Photophysical and Photochemical Properties of Dinuclear Ruthenium(II) Complexes Containing 2,2'-Bipyridine and 1,10-Phenanthroline Moieties

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The excited state and redox properties of the two mixed-ligand species [Ru(bpy)$_2$(bpt)Ru(phen)$_2$](PF$_6$)$_3$ and [Ru-(phen)$_2$(bpt)Ru(bpy)$_2$](PF$_6$)$_3$ are reported (where bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, and Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole) and compared with those obtained for [Ru(bpy)$_2$(bpt)]PF$_6$·1/2H$_2$O, [(Ru-(bpy)$_2$)$_2$(bpt)](PF$_6$)$_3$, [Ru(phen)$_2$(bpt)]PF$_6$·H$_2$O, [(Ru(phen)$_2$)$_2$(bpt)](PF$_6$)$_3$, [Ru(bpy)$_3$]$^{2+}$, and [Ru(phen)$_3$]$^{2+}$. Spectroelectrochemical data indicate that in all dinuclear compounds the ruthenium unit bound to the N1 site of the triazole ring is oxidized first. In both [Ru(bpy)$_2$(bpt)Ru(phen)$_2$]$^{3+}$ and [Ru(phen)$_2$(bpt)Ru(bpy)$_2$]$^{3+}$ the lowest ^{3}MLCT state is bpy based. Upon photolysis in MeCN only the metal center bound to the N4-site of the triazole ring is labilized. However, in MeCN/Cl$^-$ and CH$_2$Cl$_2$/Cl$^-$ solutions, both the N1 and N4 sites are photoreactive.

Introduction

There continues to be great interest in the physical properties of ruthenium polypyridyl compounds,[1–20] due to the possibility of producing compounds capable of performing useful light-induced functions and in particular their potential application in photochemically driven molecular devices.[21,22] Investigations in this area have been aimed at the synthesis and study of often oligonuclear metal complexes that might have potential for light-induced energy and electron transfer processes. Because of the rich synthetic chemistry available, many mixed-ligand complexes of the type [Ru(L$_1$)$_{n-3}$(L$_2$)$_n$]$^{2+}$ have been prepared with the aim to tune the excited-state properties.[23] To investigate such systems

many different photophysical and electrochemical techniques have been applied successfully for the identification of the excited states, in cases where the electronic properties of the ligands L$_1$ and L$_2$ are significantly different. If, however, L$_1$ and L$_2$ have very similar electronic properties, such studies are often less successful. Typical examples of such more complex systems are those containing both 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands.[24] Investigations carried out on these compounds have been less definitive in identifying the nature of the emitting state.[25]

In oligonuclear compounds the bridging ligand is an important parameter as it often controls the physical properties of the compounds.[26] Recently we reported a series of studies on the anion of 3,5-bis(pyridin-2-yl)-1,2,4-triazole (bpt$^-$)[27–30] (see Figure 1). It was found that the two nitrogen atoms of the triazole ring have quite different σ-donor properties and are therefore inequivalent and also that interaction between the two metal centers is very efficient. On the basis of this observation it was postulated that as a result in dinuclear complexes of the type [Ru(L$_2$)-bptRu(L$_2$)]$^{3+}$, the emitting state is located on the ruthenium center bound to the N1 site of the triazole ring, while photosubstitution is occurring at the N4 site of the bridging ligand[31] (see Figure 1). This would be important for the application of such compounds in molecular devices, since these differences might be used to effect vectorial energy or electron transfer. However, the differences between the two sites are small, and it has so far not been possible to obtain a good estimate of their importance for the physical properties of these compounds.

 (1) Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F.; Elliot, C. M.; Freitag, R. A.; Merkert, J. W. *Inorg. Chem.* 1986, *25*, 2440.
 (2) Hage, R.; Haasnoot, J. G.; Stufkens, D. J.; Snoek, T. L.; Vos, J. G.; Reedijk, J. *Inorg. Chem.* 1989, *28*, 1413.
 (3) Bignozzi, C. A.; Paradisi, C.; Roffia, S.; Scandola, F. *Inorg. Chem.* 1988, *27*, 408.
 (4) Curtis, J. C.; Bernstein, J. S.; Meyer, T. J. *Inorg. Chem.* 1985, *24*, 385.
 (5) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* 1982, *21*, 3849.
 (6) Murphy, W. R.; Brewer, K. J.; Gettliffe, G.; Peterson, J. D. *Inorg. Chem.* 1989, *28*, 81.
 (7) de Wolf, J. M.; Hage, R.; Haasnoot, J. G.; Reedijk, J. *New J. Chem.* 1991, *15*, 501.
 (8) Haga, M.; Matsumura-Inoue, T.; Yamabe, S. *Inorg. Chem.* 1987, *26*, 4148.
 (9) Campagna, S.; Denti, G.; De Rosa, G.; Sabatino, G.; Ciano, M.; Balzani, V. *Inorg. Chem.* 1989, *28*, 2565.
(10) Haga, M. *Inorg. Chim. Acta* 1983, *75*, 29.
(11) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, R.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* 1987, *109*, 2691.
(12) Di Marco, G.; Bartolotto, A.; Ricevuto, V.; Campagna, S.; Denti, G.; Sabatino, L.; De Rosa, G. *Inorg. Chem.* 1991, *30*, 270.
(13) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chim. Acta* 1990, *176*, 175.
(14) Akasheh, T. S.; Jibril, I.; Shraim, A. M. *Inorg. Chim. Acta* 1990, *175*, 171.
(15) Scandola, F.; Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A. *Coord. Chem. Rev.* 1990, *97*, 299.
(16) Kalyanasundaram, K.; Grätzel, M.; Nazeeruddin, M. K. *J. Chem. Soc., Dalton Trans.* 1991, 343.
(17) Serroni, S.; Denti, G.; Campagna, S.; Ciano, M.; Balzani, V. *J. Chem. Soc., Chem. Commun.* 1991, 944.
(18) Haga, M.; Ano, T.; Kano, K.; Yamabe, S. *Inorg. Chem.* 1991, *30*, 3843.
(19) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* 1988, *27*, 1146.
(20) Petersen, J. D.; Murphy, W. R., Jr.; Sahai, R.; Brewer, K. J.; Ruminiski, R. R. *Coord. Chem. Rev.* 1985, *64*, 261.
(21) Balzani, V., Scandola, F., Eds. *Supramolecular Photochemistry*; Reidel: Dordrecht, The Netherlands, 1987.
(22) Seddon, K. R.; Seddon, E. A. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1981; and references therein.
(23) Cocks, A. T.; Wright, R. D.; Seddon, K. R. *Chem. Phys. Lett.* 1982, *85*, 369.
(24) (a) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* 1980, *102*, 1309. (b) Baggot, J. E.; Gregory, G. K.; Pilling, M. J.; Anderson, S.; Seddon, K. R.; Turp, J. E. *J. Chem. Soc., Faraday Trans. 2* 1983, *79*, 195.
(25) (a) Chang, Y. J.; Xu, X.; Yabe, T.; Yu, S.; Anderson, D. R.; Orman, L. K.; and Hopkins, J. B. *J. Phys. Chem.* 1990, *94*, 729. (b) Kumar, C. V.; Barton, J. K.; Gould, I. R.; Turro, N. J.; van Houten, J. *Inorg. Chem.*, 1988, *27*, 648.
(26) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* 1983, *105*, 40.
(27) Hage, R.; Haasnoot, J. G.; Nieuwenhuis, H. A.; Reedijk, J.; De Ridder, D. J. H.; Vos, J. G. *J. Am. Chem. Soc.* 1990, *112*, 9245.
(28) De Cola, L.; Barigelletti, F.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Chem. Phys. Lett.* 1991, *178*, 491.
(29) Hage, R.; Dijkhuis, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* 1988, *27*, 2185.
(30) Barigelletti, F.; De Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* 1991, *30*, 641.
(31) Barigelletti, F.; De Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* 1989, *28*, 4344.
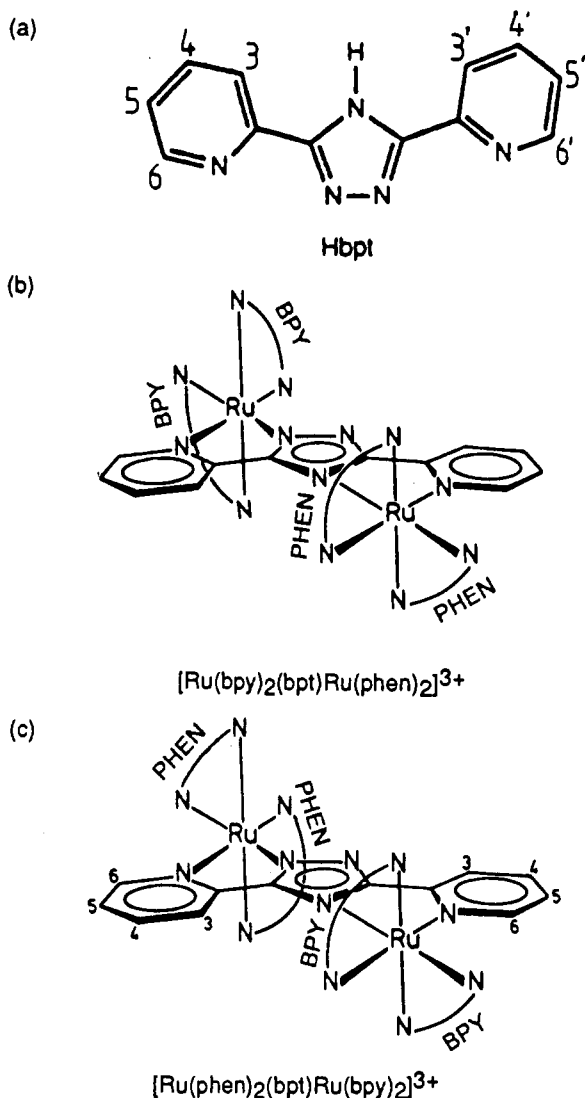
(a)

Hbpt

(b)

[Ru(bpy)₂(bpt)Ru(phen)₂]³⁺

(c)

[Ru(phen)₂(bpt)Ru(bpy)₂]³⁺

Figure 1. Structures of (a) the ligand 3,5-bis-(pyridin-2-yl)-1,2,4-triazole, (b) [Ru(bpy)₂(bpt)Ru(phen)₂]³⁺ (5), and (c) [Ru(phen)₂(bpt)Ru-(bpy)₂]³⁺ (6).

In this contribution a series of dinuclear mixed polypyridyl compounds has been prepared containing both phen and bpy moieties. With the synthetic approach recently developed in these laboratories,[32] bis(phen) and bis(bpy) units can be coordinated in a controlled manner to either the N1 or the N4 site yielding [Ru(bpy)₂(bpt)Ru(phen)₂]³⁺ and [Ru(phen)₂(bpt)Ru(bpy)₂]³⁺. It was thought that, with such mixed polypyridyl compounds, additional information about excited state and redox processes can be obtained since the UV/vis absorption spectra of phen and bpy moieties are significantly different. It was furthermore hoped that the use of dinuclear complexes would be beneficial in establishing differences between the photophysical properties of bpy and phen. The redox and excited-state properties of the resulting mixed-ligand complexes have been studied and are compared with those obtained from the [Ru(bpy)₂(bpt)Ru-(bpy)₂]³⁺ and [Ru(phen)₂(bpt)Ru(phen)₂]³⁺ species. The results obtained show that the lowest emitting state in the compounds is firmly bpy-based and that pathways for photochemically induced ligand exchange are dependent on the reaction conditions.

Experimental Section

Synthesis and Materials. 3,5-Bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) was prepared as described previously.[29] cis-[Ru(bpy)₂Cl₂]·2H₂O and cis-[Ru(phen)₂Cl₂]·2H₂O were prepared according to literature methods

from commercial grade RuCl₃·xH₂O and 2,2'-bipyridine or 1,10-phenanthroline.[25,33]

[Ru(bpy)₂(bpt)]PF₆·¹/₂H₂O (1) and [(Ru(bpy)₂)₂(bpt)](PF₆)₃ (2) have been prepared as described previously.[29] In a similar manner, the following four compounds were synthesized: [Ru(phen)₂(bpt)]PF₆·H₂O (3), [(Ru(phen)₂)₂(bpt)](PF₆)₃ (4), [Ru(bpy)₂(bpt)Ru(phen)₂](PF₆)₃ (5), and [Ru(phen)₂(bpt)Ru(bpy)₂](PF₆)₃·2H₂O (6). All compounds were purified using semi-preparative HPLC, using conditions reported previously.[34]

Anal. Calcd for [Ru(phen)₂(bpt)]PF₆ (3): C, 51.0; H, 3.0; N, 14.8. Found: C, 50.0; H, 3.0; N, 14.6. ¹H NMR of the bpt⁻ protons (ppm): H3, 8.24; H4, 7.88; H5, 7.04; H6, 7.49; H3', 7.95; H4', 7.72; H5', 7.21; H6', 8.45.

Anal. Calcd for [(Ru(phen)₂)₂(bpt)](PF₆)₃ (4): C, 42.9; H, 2.4; N, 11.7. Found: C, 43.1; H, 2.5; N, 11.5. ¹H NMR of the bpt⁻ protons for isomer 1 (ppm): H3, 6.22; H4, 6.88; H5, 6.79; H6, 7.43; H3', 8.52; H4', 7.79; H5', 7.03; H6', 7.15. ¹H NMR for isomer 2 (ppm): H3, 6.34; H4, 6.93; H5, 6.73; H6, 7.27; H3', 8.55; H4', 7.87; H5', 7.04; H6', 7.21.

Anal. Calcd for [Ru(bpy)₂(bpt)Ru(phen)₂](PF₆)₃ (5): C, 43.9; H, 2.6; N, 11.9. Found: C, 43.0; H, 2.7; N, 11.4. ¹H NMR of the bpt⁻ protons (ppm): H3, 6.43; H4, 7.00; H5, 6.88; H6, 7.33; H3', 8.64; H4', 7.63; H5', 7.33; H6', 6.86.

Anal. Calcd for [Ru(phen)₂(bpt)Ru(bpy)₂](PF₆)₃ (6): C, 43.9; H, 2.6; N, 11.9. Found: C, 42.7; H, 2.6; N, 11.2. ¹H NMR of the bpt⁻ protons (ppm): H3, 6.49; H4, 7.12; H5, 6.96; H6, 7.56; H3', 8.67; H4', 7.84; H5', 7.18; H6', 7.34.

All bpy and phen resonances were in the expected range for these complexes.

Physical Measurements. UV–vis absorption spectra were recorded in acetonitrile on a Shimadzu UV 240 instrument with 1-cm quartz cells. Extinction coefficients are accurate to 5%. ¹H and COSY experiments were performed on a Bruker WM 400-MHz spectrophotometer. All measurements were carried out in (CD₃)₂CO, with TMS as reference. For the COSY experiments 128 FID's of 16 scans, each consisting of 1K data points, were accumulated. After digital filtering (sine-bell squared), the FID was zero-filled to 512 W in the F1 dimension. Acquisition parameters were F1 = ⌀ 500 Hz, F2 = 1000 Hz, and t₁/₂ = 0.001 s. The recycle delay was 2 s. Emission spectra were obtained using a Perkin-Elmer LS50 luminescence spectrometer in acetonitrile at 298 K and in ethanol at 77 K. Lifetime measurements were carried out in a 1-cm quartz cell in deaerated CH₃CN solutions, using a Q-switched Nd-YAG Spectra Physics laser system.
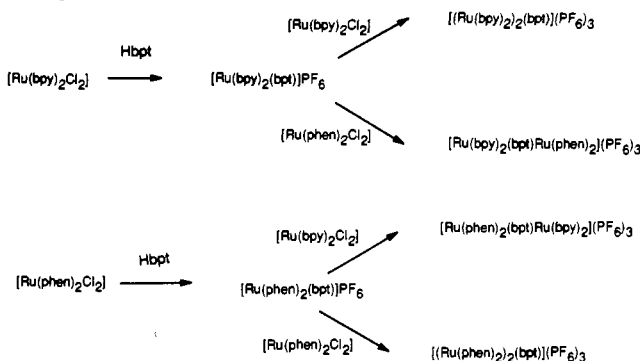
Temperature-dependent luminescent lifetime measurements were carried out using a dilute solution of the complex (10⁻⁴–10⁻⁵ M) in a 1-cm quartz cell, degassed by bubbling with argon for 30 min prior to use. The cell was placed inside an Oxford Laboratories nitrogen flow cryostat, equipped with an Oxford temperature controller. The error in the temperature was estimated to be 1 K. The analysis was performed using an in-house program.

Electrochemical measurements were carried out using an EG & G Princeton Applied Research 362 scanning potentiostat and an EG & G Princeton Applied Research 265 polarographic analyzer/stripping voltammeter. The electrolyte used was acetonitrile containing 0.1 M tetraethylammonium perchlorate (TEAP). A glassy-carbon electrode was used as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. Differential-pulse polarography (dpp) measurements were obtained at a scan rate of 5 mV s⁻¹ and cyclic voltammograms (CV) were obtained at a scan rate of 100 mV s⁻¹.

Spectroelectrochemical measurements in the range 900–300 nm were carried out using the aforementioned equipment. Electrochemical oxidation was carried out in a homemade cell with a platinum sheet as a working electrode, a platinum wire as an auxiliary electrode, and a coated silver wire electrode as a reference electrode. The electrolyte used was acetonitrile containing 0.1 M TEAP. Measurements were carried out at a number of potentials ranging from 0.9 to 1.6 V vs Ag/AgCl. The potential used to generate the mixed-valence species was 1.15 V for all dinuclear complexes.

Time-resolved resonance raman spectroscopic measurements were carried out using a Q-switched Nd/YAG laser (Quanta-Ray GCR2, pulse width ca. 9 ns) to populate and probe the excited states of the various complexes at an excitation wavelength of 355 nm. Ground-state spectra were also obtained for comparison purposes using a Spectra Physics Argon ion laser, at 364 nm and at 457.9, 465.8, 472.7, 476.5, 488.0, and

(32) Hage, R. Thesis, Leiden, The Netherlands, 1991.

(33) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

Scheme I. Synthetic Pathway for the Preparation of the Complexes

[Ru(bpy)$_2$Cl$_2$] → [(Ru(bpy)$_2$)$_2$(bpt)](PF$_6$)$_3$

[Ru(bpy)$_2$Cl$_2$] $\xrightarrow{\text{Hbpt}}$ [Ru(bpy)$_2$(bpt)]PF$_6$

[Ru(phen)$_2$Cl$_2$] → [Ru(bpy)$_2$(bpt)Ru(phen)$_2$](PF$_6$)$_3$

[Ru(bpy)$_2$Cl$_2$] → [Ru(phen)$_2$(bpt)Ru(bpy)$_2$](PF$_6$)$_3$

[Ru(phen)$_2$Cl$_2$] $\xrightarrow{\text{Hbpt}}$ [Ru(phen)$_2$(bpt)]PF$_6$

[Ru(phen)$_2$Cl$_2$] → [(Ru(phen)$_2$)$_2$(bpt)](PF$_6$)$_3$

496.5 nm. Ground-state spectra were also recorded using 396-nm excitation generated by Raman shifting the third harmonic (354.7 nm) of the Nd/YAG laser in methane. In this case the 396-nm pulse energy was held below the threshold for excited-state population. All measurements were carried out in acetone/H$_2$O solvent mixtures, degassed by argon bubbling throughout the spectral accumulation.

The photochemical experiments were carried out at room temperature in air equilibrated solutions[31] in a 1-cm quartz cell using two 250-W tungsten lamps, a glass filter ($\lambda > 390$ nm) to prevent UV radiation reaching the sample, and a water filter to prevent any thermal reactions taking place. The occurrence of photoreaction was followed by both absorption changes and by HPLC techniques, according to an established method.[34]

Results

General Characterization. An outline of the synthetic approach used to prepare complexes 1–6 is presented in Scheme I. For the structure of compounds 5 and 6 see Figure 1. For the dinuclear complexes two geometrical isomers may be present, depending on the relative orientation of the bpy (or phen) ligands, it is also possible that each geometrical isomer has a corresponding optical isomer, although these are not expected to be evident from the NMR spectra.[35,36] The ^{1}H NMR data not only confirm the purity of the complexes but also indicate the presence of only one isomer for compounds 5 and 6 and two for the [(Ru(phen)$_2$)$_2$(bpt)](PF$_6$)$_3$ (4) complex. Two isomers were also observed for compound 2.[32] The presence of these isomers is not expected to affect the physical properties of the compounds. The resonances of the bpt$^-$ protons are given in the Experimental Section. The bpy and phen resonances are in the normal range and give no additional information.

The energy of the lowest energy absorption maxima at 298 K, the emission maxima at 77 and 298 K, and the redox potentials for all complexes are summarized in Table I.

The intense absorption bands between 350 and 500 nm have been assigned as metal-to-ligand charge transfer bands (MLCT).[37–39] A substantial difference exists between the peak

shape of the bpy and phen mononuclear species (see Figure 2). This becomes important for elucidation of the photochemical processes. The state responsible for luminescence is the ^{3}MLCT excited state, which corresponds to a spin – forbidden Ru → bpy (or Ru → phen) transition.[28,40,41]

Luminescent Lifetime Measurements. Temperature dependent luminescence lifetime studies were carried out on all dinuclear species.[42–44] Plots of ln $(1/\tau)$ versus $1/T$ in the range 150–300 K are presented in Figure 3 for all four complexes. Table II lists the exponential prefactors and activation energies obtained from these measurements. Lifetimes at room temperature are presented in Table I for all mononuclear and dinuclear complexes. These indicate that in the mononuclear complexes, the phen complex is longer lived than the bpy complex, as expected. However, in the dinuclear complexes, the bis-phen complex is considerably shorter lived than the bis-bpy complex, its lifetime decreasing by a factor of 20 compared to a factor of 4 for the bpy complexes.

Excited-state absorption studies were also carried out for all four complexes. Those for the mixed-ligand species 5 and 6 are essentially identical, suggesting that the lowest MLCT states of these two complexes are likewise identical. However, it is difficult to base firm conclusions on similarities in the recorded absorbance difference spectra alone. Much more definitive evidence comes from resonance Raman data (*vide infra*).

Resonance Raman Measurements. Ground-state resonance Raman (RR) spectra have been recorded for all four complexes at excitation wavelengths of 457.9, 465.8, 472.7, 476.5, 488.0, and 496.5 nm within the MLCT absorption region of the complexes and also at 364 nm, close to the wavelength, 354.7 nm, employed for the single-color pulsed excitation transient resonance Raman studies. The RR spectra recorded throughout the MLCT absorption region for the bis-bpy (2) and bis-phen (4) complexes display features attributable to modes of bpy and phen respectively, while those of the mixed-ligand complexes, bpy-phen and phen-bpy, 5 and 6, respectively, show features due to modes of both bpy and phen. In the latter two cases the variations with excitation wavelength of the relative intensities of both sets of modes are essentially identical. This suggests that the spectral profiles corresponding to the MLCT transitions from Ru^{II} to either bpy or phen ligands are similar irrespective of whether the Ru^{II} is coordinated to the bridging ligand through the N1 or N4 nitrogens. The other excitation wavelength used for CW studies, 364 nm, is not in resonance with MLCT transitions, but the spectra display bands which can largely be correlated with those attributed to bpy and phen modes in the 458-nm excited spectra (see Figure 4).

The points of more immediate significance in the context of the present investigation relate to the 354.7-nm pulse-excited Raman spectra of the complexes, shown in Figure 5. The trace in Figure 5a shows the spectrum of [Ru(bpy)$_2$(bpt)Ru(bpy)$_2$]$^{3+}$ with terminal bpy ligands attached to both Ru(II) centers while the spectra shown in parts b and c are those recorded for complexes 5 and 6 with bpy ligands attached to the metal center bound to the N1 site and phen ligands attached to the center bound to N4 for compound 5 or vice versa for complex 6. Finally, Figure 5d shows the spectrum for the bis-phen complex (4).

Spectrum a shows prominent bands at 1210, 1287, 1427, 1497, and 1552 with other weaker features at 1177, 1321, and 1243 cm^{-1}. Apart from the band at 1243 cm^{-1} all other features listed for complex 2 correlate closely in both position and relative band intensities with the spectrum of [Ru(bpy)$_3$]$^{2+*}$ originally reported

(34) (a) Buchanan, B. E.; Wang, R.; Vos, J. G.; Hage, R.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3263. (b) Buchanan, B. E.; McGovern, E.; Harkin, P.; Vos, J. G. *Inorg. Chim. Acta* **1988**, 154.

(35) Hage, R.; Dijkhuis, A. J. H.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1988**, *45*, 1490.

(36) Fennema, B.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chim. Acta* **1990**, *171*, 223.

(37) Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3002.

(38) (a) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877. (b) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967.

(39) Curtis, J. C.; Bernstein, J. S.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 385.

(40) Ohno, T.; Nozaki, K.; Ikeda, N.; Haga, M. *ET Inorg., Org., Biol. Syst.* **1991**, *14*, 215.

(41) Cocks, A. T.; Wright, R. D.; Seddon, K. R. *Chem. Phys. Lett.* **1982**, *85*, 369.

(42) Balzani, V.; Juris, A.; Barigelletti, F.; Belser, P.; Von Zelewsky, A. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1984**, *78*, 4.

(43) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(44) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803.

(45) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(46) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(47) Buchanan, B. E.; Degn, P.; Velasco, J. M. P.; Hughes, H.; Creaven, B. S.; Long, C.; Vos, J. G.; Howie, R. A.; Hage, R.; Van Diemen, J. H.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1177.

(48) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

Table I. Absorption Bands, Luminescence Properties, and Redox Properties of the Ruthenium Complexes

compd	Absorption[a] λ_{max} (nm) (log ϵ)	emission (nm) 289 K[a] (τ/(ns))	77 K[b]	oxidn[d] poten (V vs SCE)	redcn poten (V vs SCE)
[Ru(bpy)₃]²⁺	452 (4.11)	620 (610)	582	1.26	−1.35, −1.55, −1.80
[Ru(phen)₃]²⁺	447 (4.28)	593 (920)	565	1.26	−1.36
[Ru(bpy)₂bpt]⁺	475 (4.05)	650 (354)	624	0.85	−1.44, −1.68
[Ru(phen)₂bpt]⁺	430 (4.26)	652 (592)	599	0.86	−1.47, −1.79
[(Ru(bpy)₂)₂bpt]³⁺	452 (4.30)	642 (85)	603	1.06, 1.38	−1.42, −1.67
[(Ru(phen)₂)₂bpt]³⁺	421 (4.55)	627 (33)	597	1.04, 1.34	−1.48, −1.71
[Ru(bpy)₂bptRu(phen)₂]³⁺	440 (4.37)	640 (66)	606	1.07, 1.38	−1.35, −1.71
[Ru(phen)₂bptRu(bpy)₂]³⁺	450 (4.31)	636 (51)	603	1.06, 1.37	−1.33, −1.71

[a] Acetonitrile solution. [b] Ethanol. [c] Deaerated acetonitrile solution. [d] Acetonitrile containing 0.01 M TEAP.
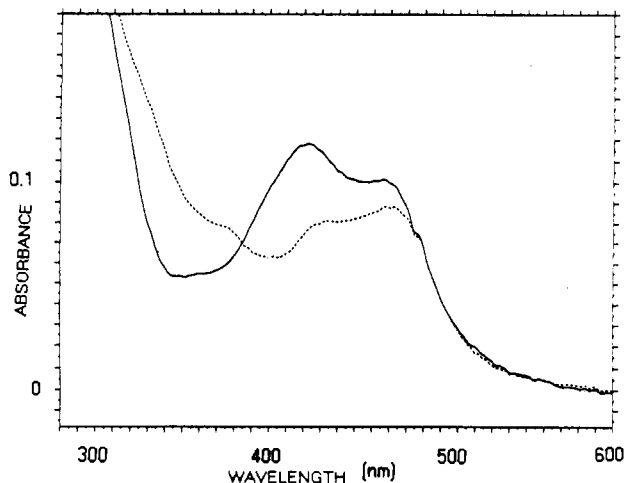

Figure 2. UV/vis absorption spectra of the compounds (A, —) [Ru-(bpy)₂(bpt)]⁺ (1) and (B, - -) [Ru(phen)₂(bpt)]⁺ (3) recorded in acetonitrile.
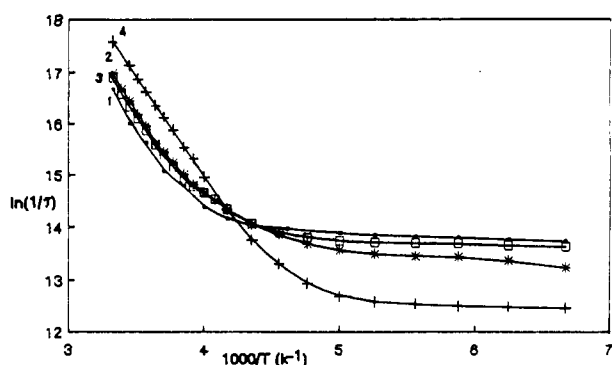

Figure 3. Temperature dependence of the luminescent lifetimes for [(Ru-(bpy)₂)₂(bpt)]³⁺ (●), [(Ru(phen)₂)₂(bpt)]³⁺ (*), [Ru(bpy)₂(bpt)Ru-(phen)₂]³⁺ (□), and [Ru(phen)₂(bpt)Ru(bpy)₂]³⁺ (+) in ethanol-methanol (4:1).

by Woodruff and Dallinger[45] (using pulsed excitation at the same wavelength, 354.7 nm, as used in the present study) and assigned to the localized MLCT excited state, [(bpy)₂Ruᴵᴵᴵ(bpy•⁻)]²⁺. We therefore formulate the above MLCT excited state of (2) as [(bpy)Ruᴵᴵᴵ(bpy•⁻) [bpt]Ruᴵᴵ(bpy)₂]³⁺, in which the Raman scattering rises predominantly from the (bpy)Ruᴵᴵᴵ(bpy•⁻) region of the complex.

Similarly, for complexes **5** and **6** the Raman spectra again very closely resemble those of the ³MLCT state of [Ru(bpy)₃]²⁺* and can therefore be attributed to excited states which contain the (bpy)Ruᴵᴵᴵ(bpy•⁻) chromophoric moiety. These states may be characterized as [(bpy)Ruᴵᴵᴵ(bpy•⁻)[bpt]Ruᴵᴵ(phen)₂]³⁺ in which the bipyridyl coordinated Ru center is attached to the N1 or N4 positions of the bpt⁻ ligand in complexes (**5**) and (**6**) respectively

(49) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.

Table II. Kinetic Parameters (Frequency Factor and Activation Energy) of the Arrhenius Term Describing a Nonradiative Process, Which Takes Place at Higher Temperatures ($T > 250$ K) for the Dinuclear Species[a]

compd	A (s⁻¹)	ΔE (cm⁻¹)
[Ru(phen)₃]²⁺	7.6 × 10¹²	3157
[Ru(bpy)₃]²⁺	1.3 × 10¹⁴	3960
[Ru(bpy)₂bpt]⁺	3.8 × 10⁸	1127
[Ru(phen)₂bpt]⁺	4.9 × 10⁸	1328
[(Ru(bpy)₂)₂(bpt)]³⁺	5.3 × 10¹⁵	4061
[(Ru(phen)₂)₂(bpt)]³⁺	2.3 × 10¹³	2747
[Ru(bpy)₂(bpt)Ru(phen)₂]³⁺	3.6 × 10¹⁴	3470
[Ru(phen)₂(bpt)Ru(bpy)₂]³⁺	2.9 × 10¹⁴	3442

[a] Measurements were carried out in ethanol-methanol (4:1).
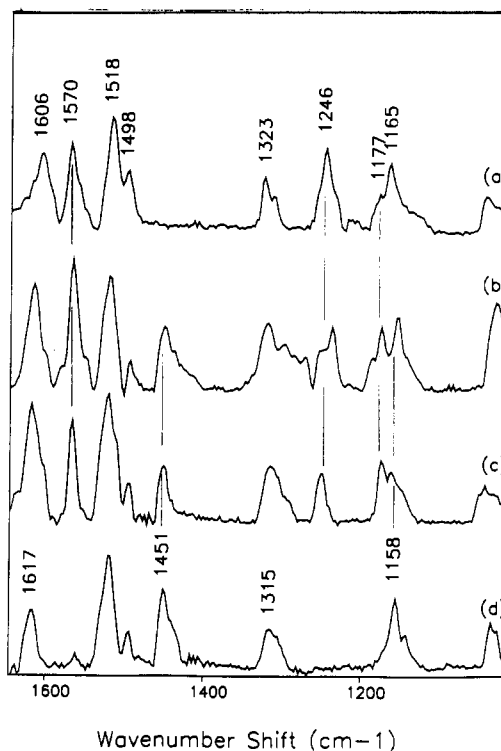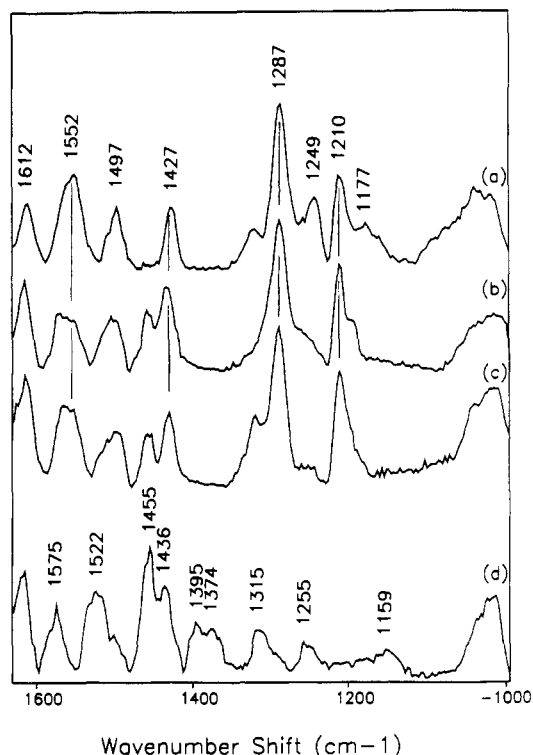

Wavenumber Shift (cm-1)

Figure 4. Ground-state resonance Raman spectra of (a) [(Ru(bpy)₂)₂-(bpt)]³⁺, (b) [Ru(bpy)₂(bpt)Ru(phen)₂]³⁺, (c) [Ru(phen)₂(bpt)Ru-(bpy)₂]³⁺, and (d) [(Ru(phen)₂)₂(bpt)]³⁺ in an acetone-water (1:4) mixture using an excitation wavelength of 363.8 nm.

i.e. the excitation is localized on the bpy-coordinated Ru center irrespective of the coordination position at the bpt⁻ ligand. Neither **5** nor **6** exhibit any of the Raman marker bands for an excited Ru(phen)₂ center (which are shown in the spectrum of complex **4** (Figure 5d)). Indeed the only differences between the spectra of excited **2**, **5**, and **6** and those of the excited mononuclear [Ru-(bpy)₃]²⁺ complex are the appearance of one extra band at 1243 cm⁻¹ in **2** and at 1458 cm⁻¹ in **5** and **6**. These extra bands in the dinuclear complexes may arise from the unexcited metal/ligand region which would be expected to continue to give "ground-state" spectra (i.e. neutral ligand modes) even in the ³MLCT

Figure 5. Transient resonance Raman spectra of (a) [(Ru(bpy)₂)₂(bpt)]³⁺, (b) [Ru(bpy)₂(bpt)Ru(phen)₂]³⁺, (c) [Ru(phen)₂(bpt)Ru(bpy)₂]³⁺, and (d) [(Ru(phen)₂)₂(bpt)]³⁺ in an acetone–water (1:4) mixture using an excitation wavelength of 354.7 nm.

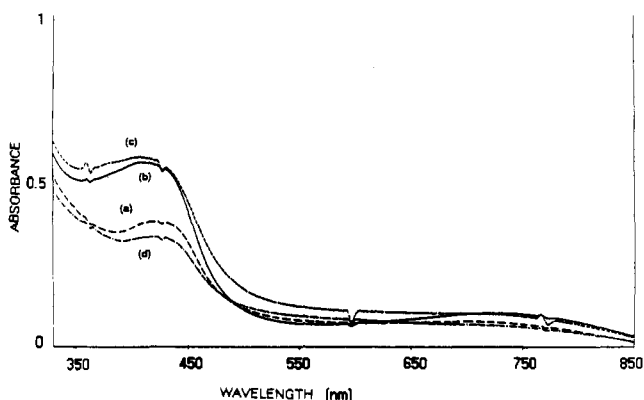**Figure 6.** Visible absorption spectra of the mixed-valence compounds (a) [(Ru(bpy)₂)₂(bpt)]⁴⁺, (b) [(Ru(phen)₂)₂(bpt)]⁴⁺, (c) [Ru(bpy)₂(bpt)-Ru(phen)₂]⁴⁺, and (d) [Ru(phen)₂(bpt)Ru(bpy)₂]⁴⁺ in acetonitrile containing 0.1 M TEAP. The applied potential is 1.15 V vs Ag/AgCl.

complexes. The band at 1243 cm⁻¹ found in **2** is also found in the ground-state spectrum of the same complex while in complexes **5** and **6** the 1458-cm⁻¹ band is close to a strong band at 1451 cm⁻¹ found in the ground-state Raman spectrum of the bis-phen complex (**4**).

Redox Properties. The redox potentials for these complexes do not vary to a large extent between ligands, showing the usual ruthenium-based oxidations and bpy or phen reductions.[46] However, spectroelectrochemistry in the visible region yielded some very interesting results. It is possible to prepare a mixed-valence species of the type M^{III}M^{II} by applying a potential of 1.15 V vs Ag/AgCl. The M^{III}/M^{III} species can be obtained by oxidation at 1.60 V vs Ag/AgCl. In the mixed-valence species the absorption spectrum in the 300–500-nm region is dominated by the M^{II} center. It, should, therefore, be possible to elucidate which metal center is being oxidized first; the N1 or the N4 center. Figure 6 represents absorption spectra obtained for the mixed-valence dimers in the 350–850-nm range. The absorption
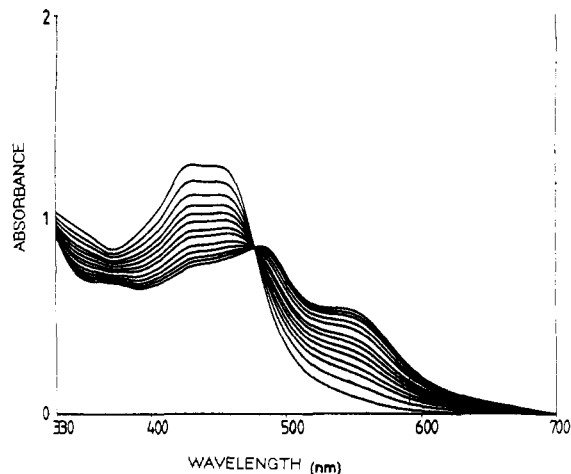

Figure 7. Changes in the UV/vis absorption spectra taken during the photolysis of compound **5** in CH₂Cl₂ containing 0.005 M Cl⁻.
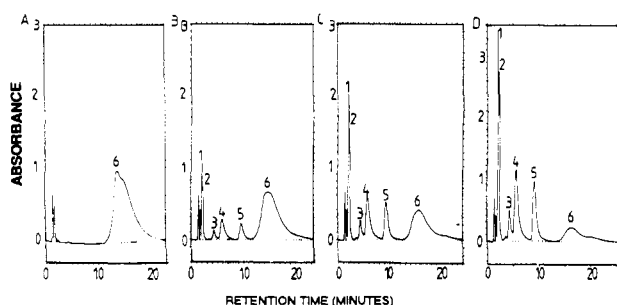

Figure 8. HPLC traces taken during the photolysis of compound **5** in CH₂Cl₂ containing 0.005 M Cl⁻. Photolysis time: (A) 0 min, (B) 10 min, (C) 29 min, and (D) 74 min. Conditions: flowrate, 2.5 cm³/min; mobile phase, 80/20 CH₃CN/H₂O containing 0.01 M LiClO₄; detection wavelength, 280 nm. For peak numbering see text.

spectra of phen-based complexes (see Figure 6b) have broader UV/vis spectra than bpy-based complexes (Figure 6a). λ_{max} for bpy is found at 425 nm, whereas λ_{max} for phen is found at 405 nm. Complex **5** shows an absorbance spectrum similar to **4**, showing that the Ru(bpy)₂ site is oxidized. Complex **6** exhibits a spectrum similar to **2** after oxidation to its mixed-valence state, suggesting that Ru(phen)₂ is oxidized. These results indicate that in compounds **5** and **6** the center attached to the N1 position of the triazole ring is oxidized first.

Photochemistry in CH₂Cl₂ Containing 0.005 M Cl⁻. During the photolysis of the mixed-ligand species **5** in CH₂Cl₂ containing 0.005 M Cl⁻, UV/vis spectra taken at specified intervals show a decrease in the absorbance as the reaction proceeds (see Figure 7). A clear isosbestic point is obtained. This confirms the results obtained by Barigelletti et al.[28]

In order to investigate the photochemical process further, HPLC analysis was carried out.[47] A typical set of traces obtained for the photolysis of **5** is given in Figure 8. From these traces it can be seen that, contrary to expectation, at least five main photoproducts are obtained. The products were identified according to UV/vis spectra and by comparison with authentic samples as follows: Peak 1, retention time 2.12 min, with an absorption maximum of 520 nm, was identified as [Ru-(phen)₂Cl₂]·2H₂O. Peak 2, retention time 2.30 min, absorption maxima at 365 and 520 nm, was found to be [Ru(bpy)₂Cl₂]·2H₂O. Taking into account the extinction coefficients of these two products at the monitoring wavelength of 280 nm, their ratios were approximately 1:1. Peak 3, retention time 4.44 min, absorption maxima 330 and 470 nm, was identified as the [Ru-(bpy)₂(MeCN)Cl]³⁺, presumably by interaction with the MeCN mobile phase. Peaks 4 and 5, which are present in almost identical proportions, have been identified as two bpt⁻-containing mononuclear complexes. Peak 4, with a retention time of 5.64 min and
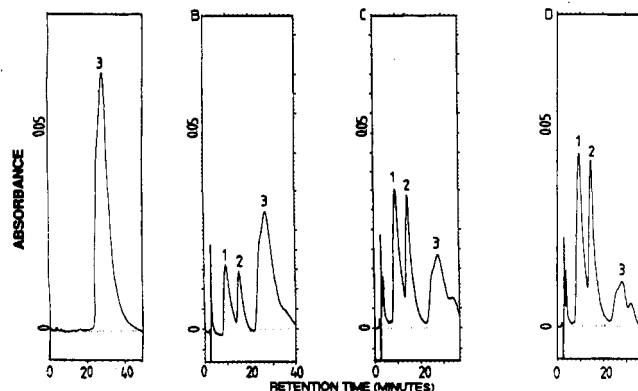
Figure 9. HPLC traces taken during the photolysis in pure MeCN of compound 4. Photolysis time: (A) 0 min, (B) 120 min, (C) 300 min, and (D) 420 min. Conditions: flowrate, 1.5 cm^3/min; mobile phase, 80/20 CH_3CN/H_2O containing 0.01 M $LiClO_4$; detection wavelength, 280 nm. For peak numbering see text.

an absorption maximum of 430 nm, was identified as [Ru(phen)$_2$-(bpt)]$^+$, the N4 isomer of compound 2 since it has a similar absorption spectra to the N1 isomer, but has a different retention time. Attempts were made to isolate this by using a large scale photolysis experiment;[47] however, sufficient amounts could not be isolated by semipreparative HPLC. Finally, peak 5, with a retention time of 9.18 min and a maximum wavelength of absorption of 475 nm, has been identified as the N1 isomer of the [Ru(bpy)$_2$(bpt)]$^+$ complex. The UV/vis spectra absorption maxima were located using the HPLC photodiode array detector, and the solvent is therefore mobile phase.

Results similar to those obtained for compound 5 were also observed during the photolysis of compounds 2, 4, and 6. The presence of both [Ru(phen)$_2$Cl$_2$] and [Ru(bpy)$_2$Cl$_2$] and the presence of two mononuclear bpt$^-$ complexes in the photolysis of these complexes confirm the results obtained for compound 5. For compound 2, both the N1 and the N4 isomers of compound 1 were present, for compound 4, both the N1 and the N4 isomers of compound 3 were present, and finally for compound 6, the N1 isomer of compound 3 was present and the N4 isomer of compound 1 was present upon irradiation.

Photochemistry in MeCN Containing 0.01 M Cl⁻. UV/vis spectra taken during the photolysis of compound 5 in MeCN containing 0.01 M Cl⁻ show clear isosbestic points, with a shift in the absorption maximum from 428 to 465 nm. However, the HPLC traces again indicate the formation of at least four main photoproducts. These were identified by retention times, by UV/vis spectra taken from the HPLC photodiode array traces, and by comparison with authentic samples. Again, both the N1 and the N4 position of the triazole are apparently photolabile in the presence of Cl⁻ ions. Photolysis of the other three dinuclear complexes, 2, 4, and 6, gave similar results. In all four cases [Ru(bpy)$_2$(MeCN)Cl]$^{2+}$, [Ru(phen)$_2$(MeCN)Cl]$^{2+}$, and two monomeric bpt-containing complexes were formed during irradiation. For compound 2, both the N1 and the N4 isomer of compound 1 were present, for compound 4, both the N1 and the N4 isomers of compound 3 were present, for compound 5, the N1 isomer of compound 1 and the N4 isomer of compound 3 were observed and for compound 6, the N1 isomer of compound 3 and the N4 isomer of compound 1 were formed.

Photochemistry in MeCN. As can be seen in Figure 9, photolysis of [(Ru(phen)$_2$)$_2$(bpt)]$^{3+}$ (4) in MeCN gave rise to only two photoproducts, which were identified as follows: Peak 1, retention time 10.10 min, λ_{max} 430 nm, was found to be the N1 isomer of the [Ru(phen)$_2$(bpt)]$^+$ (3) complex, and peak 2, retention time 15.05 min, λ_{max} 425 nm, was identified as the [Ru(phen)$_2$(MeCN)$_2$]$^{2+}$ complex. All other complexes show similar results. Upon irradiation of compound 2, only the N1 isomer of compound 1 and the [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$ complex

are formed; for compound 5, compound 1 and [Ru(phen)$_2$-(MeCN)$_2$]$^{2+}$ and for compound 6, compound 3 and [Ru(bpy)$_2$-(MeCN)$_2$]$^{2+}$ are observed.

Discussion

The purpose of this investigation is to examine how the nature of the polypyridyl ligand and the asymmetry of the bpt$^-$ bridging ligand affect the excited state properties of the dinuclear bpt$^-$ compounds. To do this the nature of the lowest energy excited states involved in the photophysical and photochemical processes has to be identified. Electrochemical measurements have often proven useful in such an investigation, since the ligand most easily reduced is normally also the one with the lowest energy excited state. Furthermore, the potential of the metal-based oxidation can be used to judge the ground-state d–d levels and, therefore, give information about the interaction between ligands and metal ions. Indeed for the two coordination isomers of the mononuclear analogue [Ru(bpy)$_2$(HPTN)]$^{2+}$, where HPTN is 3-(pyridin-2-yl)-1,2,4-triazole, a difference of about 50 mV was found between the redox potentials of N1- and N4-based coordination isomers. For the compounds reported here, however, no clear trends are observed in the redox potentials.

Of more interest are the spectroelectrochemical data. These measurements show clearly that the metal center coordinated to the N1 site of the bridging ligand is oxidized first. This confirms earlier suggestions based on the acid–base properties of pyridyl-triazole ligands that the N1 position of the triazole ring is a better σ-donor than the N4 position. This further suggests that the energy of the antibonding ^{3}MC state will be lower for the N4 position. Since population of this level is responsible for the photodecomposition of ruthenium polypyridyl complexes, this observation is of importance for the analysis of the photochemical properties of these compounds (*vide infra*).

The compounds have very similar emission properties. The low lifetime of the phen dinuclear complex is somewhat surprising as the emission of [Ru(phen)$_3$]$^{2+}$ is much longer lived than [Ru-(bpy)$_3$]$^{2+}$.[41] The decrease in the luminescent lifetimes on going from the mononuclear to the dinuclear complexes is accounted for by the fact that the negative charge on the bpt$^-$ ligand is now shared between the two Ru units for the dinuclear system, and therefore the σ-donor properties of the bridging ligand have decreased. The decrease in the case of the phen dinuclear complex is however significantly larger than for normal bpy-based complexes.

The luminescent lifetime experiments do not provide unequivocal evidence about the nature of the emitting state. In these measurements there appears to be a trend in substituting phen for bpy. The emission energies and the lifetimes suggest that in the mixed-ligand dinuclear complexes the lowest ^{3}MLCT state is bpy-based. The bpy-containing complexes have higher exponentials and higher activation energies than phen-containing complexes, which again might suggest that the emission is bpy-based. The high frequency factors (A) and the large activation energies (ΔE) suggest that at higher temperatures an activated surface crossing to a ^{3}MC excited state is occurring for compounds 2, 4, 5, and 6. Population of the ^{3}MC excited state leads to a fast deactivation to the ground state and/or decomposition of the complex,[42–44] and this is indeed observed for these compounds. The activation energies and the frequency factors for the mononuclear complexes are much lower suggesting that population of the ^{3}MC state does not occur. These complexes are found to be typically unreactive toward photosubstitution. The low prefactors suggest that the process involves the population of a state only weakly coupled to the ^{3}MLCT state.[48,49]

Ground-state resonance Raman spectra show both bpy and phen features over the whole spectral range investigated. From these data no conclusive assignment about the nature of the lowest singlet MLCT state can be made. However, direct evidence

concerning the nature of the lowest energy ^{3}MLCT state is obtained from transient resonance Raman spectroscopy data. These indicate that in compounds containing bpy, i.e. compounds **2, 5,** and **6,** the lowest excited state is bpy-based irrespective of the binding site at the triazole ligand. The only case in which phen-based emission is evident is for the dinuclear [(Ru(phen)$_2$)$_2$-(bpt)]$^{3+}$ complex. This indicates that the ^{3}MLCT excited state for bpy is indeed lower than that for phen.

The presence of Cl$^-$ ions, considerably speeds up the photochemical process, and this may account for the fact that selective photodecomposition is not encountered when these ions are present during the reaction. The efficiency of populating the ^{3}MC state from the ^{3}MLCT level (n_{ic}) can be calculated from the figures in Table II, according to

$$n_{ic} = \frac{A \exp(-E_a/RT)}{(k_0 + A \exp(-E_a/RT))}$$

where k_0 is the sum of the radiative and nonradiative rate constants. An efficiency of approximately 1 was obtained for all compounds, indicating that no other deactivation process is occurring here. The photochemical results suggest that when Cl$^-$ is present in solution, photodissociation occurs at both the N1 and the N4 positions of the triazole ring, and therefore there is no localized photodissociation from the N4 position. Photoreaction appears to take place through population of ^{3}MC levels of both Ru units. Although differences do exist (due to the nonequivalence of the coordinating nitrogens of the bridging ligand), between the positions of the lowest MLCT levels at each co-ordination site as confirmed by the spectroelectrochemical results, they appear not to be large enough to cause a large energy gap between the two ^{3}MC states.[46,48,49a] This energy gap was expected to be enhanced by the different polypyridyl ligands. However, the different properties of the polypyridyl ligands do not appear to be large enough to make a significant difference under these conditions.

In pure MeCN, a considerably slower reaction takes place, which most likely allows the different properties of the two nitrogen donor atoms (N1 vs N4) of the asymmetric ligand to become important in the photodecomposition of the complex. The results show that population of the ^{3}MC state can occur either from the triplet state on the same Ru-containing unit if bpy is attached to the N4 position of the triazole ring or from different Ru-containing units if bpy is attached to the N1 position. It appears that the energy of the reactive excited state (the ^{3}MC state) depends on the asymmetric σ-donor ability of the bridging triazole ligand, whereas the energy of the luminescent excited state, (the ^{3}MLCT state) is mainly controlled by the properties of the polypyridyl ligand attached to the Ru-containing unit.

Concluding Remarks

The data obtained in this study lead to some very interesting conclusions. Clearly the nature of the emitting state in mixed bpy/phen compounds is bpy-based. This is particularly interesting since neither the ligand-based reductions nor the ground-state resonance Raman spectra could discriminate between the ^{1}MLCT levels of the two polypyridyl ligands. Our results are, therefore, in agreement with those obtained by Hopkins and coworkers[25a] using the two color pump and probe technique for mononuclear bpy/phen complexes. Interestingly, there is what appears to be a linear relationship between the number of bis(phen) units in the dinuclear complexes and the activation energy for the population of the ^{3}MC level, with the energy decreasing with an increasing number of bis(phen) groupings. The results also indicate that the nature of the emitting charge transfer states is solely determined by the nature of the polypyridyl ligand but that on the other hand the location of the first metal-based oxidation is controlled by the asymmetry of the bpt$^-$ ligand. Photochemical experiments in MeCN suggest strongly that the ^{3}MC level of the ruthenium unit at the N4 triazole atom is lowest in energy. However, in the presence of chloride ions both the N1 and the N4 sites are labilized. The efficiency for the population of the ^{3}MC levels in all compounds is close to 1. The differences observed between the photochemical experiments carried out in pure MeCN and in the presence of chloride, are therefore most likely explained by a large increase of the rate of photodecomposition pathway with respect to radiationless decay as mechanisms for the deactivation of this metal-centered excited state.