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Energy Transfer From Tris(2,2′-Bipyridine)Ruthenium(II) or Tris(2,2′-Bipyridine)Osmium(II) To Hexacyanochromate(III) in a Pure Crystal of Double Complex Salt

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ENERGY TRANSFER FROM TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II) OR TRIS(2,2'-BIPYRIDINE)OSMIUM(II) TO HEXACYANOCHROMATE(III) IN A PURE CRYSTAL OF DOUBLE COMPLEX SALT.

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Abstract It is clarified by performing X-ray structure analysis that the crystal structure of $[Ru(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ (bpy = 2,2'-bipyridine) is the same as that of $[Os(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$. The difference of energy transfer rate from $[M(bpy)_3]^{2+}$ ($M=Ru^{2+}$ or Os^{2+}) to $[Cr(CN)_6]^{3-}$ in pure crystals of double complex salts ($[M(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$) is discussed in terms of the spectroscopic characters and lifetimes of the salts.

INTRODUCTION

The work on the relaxation processes from the photo-excited state in a pure crystal of metal-complexes[1,2] has not been done as many as that in a doped crystal. In this paper, we focus on the relationship between the optical characters and the rate of energy transfer from ^3CT state of tris(2,2'-bipyridine)ruthenium(II) or tris(2,2'-bipyridine)-osmium(II) ($[M(bpy)_3]^{2+}$; $M=Ru^{2+}$ or Os^{2+}, bpy = 2,2'-bipyridine) to ^2E_g state of hexacyanochromate(III) ($[Cr(CN)_6]^{3-}$) in the pure crystal of double complex salts ($[M(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$).

EXPERIMENTAL

Samples

$[Ru(bpy)_3]Cl_2$[3], $[Os(bpy)_3]Cl_2$[4] and $K_3[Cr(CN)_6]$[5] were prepared according to the literature. The single crystals of the two double complex salts could be obtained by careful layerring of concentrated acetone-water (vol. 1/1) solution of $[Ru(bpy)_3]^{2+}$ (or $[Os(bpy)_3]^{2+}$) upon top of an concentrated aqueous solution of $[Cr(CN)_6]^{3-}$ and by setting this aside at room temperature for a week. The double complex salts were identified by elemental analysis.

Measurement

Luminescence spectra were measured on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier. The light of 21700cm^{-1} was used as

excitation light. The samples were put into 3ϕ quartz tube and immersed directly in the coolant (liquid nitrogen). In the tube, nitrogen gas was substituted for air.

Excitation spectra were also measured on a Hitachi 850 spectrofluorometer by monitorring the luminescence maximum.

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 lifetimes were determined by a semi-logarithmic plot of the decay curve.

A full detail of X-ray structure anaysis would be published elsewhere.[6]

RESULTS AND DISCUSSION

The Crystal Structure

There are two important factors which influence the energy transfer rate from donor to acceptor; one is the distance between donor and acceptor and the other is the spectral overlap integral of donor's luminescence spectra and acceptor's absorption spectra whether the energy transfer occurs by the Dexter or Förster mechanism. Thus, the determination of crystal structure by X-ray structure analysis is required for the discussion of energy transfer. The results of the X-ray structure analysis are listed in Figure 1 and Table I.[6] The two double complex salts have almost the same crystal structure and the distance and relative orientation between donor and acceptor complexes are also equal in the salts.

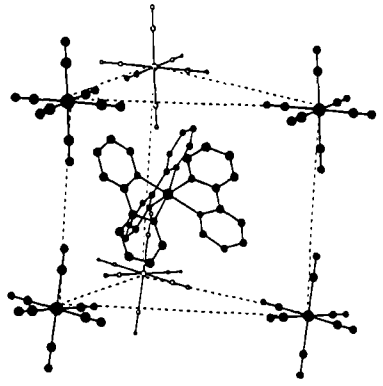

FIGURE 1 Crystal structure of $[M(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$

TABLE I Crystal data of double complex salts; $[M(bpy)_3]_2[Cr(CN)_6]Cl\cdot 8H_2O$ ($M=Ru^{2+}$, Os^{2+})

	Ru^{2+}	Os^{2+}
Space group	C2	C2
a	22.414	22.395
b	13.769	13.766
c	22.207	22.171
β	90.71	90.73

Energy Level

Figures 2(a) and (b) show luminescence and absorption spectra of donor complexes $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ in acetonitrile at room temperature, respectively. The band near at 23000 cm^{-1} is assigned to singlet metal-to-ligand charge-transfer excited state ^1CT. The luminescence near at 16000 cm^{-1} of $[Ru(bpy)_3]^{2+}$ and at 14000 cm^{-1} of $[Os(bpy)_3]^{2+}$ is assigned to a phosphorescence from ^3CT state. The energy level of ^3CT state of $[Os(bpy)_3]^{2+}$ is lower than that of $[Ru(bpy)_3]^{2+}$ (about 3500 cm^{-1}). Figure 2(c) shows absorption and luminescence spectra

of acceptor $[Cr(CN)_6]^{3-}$ in aqueous solution at room temperature and in rigid solution at 77 K, respectively. The bands near at 26000 and 32000 cm^{-1} are assigned to Laporte forbidden spin-allowed d-d transition from $^4A_{2g}$ to $^4T_{2g}$ and $^4T_{1g}$, respectively. There are a few of spin-forbidden bands near at 12500, 13000 and 18000 cm^{-1} which are assigned to ^2E_g, $^2T_{1g}$ and $^2T_{2g}$, 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 $^2E_g \rightarrow {}^4A_{2g}$. At 21700 cm^{-1} (460 nm) which is exciting wavenumber in this work, molar extinction coefficients of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ are about 14000$M^{-1}cm^{-1}$, while that of $[Cr(CN)_6]^{3-}$ is at the most 1 $M^{-1}cm^{-1}$. Therefore, $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ complexes only absorb the excitation light at 21700 cm^{-1}.

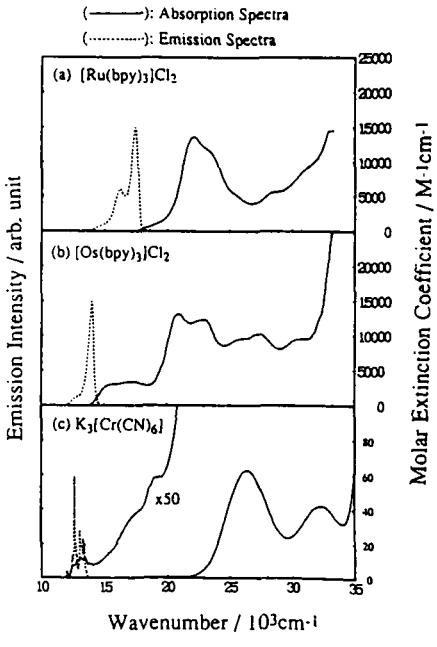

FIGURE 2 Absorption spectra in water at R.T. and emission spectra in crystal at 77K.

Luminescence and Excitation Spectra of Double Complex Salts

Figure 3 shows the luminescence spectra of the two double complex salts excited at 21700 cm^{-1}. Both double complex salts emit not only broad-band phosphorescence from ^3CT state of $[Ru(bpy)_3]^{2+}$ (near 17800 cm^{-1}) and $[Os(bpy)_3]^{2+}$ (near 14300 cm^{-1}) but also a narrow-band one from ^2E_g state of $[Cr(CN)_6]^{3-}$ (near 12500 cm^{-1}). The results indicate that excitation energy transfer occurs from $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ to $[Cr(CN)_6]^{3-}$. Irradiation of crystalline $K_3[Cr(CN)_6]$ with the light of 21700 cm^{-1} gives no phosphorescence emission because there is no appreciable absorption in this spectral region (see Figure 1 (c)).

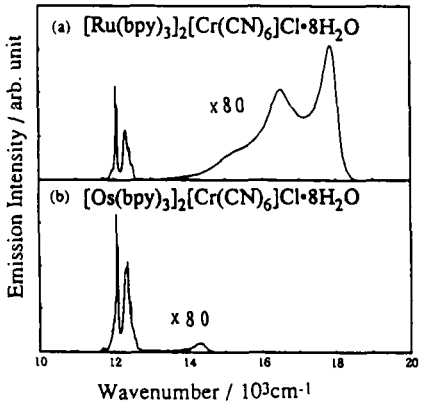

FIGURE 3 Emission spectra of the double complex salts at 77K.

The energy transfer is also supported by excitation spectra. Figures 4(a) and (b) show the excitation spectra of the single complex salts of $[Ru(bpy)_3]Cl_2$ and $K_3[Cr(CN)_6]$ at 77 K, respectively. Figure 4(c) shows the excitation spectra on monitorring the luminescence maximum of $[Cr(CN)_6]^{3-}$ (about 12000 cm^{-1}) in the crystal of $[Ru(bpy)_3]_2[Cr(CN)_6]$-$Cl{\cdot}8H_2O$ at 77 K. An agreement of Figures 4(a) and (c) shows that there is no interaction between donor's and acceptor's complexes in the ground state and the energy transfer from $[Ru(bpy)_3]^{2+}$ to ^2E_g state of $[Cr(CN)_6]^{3-}$ surely occurs. Here, the excitation spectrum of $[Ru(bpy)_3]^{2+}$ in a pure crystal is very different from the absorption spectrum of solution, since concentration of $[Ru(bpy)_3]^{2+}$ in the crystals is too high for the measurement of absorption and excitation spectra. The result of osmium(II) system is similar to that of ruthenium(II) one.

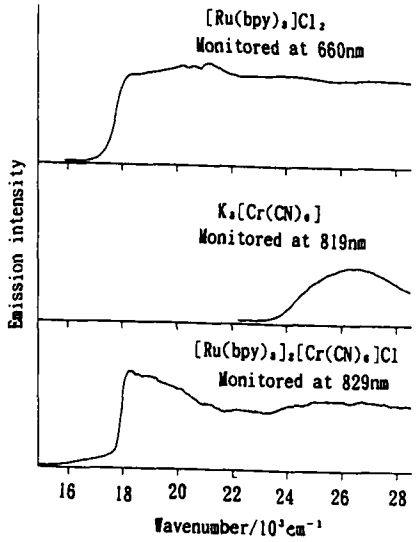

FIGURE 4 Excitation spectra of single and double complex salts at 77K.

To our great surprise, energy transfer can do occur although ruthenium(II) or osmium(II) ions are located apart from chromium (III) ion no less than 9.2 Å.

Luminescence Lifetime and Energy Transfer Rate

The lifetimes of ^3CT state of $[M(bpy)_3]^{2+}$ in various crystals are summarized in Table II. All decay curves at 77 K are single-exponential when the laser power of excitation light is lowered. The lifetimes of double complex salts are far shorter than those of single complex salts. Thus, energy transfer occurs from ^3CT state of $[M(bpy)_3]^{2+}$ to ^2E_g state

TABLE II Lifetime of $[M(bpy)_3]^{2+}$ ($M=Ru^{2+}, Os^{2+}$) and estimated rate constant of energy transfer at 77K.

Sample	Lifetime(ns)	$K_{et}/10^6(s^{-1})$
$[Ru(bpy)_3]Cl_2$	5500	
$[Ru(bpy)_3]SO_4$	3800	
1%Ru:$[Zn(bpy)_3]_2[Co(CN)_6]Cl$	5900	
$[Ru(bpy)_3]_2[Cr(CN)_6]Cl$	160	6.0
1%Ru:$[Zn(bpy)_3]_2[Cr(CN)_6]Cl$	200	4.8
$[Os(bpy)_3]Cl_2$	760	
$[Os(bpy)_3]SO_4$	700	
1%Os:$[Zn(bpy)_3]_2[Co(CN)_6]Cl$	1000	
$[Os(bpy)_3]_2[Cr(CN)_6]Cl$	20	49
1%Os:$[Zn(bpy)_3]_2[Cr(CN)_6]Cl$	25	39

of $[Cr(CN)_6]^{3-}$.

Energy levels of $[M(bpy)_3]^{2+}$ and $[Cr(CN)_6]^{3-}$ are shown in Figure 5. Energy transfer rate can be evaluated as the reciprocal of lifetime of donor's ^3CT state; $k_{ET} = 1/\tau_D$, because the lifetime does not become short in different crystals without energy transfer as shown in Table II The rate of energy migration between donor's complexes in pure crystals does not contribute to the observed luminescence lifetime because donor's lifetime in a pure crystal is almost as equal as that in a doped crystal in which energy migration between donors cannot occur. The estimated rate of energy transfer are also listed in Table II. The energy transfer rate in $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ is about the eight times larger than that in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$.

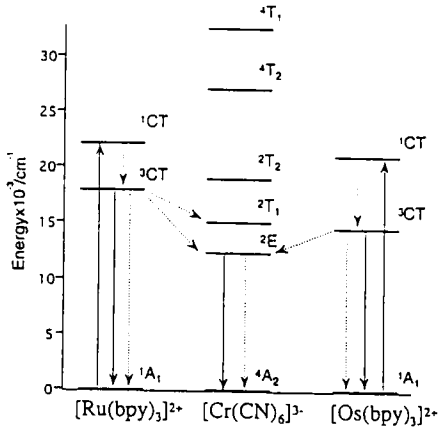

FIGURE 5 Energy diagram of double complex salts.

Energy Transfer Mechanism

Considering the value of molar-extinction coefficient of ^2E_g state of acceptor's $[Cr(CN)_6]^{3-}$ (ε=0.1), the energy transfer is thought to be caused by not dipole-dipole interaction (the Förster mecha-nism) but electron exchange interaction (the Dexter mechanism) although the distance between ruthenium(II) or osmium(II) ion and chromium(III) ion is more than 9 Å. However, this may be supported by the result that the shortest distance between the carbon-atom of bipyridine and chromium(III) ion is less than 5 Å.

Spectral Overlap Integral

The overlap of electron cloud between molecular orbital in $[M(bpy)_3]^{2+}$ and d-orbital of chromium(III) ion is almost identical in the two double complex salts because the distance and relative orientation between $[M(bpy)_3]^{2+}$ and $[Cr(CN)_6]^{3-}$ are identical in the salts. Thus, the energy transfer rate depends upon only the spectral overlap integral between the normalized luminescence spectrum of donor ($[M(bpy)_3]^{2+}$) and the normalized absorption spectrum of acceptor ($[Cr(CN)_6]^{3-}$). Unfortunately, the ^2E_g state of $[Cr(CN)_6]^{3-}$ can not be observed definitely in absorption spectrum, for the value of molar-extinction coefficient is extremely small (ε=0.1). Therefore, excitation spectrum which is obtained on monitorring the luminescence of $[Cr(CN)_6]^{3-}$ (at 12000 cm^{-1}) was used instead of absorption spectrum.

Figure 6 shows the spectral overlap integral between normalized luminescence spectrum of $[M(bpy)_3]^{2+}$ in 1%M:$[Zn(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$ at 77 K and norma-lized excitation spectrum of $[Cr(CN)_6]^{3-}$ in 10%Cr:$K_3[Co(CN)_6]$. In order to evaluate the spectral overlap integral, doped crystals were used because they are the same crystal struc-ture as pure crystals and could prevent the luminescence intensity from decreasing in consequence of high concentration. The spectral overlap integral of $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ is about eight times larger than that of $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$. This ratio is the same as that of energy transfer rate. These results indicate that energy transfer rate depends upon only the spectral overlap integral, and other interactions of $[M(bpy)_3]^{2+}$ and $[Cr(CN)_6]^{3-}$ are almost the same in the two double complex salts since the double complex salts have the identical crystal structure.

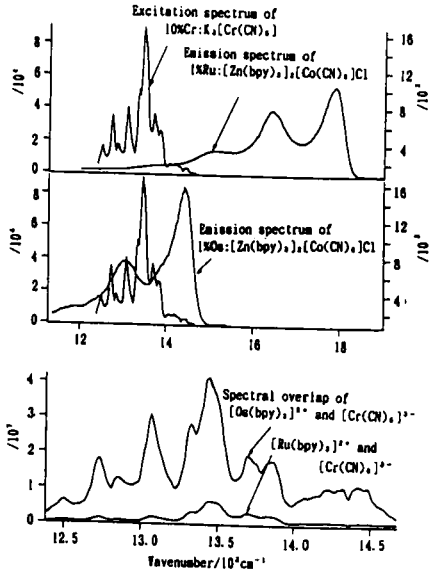

FIGURE 6 Spectral overlaps of donor and acceptor complexes.

CONCLUSION

The results of X-ray structure analysis indicate that the crystals of $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ and $[Os(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$ have almost the same crystal structure. Thus, the difference of energy transfer rate is caused by the difference of spectral overlap integral between donor's luminescence spectra and acceptor's excitation spectra in the two double complex salts.

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