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Identification of an Intermediate of the Photosubstitution of a Ruthenium(II) Diimine Complex with a Monodentate Chelating Ligand: ^{1}H NMR and HPLC Evidence

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In the reaction of the thermal and photochemical ligand substitution of a metal complex with a didentate ligand the formation of an intermediate with a monodentate potentially didentate ligand is frequently postulated or suggested.[1] However direct evidence has rarely been reported for the presence of such an intermediate, except for a group of pentacarbonyl complexes with an η^1 didentate ligand.[2] Vos and his co-workers have reported isolation of an intermediate with a monodentate 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole ligand in the photoreaction of a ruthenium(II) diimine compound.[3] However, recently they revised their conclusions and stated that the intermediate was actually a linkage isomer of the proposed intermediate, a compound with a monodentate triazole ligand coordinated not with N-2 but with N-1.[4] Isolation of stable compounds with an η^1 didentate ligand has been reported for a few systems.[5]

For the detection of an intermediate with an η^1 didentate ligand to be possible in the photosubstitution of a (didentate ligand)-ruthenium(II) complex, both the quantum yield of the formation of the intermediate and its lifetime should be large enough, and in addition, it should be readily identified. A metal complex with a 3,3′-dimethyl-2,2′-bipyridine ligand (=dmbpy), $[Ru(bpy)_2(dmbpy)]^{2+}$, was used for this purpose. The ligand has a steric hindrance for coordination between the methyl groups of its pyridine moieties which may favor the formation of an intermediate with monodentate dmbpy. The lifetime of the intermediate is expected to be long enough to allow its detection because of the steric hindrance for rechelation of the monodentate ligand. The intermediate, once formed and having sufficient lifetime may be detected by ^{1}H NMR by observing sharp methyl signals.

In our previous paper we have suggested the formation of the intermediate with a monodentate dmbpy ligand formed in the photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$ in aqueous solution on the basis of kinetic and absorption spectral evidence.[6] In this communication we will report on direct evidence, ^{1}H NMR and HPLC evidence, for the formation of the intermediate in acetonitrile solution; as far as we know, this is the first example of the identification and characterization of a true reaction intermediate with a monodentate diimine ligand for a tris(diimine) type complex.

Photoirradiation of an aqueous solution of $[Ru(bpy)_2(dmbpy)]^{2+}$ by a flash ($30\ \mu s$, $\lambda > 390$ nm) of a Xe lamp (30 J) caused an instantaneous decrease in absorbance at 400–460 nm of the solution which recovered in the dark with a half-life ($t_{1/2}$) of 7 s at 25 °C, indicating that a transient species was formed and that it returned to the original complex. In acid solution the rate of the absorbance recovery decreased remarkably with acid concentration ($t_{1/2} = 2$ min in 0.1 M CF_3SO_3H).[6]

The acid solution (a) before irradiation, (b) immediately after irradiation, (c) after an additional 22 min at 0 °C, and (d) after a further 5 min at 36 °C was analyzed by HPLC using an ODS column with an eluent of acetonitrile/water (80/20) containing 0.06 M $LiClO_4$. The chromatograms are shown in Figure 1a–d. In the figure the three small peaks in parts b–d with retention times (RT) of 1.3, 1.8, and 2.2 min have been assigned to $[Ru(bpy)_2(OH_2)_2]^{2+}$, $[Ru(bpy)_2(OH_2)(CH_3CN)]^{2+}$, and $[Ru(bpy)_2(CH_3CN)_2]^{2+}$, respectively, on the basis of the retention times of authentic samples. The main peak was of the original complex.

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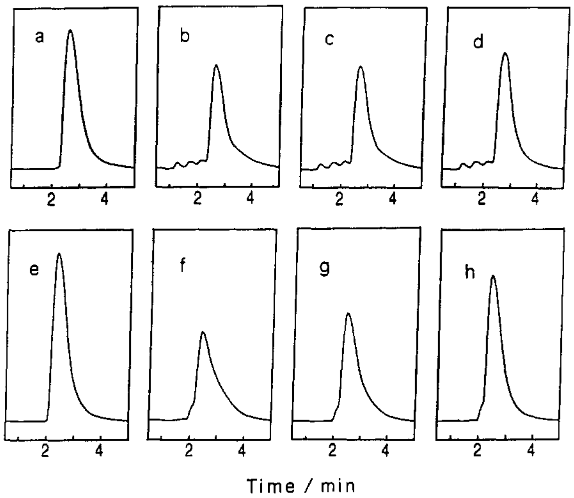

Figure 1. HPLC chromatograms (absorbance at 280 nm versus retention time) of a solution containing $[Ru(bpy)_2(dmbpy)](ClO_4)_2$ before and after photoirradiation: column, ODS 4 × 150 mm; eluent, CH_3CN/H_2O (80/20) containing 0.06 M $LiClO_4$. Key for (a)–(d) (aqueous 0.1 M CF_3SO_3H solution): (a) before irradiation; (b) immediately after irradiation; (c) after an additional 22 min at 0 °C; (d) after a further 5 min at 36 °C. Key for (e)–(h) (acetonitrile solution): (e) before irradiation; (f) immediately after irradiation; (g) after an additional 1.5 h at 25 °C; (h) after a further 3 min at 80 °C.

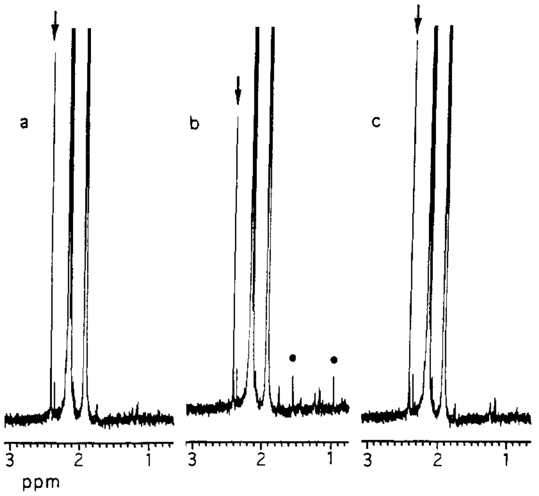

Figure 2. ^1H NMR spectra of an acetonitrile solution of 1×10^{-4} M $[Ru(bpy)_2(dmbpy)](PF_6)_2$ at 10 °C: (a) before irradiation; (b) immediately after irradiation; (c) after an additional 5 min at 60 °C. A signal marked with an arrow is that of the metal complex, and signals marked with circles are those of the intermediate. Other weak signals are those of impurities in CD_3CN (Aldrich 100% D).

The tail of the main peak which was observed for parts b and c was assigned to the intermediate with a monodentate dmbpy mentioned in our previous paper: the tail disappeared in chromatogram d with an increase in the main peak.

In various organic solvents such as pyridine, dimethyl sulfoxide, acetone, nitromethane, or chloroform, the rate of the absorbance recovery after photoflash, or the rate of the thermal reaction of the intermediate to go back to the original complex, was greater than for that in water. Only in nitrile solutions such as acetonitrile was the rate quite slow ($t_{1/2}$ = 80 min at 25 °C). HPLC analyses of the acetonitrile solution before and after photoflash gave the chromatograms shown in Fig 1e–h. There was observed one peak with a small front shoulder and a tail in chromatograms f and g. The shoulder with RT = 2.1 min was assigned to be $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ on the basis of its absorption spectrum.[7] The chromatograms f and g were similar to those of b and c in that the mother peak had a tail; the tail (RT = 3.3 min) disappeared in chromatogram h with the increase in the mother peak (RT = 2.4 min). The absorption maximum (λ_{max}) of the tail was 440 nm, close to the value of 441 nm for $[Ru(bpy)_2(3\text{-methylpyridine})(CH_3CN)]^{2+}$ and 435 nm for $[Ru(bpy)_2(pyridine)(CH_3CN)]^{2+}$, but clearly different from the λ_{max} values of other complexes.[7] The results indicated strongly that the tail was the intermediate with a formula $[Ru(bpy)_2(dmbpy)(CH_3CN)]^{2+}$.

HPLC analysis was also carried out for continuous photolysis of the dmbpy complex in acetonitrile with the light (λ = 436 nm) of a 500-W ultra-high-pressure mercury lamp. The progress of the reaction products was followed by HPLC by monitoring absorbance at 440 nm. In the initial stage of the photolysis the mother peak with RT = 2.4 min decreased continuously with the increase in the tail with RT = 3.3 min. After 30 s of photolysis the tail grew into a clear shoulder. At this stage a new small front shoulder with RT = 2.1 min appeared. With continued photolysis time, the front shoulder increased steadily while the mother peak decreased, but it was always associated with the rear shoulder. After 400 s of photolysis both the mother peak and the rear shoulder disappeared and only the one peak with RT = 2.1 min remained. The HPLC result also indicated that the rear shoulder was that of the intermediate. The intermediate was not considered to be luminescent since during photolysis the decrease in emission intensity with time of a dilute solution of the mother complex followed a first-order rate law. This is in line with the fact that neither the pyridine complex nor the 3-methylpyridine complex is luminescent.

The slow rate of disappearance of the intermediate in CH_3CN solution allowed us to measure the ^1H NMR of the intermediate. Figure 2 shows the 400-MHz ^1H NMR spectra of a CD_3CN solution containing the complex, measured at 10 °C (a) before irradiation, (b) immediately after irradiation, and (c) after an additional 5 min at 60 °C by using tetramethylammonium hexafluorophosphate (3.00 ppm) as a reference. In spectrum a there is a single CH_3 signal (2.40 ppm) of dmbpy in the complex of C_2 symmetry. In spectrum b the intensity of the signal of the mother complex decreased and two new CH_3 signals with equal intensities at 0.96 and 1.54 ppm appeared, consistent with the C_1 symmetry of the intermediate. Large upfield shifts of the signals of dmbpy in the intermediate as compared to that of the mother complex must be brought about by the twist of the two pyridine moieties of dmbpy at a right angle to each other by a rupture of a Ru–N bond: a current loop calculation[8] predicted that a CH_3 group on a pyridine ring will receive a much larger ring-current effect from the other pyridine ring of dmbpy by the twist. The methyl group on the pyridine ring with the Ru–N bond ruptured would receive larger ring-current upfield shift than the methyl group on the other pyridine moiety coordinated to the Ru center: a molecular model suggested that the former was closer to a neighboring coordinated bpy ligand and thus it would show larger ring-current upfield shift.[8] In spectrum c two CH_3 signals at 0.96 and 1.54 ppm disappeared with an increase in the intensity of the CH_3 signal at 2.40 ppm, indicating that the intermediate went back to the original complex.

In the aromatic region of the ^1H NMR spectrum several weak signals attributable to the intermediate were observed. Three of them at a field lower than 9 ppm (9.05, 9.32, 9.48) were assigned to be 6- and 6′-H on dmbpy and 6-H on a bpy in the intermediate. This indicated that the ring-current upfield shift decreased dramatically by rupture of a Ru–py bond of dmbpy and thus by a removal of a pyridine ring of dmbpy from 6-H on an adjacent bpy and consequently by a removal of 6- and 6′-H on dmbpy from

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[7] The visible absorption maxima (λ_{max}) are as follows: $[Ru(bpy)_2(OH_2)_2]^{2+}$, 480 nm; $[Ru(bpy)_2(OH_2)(CH_3CN)]^{2+}$, 451 nm; $[Ru(bpy)_2(CH_3CN)_2]^{2+}$, 424 nm; $[Ru(bpy)_2(dmbpy)]^{2+}$, 452 nm; $[Ru(bpy)_2(pyridine)(OH_2)]^{2+}$, 470 nm.

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adjacent bipyridine ligands in the intermediate. This observation provided strong evidence that dmbpy is coordinated to Ru in a monodentate manner. No indication of free dmbpy was observed in the NMR spectrum after a single photoflash (see Figure 2), but by several flashes free dmbpy dissociated from the mother complex was observed with a ^{1}H NMR CH_3 signal at 2.04 ppm.

All the results hitherto described demonstrate that an intermediate with a monodentate dmbpy was formed by photoirradiation of $[Ru(bpy)_2(dmbpy)]^{2+}$.

Studies are in progress for the thermal and photosubstitution reactivities of the intermediate and for collection of ^{1}H NMR spectra of aqueous as well as organic solutions for disclosing its structure.

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