Resonance Raman and Spectroelectrochemical Investigation of the Location of the Lowest Excited State in Mono- and Dinuclear Ruthenium(II) Complexes Containing Pyrazine Moieties

Colin G. Coates,[†] Tia E. Keyes,[‡] Helen P. Hughes,[‡] Pradeep M. Jayaweera,[†]
John J. McGarvey,*,[†] and Johannes G. Vos*,[‡]

School of Chemistry, Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland, and Inorganic Chemistry Research Centre, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

Received: January 9, 1998; In Final Form: April 16, 1998

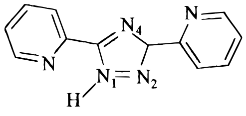
The excited-state properties of mononuclear and dinuclear Ru(bpy)$_2$ complexes with bpzt$^-$ bridging ligand (bpy = 2,2′-bipyridine, and bpzt$^-$ = 3,5-bis(pyrazin-2-yl)-1,2,4-triazole) have been probed by resonance Raman (RR), excited-state absorption (ESA), and spectroelectrochemical techniques. Excited-state RR spectroscopy provides evidence of a lowering of the π^*-level of the bridging ligand upon addition of a second Ru(bpy)$_2$ unit to the mononuclear complex, resulting in switching from a bpy-based to a bpzt-based lowest excited state, within which the data suggest there is charge polarization toward the more readily reduced pyrazine moiety. Further illustration of the sensitivity of these states to the electronic environment has also been observed in the excited-state RR spectra of the protonated mononuclear complex, where the π^*-accepting-level of bpzt is again lowered below that of bpy.

Introduction

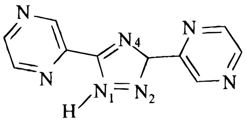
There is continuing interest in the photophysical properties of ruthenium polypyridyl complexes due to their well-recognized role in useful, photochemically driven devices.[1] Tailoring of the photophysics of such complexes is central to their adaptation for useful practical application. Moreover, the linking of mononuclear complexes via bridging ligands generally results in some degree of perturbation to the photophysical states, usually on account of the electronic communication between individual components. The extent of perturbation depends on factors such as the σ-donor/π-acceptor properties of the ligands and/or the identity of the metal centers. The nature of the bridging ligands themselves is a key factor controlling the photophysical properties of polynuclear complexes, the electronic characteristics, size, and shape having considerable bearing on the degree of interaction between linked metal-centered units. Central to the investigation of such factors is the need for effective spectroscopic probes of excited-state properties, which will be sensitive to changes resulting from either slight chemical or other modifications to the immediate external environment.[2−5]

It is well-established that the technique of resonance Raman (RR) spectroscopy is ideally suited to effective probing of the nature of the excited states of metal complexes, capable of providing information concerning the structure and electronic character of such states. In particular, the excellent selectivity of the technique for probing excited-state electronic transitions states has proven effective in characterizing the ^{3}MLCT states of mixed-ligand complexes.[6−8] Excited-state absorption (ESA) and in some cases spectroelectrochemical (thin layer electrode), methods provide a useful complement to the RR studies.[8,9]

Mixed-ligand Ru(II) complexes with electron rich 1,2,4-triazole containing bridging ligands have been investigated in considerable detail by Vos and co-workers.[10−14] Two such ligands are the anions of 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) and 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (Hbpzt). [The triazole ring in Hbpt and Hbpzt is deprotonated when coordinated, leaving a negative charge on the ligand. Throughout the paper we refer to the ligands as bpt and bpzt, omitting the negative charges for convenience.] The two coordinating nitrogen atoms of the triazole ring (N$_1$ and N$_4$) of these asymmetric ligands are inequivalent, the N$_1$ site being a better σ-donor than the N$_4$ position. Such asymmetry can be of value with regard to vectorial energy or electron transfer within photomolecular devices. The photochemistry observed for dinuclear complexes based upon these ligands has recently been reported.[13] The complex with the bpt ligand was found to be photochemically labile at both the N$_1$ and N$_4$ sites of the bridging ligand, while, for the bpzt analogue, it appeared that only the N$_4$ site was photochemically active.



Hbpt



Hbpzt

To further explore this situation, we report here detailed investigations by pulsed laser transient RR (TR^2) techniques, extending some earlier ground-state RR studies,[11] into the nature of the excited states of mono- and dinuclear complexes containing the bpzt ligand. The results obtained, supplemented by excited-state absorption (ESA) and spectroelectrochemical studies, show how relatively minor modifications to the electronic environment can substantially influence the position on which the photoexcited electron resides in the ^{3}MLCT state. Early examples of the use of RR and TR^2 methods to probe the influence of minor chemical modifications to the ligands on the excited states of mononuclear ruthenium(II) polypyridyl

---

[†] Queen's University of Belfast.
[‡] Dublin City University.

S1089-5639(98)00737-3 CCC: $15.00

complexes have been described by Kincaid and co-workers[7a] and Mabrouk and Wrighton.[7b]

Experimental Section

Chemicals. $[Ru(bpy)_2(bpzt)]^+$ (**1**) and $[(Ru(bpy)_2)_2(bpzt)]^{3+}$ (**2**) were prepared and purified using semipreparative HPLC methods as reported previously.[10,11]

Instrumentation. UV−vis absorption spectra were recorded using a diode array spectrophotometer (Hewlett-Packard Model 8452A).

Ground-state Raman spectra were recorded using a CCD detector (Princeton Instruments Model LN/UV 1152) coupled to a Jobin-Yvon HR640 spectrometer. The excitation source was an Ar^+ laser (Spectra Physics Model 2025 with outputs at 351.4 nm, at 363.8 nm, and in the visible range (450−528) nm. The laser power at the sample was typically 25−40 mW.

Laser flash photolysis and time-resolved ESA measurements employed rapid response spectrophotometric detection coupled to a digitizer (Tektronix 7912AD) for single channel transient kinetic studies. A gated, multichannel dual diode array detector (Princeton Instruments Model DIDA 700G) was used to record ESA spectra.[3] For both flash photolysis and transient Raman studies (see below), excitation wavelengths covering the range 355−600 nm were provided by Q-switched Nd:YAG lasers (Spectra Physics Models DCR2 and GCR3) operating at 355 or 532 nm, coupled to a dye laser (Spectra Physics PDL3) or a stimulated Raman wavelength-shifting cell[8] filled with H_2 or CH_4.

Most excited-state resonance Raman spectra were generated by the single-color pump and probe method[15] in which the leading edge of the laser pulse incident on the sample pumps the molecules into the excited state and the trailing edge probes the Raman scattering. Samples were contained in spinning cells in order to minimize the possibility of thermal and/or photodegradation, especially where relatively long spectral accumulation times (10−15 min) at a pulse repetition rate of 10 Hz were required to obtain transient RR spectra of good signal quality. The transient spectra were recorded using a multichannel detector (EG&G OMA III with Model 1420B intensified detector) coupled to a triple spectrometer of simple, in-house design, described earlier.[15b] Incident pulse energies for the excited-state RR experiments were typically ca. 3 mJ and for flash photolysis and ESA measurements, somewhat higher, in the region of 10 mJ. The concentrations of **1** and **2** used for resonance Raman (ground state and transient) and flash photolysis studies were typically 10^{-4} mol dm^{-3}.

Spectroelectrochemistry was carried out using an OTTLE setup comprising a homemade Pyrex glass, thin layer cell (1 mm). The optically transparent working electrode was made from platinum gauze, the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl. Spectroelectrochemistry was carried out in HPLC-grade acetonitrile, and the electrolyte employed was 0.1 M tetraethylammonium tetrafluoroborate. The working electrode was held at the required potential throughout the measurement using an EG&G PAR Model 362 scanning potentiostat. Absorption spectra of species generated in the OTTLE cell were recorded on a Shimadzu 3100 UV−vis/near-IR spectrophotometer interfaced with an Elonex PC-433.

Results

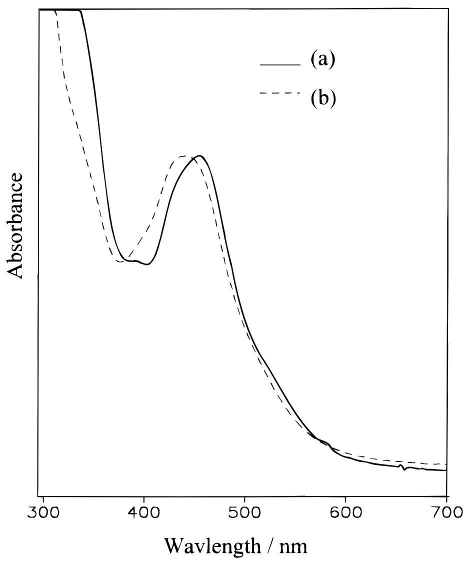


Figure 1. UV−vis spectra of (a) $[Ru(bpy)_2bpzt]^+$ and (b) $[(Ru(bpy)_2)_2bpzt]^{3+}$ in acetonitrile.

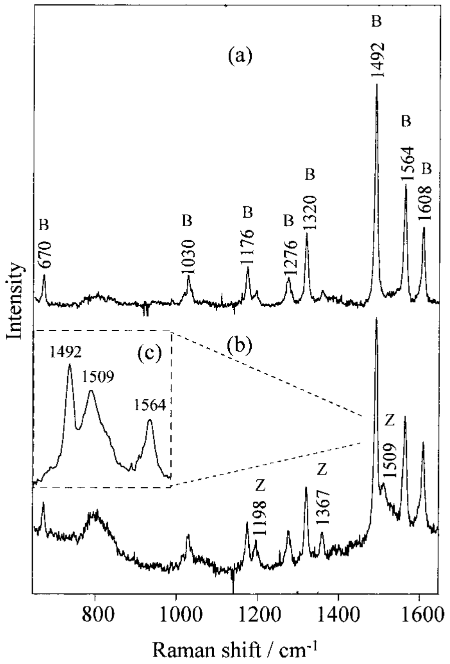


Figure 2. Ground-state RR spectra recorded at $\lambda_{ex} = 457.9$ nm of (a) $[Ru(bpy)_2bpzt]^+$ and (b) $[(Ru(bpy)_2)_2bpzt]^{3+}$ in acetonitrile (solvent peaks subtracted). (Inset c) 1492, 1509, and 1564 cm^{-1} bands of $[(Ru(bpy)_2)_2bpzt]^{3+}$ in water. B and Z denote bpy and bpzt features, respectively.

Ground State. Figure 1 shows the UV−vis spectra of both mononuclear **(1)** and dinuclear **(2)** complexes in acetonitrile. The MLCT absorption region, showing a maximum near 450 nm, is relatively unresolved for both complexes. For **1** a slight shoulder can be identified on the low-energy side of the spectrum, near 530 nm. A slight blue shift, from 450 to 445 nm, can be observed in the position of the absorption maximum upon addition of the second $Ru(bpy)_2$ moiety.

Ground electronic state RR spectra recorded using 457.9 nm excitation for each complex in acetonitrile solution are shown in Figure 2. A series of bands at 1608, 1564, 1492, 1320, 1276, 1176, and 1030 cm^{-1} are attributable to ground-state bpy modes. Also present in both spectra are some additional features, at 1509, 1367, and 1198 cm^{-1} which are somewhat more intense (relative to the bpy bands), for the dinuclear complex **2**. These are assigned to vibrational modes of the bpzt bridging ligand, enhanced through resonance with a $Ru^{II} \rightarrow$ bpzt MLCT transition occurring on the low-energy side of the MLCT

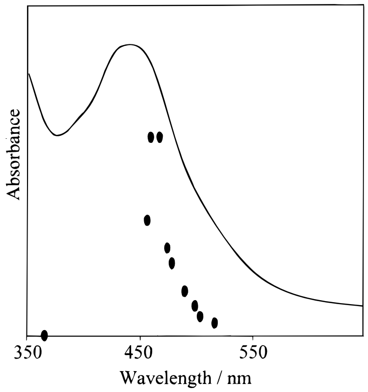


Figure 3. Excitation profile (●) for the 1509 cm^{-1} mode of [(Ru(bpy)$_2$)$_2$bpzt]$^{3+}$ in water.

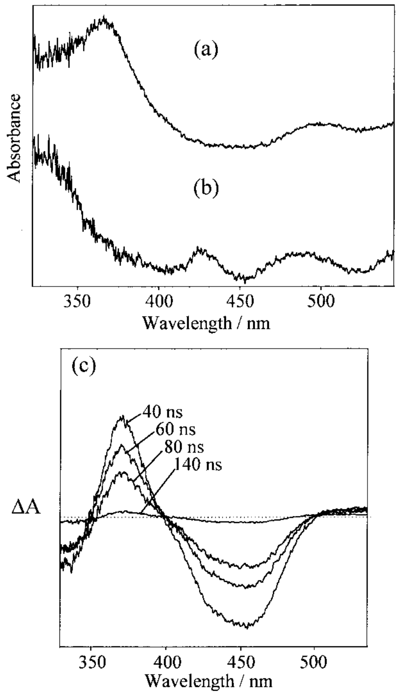


Figure 4. Excited-state absorption (ESA) spectra recorded with $\lambda_{ex} =$ 416 nm of [Ru(bpy)$_2$bpzt]$^+$ (a) and [(Ru(bpy)$_2$)$_2$bpzt]$^{3+}$ (b), using gated multichannel diode array, 20 ns after laser excitation. Spectra corrected for ground-state depletion. (c) [Ru(bpy)$_2$bpzt]$^+$at varying time delays after laser excitation, uncorrected for ground-state depletion.

absorption region. The increase in relative intensity of these bands in the spectrum of **2** is apparently due to the blue shift of the MLCT transition, bringing it more into resonance with the 457.9 nm probe wavelength. This is supported by the excitation profile shown in Figure 3 for the 1509 cm^{-1} band of **2** [not possible for **1** due to sample fluorescence] recorded in aqueous solution, suggesting that the underlying transition is most likely assignable as Ru^{II} → bpzt in character.

Excited-State Studies. Flash photolysis experiments were carried out on **1** and **2**, employing a 416 nm excitation pulse (10 mJ). Both complexes exhibited strong, exponentially decaying excited-state absorption transients in the 300−400 nm wavelength region. The excited-state lifetimes recorded in degassed acetonitrile at several monitoring wavelengths within this range were comparable, 290 ns for **1** and 260 ns for **2.** The excited-state absorption spectra of both complexes, recorded 20 ns after laser excitation, are shown in Figure 4a,b. The strong absorption band between 300 and 400 nm clearly maximizes in the case of the bimetallic species (**2**) (ca. 340 nm) to the blue of the absorbance maximum for the mononuclear species (**1**) (ca. 370 nm). Other differences are clear also, notably the band in the 500 nm region is blue shifted for the dinuclear complex (**2**), relative to that of the mononuclear complex (**1**). Further studies at increasing time delays after excitation (exemplified in trace c for **1**) showed that the spectral profiles changed only in intensity with time, suggesting in both instances the involvement of a single excited-state species over the temporal range studied.

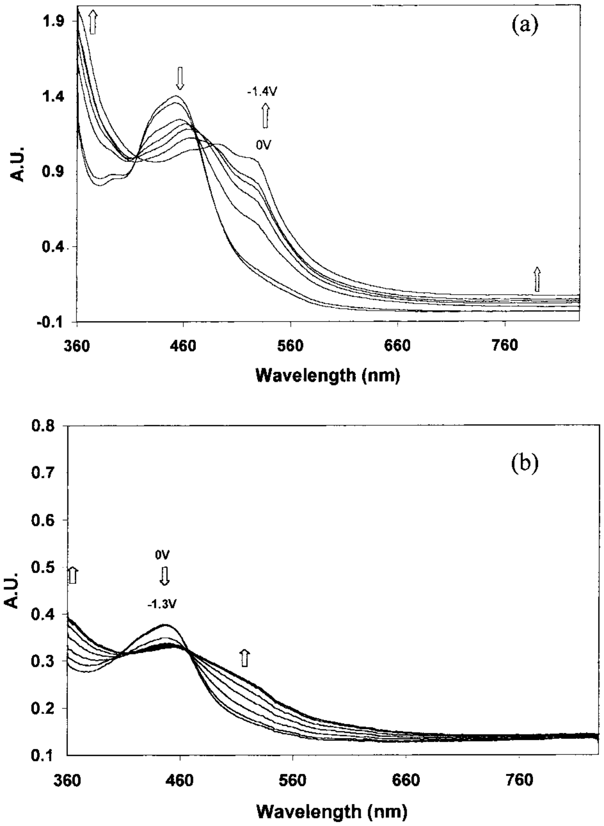


Figure 5. Spectroelectrochemistry of first reductions of (a) [Ru(bpy)$_2$(bpzt)]$^+$ at −1.4 V vs SCE and (b) [(Ru(bpy)$_2$)$_2$(bpzt)]$^{3+}$ at −1.3 V vs SCE.

As a complement to the ESA studies, UV−vis absorption changes corresponding to the first electrochemical reduction were recorded by the OTTLE technique. A potential of −1.4 V for **1** and −1.3 V for **2** was applied to the working electrode and UV−vis spectra of the complexes were recorded. The results are shown in Figure 5a,b. In each case, concomitant with depletion of the MLCT absorption bands in the visible of the unreduced complex, growth of a strong band at higher energy (300−400 nm) occurred, together with a weaker feature at lower energy (>500 nm). The effects were reversible over the potential ranges studied.

Excited-State RR Spectra. Figure 6a shows the transient resonance Raman spectrum of **1** recorded in acetonitrile using 355 nm pulsed excitation. Photon flux was sufficient to ensure a high degree of conversion to excited-state species within the laser pulse duration. The most prominent bands in the spectrum appear at 1548, 1427, 1289, 1212, 1016, and 743 cm^{-1} and are readily attributable to modes of the bpy$^{\bullet-}$ radical anion on the basis of extensive literature evidence.[15a,16] Bands at 1606, 1491, 1321, 1178, and 1030 cm^{-1} due the neutral bpy ligand are also apparent. The remaining features can reasonably be attributed to modes of the bpzt ligand. Support for this interpretation is provided by the comparison in Table 1 of the positions of these bands with those attributed to the neutral bipyrazine (bpz) ligand

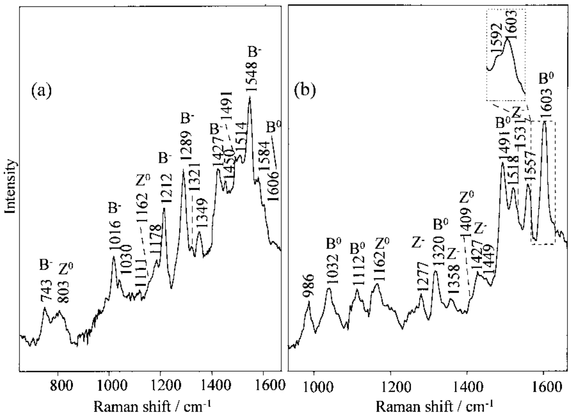


Figure 6. Excited-state RR spectra at $\lambda_{ex} = 355$ nm using the single-color pulse technique: (a) $[Ru(bpy)_2bpzt]^+$ in acetonitrile (solvent peaks subtracted) and (b) $[(Ru(bpy)_2)_2bpzt]^{3+}$ in water. B^0, B^-, Z^0, Z^- denote bands attributed to neutral and anionic ligands bpy (B) and bpzt (Z), respectively.

TABLE 1: Comparison of Bridging Ligand (bpzt) Modes Identified from 355 nm Spectrum of 1 with Neutral Ligand Modes of bpz

bpzt ligand	bpz neutral ligand	bpzt ligand	bpz neutral ligand
1514	1518	1161	1161
1409	1410	803	801
1349	1347		

TABLE 2: Comparison of Bridging Ligand (bpzt) Modes Identified from 355 nm Spectrum of 2 with Pyrazine Radical Anion Modes

bpzt features	$Bpz^{\bullet-}$ features[7]	bpzt features	$Bpz^{\bullet-}$ features[7]
1592[a]	blank	1427	1430
1531	1538	1409	1409
1518[a]	blank	1358	1358
1491	1489	1277	1274

[a] Neutral ligand features.

in the transient RR spectrum of the localized excited state (formulated as $[Ru^{III}(bpz)_2(bpz^{\bullet-})]^{2+}$) of the complex $[Ru(bpz)_3]^{2+}$, investigated by Danzer and Kincaid.[7c]

Figure 6b shows the excited-state RR spectrum recorded for the dinuclear complex **2** in water using 355 nm excitation. (A very similar spectrum was recorded in acetonitrile, but the signal: noise ratio of the spectra in water is slightly more favorable.) Absent are the characteristic $bpy^{\bullet-}$ features evident in the spectrum of **1**, but the spectrum does contain a more intense set of neutral bpy ligand features at 1603, 1557, 1491, 1320, 1112, and 1032 cm^{-1}. Of the additional bands present, several are close in position to $bpz^{\bullet-}$ (bipyrazine radical anion) modes in the 355 nm excited spectrum of $[Ru(bpz)_3]^{2+}$ reported by Kincaid and co-workers,[7c,d] listed in Table 2. Remaining features at 1592, 1518, and 1162 cm^{-1} can be attributed to bpz neutral ligand modes.

Transient RR spectra of the dinuclear complex **2** were also recorded using pulsed excitation at 460 nm, as a function of laser energy. The results are shown in Figure 7. Comparison with the spectra generated by continuous wave (cw) excitation at 457.9 nm (Figure 2) shows that increasing the laser power results in a depletion of features at 1199, 1366, and 1509 cm^{-1}, attributed earlier (Figure 2) to modes of the bpzt bridging ligand. However this wavelength is off resonance with transitions of the MLCT excited state, and there is no evidence of a concomitant growth of any excited-state features at this probe wavelength. The absence of excited-state bands was confirmed by a time-resolved resonance Raman study in which the sample was probed at 460 nm at a delay of 20 ns following 355 nm excitation. Raman spectra of electrochemically reduced **2** were also recorded in a similar spectral region ($\lambda = 476.5$ nm). In parallel with the results from the excited-state studies in Figure 7, the spectra (not shown here) indicate the depletion of bridging ligand bands upon electrochemical reduction (−1.3 V) but no new features grow in.

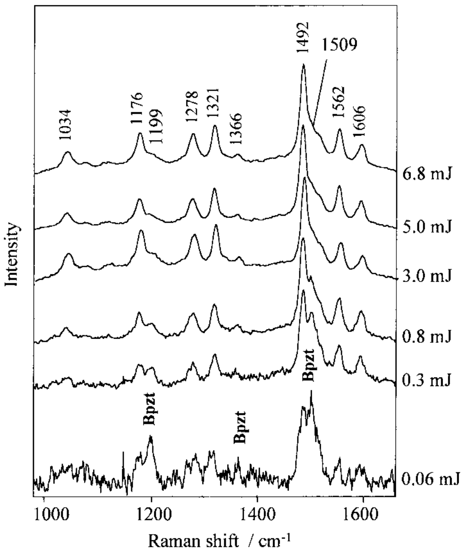


Figure 7. Excited-state RR spectra of $[(Ru(bpy)_2)_2bpzt]^{3+}$ in water recorded at increasing pulse energies using the single-color pulse technique, $\lambda_{ex} = 460$ nm.

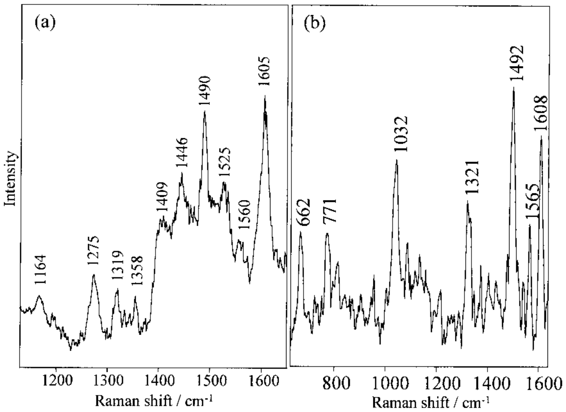


Figure 8. Excited-state RR spectra using the single-color pulse technique of $[(Ru(bpy)_2)_2bpzt]^{3+}$ in acetonitrile (solvent peaks subtracted): (a) $\lambda_{ex} = 532$ nm and (b) $\lambda_{ex} = 321$ nm.

Excited-state RR spectra of **2** recorded in acetonitrile using pulsed 532 nm excitation are shown in Figure 8a. Features are present at 1490, 1409, 1358, and 1275 cm^{-1}, which correspond closely with bands characteristic[7c,d] of pyrazine radical anion, see Table 2, as well as bands at 1605 and 1164 cm^{-1} which are attributable[7d] to modes associated with neutral pyrazine.[17] By contrast, Figure 8(b) shows an excited-state RR spectrum recorded of **2** in acetonitrile using excitation at 321 nm in order to probe the higher energy side of the excited-state absorption region between 300 and 400 nm (Figure 4). It is apparent that several prominent bands due to neutral bpy are present in this spectrum.

In Figure 9 the transient RR spectra shown were recorded using pulsed excitation at 355 nm for complex **1** in acetonitrile, following the addition of small amounts of either diethylamine (DEA), trace a, or trifluoroacetic acid (TFA), trace b. The

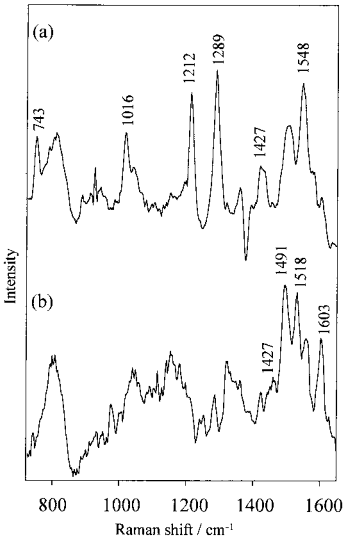


Figure 9. Excited-state RR spectra using the single-color pulse technique (laser pulse duration ca. 8 ns) at 355 nm of $[Ru(bpy)_2bpzt]^+$ in acetonitrile (subtracted) with dropwise additions of (a) diethylamine (deprotonated) and (b) trifluoroacetic acid (protonated).

spectra differ significantly, that of the complex with DEA (i.e. deprotonated) consisting of features attributable to a $bpy^{\bullet -}$-based lowest excited state. In contrast, the pattern of bands in the presence of TFA (i.e. protonated) shows a marked similarity to that observed for the dinuclear complex **2** in Figure 6b. The transient spectrum of **1** recorded in water (spectrum not shown) is also very similar to the foregoing, suggesting that protonation of the triazole ligand readily occurs in this medium. The dinuclear complex **2** cannot be protonated.

Discussion

Ground State. Ground-state RR spectra recorded at 457.9 nm (Figure 1) show that the visible region around 450 nm arises from MLCT transitions to both bpy and bpzt ligands, the $Ru^{II} \rightarrow$ bpzt transition appearing to contribute more to the low-energy side of the absorption band, as suggested by the excitation profile in Figure 3 of the 1509 cm^{-1} feature. Additionally, the bpzt (bridging ligand) bands show an increase in relative intensity in the spectrum of **2**, most likely the result of a blue shift in the latter spectrum (Figure 1), bringing it more into resonance with the excitation wavelength. Such a shift of the MLCT transitions in the dinuclear compound can be expected upon addition of a second metal center to the bridge. In the dinuclear complex, the σ-donor capacity of the triazolate anion component of the bridging ligand is shared with an extra metal center, and as a result, the metal t_{2g} orbitals are stabilized. However, it is likely that this increase in the energy gap is being counteracted for the $Ru^{II} \rightarrow$ bpzt transition because of stabilization of π^* accepting levels on the bpzt bridging ligand upon complexation to a second $Ru(bpy)_2$ moiety.[10,11]

Excited State. The ESA spectra of **1** and **2** exhibit distinctly different absorption maxima, particularly in the region of strong absorption below 400 nm (Figure 4). This in itself suggests that in the two compounds the excited electron is located on different ligands.

However, the most compelling evidence concerning the nature of the lowest excited states of the complexes comes from the transient resonance Raman spectra probed in this same spectral region. The spectrum of **1** in acetonitrile recorded using 355 nm excitation (Figure 6a) consists of features which can be associated with three distinct moieties in the complex: $bpy^{\bullet -}$ radical anion, bpy neutral ligand, and pyrazine neutral ligand, thus providing clear evidence of localization of the photoexcited electron onto a bpy ligand in the lowest energy ^{3}MLCT state. This accords with the excited-state absorption profile of this complex where the most prominent band maximum lies near 360 nm (Figure 4a). However, the enhancement of bands attributable to neutral pyrazine, as demonstrated by the comparisons in Table 1, shows that some contribution to the absorption intensity at this excitation wavelength comes from a $\pi \rightarrow \pi^*$ transition centered on pyrazine. It is interesting to note here for complex **1** that while it appears that the lowest energy ^{1}MLCT state involves the bpzt ligand, the TR^2 spectra show that the lowest energy ^{3}MLCT state is bpy-localized. A similar effect has been noted with a related compound[18] and the phenomenon is under further investigation, employing selective deuteriation and variable temperature excited-state lifetime studies.

On the basis of the comparisons in Table 2, the transient RR spectrum of **2** excited at 355 nm (Figure 6b) shows a set of features which provide evidence for electron localization on a pyrazine ring in the lowest excited state in this case. Significantly, the group of features attributable to neutral bpy ligand which also appear (Figure 6b) are markedly more intense than those in the spectrum of **1**, in Figure 6a, which is what would be expected if the excited electron in the ^{3}MLCT state in **2** is indeed localized on pyrazine, since four neutral bpy ligands would now be present. Since there is no evidence for $bpy^{\bullet -}$ features, it is apparent that coordination of a second $Ru(bpy)_2$ unit has the effect of lowering the π^* accepting level of the bridging ligand below that of the bpy ligands.[7d,11] The features appearing in the spectrum of **2** which are attributable to modes of neutral pyrazine have additional significance. Under the conditions of pulse excitation used in these studies, population of the ^{3}MLCT state of **2** is virtually complete so that the presence of bands due to neutral pyrazine cannot reasonably be ascribed to the residual ground state of **2**. Hence their appearance suggests a ^{3}MLCT state in which the electron is localized on one of the pyrazine rings, leaving the other unreduced. In effect, charge is polarized toward one pyrazine ring. The use of transient resonance Raman spectroscopy to probe charge polarization in acceptor ligand orbitals in metal polypyridyl excited states was first reported and discussed by Kincaid and co-workers.[7c,d] The conclusion arrived at in the present work is somewhat reminiscent of that reached[7c,19] in the case of complexes such as $[Ru(bpy)(bpz)_2]$ in which transient RR measurements pointed to localization of the electron on one bpz ligand in the lowest ^{3}MLCT excited state. The appearance of bands attributable to the pyrazine radical anion in the excited-state RR spectrum of **2** probed at 532 nm (Figure 8a) suggests that the weaker region of excited-state absorption maximizing near 500 nm is also due to a $\pi^*-\pi^*$ transition of the reduced bpzt ligand in the ^{3}MLCT state. Moreover, the presence of bands which could be assigned as "neutral bpz" features, analogous to what was found in the 355 nm excited spectrum, is also consistent with electron localization on one pyrazine fragment.

It is interesting that the excited-state RR spectrum of **2** recorded at 321 nm (Figure 8b) showed only strong enhancement of "neutral bpy" features. It therefore appears that the major contribution to the high-energy side of the excited-state absorption band between 300 and 400 nm (Figure 4) arises from neutral bpy-localized transitions. The $\pi^*-\pi^*$ transition localized on pyrazine radical anion then becomes the principal contributor to the lower energy side of the absorption. These conclusions help to rationalize the changes observed in this region of the ESA spectra (Figure 4), upon addition of a second Ru(bpy)$_2$ moiety, i.e., going from **1** to **2**. It would be expected that the accompanying switch from a bpy$^{\bullet -}$-localized to a pyrazine radical anion-localized ^{3}MLCT state would result in a greater contribution from neutral bpy transitions to this absorption, thus accounting for the higher energy side of the 300−400 nm band being dominant in the ESA spectrum of **2**.

The UV−vis spectra in Figure 5 recorded using the OTTLE technique of the first reduction product for **2** showed features similar to the above ESA spectra. The bands are attributable to $\pi^*-\pi^*$ transitions of the reduced ligand containing the promoted electron, in effect serving as an electrochemical model[20] of the ^{3}MLCT excited state of **2**. Although the RR investigations of **2** using pulsed 460 nm excitation (Figure 7) show no new features, but only the depletion of several ground-state bands (1199, 1366, and 1509 cm^{-1}) of the bpzt bridging ligand, the results are in fact consistent with the conclusions which emerge from the studies using 355 and 532 nm excitation, namely, that the excited electron is localized on a pyrazine ring. An excitation wavelength of 460 nm is not in resonance with pyrazine radical anion transitions and depletion of a 1509 cm^{-1} ground-state band as the only notable feature of the RR spectrum recorded following electrochemical reduction of **2** is in line with the conclusion reached above.

The influence of the chemical environment on the excited-state RR spectra of the mononuclear complex (**1**) is also interesting. It is clear from Figure 9 that, for **1**, protonation results in a lowering of the π^* accepting level below the bpy π^* level, yielding a ^{3}MLCT state in which the electron resides on the bpzt ligand. Thus, protonation of the mononuclear complex has a similar effect on the character of the lowest ^{3}MLCT excited state as does the addition of a second Ru(bpy)$_2$ moiety to the bridging ligand. The fact that the bands which appear upon protonation of **1** (Figure 9b) also match rather closely those of the pyrazine radical anion (see Table 2) suggests that the similarity between the ^{3}MLCT states of **2** and protonated **1** extends to the polarization of charge toward one of the pyrazines on the bridging ligand.

Earlier excited-state RR studies[21] of the analogous mononuclear and dinuclear complexes $[Ru(bpy)_2(bpt)]^+$ (Hbpt = 3,5′-bis(pyridinyl-2-yl)-1,2,4-triazole) and $[(Ru(bpy)_2)_2(bpt)]^{3+}$ in acetonitrile by single-color pump and probe excitation at 355 nm yielded spectra (not shown here) consisting of features attributable to bpy$^{\bullet -}$ for *both* complexes. Furthermore, no spectral changes occurred upon protonation of the triazole component of the bpt ligand. Hence, switching pyrazine to pyridyl groups to give the bpt bridging ligand has the effect of increasing the energy of the π^* accepting orbital of this ligand above that of bpy, such that complexation to a second Ru(bpy)$_2$ unit fails to stabilize the level sufficiently to result in a bpt-based excited state.

Concluding Remarks

The technique of RR spectroscopy has proven particularly successful for exploration of the nature of the excited states of the mixed-ligand complexes of Ru(II) studied here. Previous ground electronic state RR studies[11] provided information about the vertical (Franck−Condon) state reached in the electronic transition. In the TR^2 experiments the thermally equilibrated ^{3}MLCT state is addressed and in the case of dinuclear complex (**2**), the results provide direct evidence for electron localization within the reduced bpzt bridging ligand. Perturbations to the electronic environment in the mononuclear complex (**1**), effected by either protonation of the bpzt ligand or the addition of a second Ru(II) center, result in a switching of the ligand on which the LUMO is based. This observation and the evidence for charge polarization toward one pyrazine of the reduced bpzt bridge in the ^{3}MLCT state of **2** are of interest in the context of the previously reported asymmetry in the electronic nature of the bridging ligand in the lowest MLCT excited state of this complex,[13] where it has been postulated that the emitting state is located on the N1 site of the triazole ring, while photosubstitution occurs at the N4 site. This interpretation will be evaluated more thoroughly in future resonance Raman studies using partially deuterated bpzt ligand[22] which will also serve to refine the above conclusions concerning localized excited states.

Acknowledgment. The work was supported by the EC Joule program, TMR Grant CT96-0076, and by the EPSRC (Grant GRJ/01905).

References and Notes

(1) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991.

(2) Nieuwenhuis, H. A.; Stufkins, D. J.; McNicholl, R.-A.; McGarvey, J. J.; Coates, C. G., Al-Obaidi, A. H. R.; Westwell, J. R.; George, M. W.; Turner, J. J. *J. Am. Chem. Soc.* **1995**, *117*, 5579.

(3) Coates, C. G.; Jacquet, L.; McGarvey, J. J.; Bell, S. E. J.; Al-Obaidi, A. H. R.; Kelly, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 7130.

(4) Mongey, K. F.; Vos, J. G.; MacGraith, B. D.; McDonagh, C. M.; Coates, C. G.; McGarvey, J. J. *J. Mater. Chem.* **1997**, *7*, 1473.

(5) Maruszewski, K.; Kincaid, J. R. *Inorg. Chem.* **1995**, *34*, 2002.

(6) Schoonover, J.R.; Strouse, G. F. *Chem. Rev.*, in press, and references cited therein.

(7) (a) McClanahan, S. F.; Dallinger, R. F.; Holler, James, F.; Kincaid, J. R. *J. Am. Chem. Soc.*, **1985**, *107*, 4853. (b) Mabrouk, P. F.; Wrighton, M. S. *Inorg. Chem.* **1985**, *25*, 526. (c) Danzer, G. D.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 3976. (d) Danzer, G. D.; Golus, J. A.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8643.

(8) Al-Obaidi, A. H. R.; Gordon, K. C.; McGarvey, J. J.; Bell, S. E. J.; Grimshaw, J. *J. Phys. Chem.* **1993**, *97*, 10942.

(9) Gordon, K. C.; Al-Obaidi, A. H. R.; Jayaweera, P. M.; McGarvey, J. J.; Malone, J. F.; Bell, S. E. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1591.

(10) Hage, R. H.; Dijkhuis, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* **1988**, *27*, 2185.

(11) Hage, R.; Haasnoot, J. G.; Reedijk, J.; Wang, R.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 3263.

(12) Hughes, H. P.; Martin, D.; Bell, S. E. J.; McGarvey, J. J.; Vos, J. G. *Inorg, Chem.* **1993**, *32*, 4402.

(13) Hughes, H. P.; Vos, J. G. *Inorg. Chem.* **1995**, *34*, 4001.

(14) Keyes, T. E.; Vos, J. G.; Kolnaar, J. A.; Haasnoot, J. G.; Reedijk, J.; Hage, R. H. *Inorg. Chim. Acta* **1996**, 237.

(15) (a) Dallinger R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (b) Gordon, K. C.; McGarvey, J. J. *Inorg. Chem.* **1991**, *30*, 2986.

(16) Strommen, D. P.; Mallick, P. K.; Danzer, G. D.; Lumpkin, R. S.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 1357.

(17) The bands at 1605 and 1490 cm^{-1} most likely contain significant contribution from neutral bpy modes, accompanying the isolated bpy modes at 1560 and 1320 cm^{-1}.

(18) Keyes, T. E.; O'Connor, C.; Vos, J. G. *J. Chem. Soc., Chem. Commun.*, in press.

(19) Tait, C. D.; Donohoe, R, J,; DeArmond, M. K.; Wertz, D. W. *Inorg. Chem.* **1987**, *26*, 2754.

(20) For technical reasons, it was not possible to record resonance Raman spectra of the reduced species in situ in the OTTLE cell. It would clearly be of interest to have such spectra of the reduced anion, with both metal centers still in the Ru(II) state, for comparison with the spectra of the MLCT excited state of **2**. Such studies are planned.

(21) Martin, D. I. C. Ph.D. Thesis, Queen's University of Belfast, 1993.

(22) Keyes, T. E.; Weldon, F.; Muller, E.; Pechy, P.; Gratzel, M.; Vos, J. G.; *J. Chem. Soc., Dalton Trans.* **1995**, 2705.