Ru(6,6′-Diamino-2,2′-bipyridine)$_3^{2+}$: Effect of Interligand Steric Strain on the Spectroscopic, Photochemical, and Electrochemical Properties of the Complexes

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Spectroscopic, photocehmical, and electrochemical properties of a series of the Ru(II) complexes **1**—**4**, Ru(dabp)$_{3-n}$(bpy)$_n$(BF$_4$)$_2$ (n=0, 1, 2, and 3, respectively, dabp=6,6′-diamino-2,2′-bipyridine, and bpy=2,2′-bipyridine) having different degree of interligand steric strain caused by amino substituents of dabp were studied. Their metal-to-ligand charge transfer bands and oxidation–reduction potentials of a Ru(II)/Ru(III) couple were not so much different from each other. Though the complex **3** showed weak emission at around 630 nm (ϕ=6×10^{-4}), no emission of light was observed for the complexes **1** and **2**. These properties and photoanation of the complexes **1** and **3** were discussed in terms of the steric and electronic effects of the amino substituents.

Though photophysical, photochemical, and electrochemical properties of tris(2,2′-bipyridine)ruthenium(II), [Ru(bpy)$_3$]$^{2+}$, have been studied intensely, effect of intraligand[1,2] and interligand[3-6] steric strain within the complex on these properties are not well understood. Photoanation of the complex is the critical deteriorating process of the complex as a photocatalyst, and steric strain within the complex might play important role in this process.

In a preceding paper,[6] we have described the syntheses of a series of mixed-ligand complexes **1**, **2**, **3**, and **4** of 2,2′-bipyridine(bpy) and 6,6′-diamino-2,2′-bipyridine(dabp), [Ru(dabp)$_{3-n}$(bpy)$_n$](BF$_4$)$_2$ where n=0, 1, 2, and 3, respectively, having a different degree of interligand steric strain caused by the 6,6′-diamino substituents of dabp, and their structures have been elucidated by X-ray crystallography and NMR spectrometry.

Since electronic effect of the amino substituent on the bipyridine moiety of dabp has already been studied,[7,8] the complexes having different degree of interligand steric strain offer excellent probe to study systematically the effect of steric strain on the spectroscopic, electrochemical, and photochemical properties of the Ru(II) complex. We report here the properties of these complexes, and discuss the steric effect of the 6- and 6′-amino substituents on the properties of the complexes.

Experimental

Syntheses and structures of the complexes were described in the preceding paper.[6] Other chemicals were obtained commercially and some of them were purified according to the routine procedures. Ethanol used for photoanation experiments was distilled over KOH under nitrogen atmosphere, and was stored in the dark under nitrogen atmosphere.

Measurement. Sample solutions were deaerated by three times of freeze-thaw cycles, and their absorption spectra were recorded on a JASCO UVIDEC-505 or Ubest-50 spectrophotometer at 293 K, and their emission spectra on a Hitachi 850 or JASCO FP-770 spectrometer with a built-in spectral correction unit at 293 K. Emission quantum yields of the complexes were determined by using fluorescein as a standard.

Cyclic voltammetry was carried out in a 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate (TBAF)/acetonitrile solution at ambient temperature by using a Nikko NPGSFZ-2501-A potentiogalvanostat with a built-in function generator (sweep rate 0.05—0.2 V s^{-1}). Two types of cells were used for measurements. One was an airtight cell having platinum wires as working and auxiliary electrodes and a silver wire as a reference electrode, and sample solutions were deaerated by three times of freeze-thaw cycles before measurement. Observed potentials were reported in V vs. SCE after calibration with that of ferrocene. The other type of cell was equipped with glassy carbon and a platinum wire as working and auxiliary electrodes, respectively, and potentials were referenced to SCE through liquid junction. Sample solutions were kept under nitrogen atmosphere. Practically no difference was observed for the oxidation–reduction potentials obtained by using different cells.

ESR spectra were recorded on a JEOL JES-FE3X operated at X band.

Photoanation. Photoreactions of the complexes **1** and **3** in water or ethanol were carried out both under aerobic and anaerobic conditions by irradiation of a monochromated light in a JASCO CRM-FA spectroirradiator (slit width 10 mm) with a 2-kW Xenon lamp at 293 K. For this experiment, freshly distilled ethanol was used. Irradiated photon numbers were calibrated by a chemical actinometer using freshly prepared $K_3Fe(C_2O_4)_3 \cdot H_2O$ from $K_2C_2O_4$ H_2O and $FeCl_3$ according to the standard procedure.[9] Amounts of dabp liberated from the complex during the reaction were determined by measuring the emission intensity of the solution at 405 nm (λ_{ex}=340 nm), which is presumably due to the free dabp in the solution.

To isolate the reaction product, 50 mg of the complex **1** in 3 ml of ethanol was irradiated by a light of 466 nm for 24 h at 293 K under aerobic atmosphere. Analysis by thin-layer chromatography confirmed the presence of dabp in the irradiated solution. Solvent was then removed in vacuo, and a recovered residue was washed with aqueous HCl in order to remove dabp, recrystallized from water to give 35 mg of Ru(dabp)$_2$Cl$_3$·H$_2$O (complex **5**); yield 90%. Found: C, 40.2; H, 4.0; N, 19.1%. Calcd for $RuC_{20}H_{20}N_4Cl_3 \cdot H_2O$: C, 40.2, H, 3.7; N, 18.8%.

Table 1. Spectroscopic Properties of Ruthenium(II) Complexes in Ethanol–Methanol (4:1, v/v) at 293 K

Complex	Absorption/nm λ_{max} ($\varepsilon \times 10^{-4}$)	Emission/nm λ_{max} (ϕ)
Complex **1**	ca. 450 (0.63)	Not observed
Complex **2**	454 (0.89)	Not observed
Complex **3**	457 (1.04)	630 (6×10^{-4})
Complex **4**	448 (1.43)	611 (9×10^{-2})
$Ru(4,4'\text{-dabp})_3^{2+}$	504 (1.05)[a]	705 (4×10^{-3})[a]
$Ru(dmbp)_3^{2+}$	446 (0.74)[b]	589, 636, 701 (1.8×10^{-2})[b,c]
$Ru(4,4'\text{-dmbp})_3^{2+}$	455 (1.70)[a]	640 (8.6×10^{-2})[a]

a) Ref. 10. b) Ref. 4. c) 77 K in ethanol–methanol (4:1, v/v).

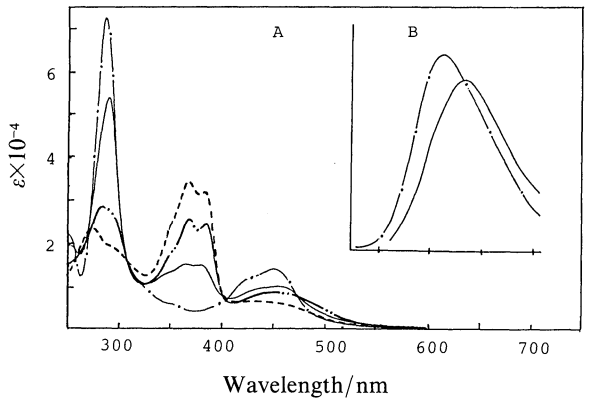

Fig. 1. Electronic Spectra of the Complexes **1**—**4** in Ethanol–Methanol (4:1 v/v) at 293 K. A: Absorption spectra of **1** (----), **2** (—··—), **3** (——), and **4** (—·—), and B: Emission spectra of **3** (——, ×150) and **4** (—·—).

Table 2. Oxidation-Reduction Potentials of Ruthenium(II) Complexes of Bipyridine Derivatives in Acetonitrile in the Presence of 0.1 mol dm^{-3} TBAF

Complex	$E_{1/2}$/V vs. SCE	ΔE/V[a]
Complex **1**	1.08	0.08
Complex **2**	1.09	0.06
Complex **3**	1.09	0.07
Complex **4**	1.29 (1.28[b])	0.06
Complex **5**	0.14	0.07
Complex **6**	0.35 (0.31[c])	0.07

a) Difference between oxidation and reduction wave maxima, sweep rate 0.1 V s^{-1}. b) Ref. 11. c) Ref. 12.

Results

Electronic Spectra and Oxidation-Reduction Potentials of the Complexes. Figure 1 shows absorption and emission spectra of the complexes **1**—**4** in ethanol–methanol (4:1 v/v). The complexes showed metal-to-ligand charge transfer (MLCT) band at around 450 nm in addition to ligand centered absorption bands at around 290 nm and/or 380 nm presumably due to π–π^* transitions of bpy and dabp, respectively.[7] The MLCT bands of these complexes are listed in Table 1 together with those of tris(6,6′-dimethyl-2,2′-bipyridine (dmbp)), tris(4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbp)), and tris(4,4′-diamino-2,2′-bipyridine (4,4′-dabp)) complexes of Ru(II) in order to facilitate the comparison.[4,10] Absorption spectra of the complexes **1** and **3** in dimethyl sulfoxide (dmso), acetonitrile, water, and 1 mol dm^{-3} aqueous HCl solution were practically identical to those in ethanol–methanol (4:1 v/v). As the pK_a of the amino group of free dabp is 2.2,[7] the amino groups of the coordinated dabp in these complexes were not protonated under these conditions.

Excitation of the MLCT band (λ_{ex}=436 nm) of the complex **3** in ethanol–methanol (4:1 v/v) showed weak emission at 630 nm (Fig. 1). Emission quantum yield of the complex **3** (λ_{ex}=436 nm) was 6×10^{-4}, which was two orders of magnitude smaller than that of the complex **4** (9×10^{-2}, reported value[10] 8.9×10^{-2}). While, the complexes **1** and **2** showed no light emission by excitation of any of their absorption band. In the case of the complex **1**, no emission was observed even at 77 K in a rigid glass state.

Cyclic voltammograms of the complexes **1**—**4** in acetonitrile in the presence of 0.1 mol dm^{-3} TBAF showed electrochemically-reversible or quasi-reversible oxidation–reduction peaks at around 1 V vs. SCE, which were ascribed to a redox couple of Ru(II)/Ru(III). The redox potentials ($E_{1/2}$) were determined as an average of the oxidation and reduction peak potentials (vs. SCE), and are listed in Table 2.

Photoanation of the Complexes 1 and 3. It was pointed out in the preceding paper that the complex **1** is photosensitive.[6] In order to clarify the role of the interligand steric strain on the photoanation of the complexes, we studied the photochemical behaviors of the complex **1** having highest steric strain and the complex **3** having relatively low steric strain.

The complex **1** in water or freshly distilled ethanol (1.5×10^{-5} mol dm^{-3}) after degassed by three times of freeze-thaw cycles was subjected to photoirradiation at 293 K. Though no spectral change was observed in the dark, irradiation of the monochromated light at 466 nm caused a change in the absorption spectrum of the solution (Fig. 2A). This spectral change completed after appropriate time of irradiation under anaerobic

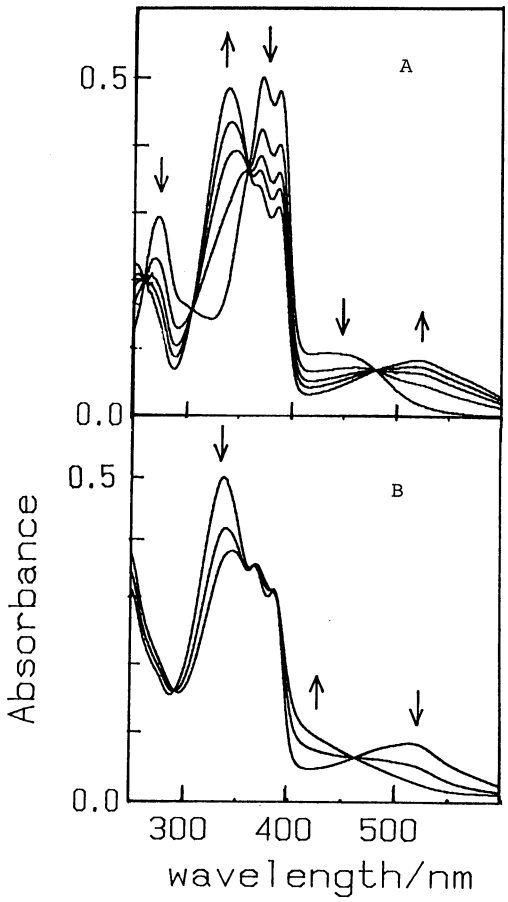

Fig. 2. Spectral Change of the Complex **1** (1.5×10^{-5} mol dm^{-3}) in Ethanol at 293 K. A: First stage of the spectral change upon irradiation (466 nm) under anaerobic conditions (0, 1, 2, 3, and 9 min of irradiation); and B: Second stage after aeration in the dark (0, 1, and 13 h after aeration).

conditions, and isosbestic points were observed throughout the spectral change. Irradiation in freshly-distilled ethanol and in water caused essentially the same spectral change, though the spectral change was much faster in ethanol. The irradiated solution showed a strong emission at 405 nm (λ_{ex}=340 nm) though no emission was observed before irradiation, and longer irradiation time resulted in a higher emission intensities. As the emission and excitation spectra of the irradiated solution were identical to those of dabp,[13] this light emission was concluded to be due to the dabp liberated from the complex **1** upon photoirradiation. The amounts of dabp liberated from the complex after completion of the spectral chenge comprised 91 mol% of the initial complex **1** in water and 87 mol% in ethanol.

The irradiated solution was then aerated and kept at room temperature. A slow spectral change took place, and different isosbestic points were observed during the second stage of the spectral change (Fig. 2B). The final spectrum after completion of the second spectral change was identical to that of a sample solution irradiated under

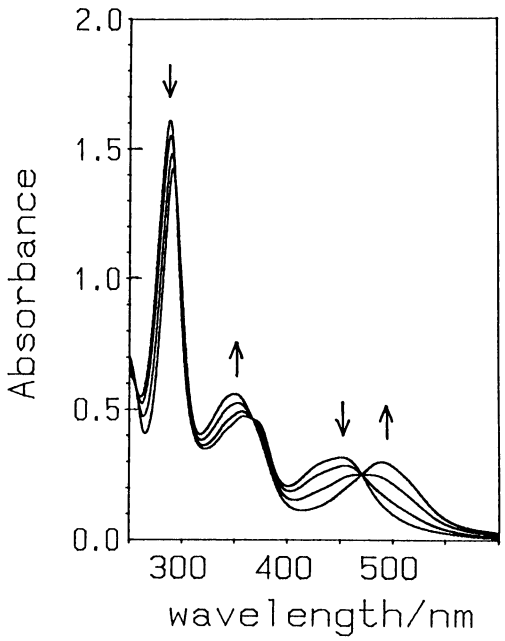

Fig. 3. Spectral Change of the Aqueous Complex **3** Solution (1.5×10^{-5} mol dm^{-3}) upon Irradiation (466 nm) at 293 K under Anaerobic Conditions (0, 1, 3.5, and 12 h).

aerobic atmosphere. A complex $Ru(dabp)_2Cl_3\cdot H_2O$ (complex **5**) was recovered from the irradiated ethanolic solution of the complex **1** under aerobic atmosphere (yield 90%). Formation of the Ru(III) species in the aerated solution was further supported by the presence of a ESR active species in the solution at 77 K,[14] which was not observed before aeration. Liberation of dabp from the complex was also confirmed by thin-layer chromatographic analysis of the irradiated solution. Therefore, these results indicated that irradiation to the complex **1** in water and ethanol caused liberation of one of its ligand, dabp, to give the bis(dabp)Ru(II) species, which was then oxidized by atmospheric oxygen in the dark to yield the bis(dabp)Ru(III) species. Quantum efficiency for the liberation of dabp was found to be 1×10^{-3} in water and 1×10^{-2} in ethanol.

Irradiation of the light at 386 nm gave essentially the same results, showing that photoanation of the complex also occurs by excitation of the π–π^* transition of dabp.

The mixed-ligand complex **3** having lower steric strain underwent similar spectral change upon irradiation of the light at 466 nm in water under anaerobic conditions (Fig. 3). Aeration of the irradiated solution after completion of the spectral change did not cause any further change. Irradiation under aerobic conditions was little different from that under anaerobic conditions. Final spectrum after completion of the spectral change was almost identical to that of *cis*-$Ru(bpy)_2Cl_2\cdot 2H_2O$ (complex **6**), and amounts of dabp liberated after completion of the spectral change comprised 89 mol% of the initial complex **3**. Therefore, the photoirradiation

caused liberation of the dabp molecule from the mixed-ligand complex **3**, and quantum efficiency for this process was found to be 5×10^{-4}. Irradiation of the light at 364 or 286 nm gave essentially the same results.

Discussion

Spectroscopic Properties and Oxidation-Reduction Potentials of the Complexes 1—4. Though relatively few pK_a values are available for disubstituted bipyridines, the basicities of the coordinating ring nitrogens of the 6,6′-disubstituted bipyridines are not so different from those of the corresponding 4,4′-disubstituted bipyridines.[15] However, Ru(II) complexes of the 6,6′-disubstituted bipyridine suffer severe interligand steric strain. X-Ray crystallographic study revealed that the complex **1** have slightly longer Ru–N(pyridine) bond, and the two pyridine rings of dabp molecules are not in a same plane but are slightly twisted in order to relieve interligand steric crowding between 6(6′)-amino substituent and adjacent pyridine ring of dabp.[6] Similar twisted structure of the dabp in the complexes **1**—**3** in solution is evidenced by ^{1}H NMR spectroscopy.[6]

Cook et al.[10,11,18,19] conducted intensive studies as to the Ru(II) complexes of wide variety of 4-, 4,4′-, and 5,5′-substituted bipyridines, and they showed that $E_{1/2}$ values of the complexes were correlated inversely with the Hammett σ of substituent groups or pK_a values of the ring nitrogens.[11] Based on the assumption that the substituent effect was limited only to the electronic effect, $E_{1/2}$ of the complex **1** can be estimated to be 0.8—0.9 V from the pK_a value of dabp. However, observed $E_{1/2}$ of the complex **1** is higher than the estimated value (Table 2), and is little different from that of the complexes **2**, **3**, or Ru(II)(4,4′-dmbp)$_3^{2+}$ (1.09 V[11] or 1.11 V[20] vs. SCE). Redox potential of a Ru(II)/Ru(III) couple is an indication of the t_{2g} level of the complex.[21] Since the complex **1** has slightly longer Ru–N(pyridine) bond, higher $E_{1/2}$ observed for the complex **1** is attributed to the weaker ligand field due to the interligand steric strain. This conclusion is further supported by the fact that the bis-dabp complex **5** suffering much less interligand strain than the tris-dabp complex **1** has lower redox potential compared to the corresponding bis-bpy complex **6** (Table 2). Thus, electronic effect of amino substituents at 6 and 6′ positions on the complex **1** is off-set in part by the steric hindrance of the amino groups.

The complexes **1**—**4** in ethanol–methanol (4 : 1, v/v) solutions showed the MLCT band at around 450 nm in addition to the ligand-centered absorption bands due to the dabp and/or bpy molecules. As the MLCT bands of 6,6′-disubstituted bipyridine complexes are smaller than those of the corresponding 4,4′-disubstituted bipyridine complexes (Table 1), decrease of the MLCT band as a number of dabp increased from the complex **4** to **1** must be due in part to the increased steric strain within the complex.

Introduction of amino group(s) at 4- and 4,4′-positions induced red shift to the MLCT absorption and the emission bands.[10] However, absorption maxima of the MLCT band of the complexes **1**—**3** are not so much different from those of the complex **4**, and are considerably shorter than that of Ru(4,4′-dabp)$_3^{2+}$.

The complex **4** showed the characteristic luminescence at around 611 nm ($\phi=9\times10^{-2}$) from its ^{3}MLCT levels. However, only the complex **3** showed very weak emission at around 630 nm ($\phi=6\times10^{-4}$) among the complexes containing dabp as a ligand, and the complex **1** did not show any light emission even at 77 K in ethanol–methanol rigid glass. Instead, the complex **1** underwent photo-induced elimination of the ligand. It is worth to note that Ru(4,4′-dabp)$_3^{2+}$ is reported to show emission at 705 nm. These spectroscopic properties of the complexes can also be explained by smaller d–d splitting caused by interligand steric strain which lowers the excited d–d level. Since the luminescent states of the tris(bpy)Ru(II) complexes are the ^{3}MLCT levels, presence of the lower-lying excited d–d level may quench efficiently the luminescence from ^{3}MLCT levels. Similar results were observed for the complexes having intraligand steric strain.[2]

Photoanation of the Complexes 1 and 3. The complex **1** having highest steric strain did not show emission but easily underwent photo-elimination of one of the dabp molecules in water and ethanol. Quantum efficiency of this process is much higher than those of the complexes **3** and **4** (reported value[22] in water at 343 K by irradiation at 436 nm, $<10^{-5}$). The liberated dabp comprised approximately 90% of the initial complex, which did not participate in any reactions such as electron-transfer reaction of tertialy amine reported by Lee et al.[23]

The resultant Ru(dabp)$_2^{2+}$ was easily oxidized by atmospheric oxygen to give Ru(dabp)$_2^{3+}$ species, though Ru(bpy)$_2^{2+}$ was not susceptible to the oxidation by atmospheric oxygen. Since elimination of one of the dabp molecules from the complex **1** reduces the interligand steric strain, this can easily be understood from the low reduction potential of the complex **5** due to the electronic effect of the amino groups. The results demonstrated again that the electronic effects of the amino groups in the complex **1** was offset in certain extent by steric strain within the complex, though stronger basicity of the ring nitrogens of dabp might contribute to the relatively high yield of the complex **1**.[6] The electronic effect of amino groups could be observed only when the steric strain was relieved by elimination of one of the dabp molecules.

In summary, spectroscopic, electrochemical, and photochemical properties of a series of the ruthenium(II) complexes **1**—**4**, Ru(dabp)$_{3-n}$(bpy)$_n$(BF$_4$)$_2$ (n=0, 1, 2, and 3, respectively) having different degree of interligand steric strain were studied, and their properties were discussed in terms of the weaker ligand field due to the

interligand strain.

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