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Tris(6,6′-diamino-2,2′-bipyridine)ruthenium(II): Effect of High Interligand Steric Strain on the Structure

Koji Araki,* Masahiro Fuse, Noriyuki Kishii, Shinsaku Shiraishi,*
Teruyuki Kodama,† and Yasuzo Uchida†
Institute of Industrial Science, The University of Tokyo, 7-22-1,
Roppongi, Minato-ku, Tokyo 106
†Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113

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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, dabp=6,6′-diamino-2,2′-bipyridine, and bpy=2,2′-bipyridine), having a different degree of interligand steric strain were synthesized, and the effect of the interligand steric strain caused by the amino substituents on their structures was examined. A crystallographic study showed that the two pyridine rings of dabp in the complex **1** were in a slightly twisted configuration in order to relieve the interligand strain. Similar twisted configurations were suggested for the bipyridine moieties of dabp and bpy in the complexes **1**—**3** in dimethyl sulfoxide solution.

A family of 2,2′-bipyridine (bpy) and its derivatives holds a considerable importance in coordination chemistry because of their ability to form a stable tris-complex with variety of transition metals. Among them, photochemical and electrochemical properties of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, have been the subject of a large number of studies because of its potential use as a photocatalyst,[1] and various substituents have been introduced to the bipyridine moiety in order to "tune" the photochemical and/or electrochemical properties of the complexes.[2—4] Though many interpretations have been made as to the electronic effect of the substituents, surprisingly little has been known as to the steric effect of the substituents. Steric strain within the complex must play an important role in photoanation of the complex and should be understood more precisely, since the photoanation is the critical deterioration process of its photocatalytic activity. Nakamaru reported the effect of an intramolecular (intraligand) steric strain of bpy caused by 3,3′-dimethyl substituents on the photochemical properties of the complex.[5] To our knowledge, however, only one report appeared so far as to the complexes having high interligand steric strains. Difficulty in synthesizing these complexes may be the major reason to limit the study. Fabian et al.[6] reported synthesis and some properties of $[Ru(dmbp)_3]^{2+}$ (dmbp=6,6′-dimethyl-2,2′-bipyridine) having high interligand strain, but no detailed discussion was provided as to the structure of the complexes. Here, we developed the way to synthesize a series of mixed-ligand complexes of bpy and 6,6′-diamino-2,2′-bipyridine (dabp), $[Ru(dabp)_{3-n}(bpy)_n]^{2+}$ (n=0—3), having a different degree of interligand steric strain caused by the 6,6′-amino substituents of dabp, and examined the effect of the 6,6′-diamino substituents on the structure of the Ru(II) complex both in crystalline state and in solution.

Results and Discussion

Syntheses of the Complexes. Though dabp forms only 1:1 complexes with most of the first-row transition metal cations due to the steric hindrance of the 6,6′-amino substituents,[7] dabp (pK_a=6.7) has higher basicity and is more stronger chelating agent than bpy (pK_a=4.5),[8] offering an interesting probe to study the electronic and steric effects of substituents on the properties of the Ru(II) complex.

Several attempts to obtain $[Ru(dabp)_3]^{2+}$ directly from $RuCl_3$ and dabp according to the usual procedures were unsuccessful,[5,9,10] though $[Ru(bpy)_3](BF_4)_2$ (**4**) was obtained in a 85% yield by the same procedure. However, the preparative procedure of Evance et al.,[11] in which intervention of $[Ru(dmso)_4]Cl_2$ (dmso=dimethyl sulfoxide), **5**, was incorporated, yielded a satisfactory result. Reaction of **5** with dabp gave $[Ru(dabp)_3]Cl_2\cdot 2H_2O$ (vide elemental analysis) in a 78% yield, which was converted quantitatively to $[Ru(dabp)_3](BF_4)_2$ (**1**) by subsequent anion exchange with $NaBF_4$. The complex **1** was photosensitive to undergo elimination of one of its ligand, and the complex should be synthesized in the dark. Fabian et al.[6] reported the formation of $[Ru(dmbp)_3]^{2+}$ from $RuCl_3$ and dmbp, but the yield of the complex was as low as 5.5%. Attempts to synthesize $[Ru(dmbp)_3]^{2+}$ from **5** did not improve the yield. Higher coordination ability of dabp might contribute to the high yield of $[Ru(dabp)_3]^{2+}$.

$[Ru(dabp)_2(bpy)](BF_4)_2$ (**2**) was obtained from *cis*-$[Ru(dabp)_2(dmso)_2]Cl_2$ and bpy in a 43% yield after column chromatographic separation using Sephadex LH-20, and $[Ru(dabp)(bpy)_2](BF_4)_2$ (**3**) from *cis*-$[Ru(bpy)_2Cl_2]$ and dabp in a 45% yield after the same procedure. The newly obtained complexes are listed in Table 1.

The Structure of $[Ru(dabp)_3]^{2+}$ in Solid State. Since the 6,6′-diamino groups of dabp are responsible

Table 1. The $[Ru(dabp)_{3-n}(bpy)_n](BF_4)_2$ Complexes (n=0—2)

Compound	Yield/%	Mp/°C[a]	Analysis (Calcd)/%		
			C	H	N
$[Ru(dabp)_3](BF_4)_2$ (**1**)	78	270 (decomp)	43.4 (43.2)	3.6 (3.2)	20.1 (20.2)
$[Ru(dabp)_2(bpy)](BF_4)_2$ (**2**)	43	260 (decomp)	44.9 (44.9)	3.5 (3.5)	17.2 (17.4)
$[Ru(dabp)(bpy)_2](BF_4)_2$ (**3**)	45	270 (decomp)	46.4 (46.6)	3.4 (3.4)	14.5 (14.5)

a) Decomp denotes decomposition of the complex.

Table 2. IR Peaks of the Amino Groups of dabp

Compound	ν_{NH}		δ_{NH}	ν_{CN}
$[Ru(dabp)_3](BF_4)_2$ (**1**)	3468	3372	1628	1291
$[Ru(dabp)_2(bpy)](BF_4)_2$ (**2**)	3464	3380	1626	1291
$[Ru(dabp)(bpy)_2](BF_4)_2$ (**3**)	—[a]	3394	1626	1288
dabp	3400	3312	1632	1280

a) Not clearly observed.

to an interligand strain, we examined the effect of interligand strain on the structure of the amino groups by IR spectrometric method (Table 2). Though the amino groups in the complexes showed slightly different absorption peaks, we could not deduce any conclusive result showing the effect of the steric strain on the structure of the amino groups.

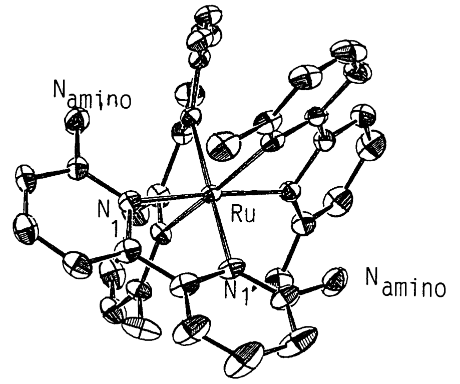

Fig. 1. Crystal structure of $[Ru(dabp)_3]^{2+}$.

A dark red granule of $[Ru(dabp)_3](PF_6)_2$ was obtained from a methanol solution of the purified sample, and was subjected to a X-ray crystallographic analysis. An ORTEP view of the $[Ru(dabp)_3]^{2+}$ is shown in Fig. 1 (R=0.081), and selected bond lengths and angles are listed in Table 3. All the three dabp molecules are serving as a bidentate ligand by coordinating with their ring-nitrogens, and the amino substituents are located close enough to the adjacent pyridine ring of other dabp molecules causing the interligand steric strains. Most characteristic feature of this result is the fact that two pyridine rings of each dabp are not in a same plane but are twisted. The dihedral angles for N1-C2-C2′-N1′ (δ) are 7.3, 14.3, and 17.3 deg for each dabp molecules, which are considerably larger than the reported value of 5.9 deg for $[Ru(bpy)_3]^{2+}$.[12] In addition, the average distance between Ru and ring-nitrogens is 2.131 Å, which is slightly longer than 2.056 Å reported for $[Ru(bpy)_3]^{2+}$.[12] These differences might be due to the interligand steric strain caused by the 6,6′-diamino substituents.

The two pyridine rings of bpy are known to be in *s*-trans configuration in a solution, and, upon complexation with metals, their configuration becomes *s*-cis form in spite of the induction of intramolecular strain due to the steric crowding of 3- and 3′-hydrogen atoms of each pyridine ring. The twisted configuration of the dabp molecules in the complex is thought to relieve this intramolecular (intraligand) steric strain

Table 3. Selected Bond Lengths and Angles of $[Ru(dabp)_3](PF_6)_2$

Bond length/Å					
Ru-N1	2.121	Ru-N2	2.114	Ru-N3	2.132
Ru-N4	2.136	Ru-N5	2.137	Ru-N6	2.143
N1-C11	1.364	N1-C15	1.364	N2-C21	1.386
N2-C25	1.349	C11-C12	1.402	C12-C13	1.386
C13-C14	1.353	C14-C15	1.411	C11-C21	1.464
C21-C22	1.392	C22-C23	1.397	C23-C24	1.364
C24-C25	1.391	N1A-C15	1.376	N2A-C25	1.368
Bond angle/deg					
N1-Ru-N2	77.48	N1-Ru-N3	153.51	N1-Ru-N4	90.08
N1-Ru-N5	105.91	N1-Ru-N6	87.90	N2-Ru-N3	89.43
N2-Ru-N4	79.45	N2-Ru-N5	176.35	N2-Ru-N6	101.79
N3-Ru-N4	77.55	N3-Ru-N5	87.46	N3-Ru-N6	104.76
N4-Ru-N5	101.71	N4-Ru-N6	177.34	N5-Ru-N6	77.19

caused by the 3,3′-hydrogen atoms in addition to the interligand strain caused by the 6,6′-diamino substituents. To understand the contribution of the intraligand steric strain on the twisted form of dabp, we studied the effect of torsional angle of the two pyridine rings on the stability of the dabp molecule.

Table 4. Effect of the Dihedral Angle (N1-C2-C2′-N1′) on the Stability of dabp[a]

Dihedral angle/deg	Potential energy difference/kJ mol^{-1}
0	=0
5	−0.5
10	−1.3
15	−2.6
20	−3.8
30	−5.9
45	−6.3
60	−3.4
90	0.0
120	−8.4
150	−20.5
180	−24.7

a) Total energies were calculated by ab initio method with STO-3G, and the potential energy differences were obtained as the total energy differences i.e., (E_{total} at given dihedral angle)−(E_{total} at 0 deg).

Differences in potential energy from the *s*-cis configuration ($\delta=0$) were calculated by ab initio method with STO-3G basis sets, and are listed in Table 4. Details of the calculation were essentially the same as those reported previously.[8] Though *s*-cis ($\delta=0$ deg) and *s*-trans ($\delta=180$ deg) configurations are electronically most stable, presence of the intramolecular steric strain makes the *s*-cis configuration as least favored one. The result showed that small deviation of the twisted angle from *s*-cis configuration did not improve the stability so much, presumably due to the loss of stabilizing effect of conjugation. Therefore, the twisted configuration of dabp in the complex **1** is most likely to be due to the interligand steric strain.

Structures of the Complexes in DMSO Solution. Structures of the complexes in solution are not necessarily the same as those in crystalline state, especially in the case of the complex like **1** having high interligand steric strain. Therefore, we examined the structures of the complexes **1**—**4** in dmso solution. In ^{1}H and ^{13}C NMR spectra of the complexes in dmso-d_6 at 27 °C, only one set of signals was observed for the pyridine moiety of dabp in the complexes **1** and **3**, and of bpy in the complexes **2** and **4**, showing that the pyridine moieties of these molecules were under the same environment.[13] Therefore, the dapb and bpy molecule(s) in these complexes were confirmed to serve

Table 5. ^{1}H NMR of the [Ru(dabp)$_{3-n}$(bpy)$_n$](BF$_4$)$_2$ in DMSO-d_6 at 27 °C

Compound	Chemical shift from TMS/ppm and Coupling constant/Hz											
	dabp					bpy						
	3,3′	4,4′	5,5′	J_{34}	J_{45}	3,3′	4,4′	5,5′	6,6′	J_{34}	J_{45}	J_{56}
[Ru(dabp)$_3$](BF$_4$)$_2$ (**1**)	7.52	7.62	6.51	7.4	8.2	—	—	—	—	—	—	—
[Ru(dabp)$_2$(bpy)](BF$_4$)$_2$ (**2**)	7.78	7.79	6.75	7.4	8.2	8.45	7.96	7.41	8.29	8.2	7	5.4
	7.67	7.41	6.21									
[Ru(dabp)(bpy)$_2$](BF$_4$)$_2$ (**3**)	7.73	7.61	6.55	7.4	8.2	8.82	8.19	7.61	8.15	8.2	7	6
						8.76	8.07	7.35	7.78			
[Ru(bpy)$_3$](BF$_4$)$_2$ (**4**)	—	—	—	—	—	8.84	8.17	7.52	7.74	7.8	7.4	5.8
dabp[a]	7.45	7.45	6.44	—	7.0	—	—	—	—	—	—	—
	(7.29)	(7.52)	(6.56)	(7.4)	(8.2)							
bpy	—	—	—	—	—	8.42	7.96	7.47	8.71	8.2	6.6	4.5

a) Figures in parentheses were those measured in CDCl$_3$.

Table 6. ^{13}C NMR Spectra of the [Ru(dabp)$_{3-n}$(bpy)$_n$](BF$_4$)$_2$ in DMSO-d_6 at 27 °C[a]

Compound	Chemical shift from TMS/ppm									
	dabp					bpy				
	2,2′	3,3′	4,4′	5,5′	6,6′	2,2′	3,3′	4,4′	5,5′	6,6′
[Ru(dabp)$_3$](BF$_4$)$_2$ (**1**)	160.0	114.2	139.4	112.0	165.8	—	—	—	—	—
[Ru(dabp)$_2$(bpy)](BF$_4$)$_2$ (**2**)	156.3	113.3	137.8	109.9	164.3	157.8	126.6	137.1	122.8	152.0
			138.0	111.2	164.5					
[Ru(dabp)(bpy)$_2$](BF$_4$)$_2$ (**3**)	156.0	113.0	138.2	111.3	163.5	157.1	127.5	137.4	124.3	151.4
						157.4	127.6	137.8	124.5	152.5
[Ru(bpy)$_3$](BF$_4$)$_2$ (**4**)	—	—	—	—	—	158.5	129.0	139.3	125.7	152.6
dabp	155.1	111.6	138.4	108.6	157.9	—	—	—	—	—
bpy	—	—	—	—	—	155.2	124.1	137.2	120.4	149.8

a) Selective decoupling technique was used for the assignment.

as a bidentate ligand. The result also showed that the three dabp molecules of the complex **1** in a solution were under the same environment within NMR time scale, though they have slightly different configurations in each other in crystalline state. While, two sets of signals were observed for the pyridine moieties of bpy and dabp in the complexes **3** and **2**, respectively. As the each pyridine unit of bpy and dabp are not under the same environment in the mixed-ligand complexes **3** and **2**, respectively,[13] the complexes obtained here were not the mixture of **1** and **4** but the mixed-ligand complexes. Thus, the complexes **1**—**4** were confirmed to have the same six-coordinated structure in dmso solution.

The 3- and 3′-protons of bpy in the *s*-cis configuration are known to suffer a strong van der Waals deshielding interaction caused by the steric crowding.[14] Therefore, the chemical shifts of these protons are the good measure of the configuration of bpy and dabp, and the difference in chemical shift of 3(3′)-proton from that of 5(5′)-proton has been used for determining configuration of bipyridine derivatives.[7,15] The doublet signals of the 3,3′-protons of dabp in the complex **3** appeared at lower magnetic field compared with those of dabp in the complex **1**, though the chemical shifts of the 5,5′-protons for both complexes were not so much different from each other. While, the signals of 3,3′-protons of bpy in the complex **2** were observed at higher magnetic field compared with those of bpy in the complex **4**. Therefore, it can be said that increase of the dabp molecules in the complexes decreased the deshielding effects of the 3,3′-protons of bpy and dabp. As the decreased deshielding effects are the indication of the increased torsional angle between two pyridine rings of bpy moieties, increase in the interligand steric strain is suggested to induce the increased torsional angle. The results is in good agreement with that observed for the complex **1** in a crystalline state.

In conclusion, $[\mathrm{Ru(dabp)}_{3-n}(\mathrm{bpy})_n]^{2+}$ (n=0—3) are obtained in moderate to high yields in spite of the presence of sterically hindering substituents at 6,6′-positions. The complex **1** in a crystalline state is found to have slightly longer Ru–N(pyridine) bond lengths, and the two pyridine rings of the dabp molecules are not in a same plane but are twisted. ^{1}H NMR studies indicated the similar twisted configuration of the two pyridine rings of dabp and bpy in these complexes in dmso solutions.

Experimental

Materials and Methods. Dabp was synthesized from 2,6-dibromopyridine according to the reported procedure.[7] $\mathrm{RuCl_3 \cdot }x\mathrm{H_2O}$, bpy, and other chemicals were purchased from Wako Pure Chemical Co., and used as received. Solvents were purified prior to use according to the routine procedures.

^{1}H and ^{13}C NMR spectra of the samples in dmso-d_6 were measured by a JEOL JNM-GX270 spectrometer operated at 270 and 67.8 MHz, respectively. The selective decoupling technique was employed to assign some of the signals. X-Ray diffraction measurement was performed on a Rigaku automated four-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation. Summary of crystal data and collection parameters are listed in Table 7. The crystal structure was solved by the heavy atom method by using the UNICS III program.[16] Atomic parameters and equivalent isotropic temperature factors are listed in Table 8. Ab initio MO calculations were carried out by GAUSSIAN-80H with STO-3G basis sets. Except for the dihedral angle (N1–C2–C2′–N1′), geometric parameters of dabp were the same as those reported previously,[8] and the potential energy differences from *s*-cis configuration were obtained as the differences in the calculated total energies (E_{total} at 0 deg= −1561584.6 kJ mol^{-1}). All calculations were performed on a HITAC M-680H at the Computer Center of the University of Tokyo.

Syntheses of the Complexes. The Complex 1: $[\mathrm{Ru(dmso)_4Cl_2}]$(**5**) was synthesized from $\mathrm{RuCl_3 \cdot xH_2O}$ according to the method of Evans et al. (yield 68%; mp 192—3 °C).[11] An ethanolic solution (30 ml) of **5** (485 mg, 1 mmol) and dabp (577 mg, 3.1 mmol) was heated to reflux for 24 h under nitrogen atmosphere in the dark. After removal of ethanol, the residue was washed with hot benzene in order to remove unreacted dabp, and then was recrystallized from a small amount of water to give $[\mathrm{Ru(dabp)_3}]\mathrm{Cl_2 \cdot 2H_2O}$ as a red granule (yield 78%), mp 280 °C (slowly decompose); Found: C, 47.2; H, 4.3; N, 21.9%. Calcd for $\mathrm{RuC_{30}H_{30}N_{12}Cl_2 \cdot 2H_2O}$: C, 47.0; H, 4.5; N, 21.9%. This was dissolved in water, and

Table 7. Summary of Crystal Data, Intensity Collections, and Structure Refinement Parameters for $[\mathrm{Ru(dabp)_3}](\mathrm{PF_6})_2$[a]

Formula (Formula weight)	$\mathrm{C_{30}H_{30}N_{12}RuP_2F_{12}}$ (949.65)
a, b, c/Å	10.602(2), 18.838(3), 9.696(2)
α, β, χ/deg	109.67(1), 93.67(2), 92.78 (2)
V/Å^{-3}	1814.7
Systematic absence	nothing
Space group	$P\bar{1}$
d_{calcd}/g cm^{-3}	1.739
d_{observed}/g cm^{-3}	1.757(1)
Z	2
F(0,0,0)	724
Crystal size/mm	0.44×0.45×0.34
μ(Mo K_α)/cm^{-1}	6.26
Data collection method	2θ–ω scan
2θ-Scan range	2.5—60.0
Scan rate (θ)/deg min^{-1}	2
Scan range (A+B tanθ)/deg	A=1.1, B=0.45
No. of standard reflection	3(2,0,0; 0,0,2; 0,8,0)
Observed reflection data	10948
Used reflection data	8013
R value/%	8.1
R_{w} value/%	11.1

a) Scattering factors and anomalous scattering factors are based on the literature.[16]

Table 8. Atomic Parameters and Equivalent Isotropic Temperature Factors

Atom	X	Y	Z	B_{eq}[a)]
Ru	0.2371	0.2391	0.2193	2.51
P1	−0.1945	0.0773	0.4931	8.24
P2	−0.2568	0.4603	0.0191	4.32
N1	0.0448	0.2256	0.1341	3.48
N2	0.1387	0.2528	0.4084	3.16
N3	0.4097	0.2767	0.3563	2.95
N4	0.2280	0.3590	0.2995	3.05
N5	0.3467	0.2235	0.0353	3.31
N6	0.2412	0.1187	0.1297	3.72
N1A	0.0726	0.1703	−0.1176	5.60
N2A	0.2846	0.2149	0.5528	5.38
N3A	0.5129	0.1652	0.2829	6.21
N4A	0.0852	0.3738	0.1169	4.52
N5A	0.3818	0.3505	0.0585	5.56
N6A	0.1001	0.0893	0.2829	5.94
C11	−0.0327	0.2586	0.2410	3.80
C12	−0.1605	0.2679	0.2094	5.54
C13	−0.2071	0.2452	0.0630	6.58
C14	−0.1331	0.2110	−0.0452	5.74
C15	−0.0058	0.2011	−0.0084	4.33
C21	0.0208	0.2793	0.3935	3.55
C22	−0.0395	0.3193	0.5164	4.87
C23	0.0184	0.3305	0.6564	5.60
C24	0.1282	0.2975	0.6696	5.33
C25	0.1825	0.2553	0.5438	3.94
C31	0.4080	0.3496	0.4527	3.35
C32	0.5019	0.3830	0.5639	4.55
C33	0.6054	0.3414	0.5771	5.28
C34	0.6089	0.2707	0.4825	4.63
C35	0.5098	0.2380	0.3732	3.92
C41	0.2992	0.3922	0.4294	3.30
C42	0.2762	0.4603	0.5288	4.55
C43	0.1770	0.4997	0.4893	5.18
C44	0.1155	0.4715	0.3537	4.75
C45	0.1428	0.4011	0.2569	3.58
C51	0.3740	0.1508	−0.0369	3.81
C52	0.4507	0.1323	−0.1508	5.09
C53	0.5051	0.1863	−0.1979	5.15
C54	0.4806	0.2603	−0.1268	4.51
C55	0.4031	0.2778	−0.0097	3.54
C61	0.3110	0.0933	0.0120	4.36
C62	0.3179	0.0170	−0.0627	7.72
C63	0.2519	−0.0352	−0.0181	9.39
C64	0.1797	−0.0119	0.0963	7.60
C65	0.1755	0.0667	0.1705	4.71

a) $B_{eq}=4/3(a^2B_{11}+b^2B_{22}+c^2B_{33}+ab\cos\gamma\cdot B_{12}+ac\cos\beta\cdot B_{13}+bc\cos\alpha\cdot B_{23})$.

addition of saturated aqueous $NaBF_4$ to the solution yielded $[Ru(dabp)_3](BF_4)_2$(**1**) as a precipitate, which was collected by filtration and dried in vacuo to give **1** quantitatively as a red powder (Table 1).

The Complex 2: Since attempts to prepare *cis*-$[Ru(dabp)_2Cl_2]$ according to the methods described in literatures did not give satisfactory results,[5,17,18)] $[Ru(dabp)_2(dmso)_2]Cl_2$ (**6**) was prepared from **5** by the following procedure. An ethanolic solution (6 ml) containing 97 mg (0.2 mmol) of **5** and 77 mg (0.41 mmol) of dabp was refluxed under N_2 stream for 24 h, and then 6.4 ml of an aqueous LiCl (1 mol dm^{-3}) solution was added. Condensation of the solution gave a precipitate, which was collected by filtration. This crude complex was purified by column chromatography with a Sephadex LH-20/ethanol system. Only a reddish-orange band was observed during column separation, and evaporation of ethanol from this fraction gave a red powder. Incorporation of dabp into the complex was confirmed by the presence of the peak at 795 cm^{-1} due to dabp in the IR spectrum of the powder, and the complex was determined to be **6** by elemental analysis (yield 70%); mp 150 °C (slowly decompose). Found: C, 41.3; H, 4.6; N, 16.3%. Calcd for $RuC_{24}H_{32}N_8S_2O_2Cl_2$: C, 41.1; H, 4.6; N, 16.0%. After refluxing 100 mg (0.14 mmol) of **6** and 222 mg (0.14 mmol) of byp in 6 ml of ethanol for 24 h under N_2 flow in the dark, the solution was directly applied to a Sephadex LH-20/ethanol column. A reddish orange fraction was collected. The residue after removal of the solvent was converted to a BF_4-salt by the procedure described in the preparation of the complex **1**, and again was purified by the Sephadex LH-20/ethanol system to give $[Ru(dabp)_2(bpy)](BF_4)_2$ as a red powder (Table 1).

The Complex 3: *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (**7**) was synthesized according to the routine method in the presence of LiCl in *N*,*N*-dimethylformamide (yield 68%).[17)] Synthesis of the mixed-ligand complex from **7** was carried out by the similar procedure as that of Nakamaru with slight modification.[5)] After reaction of 260 mg (0.5 mmol) of **7** with 100 mg (0.64 mmol) of dabp by refluxing in an ethanol–water (3:1) mixture in the presence of 500 mg of K_2HPO_4 for 24 h under nitrogen atmosphere, the solution was evaporated to dryness. Ethanol-soluble fraction of the residue was collected, and then was applied to the Sephadex LH-20/ethanol column. An orange-colored fraction was collected, and subsequent anion exchange with $NaBF_4$ gave $[Ru(dabp)(bpy)_2](BF_4)_2$ (**3**) as a dark red needle (Table 1).

The Complex 4: $[Ru(bpy)_3](BF_4)_2H_2O$ was synthesized by the reaction of $RuCl_3\cdot xH_2O$ and bpy[9)] and subsequent anion-exchange with $NaBF_4$ (yield 85%). Found: C, 47.1; H, 3.5; N, 11.1%. Calcd for $RuC_{30}H_{24}N_6B_2F_8\cdot H_2O$: C, 47.3; H, 3.3; N, 11.0%.[19)]

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