and the photophysical behavior of such complexes indicates that, in many instances, the ^{3}MLCT and ^{3}IL states interact weakly and decay independently to the ground state (e.g. thermal equilibrium in the triplet manifold is not achieved). A separate internal conversion process observed from the ^{3}MLCT state of some complexes involves formation of a triplet ligand field state (^{3}LF, not shown in the diagram) followed by ligand dissociation. The ^{3}LF state has not been observed directly but, for $[Ru(bpy)_3]^{2+}$ and many other complexes, is believed to be populated via a thermally activated process which leads to ligand loss [1,2]. The formation and reactivity of this state will not be discussed here, although there is no reason why LF reactivity cannot occur in complexes for which both intraligand and MLCT triplets coexist.

2. Detection of coexisting states

A number of experimental approaches can be used to observe involvement of multiple long-lived excited states. While definitive proof of the existence of two coexisting excited states can be obtained when both states exhibit luminescence, this is often not the case. Most traditional photochemical methods provide only necessary supporting evidence for the existence of states other than the ^{3}MLCT state. In general, more than one experimental approach must be taken to establish clearly the existence of each state. The discussion below outlines various methods used in the identification of coexisting excited states.

2.1. *Luminescence spectroscopy*

By far the most direct approach for observing the coexistence of two triplet states is luminescence spectroscopy. This approach is especially effective for low temperature matrices where ^{3}MLCT emission is usually broad and has little or no vibrational structure, whereas ^{3}IL emission often exhibits extensive vibrational structure and occurs at frequencies nearly the same as the free ligand phosphorescence. In a few instances emission from both ^{3}MLCT and ^{3}IL states has been observed. An early report is that of Wrighton and coworkers for 77 K emission from $[L_2Re^{+}(CO)_3X]^{+}$ (L = 3-benzoyl-pyridine, X = Cl^-, Br^-, I^-) [8,9]. In this work they illustrate the close correspondence between phosphorescence from the free and coordinated ligand. More recently Demas and coworkers have observed dual luminescence from $[(CO)_3XRe^{I}(L')]$ complexes (X = Cl^-, L' = substituted phen) [11]. In these complexes the two emitting states are very close in energy. Complexes also exist for which the steady state luminescence is observed from a single state, but time-resolved emission spectra indicate the existence of two emitting states. An example is shown in Fig. 3 for the complex $[(CO)_3(AN)Re(sty\_bpy)]^{+}$ (AN = CH_3CN, sty_bpy shown in Fig. 1). The structured steady state luminescence observed in low temperature glasses originates from a ^{3}IL state localized on the sty_bpy ligand. In the time-resolved emission, the spectrum obtained over the first 200 ns following excitation clearly shows luminescence from the Re(dπ) → sty_bpy(π*) ^{3}MLCT state [12].

2.2. *Measurement of intersystem crossing efficiencies to luminescent excited states*

For second- and third-row transition metal diimine complexes, intersystem crossing is the predominant process of the ^{1}MLCT state and efficiencies less than unity for populating the luminescent excited state are suggestive of intersystem crossing to another state in the triplet manifold. For $[Ru(bpy)_3]^{2+}$ and several other Ru^{2+} diimine complexes, intersystem crossing occurs with 100% efficiency [1–3]. One method for determining intersystem crossing yields is to measure the quantum yield for an irreversible bimolecular photoreaction involving the ^{3}MLCT excited state. For example, the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ reacts irreversibly with $S_2O_8^{2-}$ to produce SO_4^{2-} and the $SO_4^{-\cdot}$ radical anion, a strong oxidant [13]. The quantum

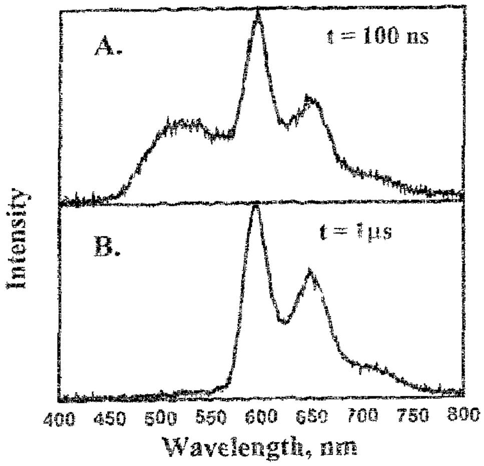

Fig. 3. Gated emission spectra of $[(CO)_3Re(AN)(sty\_bpy)]^+$ in 4:1 EtOH:MeOH at 77 K obtained (A) 100 ns following excitation and (B) 1 μs following 337 nm excitation. Gate width 100 ns.

yield for this reaction in the limit of infinite $S_2O_8^{2-}$ is 2 and that is the value found for $[Ru(bpy)_3]^{2+}$. Limiting quantum yields less than 2 suggest inefficient intersystem crossing to the ^{3}MLCT state.

A simpler and more widely applicable approach is to evaluate the ratio of the luminescence quantum yield and the lifetime of the emitting excited state. The ratio yields the product of the intersystem crossing efficiency η_{isc} and the radiative decay rate constant of the emissive state k_r:

$$\Phi_{em}/\tau_{em} = \eta_{isc}k_r \tag{1}$$

A large number of Ru(II) and Re(I) complexes having diimine ligands exhibit luminescence from ^{3}MLCT states. Among complexes for which η_{isc} is known to be unity, values of η_{isc} k_r are generally $8 \pm 4 \times 10^4$ s^{-1}, even though the emission energies span a gap of over 3000 cm^{-1} [1,2].[1] As a result, experimental values of $\eta_{isc}k_r$ which are substantially lower than 10^4 s^{-1} suggest the intersystem crossing efficiency to populate the ^{3}MLCT state is less than unity. This approach provides supporting evidence for population of a ^{3}IL or other triplet state (i.e. ligand field) directly from the ^{1}MLCT state, but is not sufficient to establish the existence of the ^{3}IL state.

2.3. *Excited state relaxation dynamics*

Even in systems where luminescence clearly arises from a single excited state, another non-emissive state may exist. If the states are not thermally equilibrated, this can result in non-exponential decay kinetics for the emitting state. For instance, in complexes having nearly isoenergetic ^{3}IL and ^{3}MLCT states, luminescence may

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[1] Note that, while $k_r \propto E_{em}^3$, this results in a decrease of k_r by a factor of only two for emission over the range of 600 to 750 nm.

occur from one state exclusively and the other state may internally convert to populate the emissive state at a rate which is slow relative to the emission. The room temperature emission of [(bpy)$_2$Ru(bpy_pyr)]$^{2+}$ (Fig. 1) represents such a case. The emission occurs exclusively from the ^{3}MLCT state in CH$_3$CN, yet the luminescence decay is double exponential with lifetimes of 900 ns and 50 μs [14]. The long decay component is associated with internal conversion from the pyrene localized ^{3}IL state to the ^{3}MLCT state of the complex (*vide infra*). Of course, a significant caveat in this approach to identifying the presence of a non-emissive state is that it is often not possible to exclude impurity luminescence as an explanation for the non-exponentiality.

2.4. Transient absorption spectroscopy

The lack of observable luminescence for complexes having MLCT absorption generally indicates that non-radiative relaxation of the ^{3}MLCT excited state is orders of magnitude faster than radiative relaxation (e.g. $k_{nr} > 10^9$ s^{-1}). However, complexes have been observed that exhibit no luminescence (even in glasses at 77 K) but have a long-lived (>100 ns) excited state absorption which can be attributed to a ^{3}IL state. One complex exhibiting this behavior is [(bpy)$_2$Ru(dmpbq)]$^{2+}$ [15]. Whereas the complex is only very weakly luminescent in solution, it exhibits transient absorbance (Fig. 4) throughout the visible with a lifetime of approximately 960 ns in degassed CH$_3$CN. The transient absorbance closely resembles the spectrum obtained from the difference between the free ligand transient absorbance and the ground state absorption (dashed line of Fig. 4).

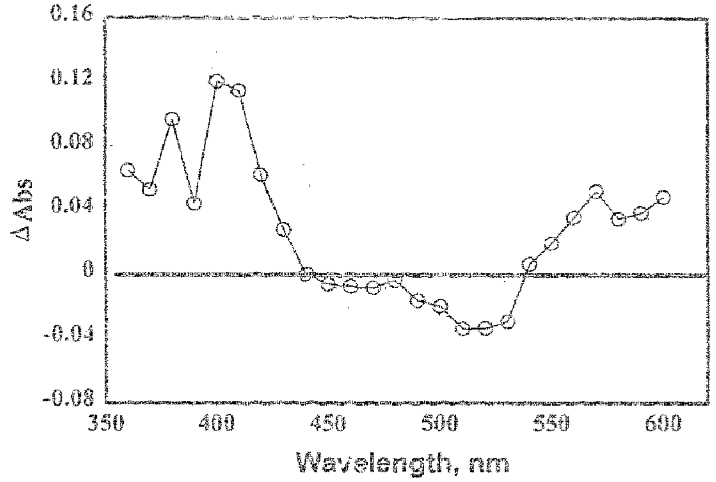

Fig. 4. Transient absorption spectrum of [(bpy)$_2$Ru(dmpbq)]$^{2+}$ in N$_2$-purged CH$_3$CN following excitation at 532 nm. Dashed line represents the spectrum calculated from the difference of ligand dmpbq transient absorbance and the complex ground-state absorption spectrum.

2.5. Photoselection techniques

Emission photoselection spectroscopy can be used to determine the relative orientation of an emitting state for randomly oriented samples (e.g. not single crystals). For complexes having two emitting states, knowledge of the relative orientation of the oscillators can aid in understanding factors that influence interconversion between the two emitting states. In addition, if the emission from both states overlaps extensively, the wavelength dependence of the emission polarization can provide evidence that two different emitting states actually exist. The technique has been employed extensively by DeArmond and coworkers in examining dual luminescence in Ru(II), Rh(III) and Ir(III) complexes [16–18].

2.6. Time-resolved infrared and Raman spectroscopy

Recent collaborative work of Stufkens and coworkers has showed that time-resolved infrared (TRIR) and time-resolved resonance Raman spectroscopy (TR^3) can be used to evaluate the nature of lowest energy excited states of d^6 diimine complexes [19]. For the series $[Ru(X)(R)(CO)_2(\alpha\text{-diimine})]$, they were able to show that the lowest energy excited state goes from being MLCT to XLCT as X is changed from Cl^- to I^- [19,20]. The conclusions are based upon the relative increase observed in the CO stretching frequency versus the relative decrease in the CN (diimine) stretches for the series. The use of TRIR and TR^3 has great potential for use in assignment of excited states and investigation of intramolecular energy migration processes.

2.7. Quenching of luminescence and transient absorption with triplet quenchers

One approach for determining the excited state energy of chromophores exhibiting either luminescence or measurable transient absorbance is to examine the free energy dependence of the rate constant for triplet quenching. The process is bimolecular, and the second-order rate constant will increase with increasing free energy ($\ln(k_{en}) \propto -\Delta G/k_b T$) until the diffusion limit is reached [21,22]. Fig. 5 shows the free energy dependence for quenching of luminescence at 14 700 cm^{-1} ($\tau_{em} = 660$ ns) and transient absorbance at 18 000 cm^{-1} ($\tau_{TA} = 1.6$ μs) for the complex $[(bpy)_2Ru(bpy\_dvb\_bpy)]^{2+}$ [23]. For the series of triplet quenchers used, the excited state absorption is not quenched efficiently by quenchers with energies above approximately 14 000 cm^{-1}, whereas the emission is quenched with rate constants in excess of 10^9 M^{-1} s^{-1} for all the triplet quenchers used. Such experiments can provide conclusive evidence of the coexistence of two non-equilibrated excited states.

2.8. Time-resolved photoacoustic calorimetry

Photoacoustic and thermal lens techniques have been used effectively for the evaluation of excited state energies and intersystem crossing efficiencies in transition

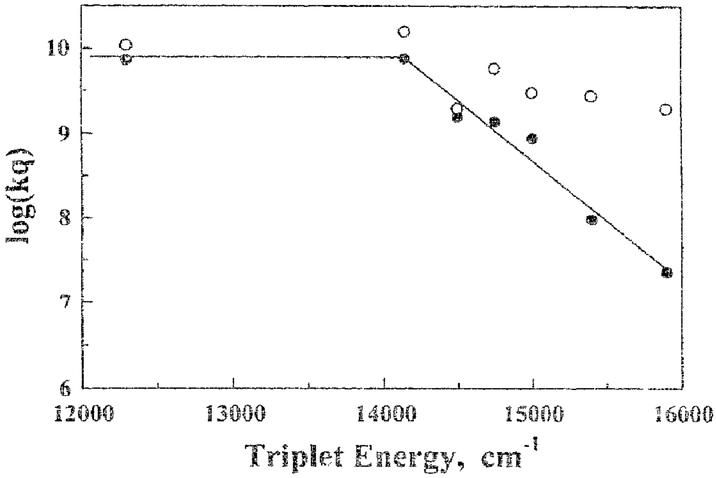

Fig. 5. Free energy dependence of luminescence (at 14 700 cm^{-1},) and transient absorbance (at 18 000 cm^{-1}, ●) for the complex $[(bpy)_2Ru(bpy\_dvb\_bpy)]^{2+}$. In order of decreasing triplet energy the quenchers are acridine, phenazine, anthracene, 9-chloroanthracene, 9,10-diphenylanthracene, 9,10-dichloroanthracene and perylene.

metal complexes [24–27]. Song and Endicott have used the technique to evaluate the energy of the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ [24]. In an application relating to the determination of excited state energy in a complex having two accessible states, Harriman and coworkers used time-resolved thermal lensing to determine the triplet state energy of $\{[(bpy)_2Ru]_2(bdpb)\}^{4+}$ [27].

3. Orbital parentage and relative energies of MLCT and IL excited states in monometallic complexes

Many of the transition metal complexes that have been shown to have multiple emissions are those for which the two states can be viewed as being spatially isolated with regard to the orbitals associated with each state. For instance, mixed ligand complexes of the type $[Rh^{3+}(bpy)_x(phen)_{3-x}]^{3+}$ ($x = 0$–3) exhibit dual luminescence from two different $^3(\pi\rightarrow\pi^*)$ excited states localized on the bpy and phen ligands [6,28,29]. Watts and coworkers also observed luminescence from both ligand field and $^3(\pi\rightarrow\pi^*)$ excited states in Ir^{3+} complexes [28,29]. In such complexes the inefficiency of internal conversion which leads to multiple emission can be associated with weak electronic interaction of the two isolated excited states.

Also interesting are complexes that have multiple excited states in the triplet manifold with similar orbital parentage. In such cases the two states are expected to be much more strongly coupled. Mentioned above are the $[(phen)_2Rh^{3+}Cl_2]^+$ complexes reported by Watts and the Re^+ benzoylpyridine complexes of Wrighton which exhibit luminescence from both a $d\pi\rightarrow\pi^*$ ^{3}MLCT state and a ^{3}IL state involving the same aromatic heterocyclic ligand [6–9]. For $[(L)_2Re^+(CO)_3X]$ (L = 3 and 4-benzoylpyridine, 3_bp and 4_bp; X = Cl), Wrighton and coworkers found that the 4_bp complex exhibits emission exclusively from the ^{3}MLCT state and the 3_bp derivative emits from both the ^{3}MLCT and ^{3}IL states at 77 K. The difference in behavior was attributed to the difference in energy between the two states in the two complexes. In the 4_bp complex the ^{3}MLCT state lies approximately 4000 cm^{-1} below the $^3(n\rightarrow\pi^*)$ state, whereas the two states are nearly isoenergetic in the 3_bp complex [8,9]. In these and other complexes, the dual luminescence behavior is observed either in single crystals or in low temperature glasses. In such media, it is generally not possible to discount the existence of multiple emitting species associated with inhomogeneities of the matrix, especially when the energy difference between the two states is small. As a result, the remainder of this discussion will focus on the behavior of complexes in solution at room temperature.

3.1. Re⁺ complexes

Numerous Re^+ complexes having *N*-heterocyclic ligands with relatively low energy ^{3}IL states exhibit phosphorescence from the ^{3}IL state which can be detected in solution [30–33]. Table 1 presents photophysical properties of Re(I) diimine complexes in acetonitrile solution [8,9,28–33,35]. Most of the complexes exhibit luminescence which decays as a single exponential, regardless of the emitting state. Those assigned as emitting from a $^3(\pi\rightarrow\pi^*)$ state exhibit structured emission in solution, whereas ^{3}MLCT state luminescence is a single broad band. It is clear from the data that values of $\eta_{isc}k_r$ vary over many orders of magnitude; complexes which emit, unperturbed, from a ^{3}MLCT state have values in excess of 10^5 s^{-1}, whereas

Table 1
Physical properties of *fac*-$[(CO)_3XRe(L')]$ complexes in CH_3CN at 298 K

X[a]	L[b]	$E_{L'}$, $\pi\rightarrow\pi^*$ (cm^{-1})[c]	E_{em} (cm^{-1})[c]	τ_{em} (μs)	$\eta_{isc}k_r$ (s^{-1})	Excited state	Ref.
AN	dmb	22 900	18 800	0.66	60 600	$d\pi\rightarrow\pi^*$	[12]
CO	dmb	22 500[d]	22 500	2.3	14 300	$\pi\rightarrow\pi^*$	[30,31]
TBI	phen	21 700[d]	19 000	7.4	65 700	$d\pi\rightarrow\pi^*$	[11]
TBI	tmphen	21 200[d]	21 000	74.6	3000	$\pi\rightarrow\pi^*$	[11]
TBI	dmphen	20 800[d]	20 800	60.1	6100	$\pi\rightarrow\pi^*$	[11]
AN	phen	20 000	18 800	0.8	NA	$d\pi\rightarrow\pi^*$	[8,9]
MPy	dppz	17 950	17 950	18.5	11	$\pi\rightarrow\pi^*$	[34]
AN	sty_bpy	16 800	17 900	0.55	1450	$d\pi\rightarrow\pi^*$	[12]
AN	bpy_dvb_bpy	14 390[d]	14 390	4.7	< 20	$\pi\rightarrow\pi^*$	[12]

[a] AN = acetonitrile, Mpy = 4-methylpyridine, TBI = t-butylisocyanide.

[b] tmphen = 3,4,7,8-tetramethylphenanthroline, dmphen = 4,7-dimethylphenanthroline.

[c] Energy approximated from triplet energy of related hydrocarbon (i.e. phen ~ phenanthrene) unless otherwise noted.

[d] Emission maximum of highest energy vibronic component.

those exhibiting structured phosphorescence can have $\eta_{isc}k_r$ values of less than $50\ s^{-1}$.

A particularly nice demonstration of the change from ^{3}MLCT to ^{3}IL excited state luminescence with changing diimine was reported by Demas and coworkers for the series *fac*-$[(CO)_3(TBI)Re^+(L)]^+$ (L = phen, dmphen and tmphen; TBI = t-butylisocyanide) [11]. The phen complex, having the highest energy ^{3}IL state, emits from the ^{3}MLCT state. Upon alkylation of the phen, the energy of the $^3(\pi\rightarrow\pi^*)$ state decreases slightly, resulting in structured ^{3}IL luminescence. These complexes have relatively large radiative decay rate constants for emission from a $^3(\pi\rightarrow\pi^*)$ state; this may reflect significant mixing with the ^{3}MLCT state. In the complexes $\{[(CO)_3(AN)Re^+]_2(bpy\_dvb\_bpy)\}^{2+}$ and $[(CO)_3(MPy)Re^+(dppz)]^+$, structured ^{3}IL luminescence is also observed in room temperature solutions [12,34]. In each of these complexes the $\eta_{isc}k_r$ value is very low ($<50\ s^{-1}$), indicating the state lacks significant ^{3}MLCT character.

One complex from Table 1 has characteristics that suggest the presence of both ^{3}IL and ^{3}MLCT states in solution at room temperature. The complex $[(sty\_bpy)Re^+(CO)_3(AN)]^+$ emits weakly from a ^{3}MLCT state with a maximum at $18\,000\ cm^{-1}$; however, the energy of the $^3(\pi\rightarrow\pi^*)$ state of the sty_bpy ligand is lower: approximately $16\,800\ cm^{-1}$ [12]. The radiative decay rate constant of the room temperature ^{3}MLCT emission ($\eta_{isc}k_r = 1400\ s^{-1}$) is very low. The implication is that either (a) the intersystem crossing efficiency is significantly less than unity for populating this state and the sty_bpy $^3(\pi\rightarrow\pi^*)$ state is providing an alternate path for relaxation of the ^{1}MLCT state or (b) the emitting ^{3}MLCT state has a much higher degree of triplet character because of mixing with the ^{3}IL state. It is possible that the ^{3}IL state is populated, but decays via trans–cis isomerization; such isomerization has been documented to occur upon photolysis of Ru^{2+} styrylpyridine complexes [36].

3.2. Ru^{2+} complexes

A few monometallic Ru^{2+} diimine complexes of the type $[(bpy)_2Ru^{2+}(L)]^{2+}$ exist which exhibit evidence for coexistence of triplet intraligand and MLCT states. Among the complexes reported, luminescence is always from the ^{3}MLCT state, represented in Table 2 as E_{MLCT}. For those ligands for which phosphorescence could not be obtained, the energy of the $^3(\pi\rightarrow\pi^*)$ state was approximated by the energy of the hydrocarbon having the structure most similar to the *N*-heterocyclic ligand (i.e. vbpy = styrene). Table 2 also reports the luminescence lifetimes of the complexes and values of $\eta_{isc}k_r$ obtained from the ratio of the emission quantum yield and the luminescence lifetime in CH_3CN. Since the energy of the ^{1}MLCT state of the complexes is at least $19\,000\ cm^{-1}$,[2] all except for the complexes of vbpy, dmb and bphb have $^3(\pi\rightarrow\pi^*)$ states which are accessible following excitation into the ^{1}MLCT absorption. The complexes of dmb, vbpy and bphb all have $\eta_{isc}k_r$ values

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[2] This is an estimate made assuming the red edge of the absorption of the complexes listed is at energies greater than or equal to $19\,000\ cm^{-1}$ (525 nm).

Table 2
Physical properties of $[(LL)_2RuL']^{2+}$ complexes in acetonitrile at 298 K

LL	L′	Analogous HC[a]	E_{HC} (cm^{-1})	E_{MLCT} (cm^{-1})[b]	Δt (cm^{-1})	τ_{em} (ns)	$\eta_{isc}k_r$ ($s^{-1} \times 10^{-4}$)	Ref.
dmb	dmb	biphenyl	22 900	15 900	7000	950	11.0	[37]
dmb	vbpy	styrene	21 700	14 900	6800	1350	5.6	[37]
dmb	bphb	*p*-terphenyl	20 200	15 800	4400	1340	7.9	[38]
bpy	dppz	1,2:3,4-dibenzanthracene	17 900	16 500	1400	663	5.0	[39]
dmb	bbpe	stilbene	16 600[c]	13 700	2900	1150	0.9	[37]
bpy	bpy_pyr	pyrene	16 300[c]	15 600	700	1300	7.5 (0.17)[d]	[14]
bpy	dmpbq	anthracene	14 900	12 800	2100	35	1.7	[15]
dmb	bpy_dvb_bpy	1,4-distyrylbenzene	14 100[c]	14 700	−600	622	0.91	[23]

[a] Hydrocarbon representing the carbon skeleton of the fused ring portion of the ligand or simple aromatic hydrocarbon of similar structure.

[b] From absorption maximum of MLCT luminescence.

[c] Triplet energy measured for the ligand from phosphorescence in low temperature matrix.

[d] This complex has a double exponential luminescence decay. The product calculated is for the short-lived luminescence component. An additional 57 μs emission exists; this, combined with Φ_{em}, yields a value for $\eta_{isc}k_r$ of 1700 s^{-1}.

greater than 50 000 s^{-1}, typical of emission from ^{3}MLCT states having unity η_{isc} values. The widely studied, DNA-binding complex $[(bpy)_2Ru^{2+}(dppz)]^{2+}$ also has an $\eta_{isc}k_r$ value large enough to suggest $^1MLCT \rightarrow ^3(\pi \rightarrow \pi^*)$ intersystem crossing is not a significant path for excited state non-radiative relaxation even though the ^{3}IL state is lower in energy than the ^{1}MLCT state [39]. The remaining complexes all exhibit unique behavior which requires discussion. The complexes all have $\eta_{isc}k_r$ values which are less than 10 000 s^{-1}, suggesting competitive intersystem crossing to some other triplet excited state in the complex.

Meyer and coworkers have thoroughly examined the photophysical behavior of $[(dmb)_2Ru^{2+}(bbpe)]^{2+}$ and have concluded that the relatively long luminescence lifetimes observed are the result of a decrease in bond displacement changes in the excited state relative to other Ru^{2+} diimine complexes [37,40]. The low radiative decay rate constant (η_{isc} is assumed to be unity) is attributed to a combination of a smaller transition dipole moment and lower emission energy for the $d\pi \rightarrow \pi^*$(bbpe) MLCT transition relative to $d\pi \rightarrow \pi^*$(dmb) transition of $[Ru(dmb)_3]^{2+}$. The approximation leads to a ratio of radiative decay rate constants $k_{r,dmb}/k_{r,bbpe} = 3.3$; the experimental ratio is 12. It is possible that the relatively low radiative decay rate constant observed reflects a contribution from direct $^1MLCT \rightarrow ^3IL$(bbpe) intersystem crossing. If the ^{3}IL state is formed in this complex, isomerization of the bbpe ligand would be expected to occur. In a separate report, weak luminescence at 15 600 cm^{-1} ($\eta_{isc}k_r = 6700$ s^{-1}) was reported from the complex $[(dmb)_2Ru^{2+}(bbdb)]^{2+}$, the butadiene-bridged bis-bipyridine analog of bbpe; however, it was not possible to discount the possibility of impurity emission in this complex [38].

A closely related complex is $[(dmb)_2Ru^{2+}(bpy\_dvb\_bpy)]^{2+}$. The reported

^{3}MLCT luminescence maximum for this complex is 1000 cm^{-1} higher in energy (14 700 cm^{-1}) and the luminescence lifetime is roughly half that (τ_{em} = 620 ns) of the bbpe complex [23]. Another related complex, [Ru^{2+}(dsty_bpy)$_3$]$^{2+}$, also has an emission maximum at 14 700 cm^{-1} and a luminescence lifetime of 720 ns ($\eta_{isc}k_r$ = 40 000 s^{-1}) [41]. For the bpy_dvb_bpy complex, the transient absorbance lifetime is 1660 ns, clearly indicating the presence of a second excited state; it was also shown that the the transient absorbance and emission differed in the free energy dependence for quenching with a series of triplet quenchers (Fig. 5). From the free energy dependence for quenching the transient absorbance, the energy of the state was estimated to be 14 200 cm^{-1}, nearly the same as the triplet energy of the structurally related hydrocarbon 1,4-distyrylbenzene reported by Sandros et al. [42]. Thus, in this case, strong evidence for population of a ^{3}IL excited state and coexistence of ^{3}MLCT and ^{3}IL states was obtained.

Another complex clearly exhibiting coexisting ^{3}IL and ^{3}MLCT states is [(bpy)$_2$Ru^{2+}(dmpbq)]$^{2+}$ [15]. The complex exhibits weak luminescence at 12 800 cm^{-1} with a lifetime of 35 ns (Table 2). The excited state absorption has a lifetime of over 900 ns; further, subtraction of the ground state absorption of the complex from the excited state spectrum of the dmpbq ligand (at wavelengths where the ground state of the ligand does not absorb) yields a calculated spectrum nearly identical to the transient spectrum of the dmpbq complex. If the triplet energy of the ligand is assumed to be nearly the same as the aromatic hydrocarbon skeleton of the fused aromatic portion of the ligand (anthracene), the ^{3}IL excited state will have an energy of approximately 14 900 cm^{-1}, 2100 cm^{-1} above the ^{3}MLCT state. The implication is that the ^{3}IL state is very weakly coupled to the ^{3}MLCT state in this complex (so weakly coupled that non-radiative relaxation of the ^{3}IL state occurs without significant internal conversion to the ^{3}MLCT state, which would give rise to a long-lived luminescence component).

Finally, [(bpy)$_2$Ru^{2+}(bpy_pyr)]$^{2+}$ represents an example of a complex wherein interconversion between the pyrene localized $^3(\pi\rightarrow\pi^*)$ state and the ^{3}MLCT state can be viewed as an intramolecular electronic energy transfer process since the pyrene is relatively spatially isolated from the coordination sphere [14]. The luminescence of this complex is relatively efficient and has a double exponential decay with components of 1300 ns and 57.4 μs, as shown in Fig. 6. The luminescence is very sensitive to the presence of O$_2$, and aerated solutions of the complex yield a single exponential decay with a lifetime of 300 ns. Time-resolved emission spectra indicate the spectral bandshape is invariant over the duration of the decay. Both the room temperature and 77 K glass emission spectra are representative of emission from a ^{3}MLCT state. At room temperature the zero–zero emission energy for the ^{3}MLCT state is approximately 16 000 cm^{-1}. The phosphorescence from the bpy_pyr ligand at 77 K in ethyl-iodide-doped glasses yields a zero–zero emission energy of 16 300 cm^{-1}. Given that energies of $^3(\pi\rightarrow\pi^*)$ states of aromatic hydrocarbons are nearly independent of temperature or the matrix, it can be concluded that the $^3(\pi\rightarrow\pi^*)$ state of the pyrene in [(bpy)$_2$Ru^{2+}(bpy_pyr)]$^{2+}$ is at slightly higher energy than the ^{3}MLCT state. Thus, the pyrene $^3(\pi\rightarrow\pi^*)$ state is serving as a reservoir for

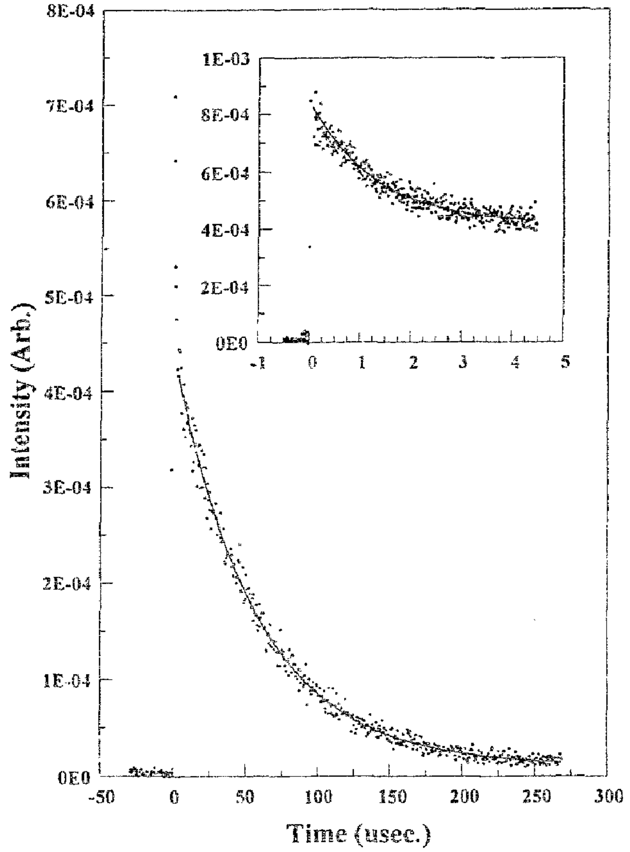

Fig. 6. Room temperature luminescence decay of $[(bpy)_2Ru(bpy\_pyr)]^{2+}$ in acetonitrile solution. The decay fits a double exponential with components of 1300 ns and 57.4 μs.

luminescence from the lower energy ^{3}MLCT state:

$$[(b)_2Ru^{II}(bpy\_{}^3pyr)]^{2+} \leftrightarrow [(b)_2Ru^{III}(bpy\_pyr^-)]$$
$$\rightarrow [(b)_2Ru^{II}(bpy\_pyr)]^{2+} + h\nu \qquad (2)$$

The dynamics of dual luminescence decays collected over a range of temperatures can be quantitatively explained by assuming that excitation into the ^{1}MLCT absorption is followed by intersystem crossing to both ^{3}IL and ^{3}MLCT states. The initially formed ^{3}MLCT state decays with a lifetime of 1300 ns and the ^{3}IL state decays via slow internal conversion to the ^{3}MLCT state, giving rise to the long-lived luminescence decay component.

4. Polyene-bridged bimetallic complexes

Several of the complexes of Fig. 1 are bis-bipyridine derivatives capable of serving as bridging ligands. The polyene-bridged bis-bipyridines exhibit large differences in

Table 3
Redox and photophysical properties of $\{[(dmb)_2Ru]_2(LL)\}^{4+}$ complexes in room temperature CH_3CN

LL	$E(5+/4+)$ (V)[a]	$E(4+/3+)$ (V)[a]	λ_{max}^{abs} (nm)	E_{em} (cm^{-1})	Φ_{em}	τ (ns)[b]	$\eta_{isc}k_r$ (s^{-1})	λ_{max}^{TA} (nm)
bbpe	1.16	−1.07	500	13 300	0.005	1310	4000	630
bbdb	1.14	−1.05	500	12 800	<0.001	540	~1800	725
bdpb	1.08	−0.90	540	NA	NA	200	NA	660

[a] Versus SSCE.

[b] Measured from luminescence of bbpe and from transient absorbance of bbdb and bdpb.

redox and photophysical behavior between the monometallic, $[(dmb)_2Ru^{2+}(L)]^{2+}$, and the bimetallic, $\{[(dmb)_2Ru^{2+}]_2L\}^{4+}$, complexes. The bimetallic complexes of bbpe, bbdb and bdpb were studied by three different research groups [37,40,38,27]. The redox and photophysical properties of the complexes are summarized in Table 3. In the bbpe and bbdb complexes the $\eta_{isc}k_r$ values are below 5000 s^{-1}, again suggesting the possibility of intersystem crossing to a state other than the ^{3}MLCT state. The triplet energies of bbdb and bdpb were estimated from the free energy dependence for quenching the ligand transient absorbance to be 14 100 cm^{-1} and 12 500 cm^{-1} respectively. Both these energies are certainly below the energy of the ^{1}MLCT state, given that the absorption maxima for the MLCT transitions are 20 000 cm^{-1} for the bimetallic bbdb complex and 18 500 cm^{-1} for the bdpb complex. All three complexes have transient absorption spectra showing bleaching of the ground state absorbance and a prominent absorbance at wavelengths greater than 550 nm (Fig. 7). The transient absorbance of the bbdb and bdpb complexes is efficiently

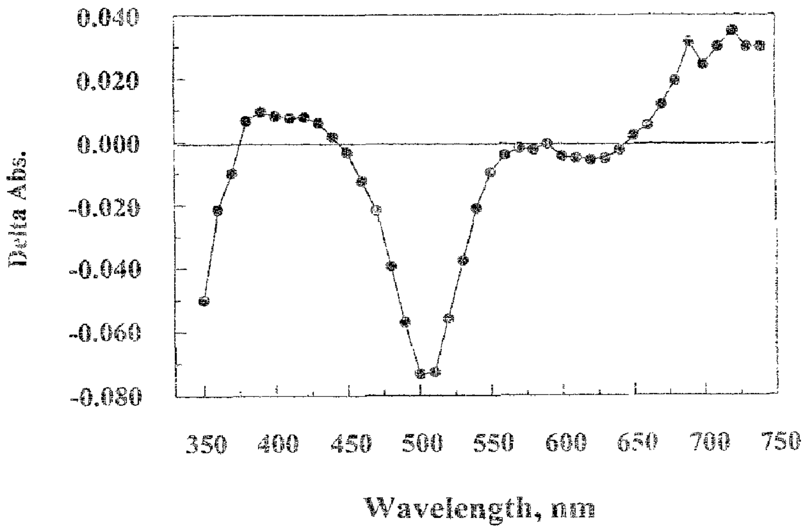

Fig. 7. Excited state absorption spectrum of $\{[(bpy)_2Ru]_2bbdb\}^{4+}$ in CH_3CN 200 ns following excitation at 532 nm.

quenched by O_2 (for bbdb the TA decays with a lifetime of less than 10 ns); this behavior is characteristic of organic triplet excited states [37,40,27]. TR^3 spectra obtained for the bbpe complex indicate that the ground state 1638 cm^{-1} C=C stretch of the ethylene moiety disappears and new bands appear at 1578 cm^{-1} and 1585 cm^{-1}. For the related hydrocarbon stilbene, the ground-state stretch at 1638 cm^{-1} shifts to 1578 cm^{-1} in the anion radical and 1586 cm^{-1} in the lowest lying triplet [37]. Thus, assignment of the excited state is inconclusive, but could be interpreted as being a mixture of coexisting ^{3}MLCT and ^{3}IL states.

5. Conclusions

The results presented here indicate that d^6 complexes of second- and third-row transition elements with *N*-heterocyclic ligands having triplet excited states accessible from the ^{1}MLCT state can exhibit behavior consistent with concomitant existence of two very weakly interacting excited states. The factors affecting intersystem crossing into each of the triplet manifolds and internal conversion between the two triplets have not been systematically investigated for these complex chromophores; there is a need for detailed spectroscopic investigations analogous to those of Gudel and coworkers [43] and Rillema and coworkers [44] for Re^+ bpy and phenanthroline complexes.

Acknowledgements

The authors wish to thank the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, under contract DE-FG02-96ER14617, and the Tulane Center for Photoinduced Processes for support of this work.

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