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Isotope and Temperature Dependence of Dual Emission in a Mononuclear Ruthenium(II) Polypyridyl Compound

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Detailed photophysical measurements on a series of $[Ru(bpy)_2(L)]^{n+}$ complexes, which are deuterated to varying degrees are reported, where bpy is 2,2′-bipyridyl and L is 3-(pyrazin-2-yl)-1,2,4- triazole (Hpztr) or 3-(pyridin-2-yl)-1,2,4-triazole (Hpytr). For the pyridinyltriazole complexes, deuteration of bpy leads to a doubling of the emission lifetime, while deuteration of the triazole ligand has no effect on the emission lifetime. For the complex containing the protonated pyrazinyltriazole ligand, deuteration of bpy does not affect the emission lifetime, but the lifetime is strongly affected by the deuteration of the triazole-containing ligand. These observations indicate that in the pyridinyltriazole complexes the emitting state is bpy based, while for the complex containing the protonated pyrazinyltriazole ligand the emission is pyrazine based. For the compound containing the deprotonated pyrazinyltriazole ligand a remarkable insensitivity of the emission lifetime to deuteration is observed. Time-resolved resonance Raman data clearly indicate that the emitting triplet state is bpy based at room temperature when the triazole is deprotonated and switches to being pyrazine based on protonation. Variable temperature emission studies on the deprotonated complex reveal a remarkable dual emission between 120 and 200 K. The two emitting states exhibit different lifetime dependences on temperature. It is proposed that the presence of these two, weakly coupled emitting states, one bpy and one pyrazine based, is responsible for the relative insensitivity of the emission lifetime of the deprotonated pyrazinyltriazole complex to deuteration.

Introduction

Mixed ligand ruthenium polypyridyl complexes have been studied in great detail because of their potential as building blocks for supramolecular devices.[1] In such complexes ligands are chosen to optimize particular photophysical and/or electrochemical characteristics.[2] Time-resolved resonance Raman spectroscopy,[3] has been widely applied as a diagnostic tool for determining the location of the emitting state, and deuteration of ligands has been applied to confirm the identity of particular vibrational features.[4] Deuteration has also been used to identify vibrational features in low-temperature emission studies.[5] Furthermore, it has been established that the emission lifetime of homoleptic metal complexes increases with deuteration of ligands.[5,6] However, the effect of deuteration on the emission lifetime of mixed ligand complexes has so far not been investigated in a systematic manner.

The application of deuteration as a tool in the study of the photophysical properties of ruthenium polypyridyl type complexes has so far been limited,[5−7] primarily by a lack of an efficient synthetic route to deuterated ligands.[8] Recently, we reported a facile one-pot synthesis, which greatly simplifies the deuteration of polypyridyl type ligands. We suggested that partial deuteration of mixed ligand complexes, in combination with emission lifetime studies, might be used to identify the location of the emitting state in such compounds.[9] It was proposed that deuteration of a ligand will only affect the emission lifetime of a compound when this ligand is directly involved in the emission process, so that deuteration of spectator ligands should not therefore influence the emission lifetime.

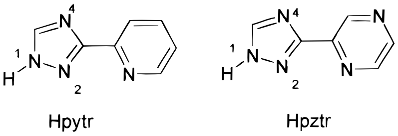

Figure 1. Structures of Hpztr and Hpytr.

In this contribution, we investigate this hypothesis in more detail and report on the photophysical behavior of a series of complexes, $[Ru(bpy)_2(L)]^{n+}$, where bpy is 2,2′-bipyridyl and L is 3-(pyridin-2-yl)-1,2,4-triazole complex (Hpytr) or 3-(pyrazin-2-yl)-1,2,4- triazole (Hpztr) (see Figure 1). These complexes may be obtained as two isomers, where either N^4 or N^2 of the triazole ring is coordinated to the metal center.[10,11] For the pyridinyltriazole complexes emission is expected to be bpy based irrespective of the protonation state of the triazole ring. Previously, ground-state resonance Raman studies suggested that

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when the pyrazine ligand is protonated, the emitting state is pyrazine based, whereas for pztr$^-$ (i.e., deprotonated) complexes the emitting state is localized on the bpy ligands.[11] These complexes are therefore very suitable for studying the effect of deuteration on the emitting properties of mixed ligand complexes. For the sake of simplicity, the present investigation concentrated on the N^2 isomers. Systematic deuteration of the various ligands has been carried out, and the consequent effect on the emitting properties of the compounds has been studied. A preliminary account of some of the results presented in this contribution has been reported previously.[12]

Experimental Section

Materials. All solvents were used without further purification.

Synthesis of Deuterated Ligands. In a typical experiment, 2,2′-bipyridyl (h$_8$-bpy) (3 g, 0.19 mol) was added to 30 cm^3 of D$_2$O (deuteration 99.9%) and the reaction mixture was allowed to react in the presence of the H−D exchange catalyst Pd/C (10% Pd, Aldrich) (0.5 g) in a Teflon-coated steel high-pressure reactor at 200 °C for 3 days. After this period, the contents of the reactor were collected and filtered hot to remove the Pd catalyst and D$_2$O was removed under vacuum to obtain the product. The Pd/C was washed with acetone to remove any product present on the surface of the catalyst. The material obtained in this manner was recrystallized from hot water. The ^{1}H NMR spectrum of the product revealed four singlets, indicating a deuteration degree of >80%. To achieve complete deuteration, the same procedure was repeated with fresh D$_2$O for another 3 days. The reaction mixture was worked up as described above. The overall yield of the fully deuterated product, d$_8$-bpy was >80%.

Deuteration of 3-(Pyridin-2-yl)-1,2,4-triazole (Hpytr) and 3-(Pyrazin-2-yl)-1,2,4-triazole (Hpztr). A 3 g sample of the triazole ligand was added to 30 cm^3 of D$_2$O, and the reaction was allowed to react in the presence of 0.5 g of Pd/C in a Teflon-coated steel high-pressure reactor at 200 °C for 6 days. The contents of the reactor were then collected and filtered to remove the Pd catalyst. The Pd catalyst was washed with acetone to remove any deuterated ligand, the acetone was then removed by rotary evaporator. On cooling, the deuterated product precipitated and was collected by vacuum filtration. The product obtained was then dried under vacuum overnight. This procedure was carried out twice, and the degree of deuteration as calculated from ^{1}H NMR was at least 95%. Overall yield 75%.

Synthesis and Purification of Metal Complexes. The undeuterated, partially deuterated, and fully deuterated N^2 and N^4 isomers of [Ru(bpy)$_2$(pytr)](PF$_6$)[10] and [Ru(bpy)$_2$(pztr)](PF$_6$)[11] were prepared using methods reported before. Separation of the N^2 and N^4 isomers was accomplished by column chromatography (neutral alumina, acetonitrile). The purity of the isomers obtained was checked by HPLC and ^{1}H NMR.

Experimental Techniques. Purification of metal complexes was carried out on a semipreparative HPLC system using a model 353 Applied Chromatography Service (ACS) pump (model RR066) and an ACS detector (model 353/UV/vis) together with a Magnum-9μ Partisil cation exchange column (10 mm × 25 cm). The mobile phase employed was acetonitrile/water (7:3, v/v) containing 0.15 mol.dm^{-3} KNO$_3$ as eluent.

Absorption spectra were measured using a Shimadzu 3100 UV−vis/NIR spectrophotometer interfaced with an Elonex PC-433. Luminescent studies were carried out on a Perkin-Elmer LS50 luminescence spectrometer, interfaced with an Epson PCAX2E personal computer. Luminescent lifetimes were measured by employing a Spectra Physics Nd:YAG frequency-tripled, Q-switched laser as an excitation source coupled in a right angled configuration to an Oriel iCCD, laser power was measured as 30 mJ per 20 ns pulse. Luminescent lifetime decay data were analyzed employing standard iterative techniques.[13]

Ground-electronic-state resonance Raman (RR) spectra were recorded using an Ar$^+$ laser (Spectra Physics model 2025) as the excitation source and the Raman scattering detected using a CCD (Princeton Instruments model LN/UV 1152) coupled to a Jobin-Yvon HR640 spectrometer fitted with a 1200 groove/mm holographic grating. The effective spectral bandwidth was 8 cm^{-1}.

Generation and study of the MLCT excited-state absorption (ESA) spectra of the various complexes were carried out by conventional nanosecond laser flash photolysis, using the frequency-doubled or -tripled output pulse from a Q-switched, Nd:YAG laser (Quanta-Ray DCR2, pulse duration ca. 9 ns), in conjunction with a hydrogen or deuterium gas-filled Raman-shifting cell, dependent upon the precise wavelength required. Laser pulse energies were typically in the range (3−10) mJ. The ESA spectra were recorded using a gated multichannel dual diode array detector (Princeton Instruments model DIDA 700G), or in single channel, “point-by-point” manner by means of rapid response spectrophotometric detection in conjunction with a transient digitizer (Tektronix 7912AD).

Transient resonance Raman (TR^2) spectra were generated and detected by the single-pulse pump and probe technique described elsewhere.[14a] This technique enables the investigation of RR scattering from transients having lifetimes that may be longer or shorter than the laser pulse duration.[14b] To enable the acquisition of more complete, time-resolved RR (TR^3) spectra, two lasers were employed in a pump−probe arrangement. The frequency-doubled or -tripled output pulse from a Q-switched, Nd:YAG laser (Quanta-Ray DCR2, pulse duration ca. 9 ns), in conjunction with a hydrogen or deuterium gas-filled Raman-shifting cell, dependent upon the precise wavelength required, served to populate the MLCT excited states. A delayed pulse from a second, Q-switched laser coupled to a pulsed dye laser or a Raman-shifting cell provided a choice of wavelengths in the range (350−650) nm to probe the RR scattering from MLCT excited states as a function of time. Delay times over the range nanosecond to microsecond between the pump and probe pulses were controlled by means of a Stanford Systems DG2 pulse generator. For both TR^2 and TR^3 studies, the excited-state spectra were recorded using a multichannel intensified diode array detector (EG&G OMA III, model 1420B) and triple spectrometer.[14a] Solutions of complexes in CH$_3$CN, typically 10^{-3} mol dm^{-3}, were contained in spinning cells to minimize the risk of thermal or photodecomposition of sample during spectral acquisition. A 50:50 (v/v) CH$_3$CN + toluene solvent mixture was used for spectral calibration in all Raman experiments.

Results

With the experimental method reported, an excellent degree of deuteration was obtained for both the 2,2′-bipyridyl- and triazole-based ligands. Some typical ^{1}H NMR spectra of complexes obtained with these ligands are shown in Figure S1 (Supporting Information). With the ligands a series of undeuterated, partially deuterated, and fully deuterated complexes containing bpy, Hpytr, and Hpztr were obtained.

Results of the studies carried out on the photophysical properties of the compounds obtained are summarized in Table 1. No significant changes were observed in the absorption or emission maxima of the compounds upon deuteration. The

TABLE 1: Emission Lifetime Data[a]

compound		lifetime, ns (λ_{max}, nm) RT	77 K	compound		lifetime, ns (λ_{max}, nm)
$[Ru(bpy)_2(pztr)]^+$	N^2	228 (660)	4450	$[Ru(bpy)_2(pytr)]^+$	N^2	145 (650)
$[Ru(d_8\text{-}bpy)_2(pztr)]^+$	N^2	283 (660)	7030	$[Ru(d_8\text{-}bpy)_2(pytr)]^+$	N^2	250 (650)
$[Ru(bpy)_2(Hpztr)]^{2+}$	N^2	230 (660)	4770	$[Ru(bpy)_2(Hpytr)]^{2+}$	N^2	− (620)
$[Ru(d_8\text{-}bpy)_2(Hpztr)]^{2+}$	N^2	230 (660)	6000	$[Ru(d_8\text{-}bpy)_2(Hpytr)]^{2+}$	N^2	− (620)
$[Ru(bpy)_2(d_4\text{-}pztr)]^+$	N^2	210 (660)	6400	$[Ru(bpy)_2(d_5\text{-}pytr)]^+$	N^2	142 (650)
$[Ru(bpy)_2(Hd_4\text{-}pztr)]^{2+}$	N^2	467 (660)	8000	$[Ru(bpy)_2(Hd_5\text{-}pytr)]^{2+}$	N^2	− (620)
$[Ru(d_8\text{-}bpy)_2(d_4\text{-}pztr)]^+$	N^2	290 (660)	9000	$[Ru(d_8\text{-}bpy)_2(d_5\text{-}pytr)]^+$	N^2	250 (650)
$[Ru(d_8\text{-}bpy)_2(Hd_4\text{-}pztr)]^2$	N^2	480 (660)	8800	$[Ru(d_8\text{-}bpy)_2(Hd_5\text{-}pytr)]^{2+}$	N^2	− (620)

[a] All measurements carried out at room temperature under nitrogen atmosphere in acetonitrile error ±10%. Lifetimes for the Hpytr complexes are too short (>20 ns) to be measured with the laser system available.

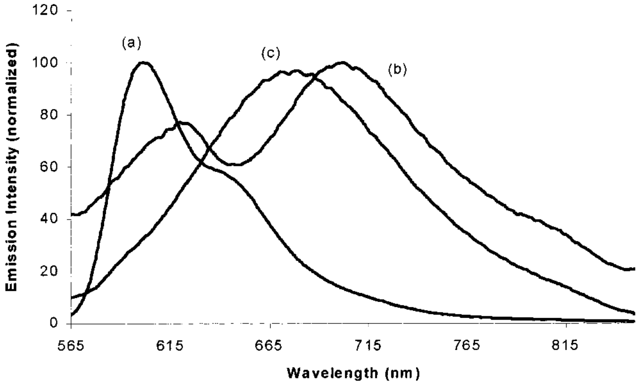

Figure 2. Temperature-dependent emission spectra of N^2-$[Ru(bpy)_2(pztr)]^+$ in ethanol/methanol (4:1 v/v) glass containing 2% diethylamine: (a) 90 K; (b) 135 K; (c) 298 K.

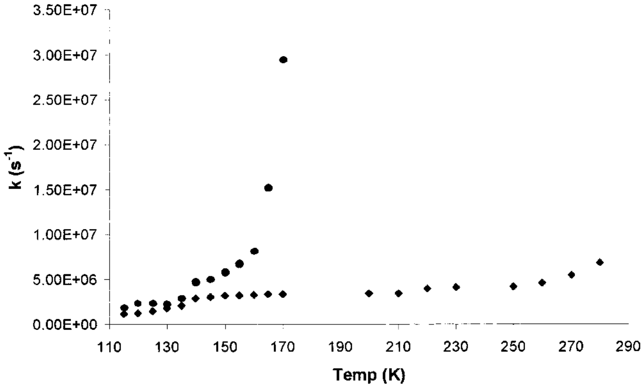

Figure 3. Temperature-dependent luminescent decay rates of N^2-$[Ru(bpy)_2(pztr)]^+$ in ethanol/methanol (4:1 v/v) glass containing 2% diethylamine, (●) monitored at 580 nm and (◆) monitored at 680 nm.

TABLE 2: Arrhenius Parameters Obtained from Temperature Dependence of the Emission of Hpztr and Hpytr Complexes

complex			E_a (cm^{-1})	A (s^{-1})
$[Ru(bpy)_2(pztr)]^+$	N^2	(700 nm)	80	6.52×10^6
$[Ru(bpy)_2(pztr)]^+$	N^2	(580 nm)	850	2.40×10^{10}
$[Ru(bpy)_2(Hpztr)]^{2+}$	N^2	(650 nm)	2610	8.2×10^{12}
$[Ru(bpy)_2(pytr)]^+$	N^2	*a*	550	4.7×10^7
$[Ru(bpy)_2(Hpytr)]^{2+}$	N^2	*a*	1710	6.0×10^{10}

[a] Data obtained from ref 15.

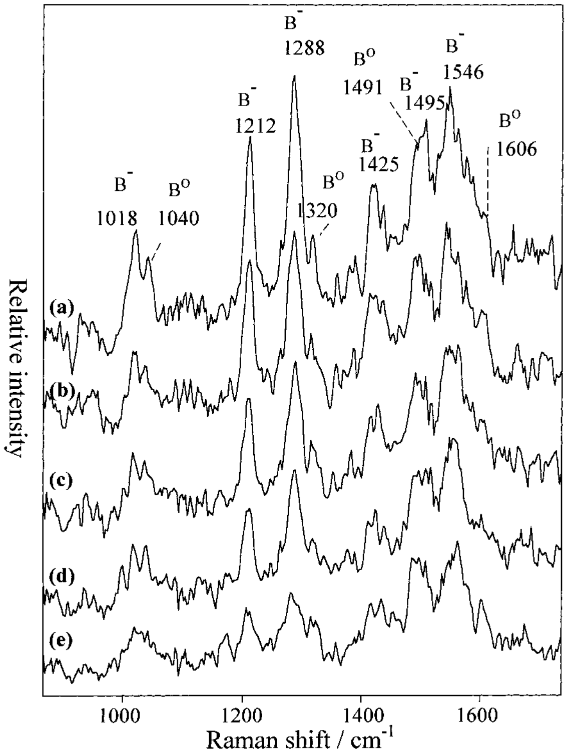

Figure 4. Time-resolved resonance spectra of deprotonated $[Ru(bpy)_2(pztr)]^+$ in MeCN (ca. 10^{-3} mol dm^{-3}). Pump pulse at 355 nm (10 mJ); probe pulse 396 nm (1 mJ). Pump−probe delays in ns: (a)10, (b) 20, (c) 40, (d) 80. (e) 396 nm probe pulse only. B^0, B^-, Z^0, Z^- denote bands attributed to neutral and anionic ligands bpy (B) and pztr (Z), respectively.

lifetimes of the protonated pyridinyltriazole complexes were too short to be measured accurately by our equipment.

The temperature dependence of the emission of $[Ru(bpy)_2(pztr)]^+$ is displayed in Figure 2, traces a−c showing emission spectra at 90, 135, and 298 K, respectively. It is clear from these that dual emission is occurring for the deprotonated complex over the temperature range 120−200 K. Two signals of roughly equal intensity are observed at 590 and 710 nm. The temperature dependence of the two emission signals observed for the deprotonated pyrazine compound is shown in Figure 3. Parameters obtained by fitting the temperature-dependent measurements on $[Ru(bpy)_2(pztr)]^+$ and its protonated analogue to an Arrhenius equation,

$$k = A\exp(-E_a/RT) \qquad (1)$$

are listed in Table 2, together with those reported for the pyridine analogues.[15] Essentially the same activation parameters were obtained for the deuterated complexes.

Ground-state RR spectra obtained for the undeuterated pztr complexes (not displayed here) recorded at excitation wavelengths of 457.9 and 488 nm showed bands at 1030, 1176, 1276, 1320, 1492, 1565, and 1608 cm^{-1}, characteristic[16,17] of the neutral bpy ligand. An additional band at 1517 cm^{-1} in the protonated complex and at 1524 cm^{-1} in the deprotonated case can be assigned to a pyrazine-associated mode.[17] The excited-

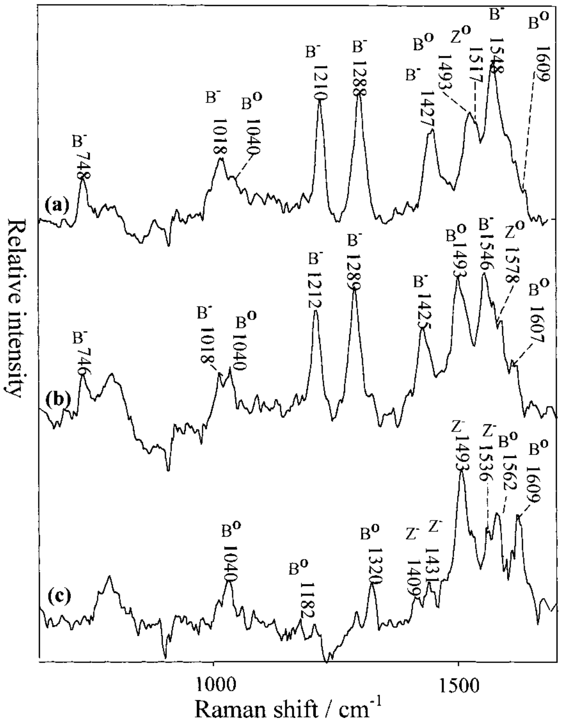

Figure 5. Excited-state resonance Raman spectra recorded at λ_{exc} = 355 nm (pulse energy 3 mJ) in MeCN, using the single-color pump and probe technique: (a) deprotonated $[Ru(bpy)_2(pztr)]^+$; (b) deprotonated $[Ru(bpy)_2(d^4\text{-}pztr)]^+$; (c) protonated $[Ru(bpy)_2(Hpztr)]^{2+}$. Bands labeled as in Figure 4. Features due to neutral bpy and anionic pztr ligands ca. 1493 cm^{-1} are nearly coincident.

state spectra showed significant differences, depending on whether the complexes are protonated or deprotonated. Preliminary data have been reported elsewhere;[18] a more complete analysis is presented here. Spectra obtained for the pyrazine-containing complexes are shown in Figures 4 and 5. For the deprotonated complex, Figure 4 shows the results of a time-resolved (i.e., TR^3) study of $[Ru(bpy)_2(pztr)]^+$ in CH_3CN using a laser pulse at 355 nm to populate the excited state and a second, delayed pulse at 396 nm to probe the Raman scattering from that state. It is clear from these spectra that the excited state is bpy localized. At the shortest pump−probe delay time of 10 ns, several bands attributable to $bpy^{\bullet-}$ radical anion are prominent, at 1018, 1212, 1288, 1425, and 1548 cm^{-1}. These decay as shown, with increasing pump−probe delay.

The effect of partial deuteration of the ligands on the excited-state spectra of the deprotonated complex is shown by the transient RR spectra in Figure 5, recorded by the single-color technique. Readily recognizable features characteristic of $bpy^{\bullet-}$ at 1210, 1288, 1427, and 1546 cm^{-1} are evident in trace a for the undeuterated complex and these are present, essentially unchanged in trace b for the same complex but with the pztr ligand deuterated, as would be anticipated for a spectrum characteristic of $bpy^{\bullet-}$, where deuteration of the pztr ligand would not be expected to cause any alteration. However, when the complex is protonated, the situation is markedly different, as exemplified by the data in Figure 5c. Bands at 1409, 1431, and 1536 cm^{-1}, convenient marker features[16,17] for the pyrazine anion, are evident, which prove to be independent of deuteration of the bpy ligands but which do shift (not displayed here) upon deuteration of the pztr ligand.

Discussion

Room-Temperature Studies. *Pyridinyltriazoles.* In an earlier publication we proposed that for mixed-ligand complexes deuteration could be used to identify the ligand from which the excited-state emission originated. In the present work it has been possible to test this proposition in more detail on two types of ruthenium polypyridyl complex, one based on *pyridinyl*triazole ligands and the second on *pyrazinyl*triazole ligands. In both cases, the triazole ring can be protonated and, as shown previously, protonation has a significant influence on the properties of the excited state.[10,11] For pyridinyltriazole complexes, the emitting excited state is bpy based, irrespective of the protonation state of the triazole ring.[10,15,16] From the emission data obtained for the deprotonated species, it is clear that deuteration of bpy leads to a significant increase in the emission lifetime but that deuteration of the triazole ligand has little effect (Table 1). These observations are in line with our earlier hypothesis concerning the effect of partial deuteration on the excited-state lifetimes of mixed ligand complexes. Only deuteration of the bpy ligand influences the emission lifetime of the compounds.

Pyrazinyltriazoles. Earlier studies based on the excited-state acid−base properties of the pyrazinyltriazole-containing compounds, demonstrated that protonation of the triazole resulted in switching of the excited state to pyrazine, from bipyridyl where it is located when the heteroligand is deprotonated.[11,16] The results obtained in the present work provide the opportunity of investigating this finding more extensively, through consideration of the effect of deuteration on both the transient resonance Raman spectra and emission properties of these complexes.

The excited-state Raman spectra show significant differences dependent upon whether the complexes are protonated or deprotonated. In the latter circumstance, the presence of several marker bands for the bipyridyl radical anion (Figure 4) provides clear evidence for a bpy-based excited state. On protonation, the spectrum is considerably different, as the data in Figure 5 demonstrate, with at least three bands at 1409, 1431, and 1536 cm^{-1} as indicated above (Figure 5c), associated with pyrazine radical anion, but no evident trace of $bpy^{\bullet-}$ features. These resonance Raman data confirm our earlier hypothesis that the site of the excited state is pH dependent, switching between the bpy and pyrazine depending on the state of protonation of the triazole moiety.

The Raman data highlight some other unusual features in the ordering of the excited-state levels. Despite the fact that the ground-electronic-state absorption spectrum of the complex, protonated or deprotonated, shows that the lowest energy singlet MLCT transition is associated with the pyrazinyltriazole ligand, it is clear from the excited-state RR spectra that in the case of the deprotonated complex, the lowest energy triplet MLCT is bpy localized. This is similar to the situation we noted previously[16] in the case of the related complex $[Ru(bpy)_2(bpzt)]^+$ (bpzt denotes the (deprotonated) bipyrazinyltriazole ligand), but contrary to what has been observed for all other examples that we are aware of in the literature, in which the lowest energy triplet MLCT excited state is localized on the same ligand as is involved in the lowest energy ground-electronic-state transition. The latter trend is in fact seen to be the case in the present work for the *protonated* complex, suggesting that the charge on the triazole ring may be a factor in deciding the energy order.

Table 1 shows that for the pyrazine-containing complexes the effect of deuteration on the emission lifetime of the compounds is significant for the protonated complex, increasing from 230 to 467 ns upon deuteration of the Hpztr ligand. The fact that the lifetime remains unchanged when the bpy ligands are deuterated instead is consistent with the Raman assignment of a pyrazine-based emitting state when the triazole ligand is protonated. However, the lifetimes of the deprotonated complexes are much less sensitive to deuteration, with the emission decay time (Table 1) increasing from 228 to 283 ns, upon deuteration of the bpy ligands, an increase that is only just outside the experimental error. This is in contrast to the situation more commonly encountered in ruthenium polypyridyl complexes where deuteration of the emitting sites results in a larger lifetime increase.[19] Therefore, while the transient resonance Raman data clearly indicate that the emitting triplet state is bpy based, the emission lifetime increase upon bpy deuteration (228 to 283 ns) is not as large as might be anticipated on the basis of our working model on the effect of deuteration on emission lifetimes, which therefore requires some further examination and amendment. Consideration of the temperature dependence of the emission lifetimes (Figure 3) provides some additional insights.

Temperature-Dependent Studies. The spectra shown in Figure 2 exhibit some rather unexpected features. For the deprotonated pyrazine complex two distinct spectral bands are observed over the temperature range 120−220 K. Monitoring the emission decay at 650 nm at a temperature of 135 K yields a biexponential kinetic trace that can be fitted to lifetimes of 2400 and 800 ns with amplitudes of 60% and 40%, respectively. Collection of decay data at 700 and 590 nm yields single exponential decays for both wavelengths, the longer lifetime belonging to the 700 nm signal. At 90 K the kinetics also fit a single-exponential decay with a lifetime of 6 μs.

Figure 2b is typical of the emission behavior of $[Ru(bpy)_2(pztr)]^+$ at temperatures between 120 and 200 K. Once protonated, $[Ru(bpy)_2(Hpztr)]^{2+}$ does not exhibit this complex behavior. Solvent and sample are identical in each case, but addition of $HClO_4$ to pH 3 ensures protonation of the complex. The emission decay of the protonated complex exhibits single-exponential behavior. The importance of this observation is 2-fold. First, since the same batch of complex was used for both measurements, this rules out the possibility of impurity contributing to the dual emission observed for $[Ru(bpy)_2(pztr)]^+$. Second, the fact that a single emission is observed over the range 120 to 200 K for $[Ru(bpy)_2(Hpztr)]^{2+}$, the region of dual emission for its deprotonated analogue, indicates that such behavior is not simply attributable to solvent effects such as high viscosity. It is also worth noting that, since the lifetimes of the two components observed for the deprotonated complex are similar, an impurity would have to have a substantial concentration and this possibility can be ruled out by the HPLC and ^1H NMR results.

Another surprising observation is that the energy of the emission observed for the deprotonated complex at 298 K is higher than at 135 K (see Figure 2). Normally, the emission energy of ruthenium polypyridyl complexes shifts to lower energy with increasing temperature. This decrease in energy is generally explained by the increased dipole moment of such compounds in the excited state. The opposite trend observed here suggests that the dipole in the excited state is less than in the ground state. This is not unreasonable since at room temperature the emission is expected to be bpy based, but the negative charge on the bpy ligand is balanced by the charge on the triazole ring, resulting in a lower dipole moment.

A somewhat complicated picture thus emerges for the deprotonated pyrazine compounds. There are two emitting states with different temperature dependences. The high-energy emission process is not observed at room temperature. The resonance Raman data strongly suggest that the low-energy emission observed at room temperature is bpy based. We therefore propose this as the origin of the 700 nm emission signal and suggest that the second state is pyrazine based. The energy separation between the two emitting states at 145 K is 2400 cm^{-1}. Interestingly, this is consistent with the potential difference of 0.33 eV between the bpy- and pyrazine-based reductions in the compound.

The lifetime vs temperature plots in Figure 3 and the corresponding Arrhenius parameters (Table 2) prompt further consideration of these proposals. The 700 nm component shows a very small temperature dependence. The very low activation energy (80 cm^{-1}) and preexponential factor (6.5×10^6 s^{-1}) in this case are indicative of population of a state that is only weakly coupled to the ^{3}MLCT manifold, analogous to what has been observed by Meyer and co-workers[20] for photostable ruthenium polypyridyl complexes and attributed to population of the so-called “fourth” MLCT state of increased singlet character, in preference to the distorted metal-based ^{3}MC state. The situation is somewhat analogous for the deprotonated pyridinyltriazoles (Table 2). This behavior is consistent with the strong ligand field splitting ability of the deprotonated triazole ring, which induces a large energy gap ($>kT$) between the bpy-based ^{3}MLCT state and the ^{3}MC level.

Examination of the temperature dependence of the high-energy emission band reveals quite different behavior. This species exhibits a significant temperature dependence for the emission. Fitting of curve a in Figure 3 to eq 1 produces E_a = 850 cm^{-1} and $A = 2.4 \times 10^{10}$ s^{-1}. These parameters are indicative of population of the ^{3}MC state. This is not unreasonable, since from λ_{max} the gap between the two emitting states is about 2400 cm^{-1}, indicating that the pyrazine-based emitting state is closer to the ^{3}MC state than is the bpy-based one. Balzani and co-workers have described in some detail[21] the interaction between emitting triplet levels in various Ru(II) complexes and the deactivating ^{3}MC state. In their description, three limiting cases are considered. For the first two cases, large prefactors are obtained, $10^{13}-10^{14}$ s^{-1}, which reflect vibrational frequencies associated with activated surface crossing processes. Preexponential factors in the third case are much lower ($\sim 10^{10}$ s^{-1}) and are considered to be indicative of a situation where the ^{3}MLCT and ^{3}MC states are in equilibrium. Under these conditions deactivation is thought to occur through a tunneling type process and is consequently not expected to involve vibrational coupling.

On the basis of this model we suggest that dual emission can be explained by the presence of two weakly coupled emitting states. Of these states deactivation of the higher energy, pyrazine-based, level occurs through the ^{3}MC state. A schematic diagram showing the relative positions of the potential energy curves is given in Figure 6. For the pyrazine-based ^{3}MLCT state the value obtained for the prefactor suggests that this state is in equilibrium with the deactivating ^{3}MC state and that, as a result, deactivation is not governed by vibrational coupling. Hence the effect of deuteration on the emission lifetime of this state is expected to be much more limited, in line with what is experimentally observed for the fully deuterated pyrazine complex (see Table 1). A significant increase in lifetime would have been expected relative to the value for $[Ru(d_8\text{-}bpy)_2(pztr)]^+$ if deactivation of the pyrazine-based triplet state had been vibrationally controlled.

The observed photophysical behavior near 90 K in the glass matrix is at present not fully understood. Only one signal is seen, which fits a single-exponential decay well, although in principle a dual emission is also anticipated in this case. The

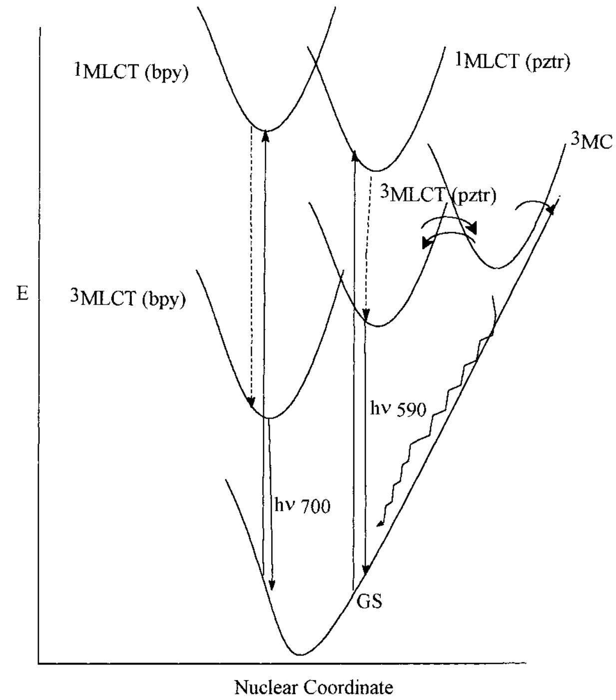

Figure 6. Model representing the excited-state behavior of N^2-[Ru(bpy)$_2$(pztr)]$^+$ and 〰 denotes nonradiative/vibrational relaxation processes.

low-temperature photophysics would be expected to originate from the bipyridyl site, although the spectrum at 90 K (Figure 2a) is also consistent with a pyrazine-based emission. It may be that the bpy-based triplet state lies at higher energy in the solid matrix because of dipole effects. Further experiments involving low-temperature resonance Raman spectroscopy and the use of different excitation wavelengths are in progress in an attempt to further elucidate the situation.

Concluding Remarks

The aim of this study was to investigate the effect of partial deuteration on the emission lifetime properties of mixed ligand ruthenium polypyridyl complexes. The data reported partly support our original hypothesis, that deuteration of a particular ligand would significantly influence the emission lifetime of a mixed ligand complex if the emitting state is based on that ligand. Interestingly, however, in the case where this assumption is not valid, the results obtained highlight a very special situation. One can expect that the presence of two strongly coupled emitting states, based on different ligands, will limit the effect of partial deuteration on the emission lifetime.[5] However, in the system reported here the limited effect of deuteration is explained by the presence of two weakly coupled emitting states, the deactivation of one of which is not strongly influenced by vibrational coupling.

The photophysical properties observed for [Ru(bpy)$_2$(pztr)]$^+$ are thus very unusual. To the best of our knowledge there is only one other example showing this behavior in solution,[22] among the very many mononuclear complexes of Ru(II) that have been studied. In this study Schmehl and Thummel and co-workers report on the interaction between a ruthenium-based ^{3}MLCT level and a pyrene-based $^3(\pi-\pi^*)$ transition that are not in equilibrium. It seems likely that solvent reorganization will play an important role in the photophysics of these systems. In a pyrazine-based excited state the electron is much more localized than when the excited state is bpy based. This is in agreement with the observation that in solid matrixes dual emission is more common.[23]

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Supporting Information Available: Figure S1. ^{1}H NMR spectra in d$_3$-acetonitrile of (a) N^2-[Ru(bpy)$_2$(pztr)]$^+$, (b) N^2-[Ru(d$_8$-bpy)$_2$(pztr)]$^+$, and (c) N^2-[Ru(bpy)$_2$(d$_4$-pztr)]$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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