# Photolysis of (Diamine)bis(2,2′-bipyridine)ruthenium(II) Complexes Using On-Line Electrospray Mass Spectrometry

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Photolysis of $Ru(bpy)_2(en)^{2+}$ and $Ru(bpy)_2(tn)^{2+}$, where bpy = 2,2′-bipyridine, en = ethylenediamine, and tn = 1,3-propylenediamine, was studied in acetonitrile using on-line electrospray mass spectrometry (ES-MS). These complexes are known to undergo a four-electron oxidation photochemically, giving the $\alpha,\alpha'$-diimine complexes. The monoimine complexes involved in this stepwise process were detectable after photoirradiation ($\lambda > 420$ nm). Also, new ligand-oxidized complexes $Ru(bpy)_2(en+14)^{2+}$ and $Ru(bpy)_2(tn+14)^{2+}$ were observed together with photosubstitution products such as $Ru(bpy)_2(AN)_2^{2+}$ and $Ru(bpy)_2(AN)_2X^+$ (AN = acetonitrile). The notation (en+14) and (tn+14) represents loss of two hydrogen atoms and addition of an oxygen atom to the en and tn ligands. Photosubstitution intermediates with the monodentate diamine, $Ru(bpy)_2(tn)(AN)^{2+}$ and $Ru(bpy)_2(tn)$-$(AN)X^+$, were detected in the ES mass spectrum of the tn complex but not in that of the en complex. Other photosubstituted intermediates with the monodentate (en+14) and (tn+14) ligands were detected by on-line mass analysis. The electrospray technique combined with use of a flow-through photoreaction cell was shown to be a useful tool for studying photolysis of inorganic metal complexes.

## Introduction

Electrospray mass spectrometry (ES-MS) has been widely used for the measurement of molecular masses of nonvolatile and thermally unstable compounds.[1−7] One of the reasons is that ES-MS is characterized by soft ionization. ES mass spectra show a simple mass pattern, which allows ready determination of molecular masses with high sensitivity. The technique has been used successfully for studies of biomolecules such as proteins and nucleic acids[3−7] and for identification of inorganic metal complexes.[8−10] We recently developed an on-line mass spectrometry system in which a photoreaction cell was attached to an electrospray interface. The system was applied to study photolysis of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and $Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine).[11] In the study of photosubstitution of $Ru(bpy)_2B^{2+}$ (B = 3,3′-Me$_2$bpy (dmbpy) and 2-(aminomethyl)-pyridine (ampy)), reaction intermediates with the monodentate ligand were directly detected for characterization of reaction pathways.[12] On-line ES-MS showed a particularly useful tool for identification of unstable reaction products or short-lived intermediates, as compared with usual methods such as UV−vis absorption, NMR spectroscopy, and separation by HPLC. The usefulness of the on-line ES-MS method enables us to examine photoinduced oxidation of ligand molecules coordinated to a metal ion, one of the fundamental reactions of photoexcited metal complexes.

Metal ions have been known to play an important role in oxidation of coordinated amines. Oxidative dehydrogenation of macrocyclic amine complexes to imine complexes, as catalyzed by the metal ions, was studied by Curtis[13] and Busch et al.[14] It was observed that $Ni^{2+}$, $Cu^{2+}$, and $Fe^{2+}$ ions promoted the oxidative dehydrogenation but $Co^{3+}$ failed to give the oxidation. This suggested that the reaction involved prior oxidation of the metal ion followed by oxidation of the ligand and reduction of the metal ion.

Oxidative dehydrogenation of aliphatic amines coordinated to ruthenium(II) has been investigated by many research groups. For the $Ru(en)_3^{2+}$ (en = ethylenediamine) complex, the reaction involved a four-electron oxidation giving the $\alpha,\alpha'$-diimine (en−4) complex of Ru(II).[15,16] $Ru(phen)_2(en)^{2+}$ also underwent the four-electron oxidation giving $Ru(phen)_2(en-4)^{2+}$ with an oxidizing agent $O_2$ or $I_2$.[17] These results showed the Ru(III) complexes were intermediates in the chemical oxidation of both $Ru(en)_3^{2+}$ and $Ru(phen)_2(en)^{2+}$ complexes. Mayer's group reported that the $Ru(bpy)_2(en)^{2+}$ complex underwent the four-electron oxidation either electrochemically or chemically, giving

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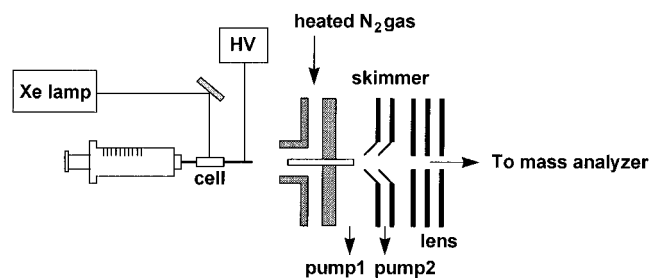(17) Mahoney, D. F.; Beattie, J. K. *Inorg. Chem.* **1973,** *12,* 2561.

**Figure 1.** Schematics of electrospray mass spectrometry for on-line analysis of photochemical reactions. The sample solution in a quartz cell is photoirradiated by a Xe lamp ($\lambda$ >420 nm; a UV-cutoff filter).

the $Ru(bpy)_2(en-4)^{2+}$ complex.[18] The results indicated that the diamine-oxidative dehydrogenation reactions are initiated by the oxidation of Ru(II) to Ru(III) and the reactions probably occur in a stepwise manner via the monoimine intermediates. Ollino and Rest[19] have found that $Ru(bpy)_2(en)^{2+}$ and $Ru(bpy)_2(tn)^{2+}$ (tn = 1,3-propylenediamine) complexes were oxidized by photoirradiation in water or acetonitrile to be changed into the corresponding $\alpha,\alpha'$-diimine complexes. However, the monoimine intermediate was not detected by absorption spectroscopy.

In this paper we will analyze photoproducts for $Ru(bpy)_2$-$(en)^{2+}$ and $Ru(bpy)_2(tn)^{2+}$ after irradiation of visible light ($\lambda$ >420 nm) using on-line ES-MS with a flow-through photoreaction cell. A variety of advantages for use of on-line ES-MS are expected to detect readily new products of the aliphatic diamine complexes except the $\alpha,\alpha'$-diimine complexes. Particularly, detection of the monoimine complex as a primary product was necessary for evidence that the photoinduced oxidation occurs in a stepwise manner. Moreover, some mechanistic details of both oxidation and substitution reactions in photolysis of the diamine complexes will be presented.

## Experimental Section

A sector-type mass spectrometer (JEOL-D300) connected with a laboratory-made ES interface was used to obtain ES mass spectra (Figure 1). A sample solution was sprayed with a flow rate of 2 $\mu$L/min at the tip of a needle applied by a voltage 3.5 kV higher than that of a counter electrode. A heated nitrogen gas flowing between the needle and the counter electrode was used to aid desolvation of charged droplets sprayed. Ions enter the vacuum system through the first and the second skimmers of a mass analyzer. The pressures of differential pumping stages were about 10 and 0.1 Torr, respectively. A rotary pump and a mechanical booster pump in their region are floating to depress a discharge. The voltage of the first skimmer was the same as that of the counter electrode and was 50 V higher than that of the second skimmer in the present case. The collision-induced dissociation with a residual gas occurs between the two skimmers.

The sample solution was irradiated with a high-pressure Xe lamp (150 W). The reaction cell was a cylindrical quartz cell of 1 mm inner diameter, installed at the middle of the needle. The size of a light spot focused by the lens was ca. 5 mm in diameter. A UV-cutoff filter was used for irradiation ($\lambda$ >420 nm). It required about 2 min for a flowing sample to pass across the light area in the cell and a few tens of seconds to arrive at the tip of needle for spraying. Thus, photoproducts with a lifetime of more than a few minutes could be detected under such spraying conditions.

The complexes $Ru(bpy)_2B(ClO_4)_2$ (B = en, tn) were prepared by similar methods described in the literature.[18] For measurements of ES mass spectra, samples were dissolved in freshly distilled acetonitrile and nothing was added to promote ionization. The concentrations of samples were kept at ~0.1 mM.

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## Results and Discussion

Positive ES mass spectra of the complexes under dark conditions and with photoirradiation by visible light ($>$420 nm) are shown in the upper (a) and lower (b) parts, respectively, of Figures 2−4. For convenience, peaks in the spectra are assigned using the abbreviations L = bpy, X = $ClO_4^-$, and AN = acetonitrile. $m/z$ values in the text were calculated from $^{102}$Ru.

**$Ru(bpy)_2(en)(ClO_4)_2$.** The mass spectrum of the en complex in acetonitrile showed three peaks corresponding to $RuL_2^{2+}$, $RuL_2(en)^{2+}$, and $RuL_2(en)X^+$ in the dark (Figure 2a). The last two are due to dissociation of the counteranion. Photoirradiation of the complex in the reaction cell promoted photoreaction and resulted in the on-line ES mass spectrum (Figure 2b). The peak intensities of $RuL_2(en)^{2+}$ and $RuL_2(en)X^+$ with irradiation relative to the dark were 0.39 and 0.38, respectively. So we can say that 60% of the complexes were transferred to photoproducts under our irradiation conditions. Some of the photoproducts were doubly charged ions $RuL_2(AN)_n^{2+}$ ($n$ = 0−2), singly charged $RuL_2(AN)_2X^+$, or $bpyH^+$, the protonated bpy liberated from the complex. Such photosubstitution products were the same as detected in the ES mass spectra obtained after photoirradiation of $Ru(bpy)_3^{2+}$, $Ru(bpz)_3^{2+}$, and $Ru(bpy)_2B^{2+}$ (B = dmbpy, ampy) complexes in acetonitrile.[11,12]

The intensities of $RuL_2^{2+}$ and $RuL_2(AN)^{2+}$ were larger than that of six-coordinate $RuL_2(AN)_2^{2+}$. This is due to a facile dissociation of acetonitrile molecules from $RuL_2(AN)_2^{2+}$ by collision-induced dissociation (CID).[8,11] Interestingly, the singly charged $RuL_2(AN)_2X^+$, a six-coordinate ion associated with a $ClO_4^-$ anion, did not yield its four- or five-coordinate species in the mass spectrum, as was detected with the doubly charged $RuL_2(AN)_2^{2+}$. The $ClO_4^-$ counterion of the singly charged ion probably protected the weakly coordinating acetonitrile molecules from CID. The appearance of the $RuL_2^{2+}$ ion in the dark (Figure 2a) is due to CID of $RuL_2(en)^{2+}$, because the signal intensity of $RuL_2^{2+}$ increased rapidly with an increase in collision energy from 50 to 80 eV. For $Ru(bpy)_3^{2+}$ and $Ru(bpz)_3^{2+}$, the CID ion $RuL_2^{2+}$ was not observed in the dark with a collision energy of 50 eV. These results indicate that the strength of bonding to the ruthenium(II) ion against CID is in the order bpy > diamines > AN. Therefore, the present collision energy represents mild collision conditions.

The products of $RuL_2(en-2)^{2+}$ and $RuL_2(en-2)X^+$ were found near the main peaks, where (en−2) represents loss of two hydrogen atoms from the en ligand. We showed the comparison of the experimental isotopic pattern with the calculated isotopic distribution to obtain more information for justifying the peak assignments. The insets of Figure 2 are the expanded spectra near the $RuL_2(en)^{2+}$ peak in the dark and with irradiation. The $m/z$ value and mass pattern for the doubly charged ion observed in the dark were consistent with the calculated ones. The mass pattern observed with irradiation suggests the production of $RuL_2(en-2)^{2+}$; this pattern could be reproduced if the complex $RuL_2(en-2)^{2+}$ overlapped as much as 10% of the en complex.

No dehydrogenation product was detected after any irradiation of $Ru(bpy)_3^{2+}$. Thus, dehydrogenation occurs in the en ligand, not in the bpy. The structures of (en−2) ligands were not determined from the present results. However, in the previous photoreactions[12] of $Ru(bpy)_2(ampy)(ClO_4)_2$ we unequivocally showed the detection of $Ru(bpy)_2(ampy-2)^{2+}$. The evidence for the (ampy−2) complex was clear because of the little overlapping. This reaction was much more photosensitive than that of the en complex. Therefore, the imine structure is more likely than the enamine for the (en−2) ligand formed by
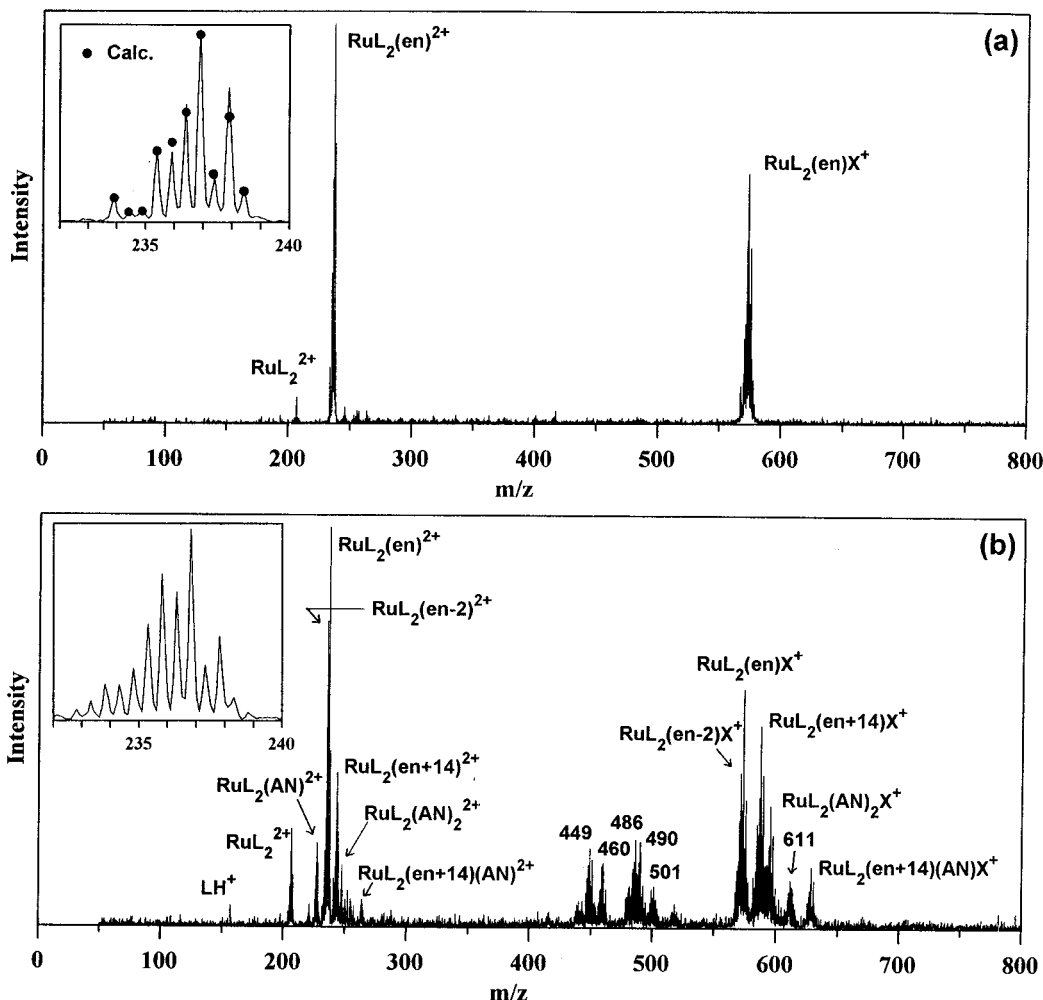
**Figure 2.** Positive ion ES mass spectra of Ru(bpy)$_2$(en)(ClO$_4$)$_2$ (bpy = 2,2′-bipyridine, en = ethylenediamine) in acetonitrile (0.1 mM) obtained under the same conditions: (a) in the dark; (b) with cell irradiation ($\lambda$ >420 nm). The relative peak intensity of irradiation vs the dark conditions was 0.39 for RuL$_2$(en)$^{2+}$. L is bpy, AN is acetonitrile, and X is ClO$_4^-$. The notations RuL$_2$(en−2)$^{2+}$ and RuL$_2$(en+14)$^{2+}$ represent the species that have masses 2 amu lower and 14 amu higher than RuL$_2$(en)$^{2+}$. The peaks given by nominal *m/z* values are unidentified.

oxidative dehydrogenation. It was reported by Meyer's group[18] that exhaustive electrolysis of an acetonitrile solution of RuL$_2$(en)$^{2+}$ at constant potential yielded the $\alpha,\alpha'$-diimine complex RuL$_2$(en−4)$^{2+}$. The complex was identified by spectral and electrochemical measurements. The electrochemical oxidation process consists of two parts: initial oxidation of the metal, Ru(II) → Ru(III), followed by oxidation of the coordinated ligand, RuL$_2$(en)$^{2+}$ → RuL$_2$(en−4)$^{2+}$ through an intermediate of the monoimine complex. The evidence for production of the (en−2) complex has not been definitely shown, because it is unstable with respect to further oxidation. It should be noticed that the (en−2) intermediates were directly detected in the ES-MS spectra. The absorption spectrum of RuL$_2$(en)(ClO$_4$)$_2$ was measured in acetonitrile. A strong visible absorption was observed near 490 nm. This band is due to a Ru(II)−(bpy) metal-to-ligand charge-transfer (MLTC) transition.[19] Accordingly, the oxidative dehydrogenation is initiated by excitation of the MLCT band in Ru(bpy)$_2$(en)$^{2+}$. One of our goals for this experiment, as mentioned in the Introduction, has been achieved. The formation of the (en−4) diimine complex was not evident from a peak analysis in the spectrum (Figure 2b). However, the RuL$_2$(en−4)$^{2+}$ ions were detected using O$_2$-purged acetonitrile with sufficient irradiation.

The complexes Ru(bpy)$_2$(en+14)$^{2+}$ and Ru(bpy)$_2$(en+14)-X$^+$ were observed together with the photosubstitution products. These notations were used to represent the species in the mass

spectra that have masses of 14 amu higher than the Ru(bpy)$_2$-(en)$^{2+}$ and Ru(bpy)$_2$(en)X$^+$ complexes, corresponding to loss of two hydrogen atoms and addition of an oxygen atom. Byproducts of the (en+14) complexes have not been reported in an oxidative dehydrogenation process of diamine complexes. (en+14) is estimated to be an oxide of ethylenediamine, e.g., NH$_2$CH$_2$CH=NOH, NH$_2$CH$_2$CONH$_2$, or NH$_2$CH$_2$C(OH)=NH. Similar oxidative products from the diimine complex of Fe(GMI)$_3^{2+}$ (GMI = CH$_3$N=CHCH=NCH$_3$) were reported by Chum and Krumholz.[20] Chemical oxidation with Ce(IV) yielded oxygenated complexes Fe(GMI)$_2$(GA)$^{3+}$ and Fe(GMI)$_2$-(GH)$^{2+}$ (GA = CH$_3$N=CHC(=O)NHCH$_3$ or CH$_3$N=CHC-(OH)=NCH$_3$; GH = CH$_3$N=CHCH=NCH$_2$OH). Therefore, the complexes RuL$_2$(en+14)$^{2+}$ and RuL$_2$(en+14)X$^+$ may be generated in a stepwise manner via the monoimine complex by photoinduced oxidation.

It was an interesting result that the peaks of RuL$_2$(en+14)-(AN)$^{2+}$ and RuL$_2$(en+14)(AN)X$^+$ were related to the photosubstitution intermediate with the monodentate (en+14) ligand. In ligand thermal substitution and photosubstitution of a metal complex with bidentate ligands, the substitution is considered to proceed stepwise (Scheme 1), and thus an intermediate with a $\eta^1$ bidentate ligand is proposed. In photosubstitution of the complex Ru(bpy)$_2$(dmbpy)$^{2+}$, the intermediates with the $\eta^1$ bidentate ligand RuL$_2$(dmbpy)(AN)$^{2+}$ and RuL$_2$(dmbpy)(AN)-

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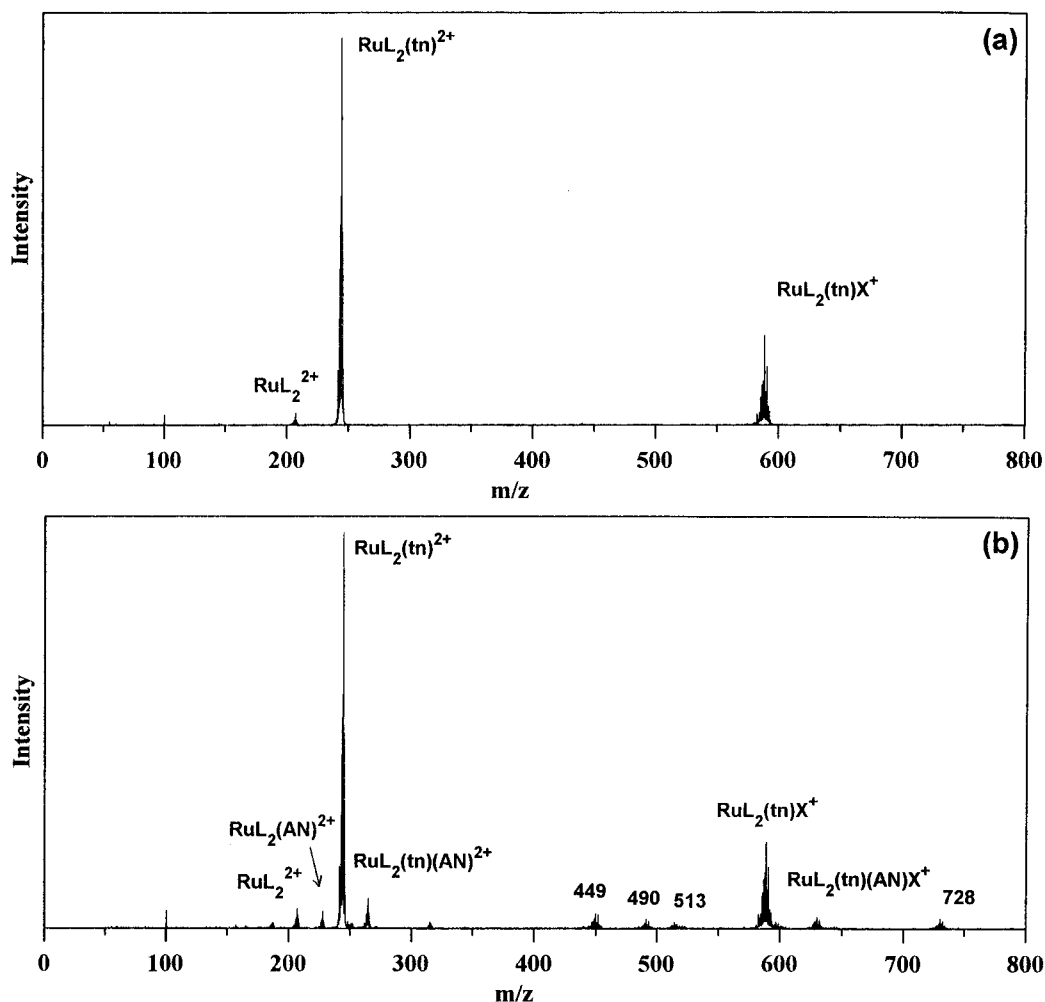
**Figure 3.** ES mass spectra of $Ru(bpy)_2(tn)(ClO_4)_2$ (tn = 1,3-propylenediamine) in deaerated (Ar purged) acetonitrile (0.1 mM); (a) in the dark; (b) with cell irradiation. The relative peak intensity of irradiation vs the dark conditions was 0.63 for $RuL_2(tn)^{2+}$.

**Scheme 1**



⬭  **Bidentate ligand**

Ⓢ  **Solvent**
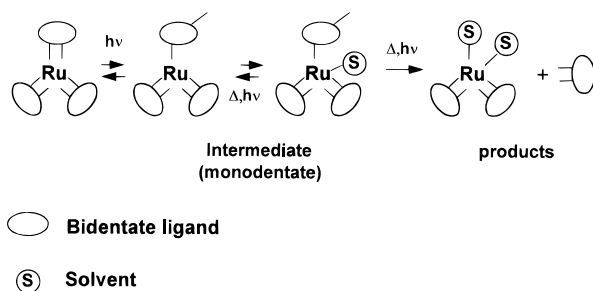
$X^+$ have been detected using on-line ES-MS. However, no intermediate was detected in the spectrum of the en complex (Figure 2b). The intermediate with the monodentate en formed by photoexcitation will undergo a fast rechelation to return to a normal state. Thus, lack of detection of the complex $RuL_2$-$(en)(AN)^{2+}$ or $RuL_2(en)(AN)X^+$ is due to a very short lifetime of the intermediate. However, once the oxidized complex $RuL_2(en+14)^{2+}$ is generated, the lifetime of the oxidized intermediate becomes longer, and thus, the intermediate with the $\eta^1$ bidentate (en+14) is detectable. Therefore, the substitution products $RuL_2(AN)_n^{2+}$ (n = 0−2) and $RuL_2(AN)_2X^+$ for the en complex were generated via the oxidized complex, not directly from the photosubstitution of $Ru(bpy)_2(en)^{2+}$. This route was supported by the spectrum obtained in deaerated solution. The sample solution was prepared under Ar atmosphere using Ar-purged acetonitrile and was irradiated

under the same conditions. There was no product other than $RuL_2^{2+}$, $RuL_2(en)^{2+}$, and $RuL_2(en)X^+$ in this solution after photoirradiation. The spectrum was the same as obtained in Figure 2a. To confirm the photoinduced oxidation of the complex with oxygen, the solution was exposed to air and was irradiated. As a result, the same spectrum of photoproducts as Figure 2b was obtained.

A number of peaks of photoreaction products appear between $m/z$ 430 and 530. $m/z$ 449 and 490 correspond to $RuL_2(Cl^-)^+$ and $RuL_2(Cl^-)(AN)^+$, respectively. The ion $RuL_2(Cl^-)^+$ has also appeared in the spectrum of $Ru(bpy)_3(ClO_4)_2$.[11] The ion $RuL_2(Cl^-)(AN)^+$ was probably formed from the coordination of $Cl^-$ released by a certain photoreaction involving $ClO_4^-$ because $Cl^-$ easily coordinates $Ru(bpy)_2^{2+}$, and the ion $RuL_2(Cl^-)^+$ was due to CID of $RuL_2(Cl^-)(AN)^+$. The other $m/z$ peaks are unidentified.

**$Ru(bpy)_2(tn)(ClO_4)_2$.** Figure 3 shows the spectra of the tn complex in the deaerated solution. The three ions $RuL_2^{2+}$, $RuL_2(tn)^{2+}$, and $RuL_2(tn)X^+$ were observed without irradiation. The monodentate intermediates of $RuL_2(tn)(AN)^{2+}$ and $RuL_2(tn)$-$(AN)X^+$ were detected with irradiation, but analogous intermediates were not detected for the en complex. This is because the lifetime of the monodentate intermediate is longer for the tn ligand than for the en ligand. In other words, the rate of rechelation for the five-coordinate complex in Scheme 1 is slower for the tn complex. The deaerated solution did not generate any oxidized species such as (tn−2) and (tn+14) after
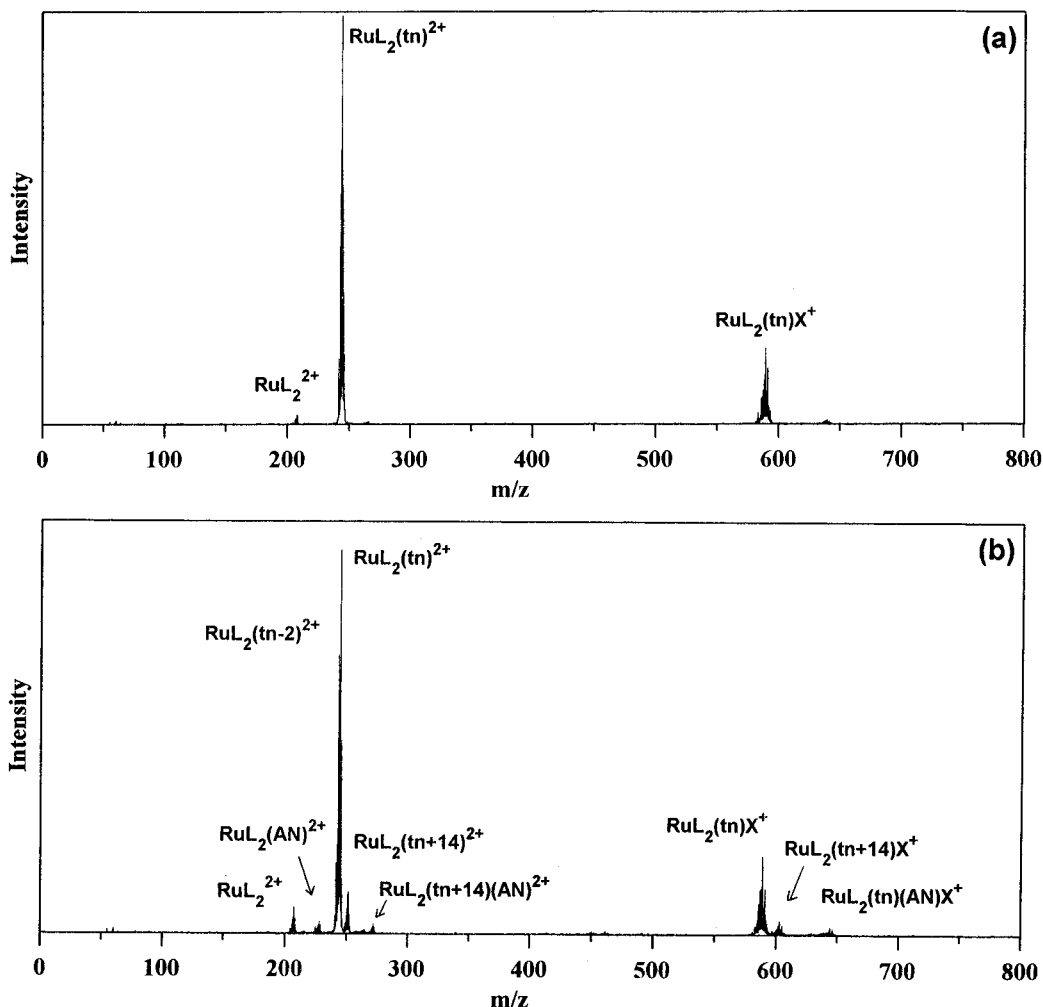
**Figure 4.** ES mass spectra of $Ru(bpy)_2(tn)(ClO_4)_2$ in non-deaerated acetonitrile (0.1 mM): (a) in the dark; (b) with cell irradiation. The relative peak intensity of irradiation vs the dark conditions was 0.69 for $RuL_2(tn)^{2+}$.

photoirradiation. This was the same as the result for the en complex. $RuL_2^{2+}$ and $RuL_2(AN)^{2+}$ ions observed for the tn complex were the CID products from the solvent-coordinated $RuL_2(AN)_2^{2+}$, which resulted from photosubstitution via the intermediate of $RuL_2(tn)(AN)^{2+}$. $m/z$ values except 449 $(RuL_2(Cl^-)^+)$ and 490 $(RuL_2(Cl^-)(AN)^+)$ were unidentified peaks.

ES mass spectra for non-deaerated solutions are shown in Figure 4. The relative intensity ratio of irradiation vs the dark conditions was 0.69 for $RuL_2(tn)^{2+}$; thus 30% of the tn complexes underwent photolysis. The oxidation products observed were analogous to those for the en complex. The monodentate intermediates of the (tn+14) complex were also clearly detected. The doubly charged ion $RuL_2(tn-2)^{2+}$ appeared near the base peak. The monodentate intermediate with the imine ligand was not seen for either the (en−2) or (tn−2) complexes. On the whole, the tn complex was less sensitive to the photoinduced oxidation than the en complex.

## Conclusion

The photolysis ($\lambda > 420$ nm) of $Ru(bpy)_2B^{2+}$ (B = en, tn) in acetonitrile was studied using on-line ES-MS. In the photooxidation of the diamine complexes, the (B−2) monoimine complexes were directly detected as primary products, which would be further oxidized to the diimine complexes. The new oxidative pathway giving $Ru(bpy)_2(B+14)^{2+}$ was observed for both complexes. In the photosubstitution reactions, the intermediates with the $\eta^1$ bidentate ligand were detected for the tn complex, but not for the en one. Another route for ligand substitution was found wherein the coordinated diamine was first oxidized to (B+14) followed by photosubstitution. Evidence was obtained by direct observation of photosubstitution intermediates with the monodentate (B+14) ligand.