# Direct Observation of Substitutional Photochemistry in Tris(bipyrazyl)ruthenium(II)

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Nanosecond laser photolysis results are presented that indicate the loss of a bipyrazine ligand upon photolysis of  $Ru(bpz)_{3}^{2+}$ in acetonitrile in the presence of chloride ions to occur very rapidly on time scales comparable to the decay of the charge-transfer excited state. Data on the triplet-state absorption spectrum in water are also presented.

# Introduction

In recent years there has been a great surge of interest in studies of the photophysics and photochemistry of transition-metal po-lypyridyl complexes.<sup>1-5</sup> Particular interest has been on the potential utility of Ru-polypryidyl complexes as sensitizers for various photoredox processes.<sup>6,7</sup> A limiting factor for practical applicatins in this context is the photochemical stability of these complexes. Though these complexes do appear to have reasonable stability in aqueous media ( $\Phi_{decomp} \leq 10^{-4}$ ), marked enhancement in the photosubstitution quantum yield has been noted in nonaqueous solvents.<sup>8-14</sup> For example,  $Ru(bpy)_3X_2$  and  $Ru(bpz)_3X_2$  (bpy = 2,2'-bipyridine, bpz = 2,2'-bipyrazine, and  $X = Cl^{-}$ , SCN<sup>-</sup>, etc.) have been reported to undergo efficient photoinduced ligand loss as in

$$[Ru(bpy)_{3}][X_{2}] \xrightarrow{h\nu} [Ru(bpy)_{2}X_{2}] + bpy$$
  
(\$\Phi = 0.068\$ for \$X = Cl\$ and \$\Phi = 0.10\$ for \$X = SCN\$)^{11b} (1\$)

$$[Ru(bpz)_{3}][X_{2}] \xrightarrow{h\nu} \\ [Ru(bpz)_{2}(CH_{3}CN)(Cl)]^{+} + bpz \quad (\Phi = 0.45)^{14} (2)$$

Extensive studies on various polypyridyl complexes in the presence of different coordinating ligands and solvents<sup>11,14</sup> have shown that the photodecomposition occurs essentially in solvents that promote ion-pair formation  $[Ru(LL)_3][X_2]$  and that the relative efficiency of ligand loss in tris, mixed ligand complexes follows the order bpyrm  $\geq$  bpz > bpy (bpyrm = 2,2'-bipyrimidine). A model has been proposed in which the photoinduced ligand loss is pictured to occur from an upper "dd" state, closely located to the <sup>3</sup>MLCT excited state as shown in Scheme I.<sup>8,11,14,15</sup> There has been hardly any time-resolved studies on the kinetic aspects

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of such photoinduced ligand loss processes. Herein we present direct nanosecond laser photolysis results on the Ru(bpz),<sup>2+</sup>chloride system in acetonitrile that indicate the ligand loss to occur on time scales comparable to the decay of the MLCT state. Data are also presented on the absorption characteristics of the triplet-triplet spectrum of this complex in water where the complex is extremely stable.

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#### SCHEME I

$$\operatorname{Ru}(LL)_{3}^{2+} \xrightarrow{X} [\operatorname{Ru}(LL)_{3}][X_{2}]$$
(3)

$$[Ru(LL)_{3}][X_{2}] \stackrel{\xrightarrow{\mu\nu}}{\underset{k_{1}}{\longrightarrow}} [Ru(LL)_{3}][X_{2}] ({}^{3}MLCT)^{*}(d\pi^{5})(\pi LL)^{1}$$
(4)

$$\overset{k_2}{\underset{k_{-2}}{\longrightarrow}} [\operatorname{Ru}(\operatorname{LL})_3][X_2]^* (\mathrm{dd})^* (\mathrm{d}\pi^5) (\mathrm{d}\sigma^*)^1 \quad (5)$$

$$(\mathrm{dd})^* \xrightarrow{k_3} [\mathrm{Ru}(\mathrm{LL})_2 \mathrm{X}_2] + (\mathrm{LL}) \text{ or } [\mathrm{Ru}(\mathrm{LL})_3][\mathrm{X}_2] \quad (6)$$

# **Experimental Section**

Materials and Methods.  $Ru(bpz)_3^{2+}$  as the  $PF_6^-$  or  $Cl^-$  salt was prepared according to published procedure.<sup>13</sup> Tetraethylammonium chloride (TEACl·H<sub>2</sub>O) was a p.a. grade chemical from Fluka and was used as such. Laser photolysis studies were carried out on a fast kinetic spectroscopy unit employing 15-ns (353 or 530 nm) light pulses from a Q-switched Nd laser (YAG oscillator, glass amplifier) as the excitation source. Triplet-state molar extinction coefficients were determined via saturation methods. Steady-state photolysis was carried out using a 250-W W-halogen lamp with water (IR) and 420-nm cutoff filters. All solutions were thoroughly degassed by passing Ar for at least 15 min prior to use.

## **Results and Discussion**

Tris(bipyrazyl)ruthenium(II),  $Ru(bpz)_3^{2+}$ , has been shown in recent years to be an efficient photosensitizer with several of the spectral, redox, and photophysical properties resembling that of the commonly used  $Ru(bpy)_3^{2+.16-19}$ 

Laser Photolysis in Water. In aqeous solutions, as with Ru- $(bpy)_{3}^{2+}$ , the bipyrazine complex shows exceptional stability under photolysis conditions. To facilitate a quantitative analysis of the photoredox processes in the presence of various quenchers and the substitutional photochemistry observed in nonaqueous solvents, we have examined the absorption spectral features of the <sup>3</sup>MLCT excited state in water by laser photolysis techniques. Figure 1 presents a transient difference absorption spectrum of Ru(bpz)<sub>3</sub>Cl<sub>2</sub> recorded at the end of 15-ns laser pulse excitation (353 nm).

The assignment of the transient spectrum as due to the <sup>3</sup>MLCT excited state has been confirmed by its matching decay characteristics (in both the presence and absence of oxygen) with the

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Figure 1. Transient difference absorption spectrum of the MLCT excited state of  $Ru(bpz)_3Cl_2$  in water recorded at 50 ns following 15-ns laser pulse excitation (353 nm).  $[Ru(bpz)_3Cl_2] = 2 \times 10^{-5} \text{ M}.$ 

MLCT excited-state emision decay monitored at 605 nm. The spectrum is characterized by maximum bleaching at wavelengths corresponding to the ground-state absorption maxima (295 and 445 nm with a shoulder around 415 nm) and two maxima at 335 and 375 nm. (Isobestic points are located at 265, 322, 397, and about 520 nm.) As expected the spectrum is very similar in features to the spectrum of the MLCT excited state of  $Ru(bpy)_3^{2+}$ with small spectral shifts and changes in relative intensities. In degassed aqueous solutions, the emission and transient absorption decay exponentially with a rate constant  $k = 0.98 \times 10^6 \text{ s}^{-1}$ (lifetime 1.02  $\mu$ s) in good agreement with earlier reported values. Saturation experiments (monitoring of the transient absorption changes as a function of laser intensity to obtain total conversion of the ground state to the MLCT state) at low Ru complex concentrations yielded  $\Delta \epsilon = +6800 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$  at 375 nm and  $\Delta \epsilon = -5700 \pm 800 \text{ M}^{-1} \text{ cm}^{-1}$  at 440 nm.

Photolysis in Acetonitrile in the Presence of Chlorine Ions. Ru(bp2)<sub>3</sub><sup>2+</sup> dissolved in acetonitrile as the PF<sub>6</sub><sup>-</sup> salt is relatively stable under photolysis conditions in the 400–500-nm region. However, if chloride ions are added, efficient photodecomposition occurs as illustrated in Figure 2. The tris complex looses a bipyrazine ligand and forms [Ru(bp2)<sub>2</sub>(CH<sub>3</sub>CN)(CL)]<sup>+</sup> as given by eq 2. The conversion is clean and quantitative as indicated by the existence of well-defined isobestic points at 350, 395, and 463 nm. (The secondary photolysis of this bis complex to give [Rub(bp2)<sub>2</sub>Cl<sub>2</sub>] (eq 7), however, is very inefficient,  $\Phi \le 0.001$ .)

$$[\operatorname{Ru}(\operatorname{bpz})_2(\operatorname{CH}_3\operatorname{CN})(\operatorname{Cl})]^+ \xrightarrow[\operatorname{Cl}]{} [\operatorname{Ru}(\operatorname{bpz})_2(\operatorname{Cl})_2]$$
(7)

The reported quantum yield for reaction 2 is quite high  $(0.37,^{13} 0.45^{14})$ .

Figure 3 presents time-resolved data on the decay of the MLCT excited state and transient absorption changes following 353-nm, 15-ns laser pulse excitation of a degassed acetonitrile solution containing the tris complex ( $[Ru(bpz)_3^{2+}] = 7 \times 10^{-5}$  M) and chloride ions ( $[TEACl] = 8 \times 10^{-4}$  M, conditions similar to those used in Figure 2). The insert in Figure 2 presents a transient difference spectrum for the long-lived (permanent) product formed, recorded at  $t = 1 \ \mu$ s after excitation of the tris complex. This difference spectrum is in excellent agreement with that calculated from the steady-state photolysis spectral changes shown in Figure 2, with isobestic points located at 463 and about 395 nm.

The decay of the MLCT excited state as monitored by its emission around 605 nm is quenched by chloride ions. For example, at [Cl<sup>-</sup>] =  $8 \times 10^{-4}$  M, the lifetime is reduced to about 370 ns, as compared to  $\tau_0 = 840$  ns observed for the PF<sub>6</sub><sup>-</sup> salt alone in the absence of any added chloride ions (trace A in Figure 3). Transient absorption changes monitored at wavelengths > 400 nm all show an initial bleaching, corresponding to the formation of the MLCT excited state (cf. eq 4 and Figure 1). This is followed by rapid bleaching recovery (at  $\lambda > 465$  nm, net positive absorptions on a long time scales and at  $\lambda < 460$  nm permanent



Wavelength (nm)

**Figure 2.** Absorption spectral changes during the photolysis (steady state) of acetonitrile solution containing  $[Ru(bpz)_3(PF_6)_2] = 8 \times 10^{-5}$  M and  $[TEACI] = 8 \times 10^{-4}$  M. ( $\lambda \ge 420$  nm.) Insert: Transient difference absorption spectrum recorded 2  $\mu$ s after laser pulse excitation of an acetonitrile solution containing  $[Ru(bpz)(PF_6)_2] = 7 \times 10^{-5}$  M and  $[TEACI] = 8 \times 10^{-4}$  M.



**Figure 3.** Typical kinetic traces obtained during the laser flash photolysis of  $\text{Ru}(\text{bpz})_3^{2+}$  (7 × 10<sup>-5</sup> M) and TEACI (8 × 10<sup>-4</sup> M) in degassed acetonitrile. A: Emission of the MLCT excited state monitored at 605 nm. B-F: Transient absorption curves at various wavelengths showing an initial bleaching (due to the formation of the MLCT state) followed by recovery (giving the bis complex as the long-lived product).

bleaching is observed as illustrated in traces B-F). At all wavelengths the formation of the long-lived product (permanent) is complete at  $t = 1 \mu s$ , with product growth kinetics comparable

to the decay of the MLCT excited state as monitored by its emission at 605 nm (trace A). Since the transient difference absorption spectrum of the long-lived product shows excellent agreement with the difference spectrum calculated from the steady-state photolysis spectra (by isolation and chemical characterization, earlier studies<sup>13,14</sup> have established the product absorbing with a maximum at 490 nm as the bis complex [Ru-(bpz)<sub>2</sub>(CH<sub>3</sub>CN)(Cl)]<sup>+</sup>), it is deduced that the product bis complex forms very rapidly on time scales comparable to the decay of the MLCT excited state.

Returning to the earlier indicated scheme that has been proposed to explain the observed photosubstitutional processes in nonaqueous media, the laser photolysis results indicate that the intermediate "dd" state responsible for the photodecomposition is extremely short-lived (lifetimes at most a few nanoseconds). Given the error limits on the transient growth, decay kinetics (about 5% even under best/optimal conditions), the present results indicate that the lifetime of the  $(dd)^*$  state is less than  $10^{-8}$  s. From an analysis of the radiative, nonradiative rate constants and quantum yields at various temperatures for various mixed, tris-(polypyridyl)ruthenium(II) complexes, Meyer et al.<sup>11,14</sup> have discussed two possible limiting situations for Scheme I: an irreversible surface crossing of the MLCT state to the (dd)\* state (with  $k_3 >> k_{-2}$ ) and a thermal equilibrium situation between MLCT and (dd)\* states (with  $k_3 \ll k_{-2}$ ). It has been deduced that tris complexes  $Ru(LL)_3^{2+}X_2$  (LL = bpy, bpz, or bpyrm) with high substitution quantum yields ( $\geq 0.1$ ) belong to the former case of irreversible surface crossing. Mixed ligand complexes of the type  $[Ru(LL)_n(LL')_{3-n}]^{2+}$  (LL, LL' = bpy, bpz, or bpyrm) with low photosubstitution quantum yields ( $\leq 10^{-2}$ ) appear to belong to the second case.<sup>20</sup>

The very short lifetime for the photoreactive  $(dd)^*$  state deduced here also explains the absence of any substitutional photochemistry for  $Ru(LL)_3Cl_2$  in water even in the presence of added chloride ions. In aqueous media the Ru complexes are fully dissociated and diffusional insertion of chloride ions (eq 8) in the (dd)\* state

$$\begin{array}{c} \operatorname{Ru}(LL)_{3}^{2+*} + \operatorname{Cl}^{-} \xrightarrow{k} \operatorname{Ru}(LL)_{2}(\operatorname{Cl})_{2} + LL \\ (\mathrm{dd})^{*} \end{array}$$
(8)

or in the intermediate species (probably one with one of the LL ligand bound to the Ru center as a monodentate) is inefficient. The inserting ligand needs to be present in the close vicinity, possibly as in an ion pair.<sup>21</sup>

There is one final aspect of the "chloride ion effect" in acetonitrile that is not yet fully understood. This concerns the efficient quenching of the MLCT state by Cl<sup>-</sup> ions (observed only in acetonitrile but not in water!). Liftime quenching studies indicate a linear Stern-Volmer behavior for Cl<sup>-</sup> concentrations up to a 100-fold excess of the Ru complex ( $k_q = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). With increasing chloride concentration, the MLCT state decays rapidly and the substitutional product, the bis complex, also appears correspondingly faster in a one-to-one fashion. Allen et al.<sup>14</sup> who also noted chloride quenching of the MLCT state of Ru(bpz)<sub>3</sub><sup>2+</sup> in CH<sub>3</sub>CN proposed the possible occurrence of redox pathways as shown in

$$\operatorname{Ru}(\operatorname{bpz})_{3}^{2+*} + \operatorname{Cl}^{-} \xrightarrow{k_{q}} \operatorname{Ru}(\operatorname{bpz})_{3}^{+} + \operatorname{Cl}$$
(9)

If this indeed is the case then the transient difference spectrum recorded during/at the end of the decay of the MLCT excited state should contain contributions from the  $Ru(bpz)_3^+$  species. Unfortunately, the reported absorption spectrum of  $Ru(bpz)_3^{+16}$  is very similar to that of the photosubstitution product, the bis complex with an absorption maximum around 490 nm. However,  $Ru(bpz)_3^+$  is known to react efficiently with oxygen and we do not see any decay of the long-lived transient absorptions in the presence of oxygen.<sup>22</sup> Also it is difficult to visualize the reasons for the absence of any such redox quenching process in aqueous medium.

An alternate explanation would be that the fraction of the ion pair responsible for the substitutional photochemisty increases with increasing Cl<sup>-</sup> concentration in a scenario where the lifetime of the MLCT state in the ion pair is very short (as in "static quenching"). But the extremely efficient substitutional photochemistry observed even in the presence of stoichiometric quantities of added chloride ions suggest very efficient formation of ion pairs in nonaqueous solvents such as CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub>. Unfortunately, the absorption, emission spectral features of Ru complexes in solvents that promote ion-pair formation and those where the complexes are fully dissociated are very similar, precluding any quantitative estimation of ion pairs present under any given conditions.

More detailed studies of the chloride ion dependence of substitutional quantum yields, the MLCT state emission intensity quenching in the steady state, and the transient product yields after the decay of the MLCT state are underway to elucidate in detail the chloride effects. These effects, however, do not largely affect the principal conclusion (demonstration?) of this study, viz., the very rapid formation of the substitutional photoproduct on time scales comparable to the decay of the MLCT excited state.

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**Registry No.** Ru(bpz)<sub>3</sub><sup>2+</sup>, 75523-96-5; [Ru(bpz)<sub>2</sub>(CH<sub>3</sub>CN)(Cl)]<sup>+</sup>, 80907-57-9; CH<sub>3</sub>CN, 75-05-8; Cl<sup>-</sup>, 16887-00-6; H<sub>2</sub>O, 7732-18-5.

<sup>(20)</sup> The absence of any chloride quenching effect on the lifetime of the MLCT state of  $Ru(bpy)_3^{2+}$  and its efficient occurrence in tris(bpz) complexes may suggest a dynamical coupling of CT, dd states in the bpz complexes. The photosubstitution in the latter can occur via a direct attack of Cl<sup>-</sup> on the Ru<sup>II</sup>-based CT state.

<sup>(21)</sup> It is also quite conceivable that in acetonitrile and water a common mechanism exists involving initial chelate ring opening and solvent capture followed by a subsequent thermal step in which chloride captures the intermediate. Given the differences in the solvation energy between acetonitrile and water, substitution by chloride may be thermodynamically favored in acetonitrile and disfavored in water.

<sup>(22)</sup> A reviewer has pointed that a rapid redox process followed by substitution and rapid back-electron transfer would still be consistent with the results since this might occur all faster than any diffusional oxygen quenching and faster than the time resolution of the xperiment.