Crystal Structure and Energy Transfer in Double-Complex Salts Composed of Tris(2,2′-bipyridine)ruthenium(II) or Tris(2,2′-bipyridine)osmium(II) and Hexacyanochromate(III)

Takuhiro Otsuka, Naoto Takahashi, Naoki Fujigasaki, Akiko Sekine, Yuji Ohashi, and Youkoh Kaizu*

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku,
Tokyo 152-8551, Japan

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In crystals of double-complex salts $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ ($M^{2+} = Ru^{2+}$, Os^{2+}; bpy = 2,2′-bipyridine), luminescence from ^{3}CT state of $[M(bpy)_3]^{2+}$ is partially quenched by $[Cr(CN)_6]^{3-}$ at 77 K and room temperature (RT). This quenching is attributed to intermolecular excitation energy transfer from the ^{3}CT state of $[M(bpy)_3]^{2+}$ to the ^2E_g state of $[Cr(CN)_6]^{3-}$. Crystal structure and crystal parameters of $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$: monoclinic, $C2$, $a = 22.384(4)$ Å, $b = 13.827(4)$ Å, $c = 22.186(3)$ Å, $\beta = 90.70(2)°$, $V = 6866(2)$ Å^3, $Z = 4$, $R = 0.0789$, $R_w = 0.1932$: are almost the same as those of $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$: monoclinic, $C2$, $a = 22.414(2)$ Å, $b = 13.7686(15)$ Å, $c = 22.207(2)$ Å, $\beta = 90.713(8)°$, $V = 6852.9(12)$ Å^3, $Z = 4$, $R = 0.0554$, $R_w = 0.1679$. Moreover, these double complex salts have the same distance and relative orientation between donor and acceptor. The rate of intermolecular energy transfer from $[M(bpy)_3]^{2+}$ to $[Cr(CN)_6]^{3-}$ was evaluated by the decay time of luminescence from ^{3}CT state of $[M(bpy)_3]^{2+}$ in single- and double-complex salts. The rate of energy transfer in $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (4.9×10^7 s^{-1}) is about eight times larger than that in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (6.0×10^6 s^{-1}) at 77 K. The difference of energy transfer rate is brought about by only the spectral overlap between the normalized luminescence spectrum from the ^{3}CT state of donor ($[M(bpy)_3]^{2+}$) and the normalized excitation spectrum of the ^2E_g state of acceptor ($[Cr(CN)_6]^{3-}$) in the salts. Decay rates of the ^{3}CT state in $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ were measured as a function of temperature. A large enhancement of a decay rate from the ^{3}CT state was obtained for $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ as the temperature was increased. This result implies that an additional path from the ^{3}CT state of $[Ru(bpy)_3]^{2+}$ to the $^2T_{2g}$ state of $[Cr(CN)_6]^{3-}$ would be opened for energy transfer with a rise in temperature in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$.

Introduction

Recently, a large number of works regarding the excitation energy transfer and migration are carried out between rare-earth metal ions in solids.[1] In a study on energy transfer between transition metal complexes, intramolecular energy transfer is mainly investigated in solution with the covalently linked binuclear systems comprising polypyridine ruthenium(II) and osmium(II) complexes [2−7] and with the bi- and trinuclear complexes that cyanide ion links ruthenium(II) ion to chromium(III) ion.[8,9] In contrast, there are only a few papers of the intermolecular energy transfer between transition-metal complexes in crystals,[10−18] although the relative orientation and distance can be determined exactly with X-ray structure analysis. It has been considered that, in solid state, environment effects can be important and the clear presentation of energy transfer is difficult.

On the study of energy transfer between chromium(III) and chromate(III) complexes in double-complex salt, it was not clear whether the energy transfer occurred or not.[12−14] However, Castelli and Forster reported that the transfer occurred in $[Cr(en)_3][Cr(CN)_6]{\cdot}2H_2O$ (en = ethylenediamine) because lifetime of the ^2E_g state of donor $[Cr(en)_3]^{3+}$ (6.0 ns) is agreement with rise time of the ^2E_g state of acceptor $[Cr(CN)_6]^{3-}$ (6.2 ns) in 1975.[15]

Fujita and Kobayashi observed the emission from the ^2E_g state of chromate(III) complex after irradiation of $[Ru(bpy)_3]^{2+}$ in the double-complex salts, $[Ru(bpy)_3]_3[Cr(A)_6]_2$ ($A = CN^-$, NCS^-) and $[Ru(bpy)_3]_3[Cr(A{-}A)_3]_2$ ($A{-}A = C_2O_4{}^{2-}$, $C_3H_2O_4{}^{2-}$) in 1970.[16−19] On the basis of luminescence intensity of

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$[Ru(bpy)_3]^{2+}$ and the viewpoint of spin conservation rule, they concluded that the main path of energy transfer was from the ^{1}CT state ($[Ru(bpy)_3]^{2+}$) to the $^4T_{2g}$ state (Cr^{3+}) when the $^4T_{2g}$ state is energetically lower than the ^{1}CT state (e.g. $[Ru(bpy)_3]_3[Cr(ox)_3]_2$, $[Ru(bpy)_3]_3[Cr(mal)_3]_2$ and $[Ru(bpy)_3]_3[Cr(NCS)_6]_2$), otherwise the path was from the ^{3}CT state ($[Ru(bpy)_3]^{2+}$) to the ^2E_g state (Cr^{3+}) (e.g. $[Ru(bpy)_3]_3[Cr(CN)_6]_2$). They also proposed that the energy-transfer efficiency of the former case was very high, while that of the latter case was low. Recently, we have briefly reported the energy transfer through the path from the ^{3}CT state to the ^2E_g state instead of the path from the ^{1}CT state to the $^4T_{2g}$ state in a crystal of the double-complex salt $Na[Ru(bpy)_3][Cr(ox)_3]$, although the $^4T_{2g}$ state is lower than the ^{1}CT state.[20]

As mentioned above, only the path of energy transfer has been discussed in the double complex in solids. On the contrary, the energy-transfer rate has not been investigated. In general, the energy-transfer rate depends on the distance, relative geometry, and spectroscopic character of donor and acceptor. In this work, we examined on a rate of the photoexcited energy transfer in the double-complex salts with the same distance and relative geometry between donor and acceptor, however, with different spectroscopic characters. We discuss the relationship of energy-transfer rates and spectroscopic character in the double-complex salts. The crystallographic character shows that $[Os(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ is almost the same crystal and molecular structures as $[Ru(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ and the distance between central metal ions ($M^{2+}-Cr^{3+}$) is about 9.2 Å^3 for both double-complex salts. The energy-transfer rate from the ^{3}CT state of $[Os(bpy)_3]^{2+}$ to the ^2E_g state of $[Cr(CN)_6]^{3-}$ in $[Os(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ (4.8×10^7 s^{-1}) is eight times larger than that in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ (6.0×10^6 s^{-1}) at 77 K. This ratio agrees with a ratio of the spectral overlap between normalized donor luminescence from the ^{3}CT state and normalized acceptor spectra of the ^2E_g state. These results show that the energy-transfer rate depends on the spectral overlap.

The temperature dependence of the decay rate of ^{3}CT in the double complex salts was examined in the temperature range of 77−300 K. The decay rates in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ increased rapidly above 240 K. From the analysis of Arrhenius plots, the activation energy was evaluated at 2300 cm^{-1} in the temperature range above 240 K. On the contrary, in $[Os(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$, the decay rates of ^{3}CT increased slowly in the temperature range 77−300 K. These results suggest that another energy-transfer path is competitive with the path from the ^{3}CT state to the ^2E_g state in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ at RT. The new path would be through the $^2T_{2g}$ state ($[Cr(CN)_6]^{3-}$) which is higher than ^{3}CT state of $[Ru(bpy)_3]^{2+}$.

Experimental Section

Compounds. $[Ru(bpy)_3]Cl_2\cdot 6H_2O$,[21] $[Zn(bpy)_3]Cl_2\cdot 6H_2O$,[22] $K_3[Cr(CN)_6]$,[23] and $K_3[Co(CN)_6]$[24] were prepared by literature procedures. $[Ru(bpy)_3]Br_2\cdot 6H_2O$ was obtained by double decomposition of sodium bromide (NaBr) and $[Ru(bpy)_3]Cl_2\cdot 6H_2O$. $[Os(bpy)_3]Cl_2\cdot 6H_2O$ was obtained by double decomposition of silver chloride (AgCl) and $[Os(bpy)_3]I_2\cdot 6H_2O$ which was prepared by a literature method modified with NH_4OsCl_6, 2,2′-bipyridine, and KI.[25] All compounds were purified by recrystallization from aqueous solutions at least three times in this work. All complexes were identified by luminescence and absorption spectra, molar extinction coefficient, and elemental analysis. The values of molar extinction coefficient were within ±5% of the literature's values. The single crystals of double-complex salts $[M(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ could be obtained by diffusion method: careful layering of concentrated acetone−water (1/1 v/v) solution of $[M(bpy)_3]^{2+}$ upon top of a concentrated aqueous solution of $[Cr(CN)_6]^{3-}$ and by setting this aside at room temperature for about a week. The double-complex salts were identified by elemental analysis. (Calcd for $[Os(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$: C, 46.49; H, 3.78; N, 14.79%. Found: C, 46.33; H, 3.66; N, 14.94. Calcd for $[Ru(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$: C, 51.92; H, 4.23; N, 16.51. Found: C, 51.76; H, 4.03; N, 16.53.) Doped crystals of 1% $M^{2+}/[Zn(bpy)_3]Cl_2\cdot 6H_2O$ and 1% $M^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ were obtained by using $[Zn(bpy)_3]^{2+}$ including 1% $[M(bpy)_3]^{2+}$.

Measurement. Luminescence spectra were measured on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier. The light of 21700 cm^{-1} was used as excitation light. The samples were put into a quartz capillary of 3 mm diameter and immersed directly in the coolant (liquid nitrogen). The capillary was filled with nitrogen gas to remove oxygen molecules in air since there is a possibility that luminescence from $[M(bpy)_3]^{2+}$ is partially quenched by oxygen molecules. Excitation spectra were also measured on a Hitachi 850 spectrofluorometer by monitoring the luminescence maximum. The sensitivity of the spectroscope and photomultiplier were corrected with *m*-dimethylaminobenzene in benzene−hexane (3/7 v/v) and 4-(dimethylamino)-4′-nitrosylbenzene in *o*-dichlorobenzene.[26]

Luminescence decay of the double-complex salt was determined by means of the two-dimensional photon-counting method (Hamamatsu Photonics model C4780 and Hamamatsu Photonics streak-scope model C4334). Subnanosecond pulses from a nitrogen-dye laser (Laser Photonics, Inc., model LN120C nitrogen laser) were used for excitation incorporated with a C500 (Exciton Chemical Co.) dye generating 525 nm pulses. To samples whose lifetime is more than 200 ns, luminescence decay was recorded on an oscillograph (Lecroy, model 9450) following excitation with the second harmonics (532 nm, fwhm 5 ns) of a Nd:YAG Laser (Spectron, model SL 401). The measurements of temperature dependence of luminescence decay were carried out with variable temperature unit (Oxford Instruments Ltd. temperature controller model ITC4 and variable temperature liquid nitrogen cryostat DN1704) at the temperature range of 77−320 K. Above 320 K, the crystal lattices of the double complex salts are destroyed by dehydration of some solvent water molecules. Lifetimes were estimated by fitting the decays to a single or double exponential function. The measurements were carried out at least five times with the samples prepared by the same procedure. The luminescence spectra and lifetimes were found to be reproducible within experimental error.

Absorption spectra were recorded on a Hitachi spectrophotometer model 330 at room temperature.

X-ray Crystal Structure Determinations. Intensity data were collected at room temperature on a Weissenberg type diffractometer with imaging plates (Rigaku, R-Axis-IIcs) within 3 h without decomposition due to desolvation. The Mo Kα radiation ($\lambda = 0.710\,73$ Å) monochromated with graphite was used. The correction for Lorentz and polarization but no absorption or extinction corrections were applied. Crystal data and refinement details for $[Os(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ are listed in Table 2. The crystal structure was solved by the direct methods with the program SHELXS-86,[27] and refined by full-matrix least squares on F^2 values using SHELXL-93.[28] Non-hydrogen atoms were refined with anisotropic temperature factors. The parameters of hydrogen atoms were obtained geometrically and refined with the riding model and isotropic temperature factors. In the final refinement (Δ/σ) max became 0.002. The maximum and minimum peaks on the final difference map were 5.31 and −5.46 e A^{-3} in the neighborhood of the Os atom.

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Table 1. Lifetime and Decay Rate of ^{3}CT State of $[M(bpy)_3]^{2+}$ ($M^{2+} = Ru^{2+}, Os^{2+}$) and Estimated Rate Constant of Energy Transfer (k_{ET}) in Various Crystals at 77 K and RT

Sample	Lifetime/ns		Decay rate/10^6 s^{-1}		k_{ET}/10^6 s^{-1}	
	77 K	RT	77 K	RT	77 K	RT
$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$	5500	960	0.18	1.0		
$[Ru(bpy)_3]SO_4 \cdot 8H_2O$	3800	730	0.26	1.4		
$[Ru(bpy)_3]I_2 \cdot 6H_2O$	3600		0.28			
$1\%Ru^{2+}:[Zn(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$	5900		0.17			
$[Ru(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	160	14	6.3	71	6.0	70
$[Ru(bpy)_3]_2[Cr(CN)_6]Br \cdot 8H_2O$	190		5.3		5.0	
$1\%Ru^{2+}:[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	200	36	5.0	28	4.8	27
$[Os(bpy)_3]Cl_2 \cdot 6H_2O$	760	130	1.3	7.7		
$[Os(bpy)_3]SO_4 \cdot 8H_2O$	700		1.4			
$1\%Os^{2+}:[Zn(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$	1000		1.0			
$[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	20	8.6	50	120	49	110
$1\%Os^{2+}:[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	25	12	40	83	39	76

Table 2. Activation Energies (ΔE/cm^{-1}) and Frequency Factors (A/s^{-1}) of ^{3}CT State

Sample	$A_1/10^7$	ΔE_1	$A_2/10^8$	ΔE_2	$A_3/10^{12}$	ΔE_3
$[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	6.0	20	1.6	210		
$1\%Os^{2+}:[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	4.0	5.0	1.3	220		
$[Ru(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	1.0	30	0.6	240	3.3	2300
$1\%Ru^{2+}:[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$	0.6	20	0.5	230	2.6	2700
$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$[a]					3.1	3200
$[Ru(bpy)_3]SO_4 \cdot 4H_2O$[a]					1.6	3040
$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$[a]					9.1	3520
$[Ru(bpy)_3]_2[Co(CN)_6]BF_4 \cdot 7H_2O$[a]					33	3280

[a] Ref. (51).

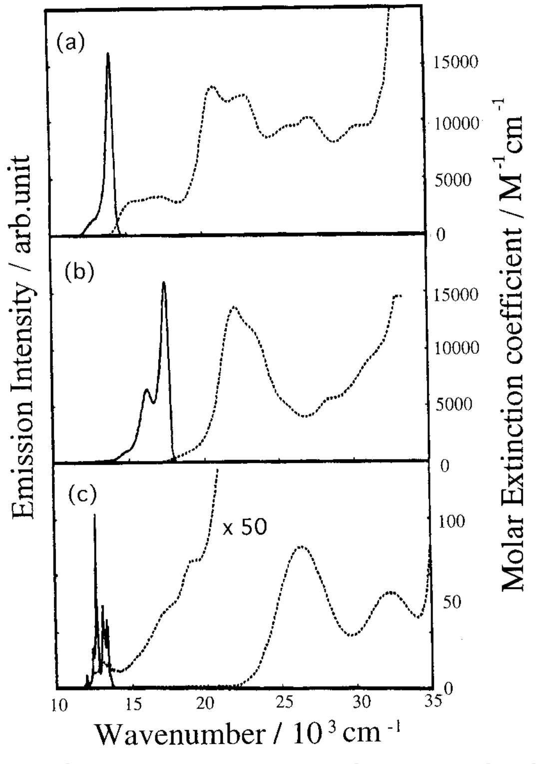

Figure 1. Absorption spectra in aqueous solution at RT (dotted line) and emission spectra in rigid solution of water−ethanol (1/1 v/v) at 77 K (solid line): (a) $[Os(bpy)_3]Cl_2 \cdot 6H_2O$; (b) $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$; (c) $K_3[Cr(CN)_6]$.

Results and Discussion

Luminescence and Absorption Spectra of Donors and Acceptor. Figure 1 shows absorption spectra in water at RT and luminescence spectra in rigid solution of water−ethanol (1/1 v/v) at 77 K. In donor complexes $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ (see Figure 1a,b), the band at 23 000 cm^{-1} is assigned to singlet metal-to-ligand charge-transfer excited state ^{1}CT,[29−32] and the band at 15 000 cm^{-1} in $[Os(bpy)_3]^{2+}$ is assigned to the ^{3}CT state.[33] The luminescence at 14 000 cm^{-1} for $[Os(bpy)_3]^{2+}$ and 16 000 cm^{-1} for $[Ru(bpy)_3]^{2+}$ is assigned to a phosphorescence from the ^{3}CT state.[29−32] The energy level of the ^{3}CT state of $[Os(bpy)_3]^{2+}$ is lower than that of $[Ru(bpy)_3]^{2+}$ by about 3500 cm^{-1}. As shown in Figure 1c, the bands at 26 000 and 32 000 cm^{-1} in acceptor $[Cr(CN)_6]^{3-}$ are assigned to Laporte-forbidden spin-allowed d−d transition from the ground state $^4A_{2g}$ to $^4T_{2g}$ and $^4T_{1g}$,[34] respectively. There are spin-forbidden bands at 12 500, 13 000, and 18 000 cm^{-1} which are assigned to ^2E_g, $^2T_{1g}$, and $^2T_{2g}$,[34] respectively. These molar extinction coefficients are very small and less than 1 M^{-1} cm^{-1}. The emission from $[Cr(CN)_6]^{3-}$ is assigned to a phosphorescence arising from $^2E_g \rightarrow {}^4A_{2g}$.[35] At 21 700 cm^{-1} (460 nm) which is exciting wavenumber in this work, molar extinction coefficients of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ are about 14 000 M^{-1} cm^{-1}, while that of $[Cr(CN)_6]^{3-}$ is at most 1 M^{-1} cm^{-1}. Therefore, $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes only absorb the excitation light at 21 700 cm^{-1} in the double-complex salts.

Luminescence and Excitation Spectra of Double-Complex Salts. Figure 2a,d shows the luminescence spectra of $[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ and $[Ru(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ excited at 21 700 cm^{-1}, respectively. Each pure double-complex salt emits not only broad-band phosphorescence from the ^{3}CT state of $[Os(bpy)_3]^{2+}$ at 14 300 cm^{-1} and $[Ru(bpy)_3]^{2+}$ at 17 800 cm^{-1} but also a narrow-band one from the ^2E_g state of $[Cr(CN)_6]^{3-}$ at 12 500 cm^{-1}. Both luminescence spectra of $[M(bpy)_3]_2[Cr(CN)_6]Br \cdot 8H_2O$ and $[M(bpy)_3]_4[Cr(CN)_6]_2SO_4 \cdot xH_2O$ agree with that of $[M(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$. Irradiation on crystalline $K_3[Cr(CN)_6]$ with the light of 21 700 cm^{-1}

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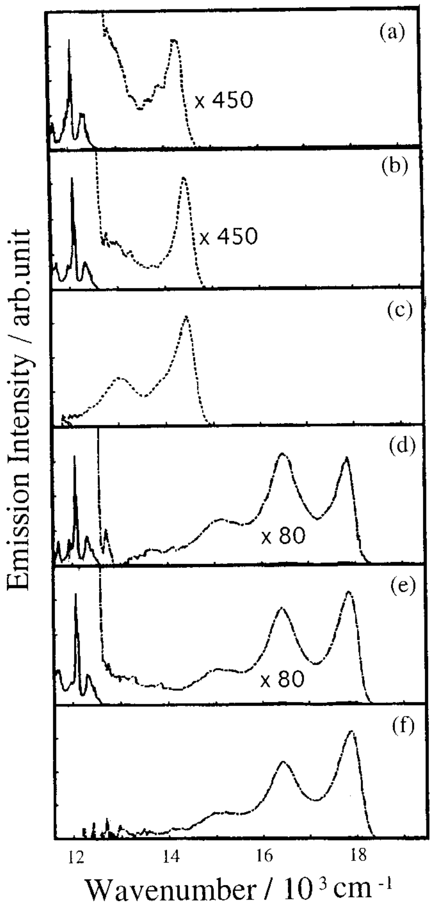

Figure 2. Emission spectra of $[Os(bpy)_3]^{2+}$ (dot line), $[Ru(bpy)_3]^{2+}$ (dashed line) and $[Cr(CN)_6]^{3-}$ (solid line) in double complex salts at 77 K: (a) $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$; (b) 1%$Os^{2+}$/$[Zn(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$; (c) 1% Os^{2+}/$[Zn(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$; (d) $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$; (e) 1% Ru^{2+}/$[Zn(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$; (f) 1% Os^{2+}/$[Zn(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$.

gives no phosphorescence because there is no appreciable absorption in this spectral region (see Figure 1c). These results indicate that excitation energy transfer occurs from $[Os(bpy)_3]^{2+}$ or $[Ru(bpy)_3]^{2+}$ to $[Cr(CN)_6]^{3-}$. As shown in Figure 2, no influence of $[M(bpy)_3]^{2+}$ on the emission spectra of $[Cr(CN)_6]^{3-}$ was observed. Since, in general, phosphorescence from chromate(III) complex is very sharp and influenced by their environment,[36-40] the agreement between the obtained emission spectra of $[Cr(CN)_6]^{3-}$ in the pure double-complex salts (see Figure 2a,d) indicates that $[Cr(CN)_6]^{3-}$ is located on the same environment in the both double-complex salts examined in this work.[41]

The energy transfer is also supported by excitation spectra. Figure 3a,b show the excitation spectra of the pure single-complex salts of $[Os(bpy)_3]Cl_2{\cdot}6H_2O$ and $K_3[Cr(CN)_6]$ at 77 K, respectively. Figure 3c shows the excitation spectrum on monitoring the luminescence maximum of $[Cr(CN)_6]^{3-}$ (at 12 000 cm^{-1}) in the crystal of $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ at 77 K. An agreement of Figure 3a,c shows that the energy transfer from $[Os(bpy)_3]^{2+}$ to $[Cr(CN)_6]^{3-}$ surely occurs and there is no interaction between donor's and acceptor's complexes in the ground state. Here, the excitation spectra of $[Os(bpy)_3]^{2+}$ in pure complex salts are very different from the absorption spectrum of solution (see Figure 1a), since concentration of $[Os(bpy)_3]^{2+}$ in the crystals is too high for the measurement of absorption and excitation spectra. In fact, an excitation spectrum of the doped double-complex salt is similar to the absorption spectrum of solution as shown in Figure 3d. The result of the ruthenium(II) analogue is similar to that of the osmium(II) one.

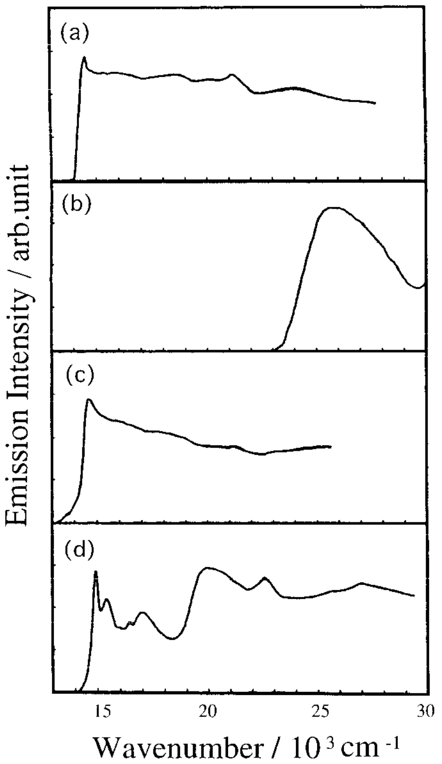

Figure 3. Excitation spectra of single- and double-complex salts at 77 K: (a) $[Os(bpy)_3]Cl_2{\cdot}6H_2O$ (monitored at 14 000 cm^{-1}); (b) $K_3[Cr(CN)_6]$ (monitored at 12 000 cm^{-1}); (c) $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (monitored at 12 000 cm^{-1}); (d) 1%Os^{2+}/$[Zn(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (monitored at 12 000 cm^{-1}).

The quenching of $[M(bpy)_3]^{2+}$ by $[Cr(CN)_6]^{3-}$ is not caused by electron transfer since the luminescence of quencher $[Cr(CN)_6]^{3-}$ is sensitized very much; moreover, electron transfer is prohibited thermodynamically.[42]

Luminescence Lifetime and Energy-Transfer Rate. The lifetimes of ^3CT state of $[M(bpy)_3]^{2+}$ in various crystals are summarized in Table 1. All decay curves at 77 K are single-exponential when the laser power of excitation light is lowered. The lifetimes of $[M(bpy)_3]^{2+}$ in pure double-complex salts are much shorter than those in pure single-complex salts. The lifetime decrease of pure double-complex salts is not brought about by a difference in the crystal lattice between single- and double-complex salts. X-ray powder patterns show that a crystal lattice of $[M(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$ is the same as that of $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ and is different from that of the single-complex salt. However, lifetimes of ^3CT state in $[M(bpy)_3]_2$-

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(41) The position of luminescence maxmum and the shape of luminescence spectra of $[Cr(CN)_6]^{3-}$ are very different in various crystals. For example; maximum of $[Cr(CN)_6]^{3-}$ at 77 K: 11 900 cm^{-1} in $[Ru(5,5'dmbpy)_3]_2[Cr(CN)_6]Cl{\cdot}xH_2O$ (5,5′dmbpy = 5,5′-dimethyl-2,2′-bipyridine), 12 100 cm^{-1} in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$, 12 600 cm^{-1} in $K_3[Cr(CN)_6]$.

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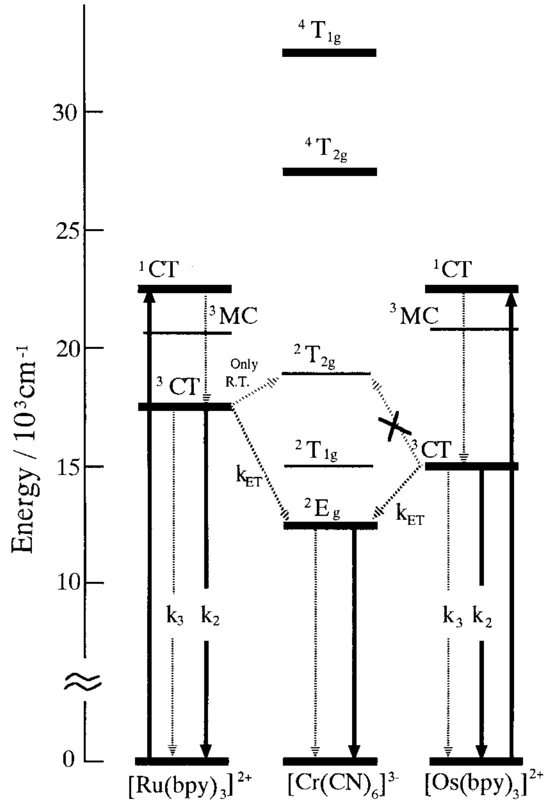

Figure 4. Energy level diagram of $[Os(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$, and $[Cr(CN)_6]^{3-}$: radiative transition (bold line); nonradiative transition (dot line).

$[Co(CN)_6]Cl \cdot 8H_2O$ are almost the same as that of the single-complex salts. In $[M(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$, energy and electron transfer from $[M(bpy)_3]^{2+}$ to $[Co(CN)_6]^{3-}$ cannot occur at 77 K. In short, the lifetime of $[M(bpy)_3]^{2+}$ is almost constant in any crystal which does not contain energy and electron acceptors. Thus, the decrease of lifetime in the double-complex salts containing $[Cr(CN)_6]^{3-}$ is caused by the excitation energy transfer from the ^3CT state of $[M(bpy)_3]^{2+}$ to the ^2E_g state of $[Cr(CN)_6]^{3-}$.

Energy levels of $[M(bpy)_3]^{2+}$ and $[Cr(CN)_6]^{3-}$ are schematically shown in Figure 4. The lifetime (τ_M) of the ^3CT state of $[M(bpy)_3]^{2+}$ in double-complex salts is represented by $\tau_M = 1/(k_2 + k_3 + k_{ET})$, where k_2 and k_3 represent the rate constants of radiative and nonradiative transition from the ^3CT to the $^1A_1$ state, respectively, and k_{ET} is the rate constant of energy transfer from ^3CT to ^2E_g. The energy-transfer rate k_{ET} is given as follows: $k_{ET} = 1/\tau_M - (k_2 + k_3)$. The ^3CT lifetime (τ_M') of $[M(bpy)_3]^{2+}$ in pure crystals of single-complex salts, in which excitation energy transfer does not occur, is written by $\tau_M' = 1/(k_2 + k_3)$. Since the value of τ_M' is almost constant for any counteranion as shown in Table 1, the value of $\{1/(k_2 + k_3)\}$ in pure double-complex salts can be assumed as the same value of the lifetime in pure single-complex salts (τ_M'). Therefore, k_{ET} is rewritten as $k_{ET} = 1/\tau_M - 1/\tau_M'$.

The evaluated rate of energy transfer are also listed in Table 1. The energy transfer rate in $[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ (4.9×10^7 s^{-1}) is about the eight times larger than that in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ (6.0×10^6 s^{-1}).

Comparison of Pure and Doped Crystals. In the pure crystals, there is a problem whether energy-migration occurs among donor complexes or not. To estimate the contribution of the energy-migration to the decay rate of ^3CT state of $[M(bpy)_3]^{2+}$ in the pure crystals, we examined in doped crystals; 1% $M^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$. In the doped crystals, the mutual interaction among donors can be effectively negligible.

Figure 2 shows the luminescence spectra of the pure and doped double-complex salts. Luminescence spectra of $[Os(bpy)_3]^{2+}$ in $Os^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ (Figure 2b) and $[Os(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$ (Figure 2c) agree with that of $[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ (Figure 2a), and phosphorescence spectra of $[Cr(CN)_6]^{3-}$ are almost the same whether in $[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ (Figure 2a) or $Os^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ (Figure 2b). The agreement of emission spectra indicates that the complexes are located in almost the same environment in the pure and doped double-complex salts. The same relation was obtained with $[Ru(bpy)_3]^{2+}$ system. Figures 2e,f show luminescence spectra of $Ru^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ and $[Ru(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$, respectively. There are not any changes of luminescence spectra of $[Ru(bpy)_3]^{2+}$ and $[Cr(CN)_6]^{3-}$ in the pure and doped double-complex salts.

As listed in Table 1, decay rates (k_d) of ^3CT state in both doped double-complex salts 1% $M^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ ($M^{2+} = Os^{2+}$, Ru^{2+}) are surely decreased by about 20% compared with those in $[M(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ at 77 K. Although transition dipole moment of ^3CT state is very different between $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes (see Figure 1a,b), the degrees of k_d decrease are the same in both the cases of $[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ and $[Ru(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$. Thus, contributions of energy migration among $[M(bpy)_3]^{2+}$ complexes to k_d are small even in the pure double-complex salts. It is reasonable to consider another reason for decrease of k_d in doped double-complex salts. The decrease of k_d in the doped double-complex salts would be caused mainly by a little difference of the distance and relative geometry between donor's and acceptor's complexes in a pure and doped crystal. In fact, lattice parameters of Zn(II) complex are somewhat different from those of the corresponding Ru(II) and Os(II) complexes; for example, $[Zn(bpy)_3](ClO_4)_2$: $C2/c$, $a =$ 17.40 Å, $b =$ 10.88 Å, $c =$ 16.13 Å, $\beta =$ 91.20°, $[Ru(bpy)_3](ClO_4)_2$: $C2/c$, $a =$ 17.62 Å, $b =$ 10.75 Å, $c =$ 15.91 Å, $\beta =$ 90.76°.[43] Cell parameters (a, b and c) of $[Zn(bpy)_3](ClO_4)_2$ are a little different from those of $[Ru(bpy)_3](ClO_4)_2$ no less than the relative error 1.28% (average value). This difference does not affect the luminescence spectra but rather the energy-transfer rate. On the other hand, $[Os(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ are different from $[Ru(bpy)_3]_2[Cr(CN)_6]Cl \cdot 8H_2O$ by only 0.09%.

Energy-Transfer Mechanism. Two mechanisms of intermolecular energy transfer have been proposed.[44] One is the Dexter mechanism, by which energy transfer can occur by electron exchange interaction.[45,46] The other is the Förster mechanism, by which the transfer is brought about by a dipole−dipole interaction.[47−49] In former case, the electron exchange interaction takes place via overlap of electron clouds and hence requires physical contact between donor and acceptor. The energy-transfer rate induced by the exchange interaction decreases exponentially as the distance between two centers

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increases. Moreover, the rate is directly proportional a spectral overlap between normalized donor's luminescence and normalized acceptor's absorption, which is independent of molar extinction coefficient. In latter case, a dipole−dipole interaction takes place via the electromagnetic field, and therefore, on the contrary, does not require physical contact between two centers. The rate induced by the dipole−dipole interaction is proportional to the inverse sixth power of the distance between donor and acceptor, and to a spectral overlap integral between the normalized donor's luminescence spectrum and the acceptor's absorption spectrum although the molar extinction coefficient of acceptor is included in the integration.

The mechanism of the intermolecular energy transfer process would be the Dexter type in the double-complex salts of $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ ($M^{2+} = Ru^{2+}, Os^{2+}$) because the molar extinction coefficient of the ^2E_g state of $[Cr(CN)_6]^{3-}$ is very small (about 0.25 M^{-1} cm^{-1}). Although the distance between the ruthenium(II) or osmium(II) ion and the chromium(III) ion is more than 9 Å (see the section Crystal Structure), the shortest distance between the carbon-atom of bipyridine and chromium(III) ion is less than 5 Å (see Table 5). This distance would be enable physical contact between molecular orbital of $[M(bpy)_3]^{2+}$ and 3d orbital Cr^{3+} ion.

Spectral Overlap. Since the distance and relative orientation between $[M(bpy)_3]^{2+}$ ($M^{2+} = Ru^{2+}, Os^{2+}$) and $[Cr(CN)_6]^{3-}$ are identical in the two double-complex salts $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (see the section Crystal Structure), the terms of orbital interactions and donor−acceptor separation is assumed identical in the salts. Thus, the energy-transfer rate depends on only the spectroscopic character of the normalized donor's ($[M(bpy)_3]^{2+}$) luminescence spectrum and the normalized acceptor's ($[Cr(CN)_6]^{3-}$) absorption spectrum. Unfortunately, the ^2E_g state of $[Cr(CN)_6]^{3-}$ cannot be observed definitely in absorption spectrum, for the value of molar extinction coefficient is extremely small ($\epsilon = 0.25$). Therefore, excitation spectrum which is obtained by monitoring the luminescence of $[Cr(CN)_6]^{3-}$ doped in $K_3[Co(CN)_6]$ at 12 000 cm^{-1} was used instead of the absorption spectrum. Figure 5 shows the spectral overlap between normalized luminescence spectrum of $[M(bpy)_3]^{2+}$ in 1% $M^{2+}/[Zn(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$ at 77 K and normalized excitation spectrum of $[Cr(CN)_6]^{3-}$ in 10% $Cr^{3+}/K_3[Co(CN)_6]$. When the spectral overlap was evaluated, doped crystals were used in order to prevent the luminescence intensity from decreasing in consequence of high concentration. The spectral overlap of $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ is about eight times larger than that of $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ since the ^3CT state of $[Os(bpy)_3]^{2+}$ is lower than that of $[Ru(bpy)_3]^{2+}$. This ratio is the same as that of the obtained energy transfer rate. These results indicate that the difference of energy transfer rate between $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ and $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ depends on only the spectral overlap, and other interactions of $[M(bpy)_3]^{2+}$ and $[Cr(CN)_6]^{3-}$ are almost the same in those two double-complex salts.

Temperature Dependence of Decay Rates. Lifetimes and decay rates of ^3CT state of $[M(bpy)_3]^{2+}$ at room temperature are also listed in Table 1. In the pure double-complex salts of $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$, a decay rate of the ^3CT state of $[Os(bpy)_3]^{2+}$ at RT (1.2×10^8 s^{-1}) becomes only about twice larger than that at 77 K (5.0×10^7 s^{-1}), while, the rate of $[Ru(bpy)_3]^{2+}$ at RT (7.1×10^7 s^{-1}) becomes eleven times larger than the value at 77 K (6.3×10^6 s^{-1}). In single-complex salts of $[M(bpy)_3]Cl_2{\cdot}6H_2O$, however, both decay rates of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ do similar behavior from 77 K to RT; i.e., the rates at RT ($Ru^{2+} = 1.0 \times 10^6$ s^{-1}, $Os^{2+} = 7.7 \times 10^6$ s^{-1}) become six times larger than those at 77 K ($Ru^{2+} = 1.8 \times 10^5$ s^{-1}, $Os^{2+} = 1.3 \times 10^6$ s^{-1}), respectively.

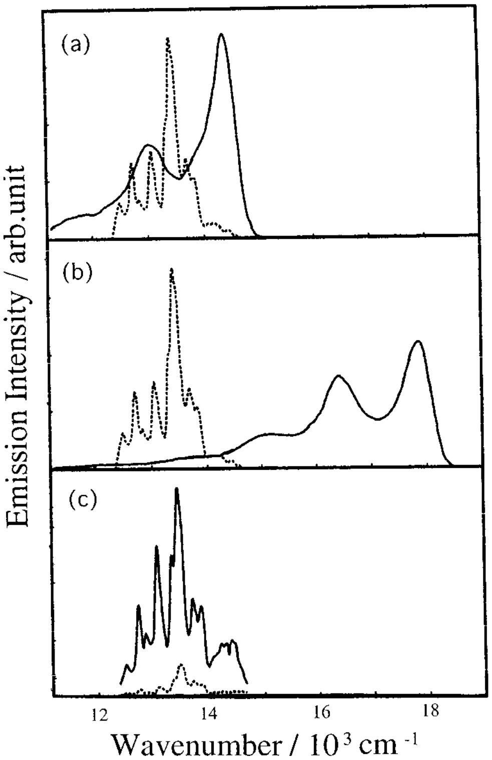

Figure 5. (a) Normalized emission spectrum of $1\%Os^{2+}/[Zn(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$ (solid line) and normalized excitation spectrum of 10% $Cr^{3+}/K_3[Co(CN)_6]$ monitored at 11 800 cm^{-1} (dashed line); (b) normalized emission spectrum of 1% $Ru^{2+}/[Zn(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$ (solid line) and normalized excitation spectrum of 10% $Cr^{3+}/K_3[Co(CN)_6]$ monitored at 12 000 cm^{-1} (dashed line); (c) spectral overlap in (a) (solid line) and in (b) (dashed line).

The large temperature dependence of $[Ru(bpy)_3]^{2+}$ decay rate in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ would be attributed to energy transfer through the path from ^3CT state ($[Ru(bpy)_3]^{2+}$) to the $^2T_{2g}$ state ($[Cr(CN)_6]^{3-}$). Increase of temperature makes the energy-transfer path from ^3CT to $^2T_{2g}$ states open since the $^2T_{2g}$ state is energetically higher than the ^3CT state by only about 1.5×10^3 cm^{-1} (see Figure 4). In $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$, the energy transfer through the path is not effective at RT, for energy difference between ^3CT and $^2T_{2g}$ states is very large (about no less than 4.7×10^3 cm^{-1}).

The new energy transfer path ($^3CT \rightarrow {}^2T_{2g}$) is supported by a temperature dependence of the decay rates. Figure 6 shows a temperature dependence of the decay rates of pure and doped double-complex salts in temperature range from 77 to 300 K. Decay rates for Os^{2+} systems increased slowly in this temperature range, while the rates for Ru^{2+} systems increased rapidly above 240 K. The obtained experimental measurements can be expressed by using two ($i = 2$; for Os^{2+} system) or three ($i = 3$; for Ru^{2+} system) temperature dependence terms,

$$k(T) = \sum_{k=1}^{i} A_k \exp(-E_k/RT) \qquad (1)$$

where A_k and E_k are the frequency factor and the activation energy for nonradiative transition including energy transfer. The values of A_k and E_k for Ru^{2+} and Os^{2+} systems are listed in Table 2. The largest activation energies (ΔE_3) evaluated by the Arrhenius plot (see Figure 6) are 2300 and 2700 cm^{-1} to $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ and $Ru^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]$-

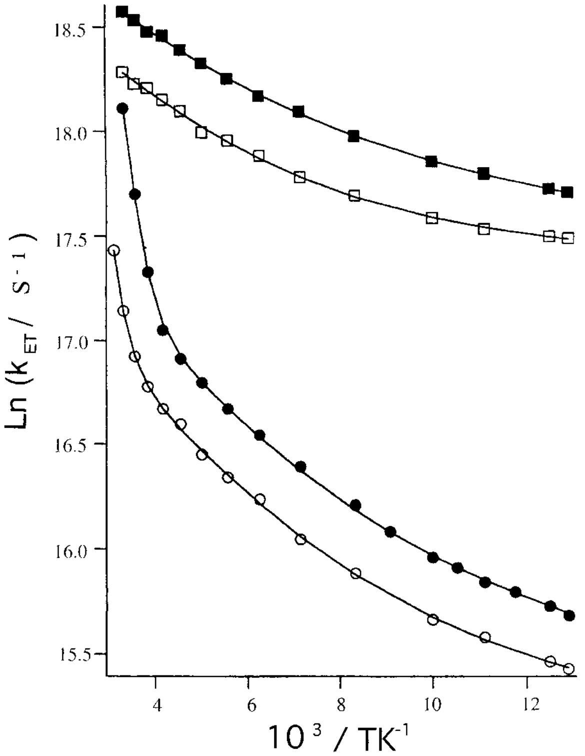

Figure 6. Temperature dependence of decay rate from ^{3}CT state: ■, $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$; □, 1% $Os^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$; ●, $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$; ○, 1% $Ru^{2+}/[Zn(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$.

$Cl{\cdot}8H_2O$, respectively, while activation energies are 3040−3520 cm^{-1} to $[Ru(bpy)_3]X_2$ (X_2 = Cl_2, SO_4, BF_4) and $[Ru(bpy)_3]_2[Co(CN)_6]BF_4{\cdot}7H_2O$. Thermal enhancement of decay rate in $[Ru(bpy)_3]X_2$ and $[Ru(bpy)_3]_2[Co(CN)_6]BF_4{\cdot}7H_2O$ is due to a ^{3}CT → ^{3}MC intramolecular transition.[51] The former activation energy is obviously smaller than the latter one. Moreover, the former decay rate constant ((2.8−7.1) × 10^7 s^{-1}) at RT is more than twenty times largrer than the latter one (1.0−1.4 × 10^6 s^{-1}). A ^{3}MC state of Ru^{2+} in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ would be near that in $[Ru(bpy)_3]_2[Co(CN)_6]BF_4{\cdot}7H_2O$ (ΔE = 3280 cm^{-1}) because the ^{3}MC state of Ru^{2+} is assigned to d−d* transition. Thermal enhancement of decay rate in the double complex salts is not attributed to ^{3}CT → ^{3}MC intramolecular transition, but another path of intermolecular transition has to be considered. Considering the activation energy (ΔE_3 = 2300−2700 cm^{-1}), the path of energy transfer from ^{3}CT to $^2T_{2g}$ is appropriate as the new path, although the frequency factor (A_3) is very large ((2.6−3.3) × 10^{12} s^{-1}). The $^2T_{2g}$ state (19 000 cm^{-1}) is energetically higher than ^{3}CT state (17 500 cm^{-1}) by about 1500 cm^{-1}.

The extremely large decay rate for Ru^{2+} system above 240 K is not caused by enhancement of ^{3}CT → ^2E_g energy transfer by the increase of spectral overlap between donor luminescence and acceptor absorption spectra with increase of temperature. The spectral overlap in $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ at RT becomes large as compared with that at 77 K on account of the red-shift of luminescence spectrum of $[M(bpy)_3]^{2+}$ with increase of temperature. However, the red-shift of luminescence spectrum of $[Os(bpy)_3]^{2+}$ with increase of temperature is much larger than that of $[Ru(bpy)_3]^{2+}$. Thus, the magnitude of change in the spectral overlap between ^{3}CT and ^2E_g states from 77 K to RT in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ is smaller than that in $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$. Increase of decay rates for Os^{2+} system with a rise in temperature would be brought about by enhancement of ^{3}CT → ^2E_g energy transfer with increase of spectral overlap.

Table 3. Summary of Crystallographic Data and Structural Analysis for $[M(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (M^{2+} = Os^{2+}, Ru^{2+}) and $[Ru(bpy)_3]_2[Cr(CN)_6]Br{\cdot}8H_2O$[a]

formula	$C_{66}H_{48}ClCrN_{18}O_8Os_2$	$C_{66}H_{48}ClCrN_{18}O_8Ru_2$	$C_{66}H_{48}BrCrN_{18}O_8Ru_2$
fw	1689.07	1510.81	1555.27
a, Å	22.384	22.414	22.414
b, Å	13.827	13.769	13.814
c, Å	22.186	22.207	22.299
α, deg	90	90	90
β, deg	90.70	90.713	90.531
γ, deg	90	90	90
Z	4	4	4
V, Å^3	6866	6853	6904
space group	*C*2	*C*2	*C*2
color, habit	black	orange	orange
D_{calc}, g cm^{-3}	1.634	1.484	1.496
μ, cm^{-1}	39.53	6.970	12.32
T, °C	20	20	20
λ, Å	0.71073	0.71073	0.71073
$2\theta_{max}$, deg	55.32	55.00	55.00
final R^b/R$_w$^{c}, %	7.89/19.32	5.54/16.79	5.88/11.18

[a] Radiation, Mo K. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w = (1/\sigma(F_o)^2)$.

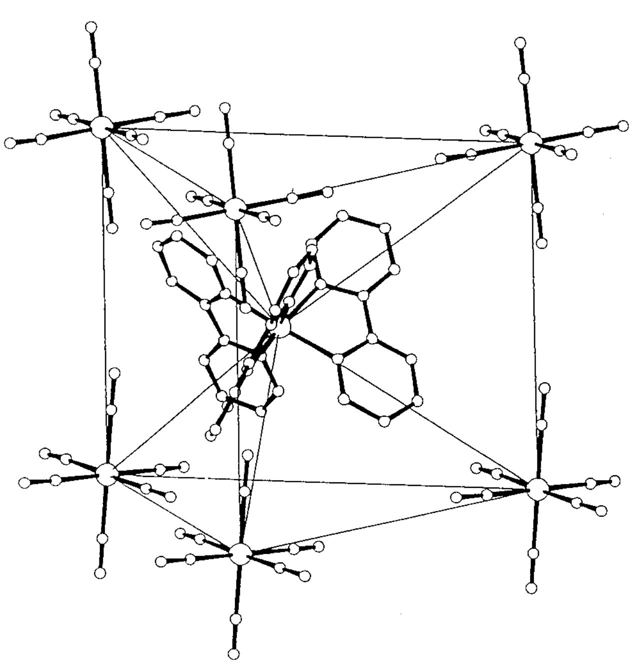

Figure 7. Relative position of $[Cr(CN)_6]^{3-}$ to $[M(bpy)_3]^{2+}$.

Crystal Structure. The results of the X-ray structure analysis for $[Ru(bpy)_3]_2[Cr(CN)_6]X{\cdot}8H_2O$ (X^- = Cl^-, Br^-)[52] and $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ are listed in Table 3. These double-complex salts have almost the same crystal and molecular structures, so the distance and relative orientation between donor and acceptor complexes are also equal in the salts. In the crystals, $[M(bpy)_3]^{2+}$ and $[Cr(CN)_6]^{3-}$ are in alternate layers. There are six acceptor complexes $[Cr(CN)_6]^{3-}$ around a donor complex $[M(bpy)_3]^{2+}$ (see Figure 7). Each chromium(III) ion of the six acceptors is almost the equivalent direction relative to the donor complex and is within 5.5 Å from the 5- or 5′-

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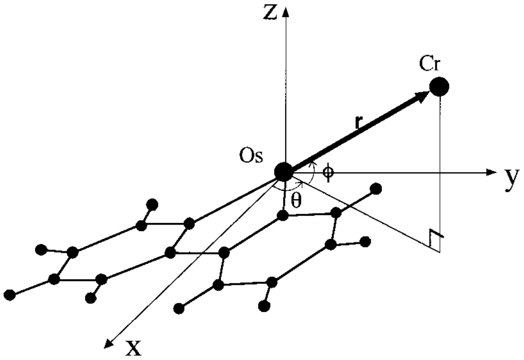

Figure 8. Relative position parameters of Cr^{3+} to ligand bypridine of $[M(bpy)_3]^{2+}$, $|\mathbf{r}|$ is the distance between osmium(II) and chromium(III) ions, θ and ϕ are the angle between x axis and projection of $\mathbf{r}$ to $x-y$ (the ligand bpy) plane and the elevation angle from the bpy plane, respectively.

Table 4. Relative Geometry Parameter in $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$

		$\lvert\mathbf{r}\rvert$ (Å)[a]	θ(°)[a]	ϕ(°)[a]	Cr−C[b]
bpy(2−3)	Cr5	9.343	29.4	14.9	4.852
	Cr3	9.296	−36.5	−21.3	4.925
bpy(4−5)	Cr2	9.890	34.8	17.6	5.441
	Cr1	9.846	−28.0	−19.0	5.445
bpy(1−6)	Cr6	9.420	34.0	20.7	4.940
	Cr4	9.204	−32.1	−14.9	4.834

[a] See Figure 8. [b] The most nearest carbon atom of ligand bipyridine from chromium(III) ion.

carbon atom of ligand 2,2′-bipyridine molecule. Each relative orientation of acceptor complex to the donor and each distance from donor are fluctuated slightly. As shown in Figure 8, relative geometry parameters are defined ($|\mathbf{r}|$, θ, and ϕ), where $|\mathbf{r}|$ is the distance between central metal ions of donor and acceptor complexes, θ and ϕ are the angles between the x axis and projection of $\mathbf{r}$ to the $x-y$ (the ligand bpy) plane and the elevation angle from the bpy plane, respectively. The relative geometry parameter ($|\mathbf{r}|$, θ, and ϕ) between donor and acceptor is listed in Table 4. The shortest distance between central metal-ions is about 9.2 Å ($M^{2+}-Cr^{3+}$) and 7.5 Å ($M^{2+}-M^{2+}$).

The crystal and molecular structures of $[M(bpy)_3]_2[Cr(CN)_6]X{\cdot}8H_2O$ do not depend on a counteranion X^-. In fact, the result of X-ray structure analysis shows that $[M(bpy)_3]_4[Cr(CN)_6]_2SO_4{\cdot}xH_2O$ has the same crystal parameter as $[M(bpy)_3]_2[Cr(CN)_6]X{\cdot}8H_2O$. X-ray powder pattern of the former salt also coincides with that of the latter salt.

Conclusion

Results of X-ray structure analysis showed that $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ is almost the same crystal and molecular structure as $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ and both salts have the same distance and relative orientation between donor and acceptor complexes. The energy-transfer rate from the ^{3}CT state of $[Os(bpy)_3]^{2+}$ to the ^2E_g state of $[Cr(CN)_6]^{3-}$ in $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (4.8×10^7 s^{-1}) is eight times larger than that in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ (6.0×10^6 s^{-1}) at 77 K. This ratio agrees with a ratio of the spectral overlap between normalized donor luminescence from ^{3}CT state and normalized acceptor excitation spectra of the ^2E_g state. These results, the very small value of molar extinction coefficient of the ^2E_g state and the very small spectral overlap indicate that the energy transfer would brought about by electron exchange interaction (Dexter mechanism). A decay rate of the ^{3}CT state of $[Ru(bpy)_3]^{2+}$ in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ from 77 K to RT changes much larger than that in $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$. We propose that increase of temperature makes the energy transfer through the path from the ^{3}CT state ($[Ru(bpy)_3]^{2+}$) to the $^2T_{2g}$ state ($[Cr(CN)_6]^{3-}$) open in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ although the transfer cannot occur at 77 K, while in $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$, the energy transfer through the path cannot occur even if at RT because the energy difference between the $^2T_{2g}$ and ^{3}CT states is very large (no less than $\sim 4.7 \times 10^3$ cm^{-1}). These results are supported by the measurements of decay rates in temperature range from 77 to 300 K and the evaluated activation energy.

Supporting Information Available: X-ray crystallographic files, in CIF format, are available free of charge via the Internet at http://pubs.acs.org.

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