

Electron transfer quenching of the excited MLCT state of Ru(II) in the double complex salts $[\text{Ru}(\text{bpy})_3]_2[\text{M}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ (M = Co and Fe)

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Abstract

The lifetimes of the excited MLCT states of ruthenium(II) diimine complex ions in the double complex salts, $[\text{Ru}(\text{bpz})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl} \cdot 14\text{H}_2\text{O}$, $[\text{Ru}(\text{bpy})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$, $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$ (bpz = 2,2'-bipyrazine; bpy = 2,2'-bipyridine), were studied in the temperature range 77–353 K. The excited states of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpz})_3^{2+}$ were very rapidly quenched in the double complex salts $[\text{Ru}(\text{bpz})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl} \cdot 14\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ even at 77 K. The lifetime of excited $\text{Ru}(\text{bpy})_3^{2+}$ in the double complex salts containing $\text{Co}(\text{CN})_6^{3-}$ with an excitation energy higher than 2.2 eV was shortened to 30–40 ns at 300 K. Three possible quenching mechanisms, electron transfer, energy transfer and internal conversion to a dissociative state, are examined. The high activation energy (230 meV) of the quenching process is ascribed to the large reorganization energy of electron transfer between the moieties of an excited ruthenium(II) ion and a cobalt(III) ion. Excitation energy transfer is unlikely because of the absence of sensitized emission and the high activation energy of the quenching process. Internal conversion to a dissociative state is less probable because it needs more activation energy (400 meV) than that obtained for the single salts $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ru}(\text{bpy})_3\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

Keywords: Photoinduced electron transfer; Double complex salt; Ruthenium complexes; Cobalt complexes; Iron complexes

1. Introduction

Electron transfer processes within covalently linked donor–acceptor composite molecules have been intensively investigated during this decade. Magnitudes of rate-determining factors, electronic exchange interaction between a donor and an acceptor [1,2] and reorganization energy of high-frequency and low-frequency vibrational modes [2–4] were estimated to interpret rates of non-adiabatic ET processes within donor–acceptor composite molecules. These studies have established that: (i) the extent of electronic exchange interaction is dependent on the electronic structure and the length of the bridging group between a donor and an acceptor [1,2]; (ii) reorientation of polar solvent molecules around a donor–acceptor composite molecules determines the rate of rapid ET for adiabatic processes [2a,3,4]; (iii) the reorganization energy of solvent low-frequency vibrational modes is the major

part of the reaction barrier for weakly exoergic processes [2b,5].

Photoinduced ion–ion reactions of ionic crystals, in which an ion is surrounded by some other ionic species with a constant separation and orientation, have been more rarely investigated. In a guest/host ionic crystal of $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2/[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine), where some sites of the host ion ($\text{Ru}(\text{bpy})_3^{2+}$) are occupied by a guest ion ($\text{Os}(\text{bpy})_3^{2+}$), a rapid excitation energy transfer from the excited host to the guest has been investigated in a wide temperature range [6]¹. Fujita and Kobayashi [7a] have clarified the mechanism of excitation energy transfer from $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Cr}(\text{CN})_6^{3-}$ in the double complex salt

¹ We have recently reported that the luminescence decays of neat crystals of Ru(II) complexes under pulse laser excitation showed excitation power dependence. The decay curves fit the kinetics derived for processes with first- and second-order components. The second-order component, the magnitude of which depends on the excitation intensity, is not attributed to the thermal effects but to exciton annihilation. The details will be published elsewhere.

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$[\text{Ru}(\text{bpy})_3]_3[\text{Cr}(\text{CN})_6]_2$ [7], in which $\text{Cr}(\text{CN})_6^{3-}$ (energy acceptor) is located at the counter-ion site of $\text{Ru}(\text{bpy})_3^{2+}$ (energy donor). The slow rate of excitation energy transfer was ascribed to a small exchange integral and a small spectral overlap integral between the absorption of an acceptor and the emission of a donor, of which the latter can be estimated from the energy gap between the initial and final states, and the Huang–Rhys factor (S) of the high-frequency averaged intramolecular vibrational mode and of the low-frequency averaged vibrational mode, and vibrational frequencies [8]. On the other hand, there is no quantitative study on the rate of electron transfer which an excited ion undergoes with its neighboring ions in double complex salts. The Franck–Condon factor for ET in crystals is expected to be larger than that in polar solutions, because the sum of reorganization energy for the solvent and the averaged, low-frequency vibrational mode is reduced in the crystal containing a few polar molecules solvating to the donor and the acceptor ions.

We report here the rapid quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$ by either $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Co}(\text{CN})_6^{3-}$ in the double complex salts $[\text{Ru}(\text{bpy})_3]_2[\text{M}(\text{CN})_6]\text{Cl}\cdot 8\text{H}_2\text{O}$ ($\text{M}=\text{Co}$ and Fe) and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4\cdot 15\text{H}_2\text{O}$. Temperature dependence of the excited state decay rates of $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl}\cdot 8\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4\cdot 15\text{H}_2\text{O}$ are compared with those of the single salts of $\text{Ru}(\text{bpy})_3^{2+}$ in the temperature range 77–353 K. Three possible mechanisms of the quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$ in the double salts, electron transfer, energy transfer and internal conversion to a dissociating state, are examined.

2. Experimental

2.1. Materials

$\text{Ru}(\text{bpy})_3\text{Cl}_2\cdot 6\text{H}_2\text{O}$ [9], $\text{Ru}(\text{phen})_3\text{Cl}_2\cdot 8\text{H}_2\text{O}$ [9] ($\text{phen}=1,10\text{-phenanthroline}$), and $\text{K}_3\text{Co}(\text{CN})_6$ [10] were synthesized and purified according to literature methods. $\text{K}_3\text{Fe}(\text{CN})_6$ and all ligands were used as purchased. $\text{Ru}(\text{dmbpy})_3\text{Cl}_2\cdot 11\text{H}_2\text{O}$ [11] ($\text{dmbpy}=4,4'\text{-dimethyl-2,2-bipyridine}$) was synthesized according to a literature method, then purified by alumina column chromatography and recrystallized.

$\text{Ru}(\text{bpz})_3\text{Cl}_2\cdot 3\text{H}_2\text{O}$ [12] ($\text{bpz}=2,2'\text{-bipyrazine}$) was kindly provided by Dr A. Yoshimura. The sulfate and tetrafluoroborate salts of $\text{Ru}(\text{bpy})_3^{2+}$ were prepared by metathesis on an anion-exchange column (Dowex 1-X8), and with NaBF_4 solution, respectively, then recrystallized from water.

Anal. $\text{Ru}(\text{bpy})_3\text{SO}_4\cdot 4\text{H}_2\text{O}$: Calc. for $\text{C}_{30}\text{H}_{24}\text{N}_6\text{SO}_4\cdot \text{Ru}\cdot 4\text{H}_2\text{O}$: C, 48.84; H, 4.37; N, 11.39. Found: C, 48.62; H, 4.66; N, 11.31%. $\text{Ru}(\text{bpy})_3\text{BF}_4\cdot 1.5\text{H}_2\text{O}$: Calc. for

$\text{C}_{30}\text{H}_{24}\text{N}_6\text{B}_2\text{F}_8\text{Ru}\cdot 1.5\text{H}_2\text{O}$: C, 46.78; H, 3.53; N, 10.91. Found: C, 46.79; H, 3.51; N, 10.88%.

2.2. Preparation of double complex salts

Crystals of $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl}\cdot 8\text{H}_2\text{O}$ were grown by using a diffusion method [13] in water at room temperature. The crystals obtained after one week were washed with water and dried in air. *Anal.* Calc. for $\text{C}_{66}\text{H}_{48}\text{N}_{18}\text{ClRu}_2\text{Co}\cdot 8\text{H}_2\text{O}$: C, 51.68; H, 4.21; N, 16.44. Found: C, 51.62; H, 4.23; N, 16.41%.

Crystals of $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{BF}_4\cdot 7\text{H}_2\text{O}$, $[\text{Ru}(\text{phen})_3]_3[\text{Co}(\text{CN})_6]_2\cdot 28\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_3[\text{Fe}(\text{CN})_6]\text{Cl}\cdot 8\text{H}_2\text{O}$ were also grown by the diffusion method.

Anal. $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{BF}_4\cdot 7\text{H}_2\text{O}$: Calc. for $\text{C}_{66}\text{H}_{48}\text{N}_{18}\text{BF}_4\text{Ru}_2\text{Co}\cdot 7\text{H}_2\text{O}$: C, 50.58; H, 3.99; N, 16.09. Found: C, 50.47; H, 3.86; N, 16.10%. $[\text{Ru}(\text{phen})_3]_3[\text{Co}(\text{CN})_6]_2\cdot 28\text{H}_2\text{O}$: Calc. for $\text{C}_{120}\text{H}_{72}\text{N}_{30}\text{Ru}_3\text{Co}_2\cdot 28\text{H}_2\text{O}$: C, 50.40; H, 4.51; N, 14.69. Found: C, 50.33; H, 4.50; N, 14.59%. $[\text{Ru}(\text{bpy})_3]_3[\text{Fe}(\text{CN})_6]\text{Cl}\cdot 8\text{H}_2\text{O}$: Calc. for $\text{C}_{66}\text{H}_{48}\text{N}_{18}\text{ClRu}_2\text{Fe}\cdot 8\text{H}_2\text{O}$: C, 51.78; H, 4.21; N, 16.47%. Found: C, 51.74; H, 4.28; N, 16.44%.

Crystals of the double complex salts were also grown by slowly evaporating the solvent, 2:1 (by volume) water/ acetonitrile at room temperature. The crystals were collected by filtration, washed with water, and then dried in air. Crystals of $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4\cdot 15\text{H}_2\text{O}$, $[\text{Ru}(\text{dmbpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl}\cdot 19\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpz})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl}\cdot 14\text{H}_2\text{O}$ were prepared by using this slow evaporation method. *Anal.* $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4\cdot 15\text{H}_2\text{O}$: Calc. for $\text{C}_{132}\text{H}_{96}\text{N}_{36}\text{SO}_4\text{Ru}_4\text{Co}_2\cdot 15\text{H}_2\text{O}$: C, 51.56; H, 4.13; N, 16.40. Found: C, 51.64; H, 4.05; N, 16.42%. $[\text{Ru}(\text{dmbpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl}\cdot 19\text{H}_2\text{O}$: Calc. for $\text{C}_{78}\text{H}_{72}\text{N}_{18}\text{ClRu}_2\text{Co}\cdot 19\text{H}_2\text{O}$: C, 49.30; H, 5.84; N, 13.27. Found: C, 49.21; H, 5.60; N, 13.29%. $[\text{Ru}(\text{bpz})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl}\cdot 14\text{H}_2\text{O}$: Calc. for $\text{C}_{54}\text{H}_{36}\text{N}_{30}\text{Ru}_2\text{FeCl}\cdot 14\text{H}_2\text{O}$: C, 39.29; H, 3.91; N, 25.46. Found: C, 39.39; H, 3.81; N, 25.58%.

2.3. Apparatus and measurements

Phosphorescence spectra of the crystals were recorded on a Hitachi MPF-4 spectrofluorometer with an R298 (Hamamatsu) photomultiplier. The sample crystals were contained in a suprasil cell of 2 mm thickness, a glass capillary of 2 mm diameter, or a copper sample holder. For the emission lifetime and lifetime quenching measurements, the SHG (532 nm, FWHM 10 ns) pulse of a Q-switched $\text{Nd}^{3+}:\text{YAG}$ laser (Quantel YG580) was used for exciting the sample crystals. It should be noted here that the excitation laser intensity was attenuated to less than $\sim 1 \mu\text{J}/\text{pulse}$ by neutral density filters to avoid non-linear photoprocesses such as triplet–triplet annihilation. Emission from the crystals was detected by using a monochromator (Jovin Yvon HR-320) with a photomultiplier (Hamamatsu R636) and a digitizer.

ing oscilloscope (HP 54510A, 8 bit, 250 MHz-1G Sampling/s).

The sample crystals on a copper holder were retained in a cryostat (Oxford DN1740) controlled by a controller (Oxford ITC4) in the temperature region 77–300 K. Above 300 K, the samples, in a thin quartz cell, were put into a circulating water bath (Neslab RTE-B5).

The redox potential of the single complex salt which was either a donor component or an acceptor component of the double complex salts was determined by means of differential-pulse voltammetry with a d.c. pulse polarograph [14]. All voltammograms were obtained at a Pt disk electrode versus SCE in water containing 0.1 M Na_2SO_4 .

3. Results

3.1. Crystals of double complex salts

The component ratio of a cation complex to an anion complex was determined from the result of weight ratio of carbon to nitrogen (C/N) in the elemental analysis. The obtained ratio was found to be 2:1 except for $[\text{Ru}(\text{phen})_3]_3[\text{Co}(\text{CN})_6]_2 \cdot 28\text{H}_2\text{O}$. Even when the stoichiometrical ratio of $\text{Ru}(\text{bpy})_3^{2+}$ – $\text{Co}(\text{CN})_6^{3-}$ was set to be 3:2 to prepare the double complex salts, the results of the component ratio showed 2:1. This was the same in both the diffusion method and the slow evaporation method. If the ratio was 3:2, the value of C/N would be 2.57. But the results of C/N value gave 3.14 which showed the component ratio of 2:1. Other possibilities such as containing K^+ ions or some ligand substitution can be excluded. The inclusion of a simple anion (SO_4^{2-} , Cl^- or BF_4^-) in the double complex salts causes a different energy and lifetime of emission. Although some studies on double complex salts with the same cation–anion combination have reported that the component ratio of the cation to the anion complex was 3:2, these component ratios are probably due to the solid samples not being crystallized but only precipitated [7b,15].

3.2. Emission spectra of double complex salts at 77 and 300 K

Every crystal of the double complex salts studied here exhibited a structured emission at 77 K as Fig. 1 shows, except for the double complex salts containing $\text{Fe}(\text{CN})_6^{3-}$. The values of the highest energy band of emission are shown in Table 1. The value of the highest energy emission band of the double complex salts, $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$, at 77 K is higher by 700–800 cm^{-1} than that of the single complex salt, $[\text{Ru}(\text{bpy})_3]\text{Cl} \cdot 6\text{H}_2\text{O}$.

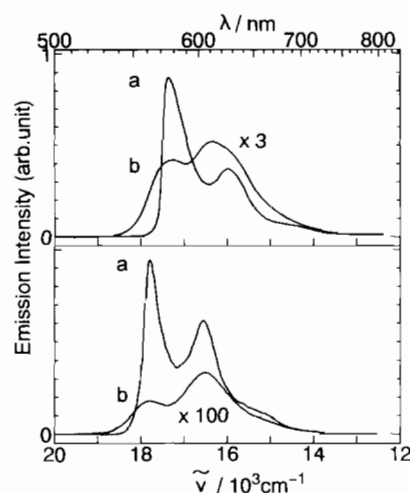


Fig. 1. Emission spectra of crystals of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ at 77 and 295 K. Top: (a) $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ at 77 K; (b) $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ at 295 K. Bottom: (a) $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ at 77 K; (b) $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ at 295 K.

The emission spectra of the crystal samples at ~ 300 K are dependent on the experimental conditions. A large crystal of the sample exhibited the highest energy band of emission as shown in Fig. 1, though the intensity of the highest energy emission band was reduced. On the other hand, the microcrystalline samples did not show the highest energy emission band so that the emission seemingly shifted to lower energy by 1400 cm^{-1} . Reabsorption of the emission at ~ 300 K causes the intensity reduction of the highest energy band, as Yersin et al. previously pointed out [16a]. Inhomogeneous broadening of the absorption band at higher temperatures [16b] might be responsible for the reabsorption of emission. No double complex salts emitted a structureless phosphorescence of $\text{Co}(\text{CN})_6^{3-}$ [17a] in the 550–800 nm region even at 77 K.

Studies on the emission spectrum of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ in the crystal form revealed that the highest energy band of emission above 15 K is a multi-phonon band [18,19]. The whole emission spectrum at 6 K is characterized by a large Huang–Rhys factor ($S=5$) for the lattice phonon modes and a small Huang–Rhys factor ($S \sim 0.1$) for the vibrational mode.

3.3. Decay rates of the excited MLCT state in the temperature range 77–353 K

The MLCT emission of all the ruthenium complexes decayed in a single exponential mode. The lifetimes (τ) at 77 and 300 K are shown in Table 1. The laser intensity for excitation was kept as weak as possible because the excited MLCT decays via T–T annihilation on excitation with the higher intensity laser. Lifetimes (τ_D) of the double complex salts $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot$

Table 1
Energy and lifetime of phosphorescence of ruthenium(II) diimine complex salts

	$\bar{\nu}_{\max}$ (cm ⁻¹) (λ_{\max} (nm)) (77 K)	τ (μ s)	
		r.t.	77 K
Ru(bpy) ₃ Cl ₂ ·6H ₂ O	17400 (574)	1.0	5.3
Ru(bpy) ₃ (BF ₄) ₂ ·1.5H ₂ O	16800 (595)	1.3	4.3
Ru(bpy) ₃ SO ₄ ·4H ₂ O	17100 (585)	0.80	5.4
Ru(bpz) ₃ Cl ₂ ·3H ₂ O	16600 (603)	0.53 ^a	3.7 ^a
Ru(dmbpy) ₃ Cl ₂ ·11H ₂ O	16500 (605)	0.71	3.4
Ru(phen) ₃ Cl ₂ ·8H ₂ O	17200 (583)	1.20	7.0
[Ru(bpy) ₃] ₂ [Co(CN) ₆]Cl·8H ₂ O	17900 (560)	0.03	5.9
[Ru(bpy) ₃] ₂ [Co(CN) ₆]BF ₄ ·7H ₂ O	17400 (576)	0.29	5.9
[Ru(bpy) ₃] ₄ [Co(CN) ₆] ₂ SO ₄ ·15H ₂ O	17800 (563)	0.03	5.1
[Ru(bpy) ₃] ₂ [Fe(CN) ₆]Cl·8H ₂ O		<0.01	<0.01
[Ru(bpz) ₃] ₂ [Fe(CN) ₆]Cl·14H ₂ O		<0.01	<0.01
[Ru(dmbpy) ₃] ₂ [Co(CN) ₆]Cl·19H ₂ O	15800 (634)	0.71	2.4
[Ru(phen) ₃] ₃ [Co(CN) ₆] ₂ ·28H ₂ O	16800 (594)	1.1	6.7

^aThe decay is not single exponential. Only the longest component is shown.

15H₂O were reduced to 30–40 ns at ~300 K. No emission was observed for the double complex salts containing Fe(CN)₆³⁻ as an anion. The ratios of the lifetime of the double complex salts (τ_D) to that of the single complex salt (τ_S) are shown in Table 2.

In the temperature range 77–200 K, the decay rate of the excited MLCT state of the double complex salts [Ru(bpy)₃]₂[Co(CN)₆]Cl·8H₂O and [Ru(bpy)₃]₄[Co(CN)₆]₂SO₄·15H₂O increased with temperature as slowly as those of the single complex salts did. Above 200 K, the decay rate of the double complex salts rapidly increased from 8×10^5 s⁻¹ at 200 K to 4×10^7 s⁻¹ at 295 K. The decay rate of the other excited double complex salt, [Ru(bpy)₃]₂[Co(CN)₆]BF₄·7H₂O,

slowly increased with temperature until 295 K, above which it rose up to 2.4×10^7 s⁻¹ at 353 K from 2×10^5 s⁻¹ at 300 K. A similarly rapid increase in the excited state decay above 300 K was seen for all the ruthenium(II) complexes, Ru(bpy)₃Cl₂·6H₂O, Ru(bpy)₃(BF₄)₂·1.5H₂O and Ru(bpy)₃SO₄·4H₂O.

4. Discussion

4.1. Possible mechanisms of MLCT state quenching

4.1.1. Electron transfer

It is known that the MLCT state of Ru(bpy)₃²⁺ in aqueous solution is quenched by Co(CN)₆³⁻ and

Table 2

Decay ratios of emission at 77 and 300 K and redox potentials of complex ions and Gibbs energy changes of redox processes Ru(NN)₃²⁺ + M(CN)₆³⁻ → Ru(NN)₃³⁺ + M(CN)₆⁴⁻, where NN is diimine ligand and M is either Fe or Co

	τ_D/τ_S ^a		$E^\circ_{\text{Ru}(3+/2+)}^b$ (V)	ΔG° ^d (eV)
	r.t.	77 K		
[Ru(bpy) ₃] ₂ [Fe(CN) ₆]Cl·8H ₂ O	<0.01	<0.002	1.030	-1.50 ^e
[Ru(bpz) ₃] ₂ [Fe(CN) ₆]Cl·14H ₂ O	<0.02	<0.003	1.60 ^e	-0.78 ^f
[Ru(bpy) ₃] ₂ [Co(CN) ₆]Cl·8H ₂ O	0.03	1.1	1.030	-0.32
[Ru(bpy) ₃] ₄ [Co(CN) ₆] ₂ SO ₄ ·15H ₂ O	0.04	0.91	1.030	-0.31
[Ru(bpy) ₃] ₂ [Co(CN) ₆]BF ₄ ·7H ₂ O	0.22	1.4	1.030	-0.26
[Ru(dmbpy) ₃] ₂ [Co(CN) ₆]Cl·19H ₂ O	1.0	0.71	0.857	-0.23
[Ru(phen) ₃] ₃ [Co(CN) ₆] ₂ ·28H ₂ O	0.92	0.96	1.040	-0.19

^a τ_S and τ_D denote the lifetime of a single complex salt and a double complex salt, respectively.

^bRedox potentials measured vs. SCE in water (see text).

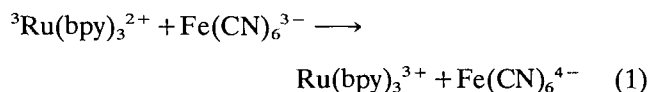
^cA value estimated in our conditions by considering the difference between the values vs. SCE in CH₃CN of Ru(bpy)₃^{3+/2+} and of Ru(bpz)₃^{3+/2+} [15c].

^dValues calculated using Eq. (2). The work term was estimated to be -0.14 eV. Redox potential of Fe(CN)₆^{3-/4-} was measured to be 0.185 V vs. SCE in water. Redox potential of Co(CN)₆^{3-/4-} was estimated to be -1.0 V in the same conditions by considering the difference between the known value (0.36 V) vs. NHE of Fe(CN)₆^{3-/4-} and the theoretical value (-0.83 V [20]) of Co(CN)₆^{3-/4-}.

^eThe excitation energy was assumed to be the same as that of [Ru(bpy)₃]₂[Co(CN)₆]Cl·8H₂O.

^fThe excitation energy was assumed to be the same as that of Ru(bpz)₃Cl₂·3H₂O.

$\text{Fe}(\text{CN})_6^{3-}$ at ambient temperature [21]. The Gibbs energy change for ET quenching of the MLCT state by $\text{Fe}(\text{CN})_6^{3-}$ (Eq. (1)) is calculated to be largely negative (-1.50 eV) for the aqueous solution by putting the redox potentials of the reactants (E°), work terms for the formation of the $\text{Ru}(\text{bpy})_3^{3+}\text{-Fe}(\text{CN})_6^{4-}$ ion-pair with an inter-metal distance (r), and excitation energy (EE) into Eq. (2).



$$\Delta G^\circ = eE^\circ(\text{Ru}^{3+}/\text{Ru}^{2+}) - eE^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + (1/4\pi\epsilon_0)(6e^2 - 12e^2)/\epsilon r + EE \quad (2)$$

The quenching rate of the MLCT state by $\text{Fe}(\text{CN})_6^{3-}$ is thought to occur rapidly, because of a large exoergonicity and small reorganization energy of the averaged low-frequency vibration mode of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ [22] and $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ [23].

As for the quenching of ${}^3\text{Ru}(\text{bpy})_3^{2+}$ by $\text{Co}(\text{CN})_6^{3-}$, whose rate constant is $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous solution at ambient temperature, electron transfer quenching is the most probable [21] because of the small exoergonicity, though the reorganization energy of the low-frequency vibrational mode of $\text{Co}(\text{CN})_6^{3-}/\text{Co}(\text{CN})_6^{4-}$ is not small [21a,c].

It is hard to estimate the extent of the exoergonicity of electron transfer in the crystal of the double complex salts. Excitation energy (EE) among the terms of Eq. (2) is only measurable, which are slightly dependent on the kinds of anions as shown in Table 2. The excitation energy of ${}^3\text{Ru}(\text{bpy})_3^{2+}$ was higher for the double complex salts containing $\text{Co}(\text{CN})_6^{3-}$ as well as for the polyanions of $\text{Cr}(\text{CN})_6^{3-}$ [7] and $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ [7]. The higher energy shift of the excitation energy may arise from the instability of the LUMO of bpy caused by the negative charge of the polyanions lying at the nearest sites. The fact that there is no shift of the excitation energy for $[\text{Ru}(\text{dmbpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 19\text{H}_2\text{O}$ is ascribed to the methyl groups of dmbpy which prevent the LUMO of dmbpy from touching $\text{Co}(\text{CN})_6^{3-}$. Both the redox potentials of the complex ions and the work terms may be less dependent on the kinds of other anions, Cl^- , BF_4^- and SO_4^{2-} , which are shared with two or four cations of $\text{Ru}(\text{bpy})_3^{2+}$.

Ergonicity of electron transfer varies with the media in general. The formation of ionic species in neutral media is much less favourable than in polar solvents. It is unclear how both the ionization potential of an ionic donor and the electron affinity of an ionic acceptor are varied in ionic crystals in comparison with those in polar solvents. In hydrous ionic crystals, the electron transfer products, $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Fe}(\text{CN})_6^{4-}$, may be stabilized by counter-ions and water molecules more than the reactants, $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{CN})_6^{3-}$, because

of the higher charges. The extent of stabilization in hydrous ionic crystals, however, may be different from that in aqueous solution.

The reorganization energy of the charge-transfer transition dipole (λ) may be a measure of the medium effect on the ergonicity of electron transfer. The similar magnitudes of λ in crystal form (65 meV) and in solution (68 meV) at 77 K for the MLCT state formation of $\text{Ru}(\text{bpy})_3^{2+}$, which are estimated from the full-width at half-maximum of the phonon-side band², implies that the MLCT transition dipole is similarly stabilized by both hydrated molecules and counter-ions in crystals and by solvent molecules in solution at 77 K. The emission of $\text{Ru}(\text{bpy})_3^{2+}$ in butyronitrile loses its structure above the melting point of solvent, which is distinct from the crystalline sample at 300 K. The unstructured emission suggests more solvation to the transition dipole in solution.

Provided that the first and the second terms of Eq. (2) for the double complex salts are the same as those in aqueous solution, ${}^3\text{Ru}(\text{bpy})_3^{2+}$ in the double complex salts is likely to be oxidized by the cyanide complexes. The large quenching rates observed for $\text{Fe}(\text{CN})_6^{3-}/\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{CN})_6^{3-}/\text{Ru}(\text{bpz})_3^{2+}$ can be accounted for by the high exoergonicity of the ET process. The rapid quenching of the MLCT emission in $[\text{Ru}(\text{bpy})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ at 77 K implies that the small reorganization energy gives rise to a small activation energy for the ET in the crystal.

As for the double complex salts containing $\text{Co}(\text{CN})_6^{3-}$, the decrease in the lifetime of ${}^3\text{Ru}(\text{bpy})_3^{2+}$ above 200 K is seen for $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$, for which the exoergonicity of electron transfer is calculated to be more than 0.30 eV by using the redox potentials in aqueous solution. No quenching of ${}^3\text{Ru}(\text{bpy})_3^{2+}$ was seen for the double complex salts for which the exoergonicity of ET is calculated in a similar manner to be smaller than 0.26 eV.

4.1.2. Energy transfer

Excitation energy transfer from $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Co}(\text{CN})_6^{3-}$ can be examined from the energetic point of view. The energy of the lowest excited state of $\text{Co}(\text{CN})_6^{3-}$ is estimated to be lower ($17\,000 \text{ cm}^{-1}$) [17a] from the structured phosphorescence at 4 K than that of ${}^3\text{Ru}(\text{bpy})_3^{2+}$, while the lowest absorption band was reported to emerge at $18\,000 \text{ cm}^{-1}$ [17b]. The absence of a sensitized emission of $\text{Co}(\text{CN})_6^{3+}$, however, indicates the low probability of energy transfer. Energy transfer via dipole-dipole interaction is im-

² The structured emission of a crystal of $\text{Ru}(\text{bpy})_3\text{X}_2$ is seen even at 300 K. The reorganization energy of the charge-transfer excitation is estimated from full-width at half-maximum ($\Delta\nu_{1/2}$) of the multi-phonon band by using $\lambda = (\Delta\nu_{1/2})^2/16 (\ln 2)k_B T$ [24].

possible because the absorption of $\text{Co}(\text{CN})_6^{3-}$ is extremely weak. The extent of electronic exchange interaction between Ru^{2+} and Co^{3+} , could be substantially small because the two-center two-electron integral required for energy transfer is small compared to the two-center one-electron integral required for electron transfer [8b].

4.1.3. Internal conversion to a dissociative state

Rapid decay channels of the MLCT state of Ru(II) polypyridine compounds are open at temperatures higher than 273 K in solution, some of which undergo a ligand-substitution reaction. The rapid decay has been described as internal conversion to a metal-centered excited state followed by bond rupture of Ru–N [25]. In crystals of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, the lifetimes of the excited state were shortened to 146 ns at 353 K. A rapid decay was seen for all the single salts at higher temperatures with the exception of anhydrous single salts of $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ and $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$. The temperature dependence of the lifetimes will be compared with those of the complex salts.

4.2. Temperature dependence of quenching rates in

$[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ and
 $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$

Decay rates of $^3\text{Ru}(\text{bpy})_3^{2+}$ in the double complex salts changed slowly in the low temperature region (77–200 K) and rapidly increased with temperature above 200 K. The observed temperature-dependent rates can be expressed by using two temperature-dependent terms,

$$k(T) = A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT) \quad (3)$$

where A_1 and E_1 are the frequency factor and the activation energy for radiationless transition in a low temperature region, respectively, and A_2 and E_2 are for radiationless transition in a high temperature region. It is presumed that the radiationless transition above 200 K is expressed as in Eq. (4) in terms of ergonicity (ΔG°) and reorganization energy (λ_0) because of either weak exoergonicity or endoergonicity

$$k_q(T) = (2\pi/\hbar)H_{\text{rp}}^2/(4\pi\lambda k_{\text{B}}T)^{1/2} \exp[-(\Delta G^\circ + \lambda)/(4\lambda k_{\text{B}}T)] \quad (4)$$

where λ and H_{rp} are reorganization energy and coupling matrix element between a donor and an acceptor. An Arrhenius plot of the quenching rate, $k_q(T) = [k(T) - A_1 \exp(-E_1/RT)]$, of $^3\text{Ru}(\text{bpy})_3^{2+}$ is linear in the tem-

³ The lifetime of $^3\text{Ru}(\text{bpy})_3^{2+}$ was very recently found not to decrease above 300 K for crystals of anhydrous $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$, in contrast to that found for hydrous compounds such as $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$. A more detailed study on the water-assisted decay channel of MLCT is in progress.

perature range 200–295 K for the double complex salts $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$. The activation energy (E_2) and the frequency factor (A_2) are written in terms of λ and H_{rp} as shown in Eqs. (5) and (6), when the entropy change is negligibly small.

$$A_2 = (2\pi/\hbar)H_{\text{rp}}^2/(4\pi\lambda k_{\text{B}}T)^{1/2} \quad (5)$$

$$E_2 = (\Delta H^\circ + \lambda)^2/4\lambda \quad (6)$$

The magnitudes of E_2 and A_2 shown in Table 3 are obtained from the slope and intercept of the plot, $\ln k_q(T) \sim 1/RT$, respectively, as shown in Figs. 2 and 3. The rapid increase in MLCT decay above 200 K implies the presence of an energy barrier (230 meV) for the radiationless process such as electron transfer, energy transfer and internal conversion to a dissociative state. In the following, the three quenching mechanisms will be examined.

4.2.1. Electron transfer

The reorganization energy is calculated to be 1.2–1.3 eV from the value of E_2 . It is regarded as the mean value of the reorganization energies of electron transfer of $\text{Co}(\text{CN})_6^{3-}/\text{Co}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$. Since the reorganization energies of the intramolecular high- and low-frequency vibrational modes of

Table 3

Activation energies (ΔE_2) and frequency factors (A_2) for the fast decay of MLCT state at high temperatures

	ΔE_2 (meV)	A_2 (10^{12} s^{-1})
$[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$	240	0.47
$[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$	230	0.32
$[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{BF}_4 \cdot 7\text{H}_2\text{O}$	410	33
$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$	400	3.1
$\text{Ru}(\text{bpy})_3\text{SO}_4 \cdot 4\text{H}_2\text{O}$	380	1.6
$\text{Ru}(\text{bpy})_3\text{BF}_4 \cdot 1.5\text{H}_2\text{O}$	440	9.1

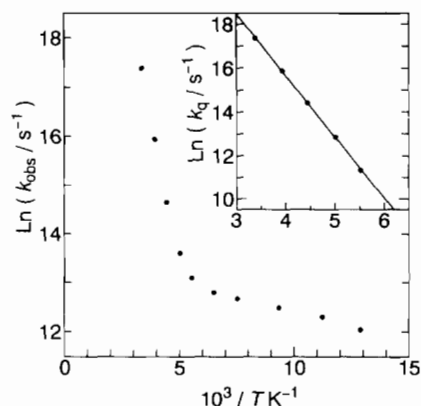


Fig. 2. Temperature dependence of emission decay (k_{obs}) of $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$. Inset: plot of $\ln k_q$ against $1/T$, where $k_q = k_{\text{obs}} - A_1 \exp(-E_1/k_{\text{B}}T)$.

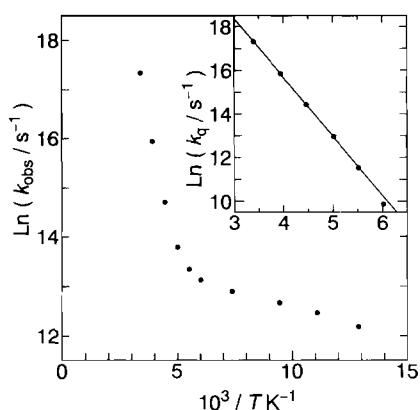


Fig. 3. Temperature dependence of emission decay (k_{obs}) of $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$. Inset: plot of $\ln k_q$ against $1/T$, where $k_q = k_{\text{obs}} - A_1 \exp(-E_1/k_B T)$.

$\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ are almost nil, $\text{Co}(\text{CN})_6^{3-}/\text{Co}(\text{CN})_6^{4-}$ must be responsible for the one observed. The reorganization energy of $\text{Co}(\text{CN})_6^{3-}/\text{Co}(\text{CN})_6^{4-}$ is estimated to be 2.4–2.6 eV from the observed averaged value. A smaller frequency factor ($\sim 4 \times 10^{12} \text{ s}^{-1}$) than the frequency of the Co–CN vibration indicates that the ET processes are non-adiabatic.

If the entropy term ($T\Delta S^\circ$) is not negligibly small as is seen for redox processes of $\text{Co}^{3+}/\text{Co}^{2+}$ [2b] and $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ [26], A_2 and E_2 are replaced by Eqs. (5') and (6'), respectively [2b].

$$A_2 = (2\pi/\hbar) H_{\text{rp}}^2 / (4\pi\lambda k_B T)^{1/2} \exp[(\Delta G^\circ + \lambda) \Delta S^\circ / 2\lambda k_B] \quad (5')$$

$$E_2 = (\Delta H^\circ + \lambda)^2 / 4\lambda - (T\Delta S^\circ)^2 / 4\lambda \quad (6')$$

The intercept (A_2) could be enhanced three hundred times by the entropy term. The second term of Eq. (6') amounts to only 23 meV when $\lambda = 1 \text{ eV}$ and $T\Delta S^\circ = 0.3 \text{ eV}$. Therefore, the value of λ estimated above is reliable.

The reorganization energy of the solvent low-frequency vibrational mode in the crystals can be smaller than that in solution because the number of water molecules solvating to the reactants are less than a quarter of the total. The inner-sphere reorganization energy of $\text{Co}(\text{CN})_6^{3-}/\text{Co}(\text{CN})_6^{4-}$ could be very large because the stable form of the reduced complex is not $\text{Co}(\text{CN})_6^{4-}$ but $\text{Co}(\text{CN})_5^{3-}$, in which one of the Co–CN bonds at the axial position is broken and the other is larger than those in the plane. The value of λ is comparable with that for $\text{Co}(\text{NH}_3)_6^{3+}/\text{Co}(\text{NH}_3)_6^{2+}$, which was calculated from the self-exchange electron transfer rate and the reorganization energy of the solvent low-frequency mode or by using the difference in the bond length between Co(II)– NH_3 and Co(III)– NH_3 and the force constants of the Co– NH_3 vibration [27,28].

4.2.2. Energy transfer

Excitation energy transfer from $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Co}(\text{CN})_6^{3-}$ is weakly exoergonic ($780\text{--}880 \text{ cm}^{-1}$). The temperature dependence of the energy transfer is expressed by Eq. (5) in terms of the reorganization energy of the reactants and the exoergonicity as in the cases of a weak exoergonic electron transfer. The magnitude of λ for the energy transfer is estimated at 350 meV, the average of $\text{Co}(\text{CN})_6^{3-}$ (560 meV) [17a] and $\text{Ru}(\text{bpy})_3^{2+}$ (130 meV). The activation energy (40 meV) calculated for the energy transfer using Eq. (6) is very close to that observed (5–40 meV) for the charge-transfer energy transfer between ruthenium(II) moieties⁴. The calculated activation energy (40 meV) is too small to account for the observed one (230 meV).

4.2.3. Internal conversion to a dissociative state

In all the single complex salts without an electron acceptor, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, $[\text{Ru}(\text{bpy})_3]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O}$, the rapid quenching process occurred above 295 K as Fig. 4 shows. Both the activation energy and frequency factor are larger (400 meV and $\sim 10^{13} \text{ s}^{-1}$, respectively) than those for the double complex salts mentioned above, irrespective of the kinds of simple anions and the number of water molecules. The differences in the activation energy between the double complex salts and the single complex salts are much larger than the experimental error. A similar temperature dependence of the decay rates above 295 K was observed for $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{BF}_4 \cdot 7\text{H}_2\text{O}$ as shown in Fig. 5. Such a higher activation

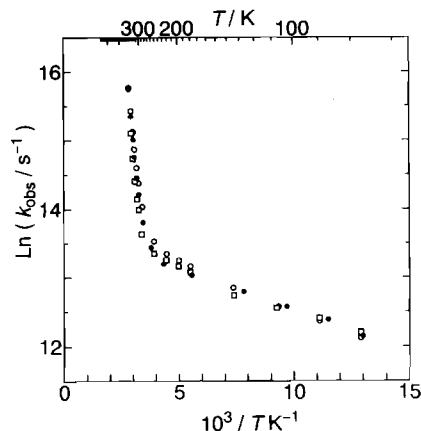


Fig. 4. Temperature dependence of emission decays (k_{obs}) of single complex salts. ●, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$; □, $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O}$; ○, $[\text{Ru}(\text{bpy})_3]\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

⁴ Activation energies were 5 meV in a frozen butyronitrile (77–110 K) and 40 meV in a fluid butyronitrile (170–330 K) for Ru^{2+} -to- Ru^{2+} energy transfer within $(\text{bpy})_2\text{Ru}(\text{bpbimH}_2)\text{Ru}(\text{dcebpy})_2^{4+}$, where bpbimH_2 and dcebpy are 1,2-(bis(2-pyridyl)dibenzimidazole) and 4,4'-dicarboethoxy-2,2'-bipyridine, respectively. Details will be published elsewhere.

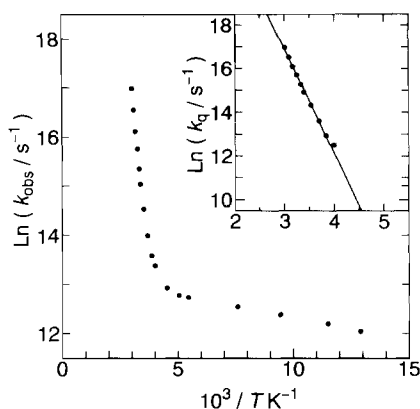


Fig. 5. Temperature dependence of emission decays (k_{obs}) of $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{BF}_4 \cdot 7\text{H}_2\text{O}$. Inset: plot of $\ln k_q$ against $1/T$, where $k_q = k_{\text{obs}} - A_1 \exp(-E_1/k_B T)$.

energy for the MLCT state decay of $\text{Ru}(\text{bpy})_3^{2+}$ in various solvents above 273 K has been ascribed to an internal conversion to a metal-center excited state followed by rupture of the Ru–N bond. Consequently, the rapid decay of $^3\text{Ru}(\text{bpy})_3^{2+}$ in the double complex salts $[\text{Ru}(\text{bpy})_3]_2[\text{Co}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_4[\text{Co}(\text{CN})_6]_2\text{SO}_4 \cdot 15\text{H}_2\text{O}$ cannot be ascribed to the internal conversion to a dissociated state.

5. Conclusions

(1) Excited MLCT states of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpz})_3^{2+}$ undergo electron transfer reaction with $\text{Fe}(\text{CN})_6^{3-}$ in the double complex salts $[\text{Ru}(\text{bpz})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl} \cdot 14\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_3]_2[\text{Fe}(\text{CN})_6]\text{Cl} \cdot 8\text{H}_2\text{O}$ at 77 and 295 K. The reorganization energy in the crystal is reduced to some extent because of the small number of water molecules in the crystals.

(2) The excitation energy of the MLCT state of $\text{Ru}(\text{bpy})_3^{2+}$ in double complex salts is affected by the negative charge of the complex counter-ions. The MLCT state of $\text{Ru}(\text{bpy})_3^{2+}$ with an excitation energy higher than 2.2 eV undergoes electron transfer above 200 K with $\text{Co}(\text{CN})_6^{3-}$ lying at the neighboring sites. The activation energy of the electron transfer process is ascribed to the large reorganization energy of the low-frequency intramolecular vibrational mode of $\text{Co}(\text{CN})_6^{3-}/\text{Co}(\text{CN})_6^{4-}$.

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