Control of Photosubstitution in Dinuclear Ruthenium Polypyridyl Complexes by Choice of Bridging Ligand

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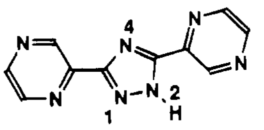
Introduction

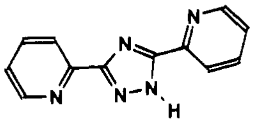
Ruthenium(II) polypyridyl complexes continue to attract great interest, due to the possibility of producing complexes capable of performing photoinduced energy migration or charge separation in photochemical molecular devices.[1] These types of complexes are excellent building blocks for the construction of such devices, and it is, therefore, not surprising that the number of investigations concerning the photochemical and photophysical behavior of dinuclear or polynuclear complexes of this type is rapidly growing.[1–6]

Key components of polynuclear complexes are the bridging ligands, since the interactions between the units and, thereby, the properties of the polynuclear complex are critically dependent on size, shape, and electronic nature of the bridge. It is of interest to examine how the nature of the bridging ligand affects the excited state properties of these complexes.

In a previous paper,[7] the synthesis and characterization of the dinuclear $[Ru(bpy)_2)_2(bpzt)]^{3+}$ (**1**) complex, where bpy = 2,2′-bipyridyl and Hbpzt (see Figure 1) is 3,5-bis(pyrazin-2-yl)-1,2,4-triazole, have been reported. In this paper, the photophysical and photochemical properties of complex **1** are reported. The results are discussed and compared with those for analogous mononuclear and dinuclear complexes containing the ligand 3,5′-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) reported previously.[8,9] The main difference between the Hbpt and the Hbpzt ligands is that in the latter the energy of the π^* level is lower. As a result, the lowest unoccupied orbital in the dinuclear bpt^- complexes is bpy based, while in the $bpzt^-$ complexes it is based on the bridging ligand. The purpose of this study is to investigate what effect these differences have on the photochemical and photophysical properties of the dinuclear compounds.



Hbpzt



Hbpt

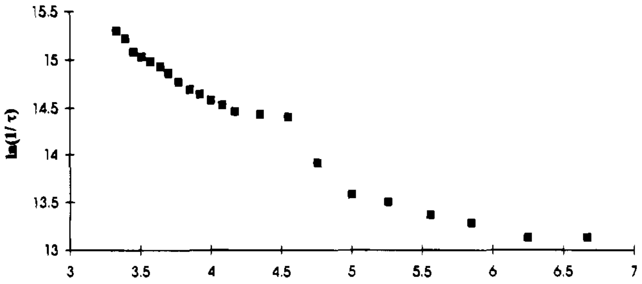


Figure 1. Temperature dependence of the luminescent lifetimes (τ) of $[(Ru(bpy)_2)_2(bpzt)]^{3+}$ in a 4:1 ethanol:methanol mixture over the temperature range 150–300 K.

Experimental Section

Materials. $[Ru(bpy)_2)_2(bpzt)]^{3+}$ was prepared and purified using semipreparative HPLC methods as reported before.[7]

Physical Measurements. Emission spectra were obtained using a Perkin-Elmer LS50 luminescence spectrometer in acetonitrile at 298 K and in 4:1 ethanol:methanol mixtures at 77 K. Lifetime measurements were carried out in a 1 cm quartz cell in deaerated CH_3CN solutions, using a Q-switched Nd-YAG Spectra Physics laser system. The excitation wavelength used was 355 nm. Temperature-dependent luminescent lifetime measurements were carried out using dilute 4:1 ethanol:methanol solutions 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 Laboratories temperature controller. The error in the temperature was estimated to be 1 K. The analysis was performed using an in-house program.

The photochemical experiments were carried out at room temperature in air-equilibrated solutions in a 1 cm quartz cell using two 250 W tungsten lamps, a glass filter (λ > 390 nm) to prevent UV radiation reaching the sample, and a water filter to prevent any thermal reactions. The photochemical reactions were followed both by absorption changes in the UV/v is part of the spectrum and by HPLC techniques using a cation exchange column, according to an established method.[10,11]

Results

$[Ru(bpy)_2)_2(bpzt)]^{3+}$ shows a strong emission at 671 nm at room temperature (degassed, acetonitrile) and at 617 nm at 77 K (ethanol/methanol glass). The emission lifetimes observed are 0.20 and 7.03 μs, respectively. Temperature-dependent-lifetime studies were also carried out. A plot of $\ln(1/\tau)$ versus $1/T$ in the range 150–300 K is presented in Figure 1. These data were analyzed by assuming that the excited state decay consists of a temperature-independent decay (k_0) from the triplet metal-to-ligand charge transfer (^{3}MLCT) state and a single thermally activated nonradiative decay process defined by k' and E_a

$$1/\tau_{obs} = k_0 + k' \exp(-E_a/RT)$$

From this analysis, a value of 3735 cm^{-1} was obtained for E_a and a value of 10^{14} s^{-1} for the preexponential factor k', with a k_0 value of 1.4×10^5 s^{-1}. These values are quite similar to those obtained for the analogous bpt complex $[(Ru(bpy)_2)_2$-

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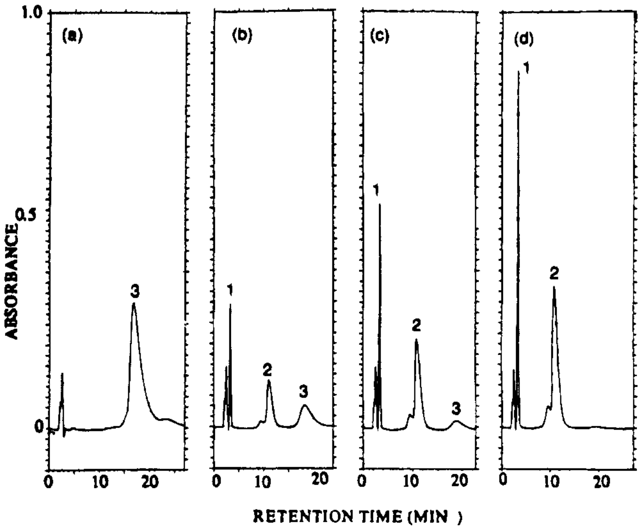

Figure 2. HPLC traces taken during the photolysis of complex **1** in dichloromethane/0.01 M LiCl. Photolysis times: (a) 0 min; (b) 4 min; (c) 8 min; (d) 17 min. Mobile phase: 80:20 acetonitrile:water mixture containing 0.06 M LiCl. Flow rate: 1.5 cm^3/min.

(bpt)]$^{3+}$ ($k' = 5.3 \times 10^{15}$ s^{-1}, $E_a = 4060$ cm^{-1}, k_0 2.4 × 10^5 s^{-1}). The high values obtained for k' and E_a indicate that the activated process observed is population of the triplet metal-centered (^{3}MC) state.[2] This suggests that the dinuclear complex is photolabile, and indeed efficient photodissociation was observed. During photolysis of this dinuclear compound in MeCN, UV/vis spectra taken at specified intervals show a shift in the absorption maximum from 450 to 430 nm and clear isosbestic points are maintained throughout the photolysis at 485 and 357 nm. Similar results were obtained upon photolysis of the compound in MeCN and dichloromethane containing 0.01 M LiCl.

We have shown before that an investigation of photochemical reactions using UV/vis spectroscopy does not always indicate clearly the nature and number of photoproducts formed.[9] So in order to investigate these photochemical processes further, HPLC analysis was carried out. A typical set of traces obtained for the photolysis of **1** in dichloromethane/LiCl is given in Figure 2. From these traces, it can be seen that only two main photoproducts are formed. These were identified as [Ru(bpy)$_2$Cl$_2$], peak 1, retention time 3.40 min, absorption maxima 365 and 525 nm, and the N1 isomer of [Ru(bpy)$_2$(bpzt)]$^+$, peak 2, retention time 10.86 min, λ_{max} 450 nm. On the basis of their extinction coefficients at the detection wavelength 280 nm, the ratio of these products is 1:1. Also for the photolysis in MeCN two photoproducts were obtained, namely [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$ and again the N1 isomer of [Ru(bpy)$_2$(bpzt)]$^+$. Upon photolysis of **1** in MeCN containing 0.01 M LiCl, the photoproducts were, apart from again the N1 isomer of the mononuclear bpzt compound, [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$, [Ru(bpy)$_2$Cl$_2$], and [Ru(bpy)$_2$(MeCN)Cl]$^+$, which were identified from their absorption spectra and by comparison with authentic samples.

For the analogous bpt$^-$ dinuclear compound at least four photoproducts were detected, including both the N1 and the N4 isomer of [Ru(bpy)$_2$(bpt)]$^+$, upon photolysis in the presence of LiCl; in pure MeCN only the N1 isomer and the bis(methyl cyanide) complex were obtained.[9]

Discussion

While much attention has been paid to the photochemical properties of mononuclear complexes, much less is known about photochemical processes in dinuclear compounds. However, if one wants to control the energy transfer properties of such complexes, a detailed investigation of their photochemical properties is needed. The photophysical and photochemical properties of dinuclear bpt systems have been investigated in great detail.[7-9] Earlier studies on mononuclear pyridyltriazole complexes have shown that the N1 site of the triazole ring is a better σ-donor than the N4 position.[12,13] It was furthermore observed that mononuclear [Ru(bpy)$_2$(bpt)]$^+$ type complexes are photostable.[7,9] From these observations one would predict that upon photolysis of dinuclear bpt$^-$ or bpzt$^-$ complexes the unit bound to the N4 triazole atom will undergo photosubstitution, since for that unit the antibonding ^{3}MC level will be lower. As a result, one would expect that the N1 isomer is formed as the primary photoproduct and not the N4 species. The photochemical investigations carried out on the dinuclear bpt$^-$ complexes showed however that this assumption is only valid for photolysis in pure MeCN; in the presence of chloride both isomers are formed in a 1:1 ratio.[9] The above model is clearly too simplistic, and more detailed investigations are needed to explain the behavior observed.

Pyrazine-based ligands are better π-acceptors than pyridine-based ligands and, hence, have lower π^*-levels.[7,14-18] This is reflected in the higher oxidation potentials and lower first reduction potentials of the bpzt$^-$ complexes. Furthermore resonance Raman spectra of **1** suggest that the π^*-orbital of bpzt$^-$ in the dinuclear complex is of lower or roughly the same energy compared to that of the corresponding bpy level.[7,19]

Photolysis of [(Ru(bpy)$_2$)$_2$(bpzt)]$^{3+}$ in any of the solvents used results solely in rupture of the Ru−N bond at the N4 site of the triazole ring. This is in agreement with the model proposed above, based only on the weaker σ-donor properties of the N4 site. We do, however, have to rationalize the different behaviors of the bpt$^-$ and bpzt$^-$ complexes; this can be done in the following manner.

The photophysical parameters obtained for **1** are similar to those reported for the analogous bpt$^-$ compounds. A possibly significant difference lies in the rates observed for population of the ^{3}MC state, k'. This rate is 50 times faster for the bpt$^-$ compound. The N1 and N4 moieties in the dinuclear molecule will have similar absorption characteristics, with the N1-based MLCT transition at somewhat lower energy than the N4 analogue.[8] Therefore, upon excitation, both ends of the dinuclear molecule have equal chances of being excited. Since in the bpt$^-$ compound the lowest π^*-level is based on the bpy ligands, both bpy-based ^{3}MLCT levels can be occupied. The photochemistry observed is now explained by postulating that in the bpt$^-$ compound population of the deactivating ^{3}MC level, k', is faster than relaxation to the lowest triplet level. This is

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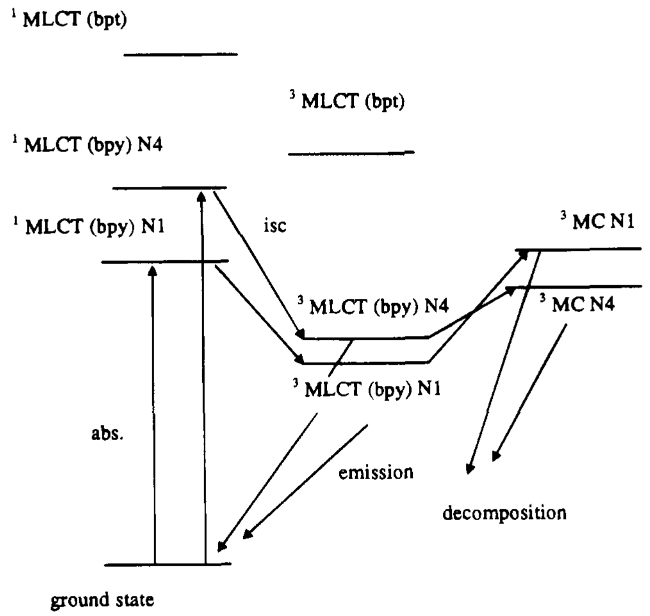

Figure 3. Jablonski diagram for the dinuclear $[Ru(bpy)_2)_2(bpt)]^{3+}$ complex.

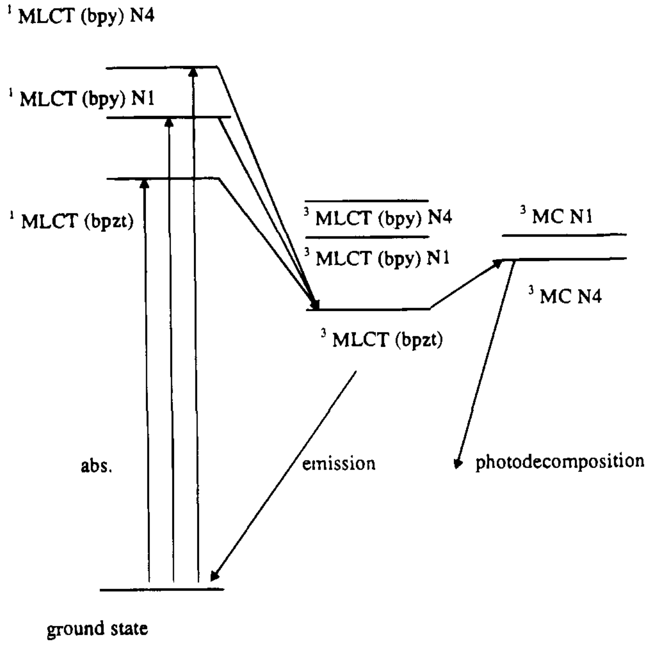

Figure 4. Jablonski diagram for the $[Ru(bpy)_2)_2(bpzt)]^{3+}$ complex.

not unreasonable since, with the high prefactors ($10^{14}-10^{15}$ s^{-1}) obtained from the temperature-dependent-lifetime measurements, it can be calculated that the efficiency for population of the ^{3}MC level at room temperature is approximately 1.[13] In this case, photodecomposition can occur from both ends, when the photochemical reaction is efficient. This process is illustrated qualitatively in the Jablonski diagram shown in Figure 3. However, if photodecomposition is not efficient (photolysis in pure acetonitrile), relaxation can occur and photolysis will occur via the lowest ^{3}MC state (on the N4 site) only. We then further postulate that since, in the case of the bpzt$^-$ compound, the lowest π^*-level is based on the bridging ligand, more central in the molecule, relaxation to a single lowest state is fast and only photolabilization from the N4 site is observed as shown in Figure 4. Of interest is also the lower k' value observed for **1**; a slower population of the ^{3}MC level will further facilitate relaxation to the lowest state. Whether the lower k' value in itself is sufficient to change the direction of the photochemical process is at this stage unclear.

Concluding Remarks

The present investigation shows that photochemical substitution reactions in dinuclear complexes can be controlled in a manner similar to that used for mononuclear complexes. Since there can be more than one ^{3}MLCT and one ^{3}MC state present in dinuclear compounds, a number of different processes can occur and control of the nature of the ligand exchange is more complicated. The results obtained suggest that, apart from the energy level of the labilizing ^{3}MC level, also the rate of relaxation to the lowest excited state plays an important role. The information obtained from such studies can be of great importance for the design of well-behaved photostable photochemically driven molecular devices.

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