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Synthetic Manipulation of Excited State Decay Pathways in a Series of Ruthenium(II) Complexes Containing Bipyrazine and Substituted Bipyridine Ligands

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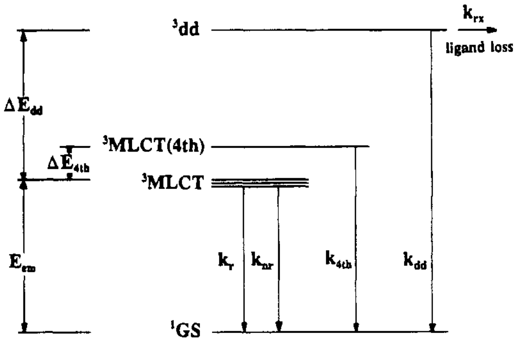
A series of heteroleptic complexes, $Ru(bpz)_2L^{2+}$ (where bpz = 2,2′-bipyrazine and L is 2,2′-bipyridine (bpy), 4,5′-diazafluorene (daf), 5-monomethyl-2,2′-bipyridine (mmb) or 4,4′-dimethyl-2,2′-bipyridine (dmb)) is studied, wherein the donor strength of the "spectator" ligand (L) is systematically increased. Attention is focused on the temperature dependence of the lifetimes of the lowest lying ^{3}MLCT states in order to reveal the relative contributions from two independent thermally activated decay pathways. One involves a high lying ligand field state (^{3}dd), while the other is associated with population of a so-called "fourth" ^{3}MLCT state which is only slightly (<1000 cm^{-1}) more energetic than the lowest energy manifold. The results show that the relative importance of each pathway is dictated by the donor strength of the spectator ligand and that in the cases of $Ru(bpz)_2(bpy)^{2+}$ and $Ru(bpz)_2(mmb)^{2+}$ both pathways participate in the overall decay.

Introduction

Intense interest in the chemistry and photophysics[1] of polypyridine complexes of ruthenium(II) continues in view of their potential utility as components of solar energy conversion devices.[2] In addition to the radiative (k_r) and direct nonradiative (k_{nr}) pathways, the relatively long-lived ^{3}MLCT excited states may relax (k_{dd} and k_{4th}) via population of two thermally accessible (so-called "ligand-field" (^{3}dd) and "fourth-MLCT" (4th)) upper states (Scheme 1).

In an exemplary series of papers, Meyer, Rillema, and coworkers[3] have shown that the nonradiative decay from the ^{3}MLCT state is governed by the energy gap law, and for most of these types of complexes the ^{3}dd state is sufficiently low in energy so as to dominate the thermal contribution to the overall relaxation rate. However, in a few cases[3a,c] the magnitude of ΔE_{dd} is sufficiently large that this pathway becomes insignificant at room temperature and below. In those cases, a different thermally activated pathway, involving another relatively low lying MLCT state, may participate substantially in the overall deactivation scheme. This state is predicted by theory[4] to possess slightly more singlet character than the manifold of the three, closely spaced, lowest energy ^{3}MLCT states.

Scheme 1. Diagram of the Excited State Deactivation Pathways in Ruthenium–Polypyridine Complexes



A better understanding of the factors which dictate the probability for population of the ^{3}dd state is desirable inasmuch as photoinduced deligation (k_{rx}) is one of the consequences associated with this decay route.[5] In fact, several strategies have been proposed to avoid this undesirable decomposition mechanism,[1] including the recent demonstrations that entrapment of such complexes within zeolite–Y supercages[6,7] apparently eliminates this decay route by increasing the magnitude of ΔE_{dd}.[7b]

In an effort to more precisely define the relative importance of the two thermally activated decay pathways as a function of ΔE_{dd}, we here report the synthesis and characterization of a series of complexes ($Ru(bpz)_2L^{2+}$ where L is the so-called spectator ligand), wherein the value of this parameter is systematically varied by utilization of several different spectator ligands of increasingly large field strength. Analysis of the temperature dependent lifetime data reveals that as the field

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strength of L is varied from weak to strong, the importance of ^{3}dd state population diminishes and that, in agreement with a previous suggestion,[3a] both thermally activated pathways are important for the complex $Ru(bpz)_2(bpy)^{2+}$.

Experimental Section

1. Materials. $RuCl_3{\cdot}3H_2O$ and the ligands 2,2′-bipyridine (bpy) and 4,4′-dimethyl-2,2′-bipyridine (dmb) were purchased from Aldrich Chemical Co. Both ligands were sublimed prior to use. All other reagents were purchased as reagent grade and used without further purification. All solvents used were reagent grade or better.

2. Preparation of Compounds. The ligands 2,2′-bipyrazine[8] (bpz) and 4,5′-diazafluorene[9a] (daf) were prepared by literature methods. The ligand 5-monomethyl-2,2′-bypiridine[10] (mmb) was available from a previous study. The $Ru(bpz)_2Cl_2$ was prepared according to the method described by Crutchley et al.[11] All tris ligated complexes were prepared by standard methods[12] and were purified by column chromatography using Sephadex LH-20 (25−100-μm bead size; Sigma Chemical Co.) as the stationary phase and 95% ethanol as the eluant. Prior to precipitation, the purity of the complexes was checked by thin layer chromatography.[12b]

Physical Measurements

1. Electronic Absorption Spectra. Electronic absorption spectra were obtained with a Hewlett-Packard Model 8452A diode array spectrometer using a 1-cm quartz cuvette. Spectra were obtained in the absorbance mode.

2. Electronic Emission Spectra. Electronic emission spectra were obtained using a conventional Raman spectrometer (Spex Model 1403 double monochromator equipped with a Spex Model DM1B controller and Hammamatsu R928 photomultiplier tube) with 457.9-nm excitation from a Spectra-Physics Model 2025-05 argon ion laser. The spinning 5-mm-i.d. NMR tube was illuminated by a laser beam focused through a glass lens, and the emission from the sample was collected with a conventional two-lens collecting system.

3. Excited State Lifetimes. The third harmonic (354.7 nm) of a Quanta-Ray (Spectra-Physics) Model GCR-11 Nd:YAG laser (operated at 20 Hz) with the beam defocused was used as the excitation source for the lifetime measurements. The emitted light was transferred through collecting and transferring lenses to a SPEX 340S spectrometer equipped with an RCA C31034A-02 photomultiplier tube (PMT). The PMT output signal was directed to a LeCroy 9450A dual 300-MHz oscilloscope. Typically 500 scans of the emission decay curve were averaged and transferred to the computer. The emission decay curves were then fitted by a monoexponential model using commercial software (PSI-Plot) based on the Marquardt−Levenberg algorithm.

$$I = I_0 \exp(-t/\tau) \qquad (1)$$

For the temperature dependent lifetime measurements, the sample was positioned into a double wall dewar cell. Prior to the measurement the sample ($<10^{-5}$ M in complex based on mass, assuming no water of crystallization) was deaerated by bubbling N_2 through the solution for approximately 30 min. During the experiment the sample was kept under a slight overpressure of N_2 and continuously stirred by a magnetic stirrer to prevent local overheating and possible decomposition of the sample. The temperature of the solution was measured with 0.1 °C accuracy using a thermocouple inserted directly into the sample. For the low temperature measurements the sample was cooled by a EtOH/ether (1:1) mixture (cooled by liquid nitrogen). The coolant mixture was then allowed to slowly warm to room temperature. During this period (3−4 h) the lifetime measurements were acquired at every 2−3 °C change in temperature. The temperature variation during the collection of the data (500 sweeps/25 s) was approximately 0.5−0.6 °C. Thus, the average value was considered as the experimental temperature for the measurement. The measurements at temperatures above 25 °C were taken with the same setup using water or silicone oil as the heating fluid. The experimentally obtained data, representing the dependence of excited state lifetimes on temperature, were then analyzed as described later.

Table 1. Summary of Room Temperature Electronic Absorption and Emission Spectra for a Series of Studied Tris Ru(II)−α-Diimine Complexes in PC

	absorption (nm)		emission[a] (nm)
complex	$d\pi \rightarrow \pi_1^*$	$\pi \rightarrow \pi^*$	$^3MLCT \rightarrow {}^1GS$
$[Ru(bpz)_2(dmb)]^{2+}$	470, 422 (sh)	298	649
$[Ru(bpz)_2(mmb)]^{2+}$	466, 420 (sh)	298	644
$[Ru(bpz)_2(bpy)]^{2+}$	465, 420 (sh)	296	639
$[Ru(bpz)_2(daf)]^{2+}$	462, 418 (sh)	298	633
$[Ru(bpz)_3]^{2+}$	442, 417 (sh)	298	601

[a] Not corrected for spectrometer response.

Results

1. Electronic Absorption and Emission Spectra. A summary of the electronic absorption and emission spectra acquired for all the heteroleptic complexes, $Ru(bpz)_2L^{2+}$, at room temperature in propylene carbonate (PC) is given in Table 1. Corresponding data for the homoleptic complex, $Ru(bpz)_3^{2+}$, is included for comparison. As had previously been shown[12a] by resonance Raman spectroscopy in the case of $Ru(bpz)_2(bpy)^{2+}$, the low energy band near 465 nm is associated with the ruthenium(II)−bipyrazine charge transfer transition, while the higher energy component is attributable to the Ru(II)−L transition. Furthermore, in all cases, the lowest energy ^{3}MLCT states are expected to be selectively localized on one of the bipyrazine ligands, a fact that had been conclusively documented by time-resolved resonance Raman (TR^3) spectroscopic measurements for the $Ru(bpz)_2(bpy)^{2+}$ complex.[12a] Given the fact that the lowest lying ^{3}MLCT states are bipyrazine localized, it is expected and observed that both the low energy ^{1}MLCT absorption band and the ^{3}MLCT emission energies are red shifted as the donor strength of the "spectator" ligand increases from the weakest (daf)[9] to the strongest (dmb),[13] this increasing field strength causing greater destabilization of dπ orbitals.

2. Lifetimes. In all cases, at all temperatures, the acquired curves are well fit by a monoexponential function, as expected. Electronic absorption and emission spectra acquired for each sample following the measurements of lifetimes were virtually identical to those obtained prior to the measurements, indicating that there is no significant sample decomposition upon exposure to the defocused laser excitation source.

Figure 1 illustrates the variation of measured lifetimes as a function of temperature for all of the complexes studied. The solid lines represent the best fit to experimental data, assuming participation of only one thermally activated pathway (see below).

Discussion

As is summarized in Scheme 1, the lowest energy ^{3}MLCT states of ruthenium(II)−polypyridine complexes may relax to the ground state via a number of routes, including population of two thermally accessible upper states, whose participation

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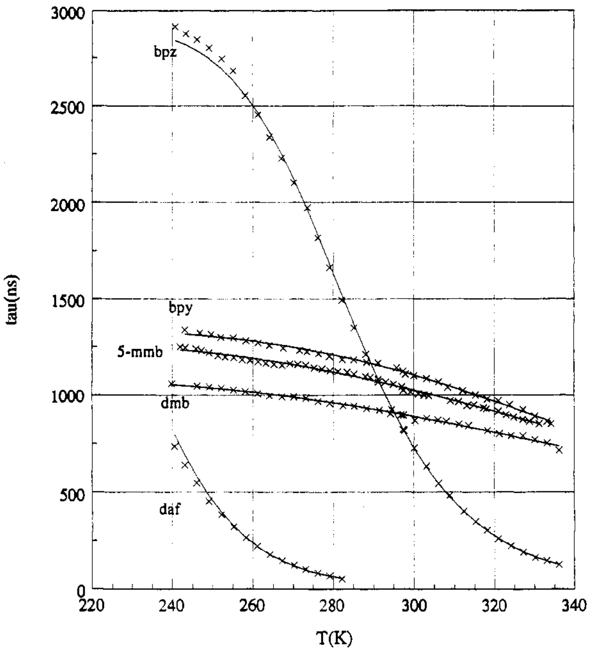

Figure 1. Temperature dependent lifetime measurements for the series of complexes with general formula $[Ru(bpz)_2(L)](PF_6)_2$ in PC: L as indicated in the figure. The solid lines represent the best fit to the monoexponential model, eq 3. Concentrations < 10^{-5} M.

can be documented by analysis of lifetime data acquired over a range of temperatures. The overall relaxation rate is given, in general, by the sum of the individual terms, as shown in eq 2, where k_{4th} as well as k_{dd} may each represent a sum of radiative

$$k_{tot} = \frac{1}{\tau} = k_r + k_{nr} + k_{4th}\exp(-\Delta E_{4th}/k_BT) + k_{dd}\exp(-\Delta E_{dd}/k_BT) + k_{rx}\exp(-\Delta E_{dd}/k_BT) \quad (2)$$

and nonradiative decay rate constants for the depopulation of the corresponding state (though the radiative contributions are typically much smaller than the nonradiative components). An evaluation of the relative importance of each term in eq 2 is available through analysis of lifetime data acquired as a function of temperature. It can be pointed out that in the case of PF_6^- salts in noncoordinating solvents, as in the case here, the k_{rx} term becomes unimportant and the last term in eq 2 can be neglected.

For the majority of known cases,[3] the temperature dependence of the lifetime data can be adequately fit using an equation which incorporates only one thermally dependent term; i.e.,

$$k_{tot} = \frac{1}{\tau} = k + k_1\exp(-\Delta E/k_BT) \quad (3)$$

where $k = k_r + k_{nr}$. Thus, in early work, Meyer, Rillema, and co-workers,[3a] using eq 3, showed that for most complexes the temperature dependent lifetime data indicated that decay through the ^{3}dd state dominated the temperature dependence, yielding preexponential factors (k_1) of $>10^{12}$ and energy gaps (ΔE) of >3000 cm^{-1}. However, in a few cases preexponential factors of $\sim 10^7$ and energy gaps of <1000 cm^{-1} were obtained. In addition, in a study of corresponding Os(II) complexes, where the ^{3}MLCT$-^3$dd energy gaps are quite large and decay via this route is negligible, analysis of temperature dependent lifetime data yielded a set of parameters whose magnitudes are similar to the latter case (i.e., $k_1 \sim 10^7$ s^{-1} and $\Delta E < 1000$ cm^{-1}).[3b]

Of special interest is the case of $Ru(bpy)_3^{2+}$ in a rigid (cellulose acetate) matrix.[14] While in fluid solution the temperature dependent lifetime data for the complex are apparently dominated by participation of the ^{3}dd state ($k_1 = 4 \times 10^{12}$ s^{-1} and $\Delta E = 3275$ cm^{-1}),[15] upon incorporation into the rigid matrix the data yielded values of $k_1 = 1.7 \times 10^7$ s^{-1} and $\Delta E = 810$ cm^{-1}. This behavior was reasonably interpreted by Meyer and co-workers to indicate that the ^{3}dd state is destabilized by the rigid matrix to the extent that it becomes inaccessible over the temperature range investigated. In this situation, participation by the so-called fourth MLCT state becomes evident. This is especially significant inasmuch as, for this complex, there is direct spectroscopic evidence[16] for the existence of such a state, the spectroscopic data yielding ΔE values (650−770 cm^{-1}) in excellent agreement with the value (810 cm^{-1}) derived from the lifetime data. It should also be pointed out that corresponding studies[7b] of this complex entrapped within the sterically confining supercages of Y−zeolite also yielded a comparable set of parameters ($k_1 = 1.1 \times 10^8$ s^{-1} and $\Delta E = 890$ cm^{-1}).

Returning to consideration of the previously acquired data[3a] for the series of complexes whose lowest energy ^{3}MLCT state is localized on bipyrazine, it can be pointed out that the data for $Ru(bpz)_3^{2+}$ and $Ru(bpy)_2(bpz)^{2+}$ are consistent with the overall model depicted in Scheme 1. Thus, in the case of the homoleptic tris complex, $Ru(bpz)_3^{2+}$, the ^{3}MLCT$-^3$dd energy gap is sufficiently small ($\sim$3900 cm^{-1}) that decay via this pathway dominates. For the heteroleptic complex, $Ru(bpy)_2(bpz)^{2+}$, where two of the bipyrazine ligands are replaced by the relatively strong field bipyridine ligand, the ^{3}dd state is sufficiently destabilized so as to render it inaccessible and the thermally activated pathway is dominated by the fourth MLCT state. As was suggested by Meyer, Rillema, and co-workers,[3a] the parameters derived from the temperature dependent lifetime data for $Ru(bpz)_2(bpy)^{2+}$ have values which are intermediate with respect to those derived for the other two members of the series and may reflect participation by both thermally accessible upper states.

In order to address this issue, the present work is focused on a series of heteroleptic complexes, $Ru(bpz)_2L^{2+}$, which are based on the $Ru(bpz)^{2+}$ core, and the field strength of the spectator ligand (L) systematically increases from the weak donor, daf, to the relatively strong field ligand, dmb. As is shown in Figure 1 and summarized in Table 2, the lifetime data over the temperature range 240−340 K are fit reasonably well by employing the equation which contains only one thermal term (eq 3). Using this approach, the derived parameters for $Ru(bpz)_3^{2+}$ and $Ru(bpz)_2(bpy)^{2+}$ are virtually identical with those obtained by Meyer, Rillema, and co-workers;[3a] i.e., the data for the latter complex yields parameters which are intermediate between those characteristic for the two pathways. Apparently, within this limited temperature range, both pathways may contribute to the thermal dependence.

To the extent that the model involving the two thermally accessible states is valid, the expanded data set (covering a wider range of temperatures) may reveal this competition between the two pathways and facilitate more accurate determinations of the associated parameters. In fact, in the cases where lifetimes have been measured over an extended range of temperatures,[17] several authors have suggested that for ruthenium(II)−polypyridine complexes, inclusion of two thermal terms is necessary in order to fit the experimental data. For this reason the lifetime

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Table 2. Temperature Dependent Lifetime Measurements for a Series of Ruthenium(II)−α-Diimine Complexes in PC[a]

complex	T^b (K)	τ(298 K) (ns)	k (s^{-1})	k_l (s^{-1})	ΔE (cm^{-1})
$Ru(bpz)_2(dmb)$	243−330	875	$(9.1 \pm 0.1) \times 10^5$	$(1.9 \pm 0.7) \times 10^8$	1426 ± 82
$Ru(bpz)_2(mmb)$	243−330	1070	$(7.76 \pm 0.06) \times 10^5$	$(3.0 \pm 0.8) \times 10^8$	1521 ± 61
$Ru(bpz)_2(bpy)$	243−330	1110	$(7.39 \pm 0.05) \times 10^5$	$(1.3 \pm 0.3) \times 10^9$	1859 ± 64
$Ru(bpz)_2(daf)$	243−283	21[c]	$(5.2 \pm 1.5) \times 10^5$	$(1.94 \pm 0.03) \times 10^{15}$	3627 ± 4
$Ru(bpz)_3$	243−330	815	$(3.42 \pm 0.07) \times 10^5$	$(1.4 \pm 0.1 \times 10^{14}$	3902 ± 25

[a] Parameters listed obtained from fit to monoexponential model. [b] Temperature range studied. [c] Estimated from the fitted curve.

Table 3. Temperature Dependent Lifetime Measurements over an Extended Temperature Range

complex	T^a (K)	k (s^{-1})	k_{4th} (s^{-1})	ΔE_{4th} (cm^{-1})	k_{dd} (s^{-1})	ΔE_{dd} (cm^{-1})
$Ru(bpz)_2(mmb)^b$	243−373	$(6.7 \pm 0.3 \times 10^5$	$(8 \pm 3) \times 10^6$	706 ± 98	$(9.0 \pm 0.2) \times 10^{13}$	4720 ± 8
$Ru(bpz)_2(bpy)^b$	243−373	$(6.4 \pm 0.5) \times 10^5$	$(8 \pm 7) \times 10^6$	736 ± 206	$(9 \pm 5) \times 10^{13}$	4632 ± 153
$Ru(bpz)_3$	243−330	$(3.42 \pm 0.07) \times 10^5$			$(1.4 \pm 0.1) \times 10^{14}$	3902 ± 25
$Ru(bpz)_3{-}Z^c$	200−298	4.1×10^5	1.1×10^7	765		
$Ru(bpy)_2(bpz)^d$	210−345	$(2.1 \pm 0.2) \times 10^6$	$(3 \pm 9) \times 10^7$	800 ± 600		
$Ru(bpy)_2(bpz){-}Z^c$	200−298	5.4×10^5	1.9×10^8	894		

[a] Temperature range studied. [b] Parameters listed were obtained from fit using eq 2. [c] Data from ref 7b. [d] Data from ref 3a.

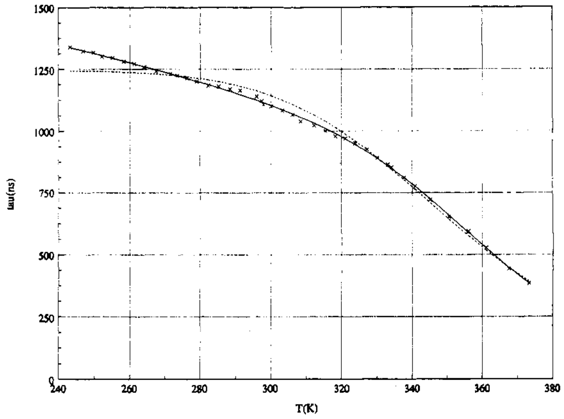

Figure 2. Temperature dependent lifetime measurements for $Ru(bpz)_2(bpy)^{2+}$ over an extended temperature range. The lines represent the best fits to eq 2 (—) and to eq 3 (- -). Concentrations < 10^{-5} M.

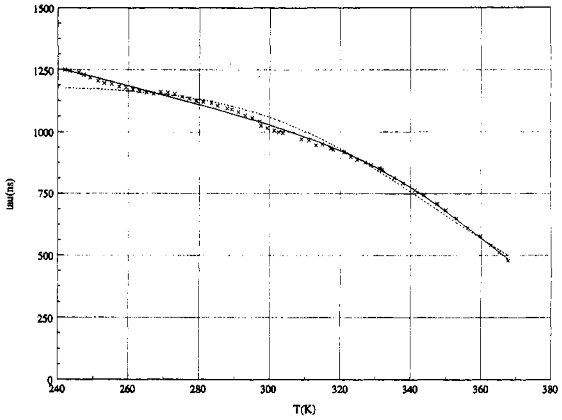

Figure 3. Temperature dependent lifetime measurements for $Ru(bpz)_2(mmb)^{2+}$ over an extended temperature range. The lines represent the best fits to eq 2 (—) and to eq 3 (- -). Concentrations < 10^{-5} M.

data for two of the complexes, $Ru(bpz)_2(bpy)^{2+}$ and $Ru(bpz)_2(mmb)^{2+}$, studied here were acquired over the temperature range from 240 to 370 K. The data acquired for the former complex are shown in Figure 2. In the figure the best fit obtainable using eq 3 (i.e., employing a single temperature dependent term) is given by the dashed line, while that obtained using the more general, eq 2, incorporating both temperature dependent terms, is shown as a solid line. Clearly, this expanded data set is not adequately fit using eq 3, and the inclusion of both temperature dependent terms is necessary. The parameters for one of the derived thermal terms are $k = 9 \times 10^{13}$ s^{-1} and $\Delta E = 4632$ cm^{-1}, values which are quite similar to those obtained for the majority of complexes which have an accessible ^{3}dd state. The derived parameters for the other temperature dependent term are $k = 8 \times 10^6$ s^{-1} and $\Delta E = 736$ cm^{-1}, the magnitudes of which are close to those previously obtained[3] for the few complexes whose ^{3}dd states are known to be inaccessible. Thus, it is reasonable to associate the two thermal terms with these two individual pathways, as is done in Table 3, which summarizes the results for both $Ru(bpz)_2(bpy)^{2+}$ and $Ru(bpz)_2(mmb)^{2+}$ (Figure 3), along with those for several other complexes whose lowest lying ^{3}MLCT states are localized on a bipyrazine ligand.

Clearly, the behavior observed over the extended range of temperatures is consistent with the concept suggested by Meyer, Rillema, and co-workers[3] that for certain complexes, including $Ru(bpz)_2(bpy)^{2+}$ and $Ru(bpz)_2(mmb)^{2+}$, both states are thermally accessible and may influence the temperature dependent lifetime curves, depending on the range of temperatures studied. For such cases it is necessary to investigate a larger range of temperatures and employ the more general approach involving both temperature dependent terms (i.e., eq 2). This rather dramatic effect of slightly extending the temperature range (to 370 vs 340 K) comes about because the preexponential factor for decay from the higher (^{3}dd) state is a factor of 10^7 greater than that for the lower (4th-MLCT) state, i.e., $\sim 10^{14}$ vs $\sim 10^7$. It is also worth noting that the relative magnitudes of the derived linear terms (k in eqs 2 and 3 and Tables 2 and 3) are consistent with energy gap law; i.e., k decreases with increasing ^{3}MLCT−^{1}GS energy gap, as shown by the corresponding relative values in Table 1.

It is instructive to consider the behavior observed for the various species listed in Table 3. For the tris(bipyrazine) complex ($Ru(bpz)_3^{2+}$) in PC solution, where the two spectator ligands are other bipyrazine ligands, having a low ligand field strength, the ΔE_{dd} value is only $\sim$3900 cm^{-1} and the temperature dependence is dominated by the ^{3}dd pathway. As one of the spectator ligands is replaced by the stronger field bipyridine ligand (i.e., $Ru(bpz)_2(bpy)^{2+}$), the ΔE_{dd} rises in energy and both pathways participate in the temperature dependent decay.

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[17] See, for example: (a) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: San Diego, CA, 1992; pp 128, and references cited therein. (b) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J. *J. Chem. Soc., Farad. Trans. 1* **1978**, *74*, 1275. (c) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; Von Zelewski, A. *Inorg. Chem.* **1983**, *22*, 3335. (d) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; Von Zelewski, A. *J. Phys. Chem.* **1986**, *90*, 5190. (e) Kawanishi, Y.; Kitamura, N.; Tazuke, S. *Inorg. Chem.* **1989**, *28*, 2968.

However, where two of the bipyrazine ligands are replaced by bipyridine (i.e., in the case of $Ru(bpy)_2(bpz)^{2+}$), the ΔE_{dd} becomes sufficiently large that the temperature dependent data are reasonably well modeled using only one thermal term whose parameters are characteristic of decay via the fourth MLCT state.

The behavior of the two zeolite-entrapped complexes listed in Table 3 is also consistent with these concepts. As is discussed in detail elsewhere,[7b,c] the principal effect of entrapment of such complexes within the sterically confining Y−zeolite supercage is to raise the energy of the ^{3}dd state. Thus, the zeolite entrapped tris(bipyrazine) complex, $Z-Ru(bpz)_3^{2+}$, exhibits a temperature dependent lifetime curve which is dominated by involvement of the fourth MLCT state. The parameters for the zeolite-entrapped heteroleptic complex, $Z-Ru(bpy)_2(bpz)^{2+}$, are not substantially different from those of the complex in PC solution inasmuch as, in this case, the ^{3}dd is already sufficiently destabilized by the two relatively strong field bipyridine ligands.

Finally, it is interesting to note that the value of the derived ΔE_{4th} parameter for all of these bipyrazine-localized excited states all are within experimental error of 800 cm^{-1} and that the associated preexponential factors are within a factor of 10 of the value previously derived by Meyer, Rillema, and co-workers.[3a] Thus, the ΔE_{4th} energy gap appears to be relatively ligand specific, whereas the ΔE_{dd} gap is controlled by the donor strength of the spectator ligands. The slightly larger variation of the k_{4th} values among the complexes listed in Table 3 is not surprising inasmuch as the nonradiative relaxation from this state is expected to be sensitive to environmental conditions (i.e., PC vs the zeolite supercage).

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