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A Long-Lived Intermediate with a Unidentate Dmbpy Ligand in the Photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$ (dmbpy=3,3'-dimethyl-2,2'-bipyridine)[1)]

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Photoirradiation of a solution of $[Ru(bpy)_2(dmbpy)]^{2+}$ for a short moment produced an intermediate with a unidentate dmbpy ligand having a long half-life of 0.2-10 min in neutral to 1 mol dm^{-3} acid solutions at 25 °C.

In thermal- or photo-ligand substitution of a tris(bidentate)metal chelate, an intermediate with a half-bound bidentate ligand is usually postulated in the reaction mechanism for the understanding of its kinetic behavior.[2,3)] However it is quite difficult to obtain direct evidence for such an intermediate. Thus, in systems with 1,2-diimine or polypyridine ligand, very few cases have been reported for an intermediate[4,5)] or species[6)] with a half-bound bidentate ligand with indirect or less reliable evidence. In this letter we report on a novel example of a long-lived intermediate with a unidentate polypyridine ligand.

Preparation of $[Ru(bpy)_2(dmbpy)]Br_2$ was reported previously.[7)] Photoreaction was performed in CF_3SO_3H and in HCl solutions containing $2.5X10^{-5}$ M metal complex. A 2.5 ml solution in a 1 cm square quartz cell was purged by Ar gas for 30 min and then the solution, under stirring, was photoirradiated for a short moment with a light at 436 nm of an intensity of $7X10^{-5}$ einstein l^{-1} s^{-1}. Right after the photoirradiation the absorption spectrum, or the absorbance at 450 nm, of the solution was measured repeatedly with proper time intervals.

Photoirradiation of a solution of $[Ru(bpy)_2(dmbpy)]^{2+}$ for a short moment (10-30 s) caused an instantaneous decrease in absorbance at 400-460 nm. Leaving the solution in the dark, the absorbance recovered gradually with time to a final value slightly smaller than the original absorbance. In Fig. 1 is shown the change in absorption spectrum of a 0.5 M CF_3SO_3H solution containing the metal complex when it was repeatedly photoirradiated for 0.5, 1, 2, and 5 min. After each photoirradiation the absorption spectrum of the solution was measured repeatedly for 10 min, during which the spectrum once decreased its intensity by photoirradiation recovered partly. In the figure the top curve at 400-460 nm is an original spectrum of the complex, a group of spectra next to the original one are those obtained after 0.5 min of photoirradiation, where the bottom is a spectrum right after the photoirradiation, the top is that of a recovered 10 min after the irradiation, and the next group of spectra are those after 1 min of photoirradiation, etc. Absorption spectrum obtained after 5 min of photoirradiation (the spectrum at extreme right in Fig. 1) showed that the final product was $[Ru(bpy)_2(OH_2)_2]^{2+}$. Since initial change in absorption spectrum right after the photoirradiation was different from that expected from the final product, the change in the absorption spectrum must be brought about by the formation of a transient species.

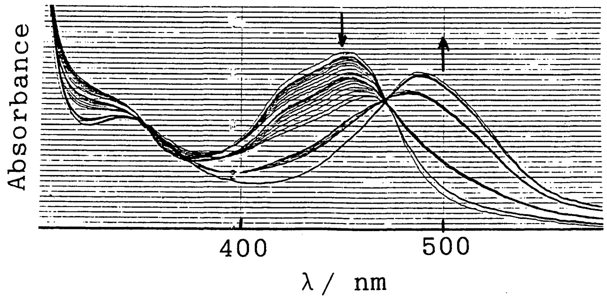

Fig. 1. Change in absorption spectrum by repeated photoirradiation in 0.5 M CF_3SO_3H solution

Figure 2 shows an example of the changes in absorbance at 450 nm with time in the dark of a 0.5 M CF_3SO_3H solution containing the complex after repeated photoirradiation (30") at 25 °C. Recovery of the absorbance with time shown in the figure followed the first order rate law: a linear plot of a logalithm of an absorbance at time t (A_t) minus an absorbance at infinite time (A_∞), $\log(A_t - A_\infty)$, vs. time was shown in the insert of the figure. The first-order rate constants obtained at any stage of the reaction were nearly constant as listed in Table 1, indicating that the reaction was solely related to a start-

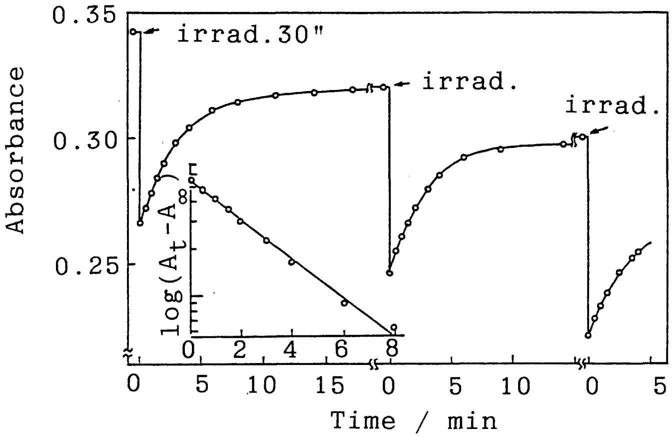

Fig. 2. The decrease in absorbance at 450 nm by photoirradiation and the subsequent recovery in the dark (Insert: First-order plot of the recovery process)

ing material and that the rate constant did not depend on the initial concentration of the complex. It did not change in the presence of free bpy ligand ($4X10^{-4}$ M)(see Table 1), suggesting that the reaction was an intramolecular process and not the recombination of a free bpy or a dmbpy ligand once dissociated completely from the complex.

The rate constant of the dark reaction decreased remarkably with the increase in acid concentration of the solution as shown in Fig. 3. The acid dependence was readily rationalized if photoirradiation induced the formation of an intermediate with a unidentate dmbpy ligand as shown in Fig. 4. Protonation to a free nitrogen atom of the unidentate dmbpy prevents from the chelate ring closing (k_{-1} path) to go back to the orignal tris-type complex again. The recovery of an absorbance in the dark right after photoirradiation corresponded to the chelate ring closing process. Thus based on the mechanism shown in Fig. 4 the observed rate constant of the recovery process in acid solution was expressed as:

$$k^{obs} = \frac{k_{-1}k_{-2} + k'_{-1}k_2[H^+]}{k_{-1} + k_2[H^+]} \qquad (1)$$

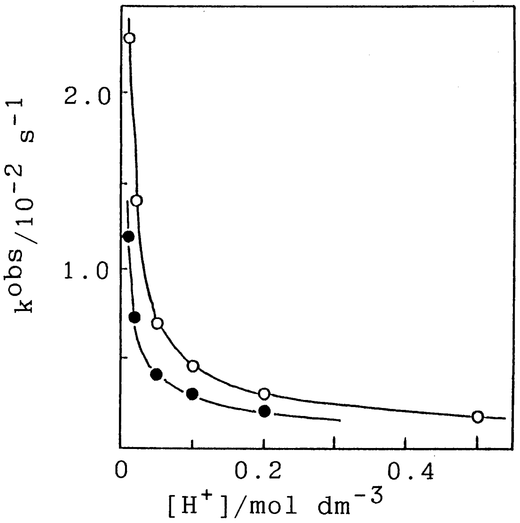

Fig. 3. Acid dependence of the rate constants of the recovery process in HCl (●) and CF_3SO_3H (○) solutions at 25 °C (I=1.0 M, NaX)

Table 1. Net decrease in absorbance by repeated photoirradiation and the rate constants of the absorbance recovery process in 0.5 M CF_3SO_3H solution(I=1.0M) at 30 °C

$\Delta t_{irrad.}$	Abs.(450 nm)	$k/10^{-3}$ s^{-1}
0	0.367	--
30"	0.342	--
30"	0.320	4.83 ± 0.14
30"	0.300	4.85 ± 0.15
1'	0.267	4.87 ± 0.15
1'	0.240	5.09 ± 0.15
2'	0.205	4.87 ± 0.15
In the presence of $4X10^{-4}$ M bpy		
0	0.376	--
30"	0.350	4.58 ± 0.23
30"	0.325	4.98 ± 0.15

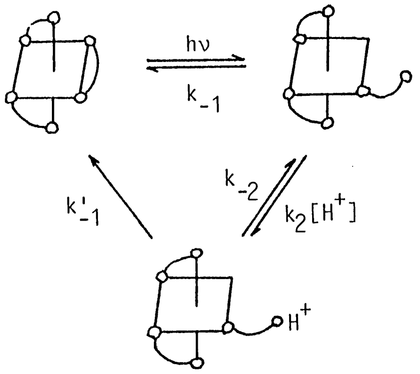

Fig. 4. The reaction scheme for the recovery process in acid media

Analysis of the data in Fig. 3 by Eq. 1 gave the values of $k_{-1}=(6.0 \pm 0.7)\mathrm{X}10^{-2}$ s^{-1}, $k_{-1}'=(0.12 \pm 0.02)\mathrm{X}10^{-2}$ s^{-1} and $k_{-2}/k_2=(5.9 \pm 0.7)\mathrm{X}10^{-3}$ mol dm^{-3} in CF_3SO_3H solution and $k_{-1}=(2.75 \pm 0.14)\mathrm{X}10^{-2}$ s^{-1}, $k_{-1}'=(0.12 \pm 0.02)\mathrm{X}10^{-3}$ s^{-1}, $k_{-2}/k_2=(6.5 \pm 0.3)\mathrm{X}10^{-3}$ mol dm^{-3} in HCl solution. The solid curves in the figure are those calculated based on the Eq. 1 and the parameter values. The difference in the value of k_{-1} between in solution of CF_3SO_3H and in solution of HCl suggests that a water molecule or a chloride ion occupied the sixth coordination site which had been possessed by the free nitrogen atom of the unidentate dmbpy ligand. Similarity in the value of k_{-2}/k_2 between the two kinds of acid solutions is natural since the value is related to the basicity of the unidentate dmbpy ligand.

A phenomenon similar to that shown in Figs. 1 and 2 was also observed for $[Ru(bpy)(dmbpy)_2]^{2+}$ and $[Ru(dmbpy)_3]^{2+}$ complexes. Since the dmbpy ligand coordinates to Ru(II) with its two pyridine moieties twisted to each other because of the steric repulsion between 3 and 3' methyl groups the Ru-N (dmbpy) bond must be weak in the complexes. The weak bond lead to a photochemical formation of the unidentate intermediate with a larger quantum yield (0.01-0.03) than that of $[Ru(bpy)_3]^{2+}$.8) Having an inert nature of Ru(II) ion the unidentate intermediate had a novel long lifetime (0.2-10 min) as a reaction intermediate with a half-bound bidentate ligand.

References

1) Presented at the International Symposium on Photochemistry and Photophysics of Coordination Compounds, Fribourg, Switzerland, July, 1991.
2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York (1967).
3) B. Durham, J. L. Casper, J. K. Nagel, and T. J. Meyer, J. Am. Chem. Soc., 104, 4803 (1982).
4) B. Durham, J. L. Walsh, C. L. Carter, and T. J. Meyer, Inorg. Chem., 19, 860 (1980).
5) J. Lilie, W. L. Walty, S. H. Lee, and L. L. Gregor, Inorg. Chem., 25, 4487 (1986).
6) R. J. Watts, J. S. Harrington, and J. Van Houten, J. Am. Chem. Soc., 99, 2179 (1977).
7) K. Nakamaru, Bull. Chem. Soc. Jpn., 55, 2697 (1982).
8) S. Tachiyashiki and K. Mizumachi, Chem. Lett., 1989, 1153.

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