Synthesis, Luminescence Quantum Yields, and Lifetimes of Trischelated Ruthenium(II) Mixed-ligand Complexes Including 3,3′-Dimethyl-2,2′-bipyridyl

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New five complexes of the type of $[RuL_{3-x}(dmby)_x]X_2$(x=1,2,3, L=2,2′-bipyridyl or 1,10-phenanthroline, dmby=3,3′-dimethyl-2,2′-bipyridyl, X=halide ion) have been synthesized in order to investigate the effects of two methyl groups of dmby on the absorption and emission spectra, luminescence quantum yields, and lifetimes. Values of the radiative and nonradiative rate constants have been calculated from these data at 77 K. Although the absorption and emission maxima and the lifetimes are not much affected by the dmby ligand substitution, the molar extinction coefficients and emission quantum yields are decreased compared with trischelated complexes of the parent bipyridyl or phenanthroline ligands. At 25 °C the emission yields of the complexes containing dmby decrease by 3—4 orders of magnitude than at 77 K. Possible causes of the decrease in the quantum yields are discussed.

Tris(2,2′-bipyridyl)ruthenium(II) ion, $[Ru(bpy)_3]^{2+}$, has attracted widespread attention in recent years because of its strong charge transfer (CT) luminescence[1,2] even in fluid solutions at room temperature as well as at 77 K and because of higher redox ability in the excited state than in the ground state.[3—5] In particular, the latter property has accelerated many investigations on photoredox chemistry of this ion and related complexes in the hope of possible catalytic activity in solar energy conversion to chemical potential energy.[6—10]

There have been a few studies on the effects of ligand substituents on the spectral and excited state properties of bipyridyl or 1,10-phenanthroline (phen) complexes with ruthenium(II). Phenyl substitution on the 4,4′-positions of bipyridyl and 4,7-positions of phenanthroline ligands has been shown to produce an increase in the luminescence quantum yields and a slight decrease in the measured lifetimes. These effects have been interpreted on the basis of a model of intensity borrowing *via* spin-orbit coupling interaction between a luminescing triplet state and a lending singlet state.[11—13] Temperature dependence of the quantum yields and lifetimes of ruthenium(II) complexes with the unsubstituted and methyl- or phenyl-substituted ligands at low temperature has been reported[14,15] (at higher temperatures, only for the $[Ru(bpy)_3]^{2+}$ [16,17]). Recently, some sterically hindering bi- and tridentate ligand complexes have been prepared and their effects on the relaxation processes of the excited state have been discussed.[18—20]

3,3′-Dimethyl-2,2′-bipyridyl(dmby), which was first synthesized by Case,[21] is an interesting ligand in that upon coordination to metal it is expected to take a twisted, and hence non-coplanar conformation owing to the steric hindrance of the two methyl groups.[22,23] Photophysical and photochemical studies, however, on the transition metal complexes with this dmby have scarcely been found. This paper reports the preparation of several trischelated ruthenium(II) complexes including dmby and bipyridyl (or phenanthroline); also the effects of dmby on the absorption and emission spectra, emission quantum yields, and lifetimes of these complexes.

Experimental

Materials. $RuCl_3 \cdot 3H_2O$ (Aldrich Chemical Co.), 2,2′-bipyridyl and 1,10-phenanthroline (Wako Pure Chemicals Co.), and substituted ligands (G. Frederick Smith Chemical Co.) other than dmby were used as obtained. 2-Amino-3-methylpyridine was prepared by reflux of 3-methylpyridine with sodium amide in xylene.[24] 2-Bromo-3-methylpyridine was synthesized from 2-amino-3-methylpyridine by the Sandmeyer reaction.[25]

Preparation of 3,3′-Dimethyl-2,2′-bipyridyl. A slight modification of the method of Case[21] was used. A dried mixture of 200 ml of *p*-cymene, 75 g of copper powder, and 75 g of sodium chloride was refluxed with stirring in an oil bath. To this 120 g of 2-bromo-3-methylpyridine was added slowly and the reflux continued for two hours at 180—200 °C. After cooling to 100 °C, 200 ml of 6 mol dm^{-3} HCl was added. This reaction mixture was made alkaline with NaOH and distilled with steam. About 10 L of the aqueous distillate was extracted with chloroform. After the chloroform was removed, the remainder was distilled under reduced pressure. On redistillation 26 g of pale yellow liquid boiling at 157—158 °C (20 mmHg, 1 mmHg$\approx$133.322 Pa) was obtained (yield, 40%). Purification of the crude product was accomplished by conversion of the base to its hydrochloric acid salt and repeated recrystallization from 330 ml of the mixture of ethanol and concentrated HCl (90:10%, v/v). 19 g of the pure white crystals (yield, 21%) were again converted to the base with NaOH and the liberated product was extracted with diethyl ether. Evaporation of the ether gave 12 g of viscous, colorless liquid (final yield, 19%). Its absorption spectrum agreed well with the authentic sample.[23]

cis-$[Ru(bpy)_2Cl_2] \cdot 2H_2O$ and *cis*-$[Ru(phen)_2Cl_2] \cdot 3H_2O$ were prepared by the method described in the literature.[26]

Preparation of cis-$[Ru(dmby)_2Cl_2] \cdot 3H_2O$. Since all attempts to prepare this compound according to the method described in literature were unsuccessful, the following procedure was adopted. 3.0 g of $RuCl_3 \cdot 3H_2O$ and 4.3 g of dmby in 104 ml of *N,N*-dimethylformamide and 12 ml of 0.2 M (1 M=1 mol dm^{-3}) phosphate buffer solution (pH 6.8—7.0) were refluxed together for 6 h. The solvent was distilled off, and the residue was dissolved in about 400 ml of hot water containing 10 ml of phosphate buffer solution. The dark red brown solution was quickly filtered and 57 g of LiCl added to the filtrate. The product, which precipitated on standing overnight in refrigerator, was collected by suction filtration, washed several times with cold water and

TABLE 1. ANALYTICAL RESULTS

Compound	C (%)		H (%)		N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
$[Ru(bpy)_3]Cl_2 \cdot 3H_2O$	49.32	48.88	4.69	4.51	11.50	11.67
$[Ru(bpy)_2(dmby)]I_2 \cdot 2H_2O$	43.31	43.14	3.63	3.42	9.47	9.30
$[Ru(bpy)(dmby)_2]I_2 \cdot 3H_2O$	43.74	43.84	4.10	3.88	9.00	8.95
$[Ru(dmby)_3]Br_2 \cdot 7H_2O$	46.01	46.17	5.36	5.02	8.94	8.96
$[Ru(phen)_3]Cl_2 \cdot 7H_2O$	51.55	51.34	4.57	4.17	10.02	10.00
$[Ru(phen)_2(dmby)]Cl_2 \cdot 8H_2O$	50.23	49.94	5.15	4.89	9.76	10.05
$[Ru(phen)(dmby)_2]Cl_2 \cdot 7H_2O$	51.06	50.58	5.48	5.07	9.92	9.89
$[Ru(4,4'\text{-dimethylbpy})_3]Cl_2 \cdot 7H_2O$	50.82	50.85	5.92	5.56	9.87	9.75
$[Ru(4,7\text{-diphenylphen})_3]Cl_2 \cdot 5H_2O$	68.67	69.11	4.64	4.33	6.67	6.83
cis-$[Ru(dmby)_2Cl_2] \cdot 3H_2O$	48.49	48.55	5.09	4.37	9.47	9.76

dried. The dark, almost black, fine powder product was obtained in 44% yield (4.0 g).

$[Ru(bpy)_3]Cl_2 \cdot 5H_2O$ was prepared according to the method reported.[27] $[Ru(4,4'\text{-dimethylbpy})_3]Cl_2 \cdot 7H_2O$, $[Ru(4,4'\text{-diphenylbpy})_3]Cl_2 \cdot 5H_2O$, $[Ru(dmby)_3]Br_2 \cdot 7H_2O$, $[Ru(phen)_3]Cl_2 \cdot 7H_2O$, and $[Ru(4,7\text{-diphenylphen})_3]Cl_2 \cdot 5H_2O$ were prepared analogously.

Preparation of $[RuL_{3-x}(dmby)_x]X_2(x=1,2)$. The preparation of this type of compounds all follows the same procedure as described for $[Ru(phen)_2(dmby)]Cl_2 \cdot 8H_2O$.

$[Ru(phen)_2(dmby)]Cl_2 \cdot 8H_2O$: 2.0 g of *cis*-$[Ru(phen)_2Cl_2] \cdot 3H_2O$ (3.2 mM) and 0.7 g of dmby (3.8 mM) in 200 ml of ethanol and 15 ml of 0.2 M phosphate buffer solution were refluxed for 72 h. The dark red brown solution was filtered and then evaporated to dryness. The residue was first purified on a column of silica gel eluting with acetone–ethanol (1:2, v/v). Final purification was achieved by repeated recrystallization from water. The pure chloride product is a deep red brown crystalline material.

For the preparation of the other trischelated complexes, *cis*-$[Ru(bpy)_2Cl_2] \cdot 2H_2O$ or *cis*-$[Ru(dmby)_2Cl_2] \cdot 3H_2O$ was used as the starting material instead of *cis*-$[Ru(phen)_2Cl_2] \cdot 2H_2O$. The chloride and bromide salts of $[Ru(bpy)_2(dmby)]^{2+}$ and $[Ru(bpy)(dmby)_2]^{2+}$ were too soluble to crystallize from water. Hence, for the purpose of elemental analysis, they were converted to the iodide salts by treatment with KI. For the same reasons, the chloride salt of $[Ru(dmby)_3]^{2+}$ was converted to the bromide salt by KBr. Elemental analysis was performed by Chem. Dept., Fac. Sci., Tohoku Univ. and the results are listed in Table 1.

Spectroscopic Measurements. Absorption spectra were measured with a Hitachi 124 double-beam spectrophotometer thermostated at 25 °C. All luminescence measurements were made with a Hitachi MPF-4 fluorescence spectrophotometer. Emission spectra were corrected using 2-naphthol in (0.020 ± 0.001) mol dm^{-3} sodium acetate–acetic acid buffer solution, *N*,*N*-dimethyl-*m*-nitroaniline in benzene–hexane (30:70%, v/v), and 4-dimethylamino-4′-nitrostilbene in *o*-dichlorobenzene as the standard. The true emission spectra of these substances were reported by Lippert *et al.*[28] For emission measurements at 77 K the complexes were dissolved in methanol–ethanol (1:4, v/v) mixed-solvent and frozen in liquid nitrogen by immersion of a 5-mm quartz tube. The sample absorbance at an exciting wavelength was kept as low as possible to avoid fluorescence errors. The usual concentrations were $(3-5) \times 10^{-6}$ M. For excitation at 436 nm, light from a 150 W xenon lamp was passed through a monochromater and a Toshiba V-Y43 cut-off filter. For the emission intensity measurements a Toshiba V-O58 cut-off filter was further placed in front of the PM tube.

Quantum yields were measured by the modified Parker and Rees method.[29] As the quantum yield standard, $[Ru(4,7\text{-diphenylphen})_3]Cl_2$ was used assuming a value of 0.682.[13] Preliminary measurements using $[Ru(4,4'\text{-diphenylbpy})_3]Cl_2$ as a test sample gave a value of 0.563 ± 0.014, in good agreement with the reported value of 0.573 ± 0.032.[13]

Measurements at 25 °C were done in aqueous solutions with the same apparatus and procedures except that the usual fluorescence cell was used and that the emission quantum yield standard was fluorescein in 0.1 mol dm^{-3} NaOH or $[Ru(bpy)_3]Cl_2$ in air saturated aqueous solution. Each yield is 0.90[13] and 0.028,[30] respectively. All the ruthenium(II) complexes in H_2O were thermally stable, but the samples were daily prepared prior to use. If necessary, nitrogen was bubbled through the sample solutions for 15 min. More details have been described previously.[30]

For the lifetime measurements, an apparatus constructed by Kokubun (Chem. Dept., Fac. Sci., Tohoku Univ.) was used. The sample was excited at 337 nm with a pulsed nitrogen laser. Lifetimes were determined from the slope of a linear plot of ln intensity *vs.* time.

The absorption spectra of the iodide salts of $[Ru(bpy)_2(dmby)]^{2+}$ and $[Ru(bpy)(dmby)_2]^{2+}$ differ in the ultraviolet region from their chloride or bromide salts owing to the iodide absorption. Therefore the chloride salts of these complexes were used for the absorption measurements. For the emission measurements, however, the iodide salts of these complexes and the bromide salt of $[Ru(dmby)_3]^{2+}$ were used since no effect of the counterions was observed on the emission spectra and intensities.

Results

The absorption and luminescence spectra of the ruthenium(II) complexes studied are shown in Figs. 1—3. The wavelengths of the absorption maxima and the corresponding molar extinction coefficients as well as the wavelengths of the emission maxima for all the ruthenium(II) complexes are summarized in Table 2.

The quantum yields and lifetimes for all the complexes at 77 K are tabulated in Table 3. A value of the quantum yield, 0.328, for the $[Ru(bpy)_3]Cl_2$ is smaller than that of 0.376 reported by Demas and Crosby.[11] A once recrystallized sample also gave the same value. When $[Ru(4,4'\text{-diphenylbpy})_3]Cl_2$ was used as the quantum yield standard with a value of 0.563 measured in this study, again the same result

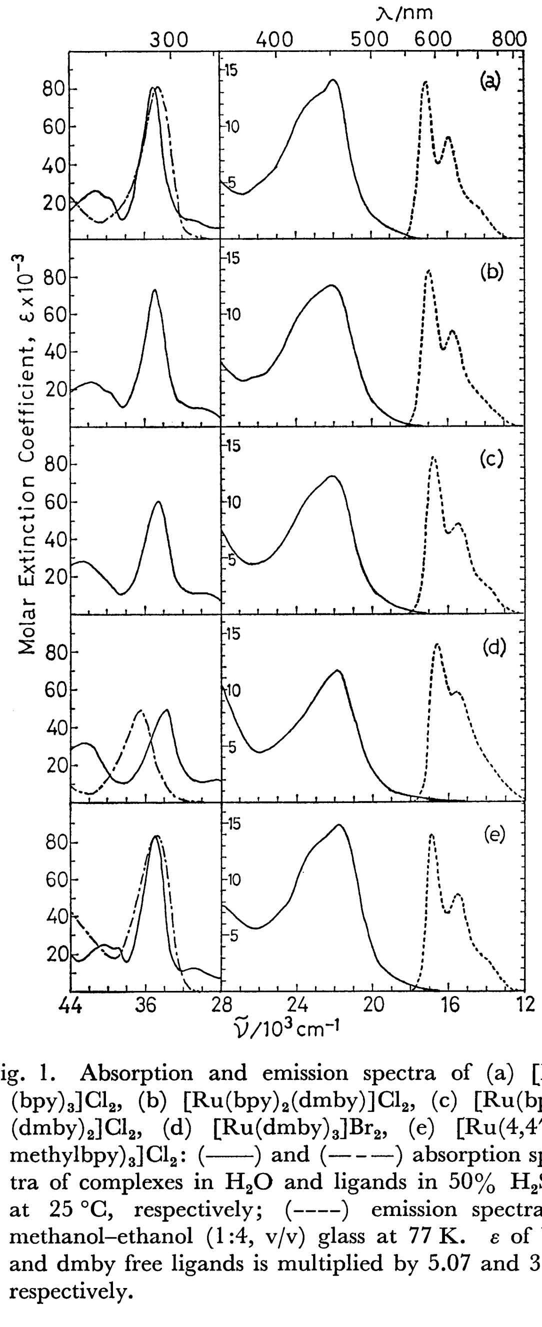

Fig. 1. Absorption and emission spectra of (a) [Ru($bpy)_3]Cl_2$, (b) [Ru$(bpy)_2$(dmby)]Cl_2, (c) [Ru(bpy)(dmby)$_2$]Cl_2, (d) [Ru$(dmby)_3$]Br_2, (e) [Ru(4,4′-dimethylbpy)$_3$]Cl_2: (——) and (— — —) absorption spectra of complexes in H_2O and ligands in 50% H_2SO_4 at 25 °C, respectively; (----) emission spectra in methanol–ethanol (1:4, v/v) glass at 77 K. ε of bpy and dmby free ligands is multiplied by 5.07 and 3.54, respectively.

was obtained. The quantum yield, 0.328, for the [Ru(bpy)$_3$]Cl_2 complex is acceptable in view of the fact that the present quantum yields for the [Ru(phen)$_3$]Cl_2 (0.578) and [Ru(4,4′-diphenylbpy)$_3$]Cl_2 (0.563) agree well with the values of 0.584 and 0.573 measured by Demas and Crosby,[11,13] respectively, and the lifetimes for [Ru(bpy)$_3$]Cl_2, [Ru(4,4′-diphenylbpy)$_3$]Cl_2, [Ru(phen)$_3$]Cl_2, and [Ru(4,7-diphenylphen)$_3$]Cl_2 (5.1, 4.8, 9.9, and 10.2 μs, respectively) are also in good agreement with the values reported for these complexes (5.21, 4.68, 9.79, and 9.58 μs, respectively[11,13]).

Radiative (k_r) and nonradiative (k_{nr}) rate constants were calculated using the following expressions,

$$Q = k_r/(k_r+k_{nr}) = k_r\tau_m, \quad (1)$$

$$k_{nr} = \tau_m^{-1} - \tau_r^{-1}, \quad (2)$$

where Q is the emission quantum yield, τ_m is the measured lifetime, and τ_r is the radiative lifetime ($=1/k_r$). In Eq. 1 the efficiency of populating the emitting CTTL excited state (see Discussion) is assumed to be unity as is generally accepted.[2,31] The results are included in Table 3.

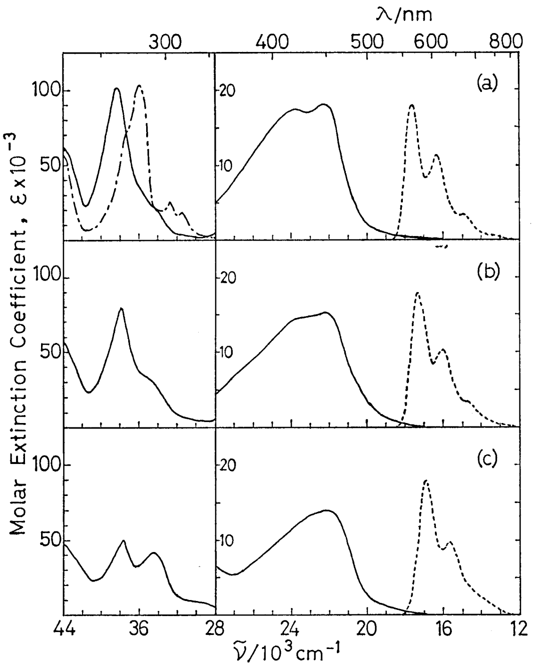

Fig. 2. Absorption and emission spectra of (a) [Ru(phen)$_3$]Cl_2, (b) [Ru(phen)$_2$(dmby)]Cl_2, (c) [Ru(phen)(dmby)$_2$]Cl_2: (——) and (— — —) absorption spectra of complexes in H_2O and ligands in 50% H_2SO_4 at 25 °C, respectively; (- - -) emission spectra in methanol–ethanol (1:4, v/v) glass at 77 K. ε of phen and dmby free ligands is multiplied by 2.52 and 3.54, respectively.

At 25 °C the emission intensity largely decreases, especially for the complexes including the dmby ligand. This is the reason why the lifetimes of the complexes including dmby (except that of [Ru(bpy)$_2$(dmby)]Cl_2) and the quantum yield of [Ru(dmby)$_3$]Br_2 could not be measured. As for the two complexes of [Ru(bpy)(dmby)$_2$]I_2 and [Ru(phen)(dmby)$_2$]Cl_2, it was difficult to obtain the exact corrected emission spectra because of their low intensities. The yields were estimated, however, by an assumption that the ratio of the integrated area under the corrected emission spectrum to the intensity in height at the observed wavelength (600 nm)[29] is equal to those of [Ru(bpy)$_2$(dmby)]I_2 and [Ru(phen)$_2$(dmby)]Cl_2, respectively. The errors in these procedures mainly stem from the estimate of the height in the ratio because the area is almost the same within the bipyridyl or phenanthroline complex series. Since the red shift in the emission spectra on introduction of dmby is evident but small (Table 2), the errors caused by the above assumption seem not so large that the order in the yield is varied. The results are listed in Table 4. The quantum yields using the excitation wavelength of 480 nm agreed well with those at 436 nm. Moreover, an excellent coincidence was seen between the yields obtained by means of fluorescein and [Ru(bpy)$_3$]Cl_2 as the standard.

Table 2. Absorption and emission spectral data for ligands and Ru(II) complexes

Compound	Absorption[a)]				Emission[a)]	Emission[d)]
	λ_{max}/nm	$\frac{\varepsilon_{max}\times 10^{-4}}{M^{-1}\,cm^{-1}}$	$\frac{\delta^{b)}}{cm^{-1}}$	$f^{c)}$	λ_{max}/nm	λ_{max}/nm
$[Ru(bpy)_3]Cl_2$	452	1.40	2300	0.15	628	582, 629
	286, 243	8.14, 2.55				
$[Ru(bpy)_2(dmby)]Cl_2$	453	1.26	2700	0.16	630	588, 636
	287, 239	7.14, 2.43				
$[Ru(bpy)(dmby)_2]Cl_2$	454, 342	1.23, 1.09	2700	0.15		597, 641
	289, 235	6.06, 2.82				
$[Ru(dmby)_3]Br_2$	456, 348	1.16, 1.18	2800	0.15		601, 638
	296, 236	4.94, 3.23				
$[Ru(phen)_3]Cl_2$	447, 420	1.81, 1.74	2500	0.21	604	566, 610
	262, 222	10.8, 7.89				
$[Ru(phen)_2(dmby)]Cl_2$	450, 423	1.52, 1.47	3000	0.21	611	576, 623
	264, 224	7.96, 6.04				
$[Ru(phen)(dmby)_2]Cl_2$	451, 423	1.40, 1.24	2800	0.18		591, 638
	289, 265, 226	4.22, 5.08, 4.53				
$[Ru(4,4'\text{-dimethylbpy})_3]Cl_2$	459	1.49	2600	0.18	642	593, 641
	285, 247	8.00, 2.52				
bpy[e)]	289 (280)	1.61 (1.29)				
dmby[e)]	274 (271, 266)	1.40 (0.85, 0.85)				
4,4′-Dimethylbpy[e)]	286 (279)	1.58 (1.24)				
phen[e)]	278 (264)	4.28 (2.91)				

a) In water at 25 °C. b) Bandwidth at half-height of CT-absorption band estimated by drawing gaussian curves eliminating shoulders. c) Oscillator strengths, f, were calculated using the expression, $f=4.60\times 10^{-9}\,\varepsilon_{max}\delta$, from C. J. Ballhausen, *Prog. Inorg. Chem.*, **2**, 251 (1960). d) In methanol-ethanol(1:4, v/v) rigid glass at 77 K. e) In 50% H_2SO_4. Values in 0.1 M NaOH were indicated in parentheses.

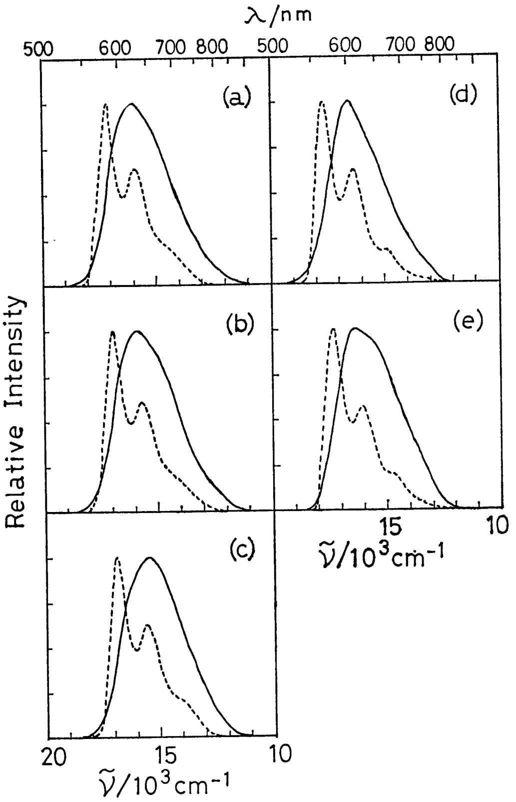

Fig. 3. Emission spectra of (a) $[Ru(bpy)_3]Cl_2$, (b) $[Ru(bpy)_2(dmby)]I_2$, (c) $[Ru(4,4'\text{-dimethylbpy})_3]Cl_2$, (d) $[Ru(phen)_3]Cl_2$, (e) $[Ru(phen)_2(dmby)]Cl_2$: (——) in H_2O at 25 °C; (- - -) in methanol-ethanol (1:4, v/v) glass at 77 K.

Discussion

Absorption and Emission Spectra. The intense visible absorption bands of the tris-type ruthenium(II) complexes of bipyridyl,[2)] phenanthroline,[2,32)] and 4,4′-dimethylbipyridyl[14)] have been all assigned to the spin-allowed charge transfer transitions from the metal d orbitals to the ligand π* orbitals (CTTL), while the more intense bands below 300 nm have been assigned to intraligand π-π* transitions.[14,33)] Because of the similarities in the spectra of the complexes containing the dmby ligand, the same band assignments can be made for the new complexes reported here.

The following features can be seen from Figs. 1 and 2 or Table 2. First, the absorption spectra of the parent complexes of $[Ru(bpy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ regularly change to that of $[Ru(dmby)_3]^{2+}$ without any appearance of new bands in the mixed-ligand complexes other than the characteristic bands already present in these three homotrischelated complexes. Moreover, a slight red shift is seen except for the 240 nm band in the bipyridyl complex series which shows a blue shift. Secondly, the π-π* absorption maximum of the dmby free ligand lies in a considerable shorter wavelength than that of the parent bipyridyl. This contrasts with 4,4′-dimethylbipyridyl in which the position and intensity of the absorption maximum are comparable with the parent ligand, and hence suggests that due to the steric interactions of the two methyl groups of dmby the delocalization of π-electrons is limited to a narrow range. Such hypsochromic effect of a substituent(s) at the sterically hindering

Table 3. Quantum yields, lifetimes, and rate constants for Ru(II) complexes at 77 K a)

Complex	Q b)	τ_m c) / μs	τ_r d) / μs	k_r e) / μs^{-1}	k_{nr} f) / μs^{-1}	Q_h g)
$\mathrm{[Ru(bpy)_3]Cl_2}$	0.328±0.011	5.1±0.2	16	0.064	0.14	
$\mathrm{[Ru(bpy)_2(dmby)]I_2}$	0.252±0.008	5.2±0.1	21	0.048	0.14	0.255
$\mathrm{[Ru(bpy)(dmby)_2]I_2}$	0.192±0.003	5.4±0.2	28	0.036	0.15	0.205
$\mathrm{[Ru(dmby)_3]Br_2}$	0.113±0.014	6.4±0.2	57	0.018	0.14	0.114
$\mathrm{[Ru(phen)_3]Cl_2}$	0.578±0.007	9.9±0.3	17	0.058	0.042	
$\mathrm{[Ru(phen)_2(dmby)]Cl_2}$	0.422±0.011	9.4±0.2	22	0.045	0.065	0.517
$\mathrm{[Ru(phen)(dmby)_2]Cl_2}$	0.281±0.013	9.3±0.2	33	0.030	0.080	0.417
$\mathrm{[Ru(dmby)_3]Br_2}$	0.113±0.014	6.4±0.2	57	0.018	0.14	0.300
$\mathrm{[Ru(4,4'\text{-}dimethylbpy)_3]Cl_2}$	0.283±0.007	4.6±0.2	16	0.062	0.093	0.307

a) Measured in methanol-ethanol(1:4, v/v) rigid glass. b) Luminescence quantum yields. Excited at 436 nm. c) Measured lifetimes. Excited at 337 nm. d) Radiative lifetimes calculated from τ_m/Q. e) Radiative rate constant calculated from $1/\tau_r$. f) Nonradiative rate constants calculated from $\tau_m^{-1}-\tau_r^{-1}$. g) Hypothetical quantum yield (see context).

Table 4. Luminescence quantum yields for Ru(II) complexes at 25 °C a)

Complex	N$_2$-saturated b)		Air-saturated b)	
	Q(F)	Q(R)	Q(F)	Q(R)
$\mathrm{[Ru(bpy)_3]Cl_2}$ c)	0.042±0.002		0.028±0.002	
$\mathrm{[Ru(bpy)_2(dmby)]I_2}$	(3.6±0.2)×10^{-4}	(3.6±0.3)×10^{-4}	(3.0±0.2)×10^{-4}	(3.1±0.2)×10^{-4}
$\mathrm{[Ru(bpy)(dmby)_2]I_2}$ d)	(1.3±0.3)×10^{-5}	(1.9±0.8)×10^{-5}	(0.8±0.2)×10^{-5}	(1.1±0.3)×10^{-5}
$\mathrm{[Ru(phen)_3]Cl_2}$ c)	0.058±0.005	0.058±0.004	0.032±0.002	0.030±0.002
$\mathrm{[Ru(phen)_2(dmby)]Cl_2}$	(4.0±0.5)×10^{-5}	(4.0±0.4)×10^{-5}	(4.6±0.6)×10^{-5}	(4.9±0.7)×10^{-5}
$\mathrm{[Ru(phen)(dmby)_2]Cl_2}$ d)	(6±3)×10^{-6}	(9±3)×10^{-6}	(5±2)×10^{-6}	(8±2)×10^{-6}
$\mathrm{[Ru(4,4'\text{-}dimethylbpy)_3]Cl_2}$ c)	0.026±0.002	0.025±0.002	0.021±0.002	0.021±0.002

a) In water at 25 °C. b) Luminescence quantum yields. Excited at 436 nm. Q(F) and Q(R) denote the yields measured by using fluorescein and $\mathrm{[Ru(bpy)_3]Cl_2}$ as the standard, respectively. c) Value from Ref. 30. d) As for the procedures to obtain these values, see Results.

positions of various organic compounds is well known (for example, biphenyl, a similar compound to 2,2′-bipyridyl).34) The π-π* absorption maximum of dmby (274 nm), however, greatly shifts to the longer wavelength (296 nm) upon coordination to ruthenium, contrasted with that of phenanthroline (278 nm) which shifts to shorter wavelength (262 nm). Finally, as the number of the dmby ligand increases, maximum molar extinction coefficients decrease step by step except also for the 240 nm band, where an increase rather than a decrease is observed. This decrease can be explained, at least in part, by a broadening of the visible CT band.18) The oscillator strengths in Table 2, though by a rough calculation, are almost the same; a reduction in the extinction coefficients is recovered by an increase in the bandwidths.

The emission at 77 K from the trischelated ruthenium(II) complexes with the unsubstituted and substituted bipyridyl or phenanthroline arises from a CTTL excited state.11,13,14) However, a discussion about the assignment of a spin multiplicity is inappropriate due to strong spin-orbit coupling.35) As is similar to these complexes, the emission spectra reported here clearly show the vibrational progression indicative of a CT luminescence2) although the vibrational structure is somewhat obscure in the tris(dmby) complex. It is therefore concluded that the observed luminescence of the complexes including dmby is also due to the radiative transitions from the CTTL excited state. It should be pointed out that the red shift of the emission peak of $\mathrm{[Ru(dmby)_3]^{2+}}$ from that of $\mathrm{[Ru(bpy)_3]^{2+}}$ is larger than any other ruthenium(II) complexes of substituted bipyridyls reported until now.

The emission spectra at 25 °C (Fig. 3) are broader and indicate red shifts in comparison with those at 77 K. These large changes in the shape of the spectra when the solvent medium is transformed from a rigid glass to a fluid have been used as an evidence for the argument that in fluid solutions charge transfer to solvent (CTTS) configurations interact with the CTTL excited state of $\mathrm{[Ru(bpy)_3]^{2+}}$.16,17)

Lifetimes and Quantum Yields. The observed lifetimes for the bipyridyl complex series produce only a relatively minor variation as well as for the phenanthroline series. The longer lifetimes for the latter are plain enough.

The most notable effect of dmby is seen in a large decrease in the emission quantum yield of its tris complex, that is, 66% and 80% decreases compared with the parent complexes of bipyridyl and phenanthroline, respectively. Dimethyl substitution on the normal (sterically not hindering) positions such as 4,4′- for bipyridyl or 4,7- and 5,6-positions for phenanthroline has been known to result in relatively slight changes in the yields (3—12%), whereas diphenyl substitution causes a larger increase (20—50%).14,15,36) However,

Table 5. Reproduction of the emission quantum yields of the mixed ligand Ru(II) complexes

	$k_r/\mu s^{-1}$		$k_{nr}/\mu s^{-1}$		$\tau/\mu s$		Q	
	Calcd[a]	Obsd	Calcd[b]	Obsd	Calcd[c]	Obsd	Calcd[d]	Obsd
$[Ru(bpy)_2(dmby)]I_2$	0.0486	0.048	0.140	0.14	5.29	5.2	0.257	0.252
$[Ru(bpy)(dmby)_2]I_2$	0.0333	0.036	0.140	0.15	5.78	5.4	0.192	0.192
$[Ru(phen)_2(dmby)]Cl_2$	0.0446	0.045	0.0747	0.065	8.40	9.4	0.375	0.422
$[Ru(phen)(dmby)_2]Cl_2$	0.0313	0.030	0.107	0.080	7.25	9.3	0.227	0.281

a) Calculated using the values of 0.0213 for a bpy, 0.0193 for a phen, and 0.006 μs^{-1} for a dmby. These values were obtained by division of k_r for the corresponding parent tris complexes by 3. b) Calculated using the values of 0.0467 for a bpy, 0.014 for a phen, and 0.0467 μs^{-1} for a dmby obtained by division of k_{nr} for the corresponding parent tris complexes by 3. c) Calculated from $1/(k_r+k_{nr})$. d) Calculated from $k_r\tau$.

methyl- or dimethyl-substitution on the sterically hindering positions such as 6,6′- for bipyridyl or 2,9-positions for phenanthroline has been shown to bring about a great decrease in the yields (72% for the monomethyl and 92% for the dimethyl ligands).[20] It should be noted that the latter values are comparable to the present case.

A perusal of Table 3 shows that introduction of the dmby ligand into the parent tris complexes causes a decrease in the yields at almost the same rate for both series of complexes. According to Hipps and Crosby,[37] the lowest CTTL excited state of the ruthenium(II) complexes is viewed as the one in which an electron has been essentially promoted from the central metal core to an antibonding orbital delocalized over the three ligands. Therefore the electronic properties of the excited state are described as weighted averages of the properties of the individual ligands. In line with this point of view, the quantum yields of the mixed-ligand complexes can be calculated as follows. An assumption that the values of radiative and nonradiative rate constant for the tris(bipyridyl) complexes can be alloted equally to each of three bipyridyl molecules gives the values of 0.0213 and 0.0467 μs^{-1}, respectively. An analogous procedure for the tris(phenanthroline or dmby) complexes gives 0.0193 and 0.014 μs^{-1} for a phenanthroline, 0.006 and 0.0467 μs^{-1} for a dmby. Then using these values the quantum yields are computed by Eq. 1 and the results are listed in Table 5. It is seen that the calculated and observed quantum yields agree well although somewhat low calculated values are obtained for the phenanthroline mixed-ligand complexes.

As Eq. 1 shows, the observed decrease of the emission quantum yield is due both to the decrease in k_r and to the increase in k_{nr}. The relative contributions of these two factors to the decrease in the yield are illustrated in Fig. 4. The line on the left of each diagram represents the quantum yield of the parent complex while the line on the right represents the observed quantum yield of the complex including dmby. The line in the middle represents the hypothetical quantum yield (Q_h) that the dmby complex would have if only a change in the radiative rate constant (Δk_r) were caused by the dmby ligand substitution (the values of Q_h are also listed in Table 3). Δk_{nr} represents the change in the quantum yield due to the change in k_{nr}. The figure shows that both factors comparably contribute to the decrease in the yield for the phenanthroline complexes, although a detailed examination indicates that as the number of dmby increases the role of Δk_r factor becomes more important while the role of Δk_{nr} factor decreases. In sharp contrast to the phenanthroline complexes, however, the decrease in the yield for the bipyridyl complexes is almost ascribed to the decrease in k_r. Similar results have been also reported for the other ruthenium(II) complexes.[38]

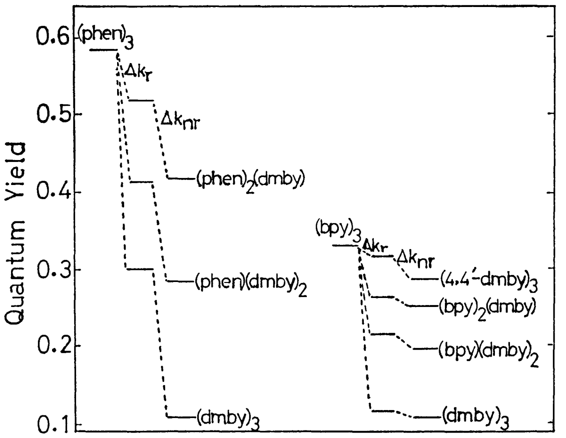

Fig. 4. Dmby substitution-induced changes in quantum yields resolved into radiative(Δk_r) and nonradiative(Δk_{nr}) factors for Ru(II) complexes in methanol–ethanol (1:4, v/v) glass at 77 K.

The decrease in k_r can be, at least qualitatively, explained by the model by Demas and Crosby[11] which assumes that the emitting (triplet) state (the energy, E_T) borrows intensity from the lending, highly spin-allowed (singlet) state (the energy, E_S) through the spin-orbit coupling interaction (magnitude, $K|M_{SO}|^2$). On the basis of this model, they have expressed the radiative rate constant as follows:

$$k_r = \varepsilon(S)K|M_{SO}|^2(E_T^3/E_S)/(E_T-E_S)^2, \tag{3}$$

where $\varepsilon(S)$ is the maximum molar extinction coefficient of the first visible CT band. E_S is taken as the energy of the first absorption maximum of the highly allowed CT band, and E_T is assumed to be the energy of the shortest wavelength emission peak.[11] In calculating the radiative rate constant by Eq. 3, two additional approximations are made. First, the values of $\varepsilon(S)$ at 25 °C in Table 2 are used because the absorption spectra have not been measured at 77

Table 6. Caculated and experimental radiative rate constants of Ru(II) complexes at 77 K*)

Complex	ε(S)a)	E_S b)	E_T c)	k_r(calcd)d) / μs^{-1}	k_r(exptl)e) / μs^{-1}
$[\mathrm{Ru(bpy)_3}]\mathrm{Cl_2}$	1.40	22.1	17.2	0.064(1.00)	0.064(1.00)
$[\mathrm{Ru(bpy)_2(dmby)}]\mathrm{I_2}$	1.26	22.1	17.0	0.053(0.83)	0.048(0.75)
$[\mathrm{Ru(bpy)(dmby)_2}]\mathrm{I_2}$	1.23	22.0	16.8	0.046(0.72)	0.036(0.56)
$[\mathrm{Ru(dmby)_3}]\mathrm{Br_2}$	1.16	21.9	16.6	0.042(0.66)	0.018(0.28)
$[\mathrm{Ru(phen)_3}]\mathrm{Cl_2}$	1.81	22.4	17.7	0.058(1.00)	0.058(1.00)
$[\mathrm{Ru(phen)_2(dmby)}]\mathrm{Cl_2}$	1.52	22.2	17.4	0.044(0.75)	0.045(0.78)
$[\mathrm{Ru(phen)(dmby)_2}]\mathrm{Cl_2}$	1.40	22.2	16.9	0.032(0.55)	0.030(0.52)
$[\mathrm{Ru(dmby)_3}]\mathrm{Br_2}$	1.16	21.9	16.6	0.025(0.43)	0.018(0.31)
$[\mathrm{Ru(4,4'\text{-}dimethylbpy)_3}]\mathrm{Cl_2}$	1.49	21.8	16.9	0.066(1.03)	0.062(0.97)

a) Maximum molar extinction coefficient of the first visible CT band (in unit of $10^4\ \mathrm{M^{-1}\,cm^{-1}}$). b) Singlet state energy of the absorption maximum of the first visible CT band(in unit of $10^3\ \mathrm{cm^{-1}}$). c) Triplet state energy assumed to be the energy of the shortest emission peak at 77 K(in unit of $10^3\ \mathrm{cm^{-1}}$). d) Calculated radiative rate constant using a value of $K|M_{SO}|^2$ of 4.87×10^{-7} for the bipyridyl complexes and 2.87×10^{-7} ($\mathrm{M\,cm\,\mu s^{-1}}$) for the phenanthroline complexes. e) Experimentally obtained radiative rate constant (see Table 3). *) Normalized figures of k_r for the bipyridyl and phenanthroline complexes are shown in parentheses.

Table 7. Lifetimes of $[\mathrm{Ru(bpy)_3}]\mathrm{Cl_2}$ and $[\mathrm{Ru(bpy)_2(dmby)}]\mathrm{Cl_2}$ in various solvents at 25 °Ca)

Solvent	$[\mathrm{Ru(bpy)_3}]\mathrm{Cl_2}$ b) $\tau_m/\mu s$	$[\mathrm{Ru(bpy)_2(dmby)}]\mathrm{Cl_2}$ $\tau_m/\mu s$	ANc)
Water	0.65±0.02	0.41±0.03	54.8
Methanol	0.72±0.03	0.44±0.02	41.3
Ethanol	0.74±0.02	0.39±0.02	37.1
Acetonitrile	0.89±0.03	0.59±0.02	19.3
Pyridine	0.92±0.05	0.63±0.03	14.2

a) In nitrogen-bubbled solutions. Excited at 337 nm. b) Ref. 40. c) Gutmann's acceptor number from Ref. 39.

K. Secondly, value of $K|M_{SO}|^2$ is assumed not to be so much affected by dmby substitution. Hence, a value of 4.87×10^{-7} and 2.87×10^{-7} ($\mathrm{M\,cm\,\mu s^{-1}}$) is used as $K|M_{SO}|^2$ for the bipyridyl and phenanthroline complexes, respectively, in order to normalize the calculated values to the experimentally obtained radiative rate constants for the parent complexes (the latter value reasonably agrees with 2.43×10^{-7} for $[\mathrm{Ru(phen)_3}]^{2+}$, but the former is somewhat larger than 3.78×10^{-7} for $[\mathrm{Ru(bpy)_3}]^{2+}$ reported by Demas and Crosby[11]). The results in Table 6 show that agreement between the calculated and experimental radiative rate constant is excellent for the phenanthroline complexes, whereas poor agreement is observed for the bipyridyl complexes. However, it may safely be said that the observed decrease in k_r is, at least qualitatively, due to the decrease in ε(S) and E_T^3/E_S term and the increase in the energy gap term for both the complex series as is expected from Eq. 3.

The larger nonradiative rate constant for the parent bipyridyl complex than for the parent phenanthroline complex is attributed to the difference between the structure of the two ligands; the rigid ring system and planarity of phenanthroline considerably slow down the nonradiative processes. The effect of dmby substitution on the nonradiative rate constant would be largely observed for the complex which has a small value of k_{nr}, *i.e.* the phenanthroline complexes as compared with the bipyridyl complexes. In such a case the values of k_{nr} for the bipyridyl complexes are hardly influenced by dmby if the effect is not large. Nearly the constant values of k_{nr} observed for the bipyridyl complexes may be a reflection of such circumstances.

The above discussion reveals that methyl substituents on the 3,3′-positions of the bipyridyl ligand decrease the visible CTTL absorption intensity and increase the energy gap between the intensity-lending singlet and the emitting triplet state, and that this leads to the decrease in k_r and hence the emission quantum yield. On the contrary, methyl substitution on the 4,4′-positions of the parent ligand, which is considered not to change chelate conformation of the parent ligand believed to be coplanar, produces only a minor change in these factors and thus a relatively small decrease in the yield. Fabian, *et al.*,[20] have reported more marked decreases in the absorption intensities and emission yields of the ruthenium(II) complexes caused by methyl substituents on the sterically hindering 6,6′-positions for bipyridyl and 2,9-positions for phenanthroline than the complexes reported here, and have pointed out that the effects can be reduced to some extent by relief of the steric hindrance by twisting of the ligands. From these comparisons with the other substituted ligand complexes, it may be reasonable to consider that 3,3′-dimethyl-2,2′-bipyridyl in the ruthenium(II) complexes studied takes a twisted, noncoplanar conformation owing to the steric hindrance of the two methyl groups.

At 25 °C, only the lifetime of $[\mathrm{Ru(bpy)_2(dmby)}]\mathrm{Cl_2}$ in the dmby-mixed complexes can be measured because of the low emission intensities. As is seen from Table 7, the lifetimes of the bis(bipyridyl) complex in several solvents are about 2/3 compared with those of the tris(bipyridyl) complex and increase with the decrease in the Gutmann's acceptor number[39] as in the parent complex. This may suggest that the emitting state of the bis(bipyridyl) complex is similar to that of the tris(bipyridyl) complex, *i.e.* CTTL excited state contributed by the CTTS configurations.[16,17]

Values of the radiative (k_r) and nonradiative (k_{nr}) rate constants calculated from Eqs. 1 and 2 using the data in H_2O are 0.065, 1.5 μs^{-1} for $[Ru(bpy)_3]Cl_2$ and 8.8×10^{-4}, 2.4 μs^{-1} for $[Ru(bpy)_2(dmby)]Cl_2$, respectively; namely, the drastical decrease in the yield of the bis(bipyridyl) complex at 25 °C is due mainly to the large decrease in k_r. However, such a result does not agree with the usual understanding that the radiative rate constant is characteristic of a molecule and not dependent on the surrounding conditions, such as temperature or solvent properties. In fact, the value of k_r for $[Ru(bpy)_3]Cl_2$ is nearly the same both at 77 K and 25 °C. On the other hand, the above calculations show another important point that the nonradiative rate constant of the bis(bipyridyl) complex at 25 °C is only slightly larger than that of the parent tris complex, and thus the large decrease in the yield of the bis(bipyridyl) complex cannot be ascribed to the increase in k_{nr}. Consequently two reasons are possible for the decrease in the yield of the bis(bipyridyl) complex at 25 °C; (i) decrease of the formation efficiency of the emitting state (φ_{isc}) and (ii) changes of the circumstances of the excited states in contrast with those at 77 K. According to the first alternative, Eq. 1 does not hold any more and must be replaced by the following expression:

$$Q = \varphi_{isc}k_r/(k_r+k_{nr}) = \varphi_{isc}k_r\tau_m. \qquad (4)$$

φ_{isc} can be estimated if k_r at 25 °C is assumed to be the same as that at 77 K (0.048 μs^{-1}). The value of φ_{isc} obtained in this way is 1.8×10^{-2}, *i.e.* decreased by two orders of magnitude. The cause of the large decrease in φ_{isc}, however, is not obvious at this stage. In order to argue about the second alternative, it is necessary to know about various aspects such as the contributions of the CTTS configurations to the emitting state,[16,17] equilibrium between the CTTL and d-d excited state (this problem is neglected at 77 K),[17,41] as well as the detailed knowledge of the energy levels of each excited states. These data, however, are also insufficient. It is likely that changes in the excited state features result in the decrease of φ_{isc}, but further experiments are needed to establish this view.

Finally it should be noted that the quenching effect of dissolved oxygen in the solvent reported for the tris(bipyridyl)ruthenium(II) complex[42] is also seen in the complexes studied here (Table 4).

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methyl or 2,9-dimethylphen complexes the decrease in the quantum yields is due more to the increase in the nonradiative rate constant. However, recalculations of Q_h using their data suggest that these conclusions seem not to be correct.

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