

SELECTIVE PERTURBATION OF LIGAND FIELD EXCITED STATES[†]

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Summary

The photophysics of polypyridine ruthenium(II) complexes have generated intense interest recently. One controversial process involves the thermal population of a higher-lying ligand field (LF) state during the lifetime of the lowest excited triplet metal-to-ligand charge transfer (MLCT) state. In order to substantiate this thermal process, several series of closely related complexes were prepared and their photophysics examined. The results clearly suggest thermal population of an LF state. In one example, the LF state was selectively perturbed while the MLCT states were nearly unchanged energetically. This approach which involves a novel ligand, 4,5-diazafluorene, nicely complements selective perturbation of MLCT states by introduction of electron-withdrawing substituents.

1. Introduction

In recent years, the photophysical and photochemical behavior of polypyridine ruthenium complexes has been extensively examined. (The literature in this field is indeed rich with many more important contributions than can be listed; thus only a representative review is offered [1].) The interest in these complexes stems from several facts. First, these complexes often exhibit intense emission from long-lived excited states which greatly facilitates their investigation. Hence, many of the currently emerging concepts of organometallic and inorganic photochemistry have been quantitatively verified using these complexes [1]. Second, these complexes have been extensively investigated as potential components in systems capable of photochemically producing hydrogen from water [2].

The solution phase UV-visible absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} \equiv 2,2'$ -bipyridine) consists of three major absorption bands, centered at 244, 285 and 438 nm [1]. The first and third bands exhibit fine structure and have been assigned as metal-to-ligand charge transfer (MLCT) transitions

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[1]. The second band occurs in the same region as the $\pi-\pi^*$ transition of the diprotonated form of bipyridine and has consequently been assigned as an intraligand transition.

The $\text{Ru}(\text{bpy})_3^{2+}$ complex displays a relatively intense emission whose quantum efficiency is wavelength independent. Thus, excitation at any wavelength below approximately 560 nm results in rapid formation of the lowest excited MLCT state. This initially formed state has been suggested to contain largely singlet character and to undergo intersystem crossing with unit efficiency to the corresponding triplet MLCT state [3]. The emission is then assigned as phosphorescence from this $^3\text{MLCT}$ state. Since rather large spin-orbit coupling obtains in $\text{Ru}(\text{bpy})_3^{2+}$ the use of pure spin labels may not be justified [4]. However, most photophysical features of $\text{Ru}(\text{bpy})_3^{2+}$ can be rationalized in terms of a model assuming D_3 symmetry and incorporating spin-orbit coupling for the d^5 ruthenium(III) core [5]. Hence, the use of these spin labels will be maintained with the understanding that singlet-triplet mixing does occur.

Because of the readily observed emission, this lowest excited $^3\text{MLCT}$ state has been extensively investigated. On the basis of low temperature studies, Baker and Crosby [6] have concluded that this state actually consists of three closely spaced states that have widely different lifetimes. However, at 298 K all three states are populated and hence can be considered to be an "average state". The symmetry of this excited state also appears to be C_2 rather than D_3 [7]. Thus, this $^3\text{MLCT}$ state can best be described as $\text{Ru}(\text{III})(\text{bpy})_2(\text{bpy}^-)$, *i.e.* the excitation is not delocalized over all three bipyridine ligands but rather is localized on a single ligand.

This $^3\text{MLCT}$ state is reasonably long lived (about 0.6 μs in water at 298 K) and is thought to be deactivated by the three processes shown in Fig. 1. One process is the radiative decay to the ground state with the accompanying emission occurring around 600 nm. For a large number of polypyridine ruthenium complexes, the values for the radiative rate constant are found to lie between 10^4 and 10^5 s^{-1} [8, 9].

A radiationless deactivation pathway is also available to this excited state. The rate constant for this process is theoretically predicted to depend

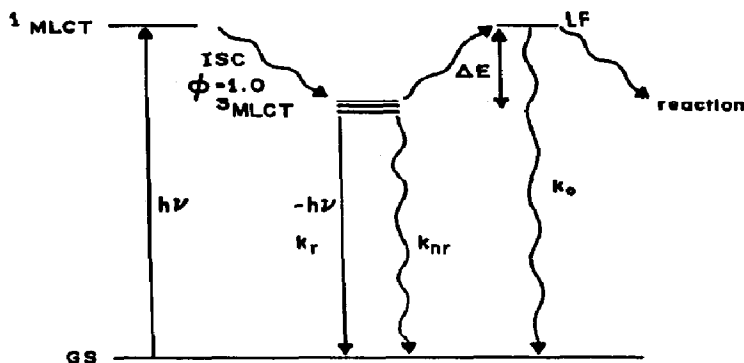


Fig. 1. Photophysical processes in $\text{Ru}(\text{bpy})_3^{2+}$.

exponentially on the energy difference between the initial ($^3\text{MLCT}$) and the final (ground) state [10]. Meyer and coworkers [11, 12] have indeed verified this expected dependence for numerous ruthenium and osmium complexes.

The radiationless rate constant is subject to a large solvent isotope effect, being 1.8 in $\text{H}_2\text{O}-\text{D}_2\text{O}$ at 298 K [13]. This large isotope effect has led Van Houten and Watts [13] to suggest that the luminescent state contains some metal-to-solvent charge transfer MSCT character. In fact, by evaluating k_{nr} for $\text{Ru}(\text{bpy})_3^{2+}$ in different solvents, Nakamura [14] estimated the relative ratio of MLCT to MSCT to be nearly unity in water.

Above 77 K, the three closely spaced $^3\text{MLCT}$ excited states are nearly equally populated and they can be thought of as an average state. The luminescence from this average triplet state displays an additional temperature dependence in the range 273 - 373 K [13, 15]. This behavior has led to the postulate that another excited state is approximately 3600 cm^{-1} above the emitting state and that this state can be thermally populated during the lifetime of the $^3\text{MLCT}$ state. The facts that this thermally populated state is non-luminescent, rapidly decays to the ground state and results in a photo-substitution reaction indicate that its identity is most likely to be a ligand field (LF) excited state [13, 15, 16].

However, Fasano and Hoggard [17] have recently studied the quenching of both emission and photosubstitution by ferrocene. Both Stern-Volmer plots were linear but had different slopes. These researchers concluded that two excited states are involved but they are not in thermal equilibrium.

In order to gain further insight into the excited state behavior of these complexes, the photophysics of several closely related complexes have been examined. The first series of complexes was selected on the basis of the expected variation in the energy of the MLCT excited states. In particular, the energy of this state has been systematically lowered and the effect on the excited state properties determined. Next, the energy of the LF state was selectively varied and the effect on the excited state properties again evaluated. This perturbation of the LF state involved the use of a novel ligand, 4,5-diazafluorene, and was selective in that the MLCT state was unaffected.

2. Experimental details

$\text{Ru}(\text{bpy})_3\text{Cl}_2$ was obtained from G. F. Smith Inc. The 4,4'-dicarboxyl-2,2'-bipyridine was prepared as described by Sprintschnik *et al.* [18] and the 4,5-diazafluorene as described by Kloc *et al.* [19].

The ruthenium complexes were prepared according to standard procedures given in the literature [18]. In all cases, acceptable elemental analyses (Galbraith Laboratories, Knoxville, TN) were obtained.

2.1. Spectra

All the absorption spectra were recorded on a Cary 14 spectrometer. All the emission spectra were recorded on an SLM4800 spectrofluorometer and are corrected for the photomultiplier response.

2.2. Quantum yield determinations

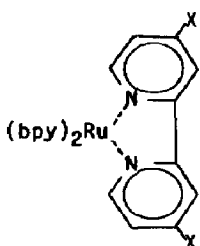
The quantum yields were determined with $\text{Ru}(\text{bpy})_3^{2+}$ in water as a standard ($\phi = 0.042$ [13, 15]). The spectra were corrected for variations in the lamp intensity and the photomultiplier response. The spectra were integrated in wavenumbers.

2.3. Lifetimes

The lifetimes were determined by the single-photon counting method [20]. The temperature was maintained by adjusting the flow of pre-cooled nitrogen gas. The sample temperature was monitored with a copper-constantan thermocouple.

3. Results and discussion

The introduction of an electron-accepting group in the *para* positions of the bipyridine ligand results in a substantial decrease in the MLCT excited state energy. This is demonstrated for I - III



- I: X \equiv H
 II: X \equiv CO₂⁻
 III: X \equiv CO₂H

in Table 1. The lifetimes at 300 K are also reported in Table 1. These lifetimes showed a pronounced temperature dependence. For both I and II, the temperature dependence is best described by

$$k_{\text{exp}} = \frac{1}{\tau} = k_r + k_{\text{nr}} + k_0 \exp\left(-\frac{\Delta E}{RT}\right) \quad (1)$$

The experimental data were fitted to eqn. (1) using a non-linear least-squares routine and the resulting parameters are shown in Table 2. In contrast, III showed a much smaller temperature dependence which was adequately

TABLE 1

Emission maxima, quantum yields and lifetimes for I - III

Complex	Solvent	λ_{max} (nm)	ϕ	τ^a (μs)
I	H ₂ O	627	0.053	0.63
II	H ₂ O	659	0.039	0.62
III	H ₂ O	686	0.006	0.29

^a300 K.

TABLE 2
Photophysical rate constants for I - III

Complex	$k_r (\times 10^5 \text{ s}^{-1})$	$k_{nr} (\times 10^5 \text{ s}^{-1})$	$k_0 (\times 10^{-13} \text{ s}^{-1})$	$\Delta E (\text{cm}^{-1})$
I ^a	0.69	1.22	1.0	3559
II	0.63	1.54	1.0	4230
III	0.21	3.43	—	310 ^b

^aRefs. 13 and 15.

^bEvaluated by using the usual Arrhenius equation.

described by an Arrhenius equation. The resulting parameters are also shown in Table 2.

The MLCT excited state varies in an orderly fashion for I - III. On the basis of their emission maxima, the energies for I, II and III are 15949 cm^{-1} , 15175 cm^{-1} and 14575 cm^{-1} respectively. If the ³MLCT and LF states do thermally communicate with one another, this bathochromic shift in the ³MLCT state should be reflected in an increased ΔE (Fig. 1). Indeed, the bathochromic shift for II is 774 cm^{-1} while the increase in ΔE is 627 cm^{-1} , and the agreement is reasonable considering the experimental difficulty.

For III, the temperature dependence of the lifetime no longer requires eqn. (1) but rather displays the usual Arrhenius behavior. This can be traced to both the increase in the activation energy for the population of the LF state and the increase in k_{nr} on protonation. The activation energy should increase by approximately 1200 cm^{-1} relative to that of I. With this activation energy, the observed decay rate due to thermal population of the LF state at 373 K can be estimated as $8 \times 10^4 \text{ s}^{-1}$. At this same temperature, the first two terms in eqn. (1) are approximately $4.5 \times 10^6 \text{ s}^{-1}$ so that the second term in eqn. (1), *i.e.* decay via the LF state, represents only a 2% change in k_{exp} . Hence, population of the LF state does not significantly compete with the direct (mostly non-radiative) decay of the ³MLCT state.

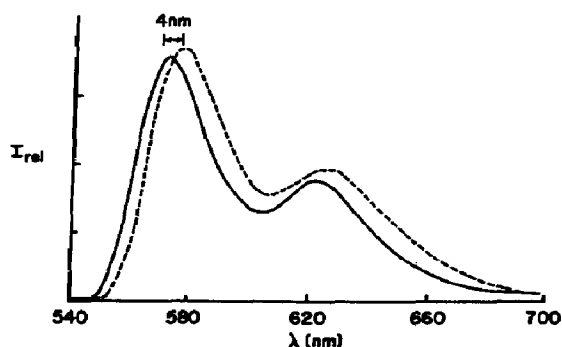
Clearly, these results implicate thermal population of the LF state from the ³MLCT state. However, further support could be obtained by selective perturbation of the LF state. Furthermore, this method would certainly be useful in numerous other complexes as a complement to selective perturbation of MLCT states.

The physical and spectroscopic properties of 4,5-diazafluorene agreed with those in the literature [19]. In order to verify that 4,5-diazafluorene is indeed a weaker ligand than bipyridine, complexes of nickel(II) were prepared. The selection of nickel(II) was based on the readily identifiable LF states for amine complexes [21]. As seen in Table 3, the LF transitions were found to undergo a bathochromic shift as the ligand was varied from bipyridine to 4,5-diazafluorene to water. Clearly, 4,5-diazafluorene is a weaker σ bonding ligand than bipyridine. (Further evidence is provided by the structure of $\text{Ni}(\text{diaz})_3^{2+}$ ($\text{diaz} \equiv 4,5\text{-diazfluorene}$), where the average

TABLE 3

Absorption spectra for nickel(II) complexes^a

Complex	${}^3A_2 \rightarrow {}^3T_2$ (cm^{-1})	${}^3A_2 \rightarrow {}^3T_1$ (cm^{-1})
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	8850	14900
$\text{Ni}(\text{diaz})_3^{2+}$ ^b	10250	16950
$\text{Ni}(\text{bpy})_3^{2+}$	12660	20830

^aWater-acetone solvent (2:1) at 298 K.^bdiaz, 4,5-diazafluorene.Fig. 2. Emission spectra for $\text{Ru}(\text{bpy})_3^{2+}$ (---) and $\text{Ru}(\text{bpy})_2(\text{diaz})^{2+}$ (—) at 77 K in EtOH-MeOH (4:1).

Ni-N bond length was determined to be 2.149 Å. The corresponding bond length in $\text{Ni}(\text{bpy})_3^{2+}$ has been reported to be 2.0891 Å [22].

The absorption spectra of I and $\text{Ru}(\text{bpy})_2(\text{diaz})^{2+}$ IV were found to be nearly superimposable. The low temperature (77 K) emission spectra for I and IV are shown in Fig. 2. The intensities and lifetimes were comparable (Table 4) and the radiative and radiationless decay rate constants were found to be similar for both complexes (Table 5). Furthermore, very few differences in the band shapes of these spectra were apparent. The small 4 nm bathochromic shift noted for I supports the contention that any MLCTs are only slightly affected by substitution of 4,5-diazafluorene for bipyridine. As the temperature is raised to 298 K, both spectra underwent a substantial bathochromic shift and a loss of fine structure. However, the most spectacular change was noted in their relative emission intensities (Table 3). At this temperature, the emission intensity for I was almost fiftyfold larger than that for IV. In fact, the emission intensity from IV was so low that the lifetime could not be evaluated.

The above results can be readily rationalized within the context of Fig. 1. As mentioned earlier, the lowest excited MLCT state is deactivated by three processes: radiative decay (k_r), radiationless decay (k_{nr}) and thermal population of a higher excited LF state ($k_0 \exp(-\Delta E/RT)$). This LF state

TABLE 4
Emission parameters for ruthenium(II) complexes

Complex	λ_{\max}^a (nm)	$\phi(77)^b$	$\tau(77)^c$ (μs)	$\phi(298)^d$	$\tau(298)^e$ (ns)
$\text{Ru}(\text{bpy})_3^{2+}$	578	0.33	5.2	4.2×10^{-2}	630
$\text{Ru}(\text{bpy})_2(\text{diaz})^{2+}$	574	0.56	5.9	8×10^{-4}	f
$\text{Ru}(\text{bpy})_2(\text{diazO})^{2+} \text{ g}$	609	0.23	4.3	5.6×10^{-3}	137
$\text{Ru}(\text{diaz})_3^{2+}$	$\approx 585^h$	Low	—	—	—

^aCorrected emission maximum at 77 K in EtOH–MeOH (4:1).

^bEmission quantum yield at 77 K in EtOH–MeOH (4:1); $\pm 20\%$.

^cEmission lifetime at 77 K in EtOH–MeOH (4:1); $\pm 10\%$.

^dEmission quantum yield at 298 K in water; $\pm 5\%$.

^eEmission lifetime at 298 K in water; $\pm 10\%$.

^fToo weak to measure.

^gdiazO, 4,5-diazafluorenone.

^hVery weak emission.

TABLE 5
Radiative and radiationless decay rate constants for polypyridine ruthenium complexes at 77 K

	$k_r^{a,b}$ ($\times 10^4 \text{ s}^{-1}$)	$k_{nr}^{a,c}$ ($\times 10^5 \text{ s}^{-1}$)
$\text{Ru}(\text{bpy})_3^{2+}$	6.3	1.3
$\text{Ru}(\text{bpy})_2(\text{diaz})^{2+}$	9.5	0.8
$\text{Ru}(\text{bpy})_2(\text{diazO})^{2+}$	5.4	1.8

^aAt 77 K in EtOH–MeOH (4:1).

^bEvaluated from $\phi(77)/\tau(77)$.

^cEvaluated from $1/\tau(77) - k_r$.

undergoes very efficient radiationless decay to the ground state. At 77 K, just the first two processes are operational and both IV and I have similar emission lifetimes and intensities. Only when the temperature is raised does thermal population of the LF state become important. Since this LF state is energetically lower in IV than in I, population is much more efficient for IV at 298 K. This results in the drastic reduction in the emission intensity noted for IV relative to that for I.

In order to substantiate these conclusions further, several other complexes have been investigated. First, $\text{Ru}(\text{bpy})_2(\text{diazO})^{2+}$ V (diazO \equiv 4,5-diazafluorenone) has been prepared and its emission properties have been examined. As seen in Table 3, the emission lifetime and intensity for this complex were found to be intermediate between those of IV and those of I. This results from the fact that 4,5-diazafluorenone is more easily reduced than 4,5-diazafluorene which necessitates a lower MLCT state. This conclusion is confirmed by the substantial bathochromic shift in the emission maximum. Consequently, both the LF and the MLCT states have been

energetically lowered with the result that their energy difference is not varied dramatically by the substitution of 4,5-diazafluorenone for bipyridine.

Additionally, $\text{Ru}(\text{diaz})_3^{2+}$ has been prepared and, again, its spectroscopic properties have been investigated. In contrast with the previous complexes, this complex did not emit at 298 K. In fact, only a very weak emission was observed even at 77 K. This weak emission displayed none of the fine structure apparent in IV and I. Consequently, we suggest that this polypyridine ruthenium(II) complex has a lowest excited state characterized by mainly a LF configuration. When the small bathochromic shift that is observed in the MLCT state is taken into account, these results suggest that the energy of the LF state has been reduced by approximately 3000 cm^{-1} . On the basis of the results for the nickel(II) complexes, this seems to be a reasonable estimate.

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