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Complexation, Luminescence and Energy Transfer in the Ce(III)–2,2′-Bipyridine Complexes

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Abstract

Fluorescence characteristics and energy transfer of a cerium complex with 2,2′-bipyridine (bpy) in methanol are described. Stoichiometries and the stability constant of the Ce(III)–bpy complex in methanol were determined by use of the molar ratio method. A fluorescence lifetime and a quantum yield have been measured for the 2:1 complex. Decay times and time-resolved (T–S) emission spectra for Ce(III)–bpy and $CeCl_3$ were measured in methanol at room temperature. An energy transfer rate constant was determined from the luminescence lifetime and the quantum yield. The mechanism of energy transfer from the lowest excited singlet state S_1 to the 5d level of the Ce(III) in the Ce(III)–bpy complex system is discussed in some detail.

Introduction

The luminescence of organic complexes of transition metals coordinated by bpy, for example, the tris(bpy)–Ru(III) system, is well known [1–5]. Sinha [6–9] and Ferraro *et al.* [10] have published preparations and spectroscopic properties for bpy complexes of rare earths (RE) having an f–f transition, *i.e.* Eu(III), Tb(III) and Nd(III), etc. IR and fluorescence spectra indicate complex formation of a RE ion with the bpy ligand through direct bonding between the RE ion and nitrogen atoms in the ligand [7]. Energy transfer for the complex of bpy with Ce(III) ion, having an f–d transition system, however, has not yet been reported.

An intramolecular energy transfer from an organic ligand to an RE ion has been proposed [11–15]. The emission is due to indirect excitation of the RE ion via radiation-less transfer of energy predominantly from the lowest triplet level of the complexes, if the lowest triplet level of the complexed ligand lies above the emissive level of the RE ion. On the other hand, Bhaumik and El-Sayed [13, 16] proposed a diffusion-controlled intermolecular energy transfer mechanism. Although another mechanism of energy transfer arising from the ligand through the lowest excited singlet state has been considered previously [17], details have scarcely been discussed before.

In this paper, we report complexation and fluorescence characteristics and energy transfer for a new Ce(III)–bpy complex system in methanol. It is especially interesting because the acceptor of energy transfer is a complexed Ce(III) ion having an f–d transition.

Experimental

Materials

Methanol, ethanol and bpy were purchased from Wako Pure Chemicals, Osaka, Japan.

The 2,2′-bipyridine was found to contain a very small amount of an impurity (probably 4,4′-bipyridine) from UV spectra of the reagent as obtained (refs. 18 and 19). The 2,2′-bpy was, however, used as purchased because 4,4′-bipyridine does not form any stable complex with Ce(III) [20].

Preparation of anhydrous $CeCl_3$ powder has been described previously [21]. A Ce(III)–bpy complex solution was prepared by mixing bpy and anhydrous $CeCl_3$ powder in methanol. Ethanol was used as the solvent for the Ce(III)–bpy complex system for phosphorescence measurements at liquid nitrogen temperature (LN).

Instruments and Procedures

The molar ratio [L/M] was determined by measuring the dependence of the ligand molar concentration on the absorbance of uncomplexed $CeCl_3$ in the Ce(III)–bpy complex solution.

Fluorescence emission and excitation spectra were determined on a Shiomadzu Absolute Spectrofluorophotometer, model RF-502, using an automatic compensation and calibration system. Phosphorescence properties at LN were taken on a Hitachi Absolute Spectrofluorophotometer, model 850,

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equipped with a phosphorescence measurement apparatus. A fluorescence quantum yield of the complex was determined by comparison with that of a 1×10^{-5} M quinine bisulfate–0.1 N H_2SO_4 solution ($\phi = 0.55$) [22]. Time-resolved emission spectra and the lifetime of the complex were measured by use of a Horiba Time-resolution Spectrofluorometer, NAES-1100, equipped with a high pressure hydrogen lamp (pressure 1 Mpa, halfwidth of the pulse 2 ns). The emission was monitored by using a Hamamatsu 1p28 photomultiplier (for a starting pulse) and a Hamamatsu R928p photomultiplier (for a stop pulse).

The T–S spectrum and fluorescence decay times were analysed using a built-in microcomputer (Intel 8085). Lifetimes were obtained by averaging several measurements, the scattering being less than 10%. The excitating light was passed through a filter train consisting of a 2.5-cm cell of $NiSO_4$ (500 g/l) and a Hoya U-340 glass filter for the measurements. The combination transmits in the region of the excitation wavelength of about 310–320 nm. Absorption spectra were observed using a Shimadzu double-beam spectrophotometer, model UV 180. All measurements were performed at room temperature except phosphorescence which was at LN.

Results and Discussion

Stoichiometries and Stability Constants of the Ce(III)–bpy Complexes

The establishment of stoichiometry and the calculation of the stability constants of the complexes were attempted by means of the molar ratio method for the Ce(III)–bpy system in methanol. For the Ce(III)–bpy complex, the ligand-to-Ce(III) ratio was found to be 2:1, as shown in Fig. 1, which shows plots of absorbance of Ce(III) against L/M in the Ce(III) ion, bpy and methanol system. Thus, the number of nitrogen atoms which coordinate directly with the Ce(III) ion in the Ce(III)–bpy complex should be four.

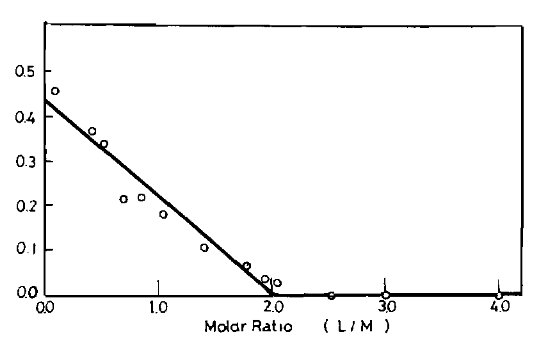

Fig. 1. Molar ratio [L/M] plots of uncomplexed Ce(III) ion absorbancy for the Ce(III)–bpy complex system.

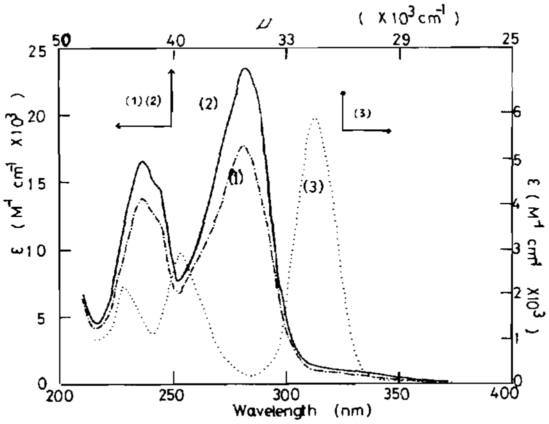

Fig. 2. Absorption spectra for bpy (1), Ce(III)–bpy complex (2) and $CeCl_3$ (3) in methanol.

The stability constants for Ce(III)–bpy complexes were also determined using the molar ratio method. The log K value calculated from Fig. 1 is about 9.4. Therefore it may be considered that the complex reaction of Ce(III) ion with bpy occurs more easily.

Fluorescence Properties

The relative fluorescence quantum yield observed from an absorption coefficient is about 6.2%.

The absorption spectrum of a given complex did not show any significant modification on adding the metallic ion and actually the spectra are very similar to that of the bpy ligand [Fig. 2(1) and (2)] but differ from uncomplexed $CeCl_3$ [Fig. 2(3)]. This indicates that the absorption spectrum is characteristic of ligand groups surrounding the ion, because the absorption band is due to the same kind of electronic transition in each case, probably a $\pi^* \leftarrow \pi$ type or a 'K' transition associated with conjugated systems of bpy. Excitation and emission spectra are displayed in Fig. 3, in which ex_1 and em_1 indicate excitation and emission bands of bpy, and ex_2 and em_2 show excitation and emission bands of the Ce(III)–bpy complex,

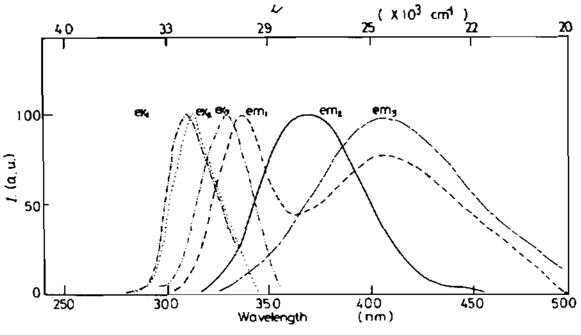

Fig. 3. Excitation and emission spectra of bpy (ex_1, em_1) and the Ce(III)–bpy complexes (ex_2, em_2), as well as 4,4′-bpy which is an isomer of 2,2′-bpy (ex_3, em_3).

respectively. It is noteworthy that the emission spectrum (em_1) is composed of two bands at 340 nm and at 400 nm, but emission spectrum (em_3) is almost completely composed of one band at 400 nm under excitation at 325 nm (ex_3). Thus the em_1 band is considered to be a result of the overlap of the 340 nm band with the 400 nm band, which is presumably generated from the emission of 2,2′-bpy and its isomer, probably 4,4′-bpy, in methanol solution, respectively [18, 19]. The 4,4′-bpy may exist in 2,2′-bpy as an impurity. A discernible shoulder at 345 nm in the absorption band (1) or (2) in Fig. 2 provides evidence for the presence of 4,4′-bpy in the methanol solution of Ce(III)–complex as indicated from the absorption spectrum of bpy. The excitation spectra (ex_1 and ex_2) of the fluorescence correspond well to the absorption spectra for the Ce(III)–bpy complexes, as shown by comparison of Fig. 2(2) and Fig. 3 (ex_2), and are also very similar in position to that of bpy itself, as shown in Fig. 3 (ex_1 and ex_2). The emission spectrum of the Ce(III)–bpy complex is composed of a broad band centered at 365 nm [Fig. 3 (em_2)]. The decay time of the complex is about 30 ns, resembling other Ce(III) luminescent materials.

Energy transfer

(i) Absorption and excitation

As indicated in Fig. 2, the absorption spectrum of the Ce(III)–bpy complex is the same as that of the bpy ligand, and the excitation spectrum of Ce(III) fluorescence of the complexes is close to the ex_1 of the bpy luminescence (340 nm emission band). Therefore, an energy transfer from the bpy ligand to the Ce(III) ion in the Ce(III) complex would take place. As mentioned above, the absorption bands of uncomplexed $CeCl_3$ in the Ce(III)–bpy methanol system disappear [Fig. 2(2)], but an emission band of the complex is generated from Ce(III), no longer from the bpy. Although there are 2,2′-bpy and its isomer, 4,4′-bpy present, the complexes of the 2,2′-bpy with Ce(III) ion would only occur and the occurrence of an emission band of 340 nm was dominantly observed in T–S emission spectra (see later Fig. 8). The results were also supported by the luminescence of the ligand in the Y(III)–bpy complex in which Y(III) is a non-luminescent lanthanide. That is, the intensity of the 340 nm band strongly increased while the bpy complexed with the Y(III) ion, as indicated in Fig. 4. The enhancement of the 340 nm band is due to the reduction of the vibrations of bpy itself in the complex. The fact that 2,2′-bpy coordinates with the Ce(III) ion is because bpy functions as a typical bidentate chelate molecule through the nitrogen atoms with the formation of five-membered rings, but its 4,4′-isomer does not form stable complexes, although the isomer may well attach to other metals as a monodentate ligand [20].

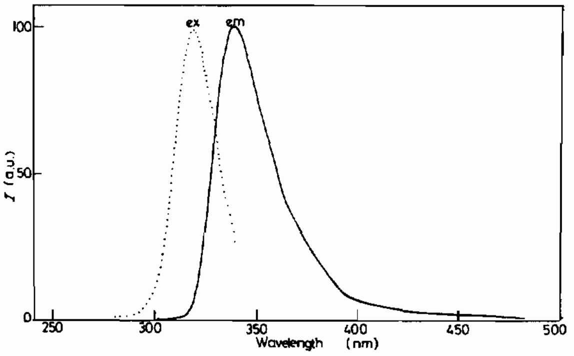

Fig. 4. Excitation and emission spectrum of the Y(III)–bpy complex in methanol.

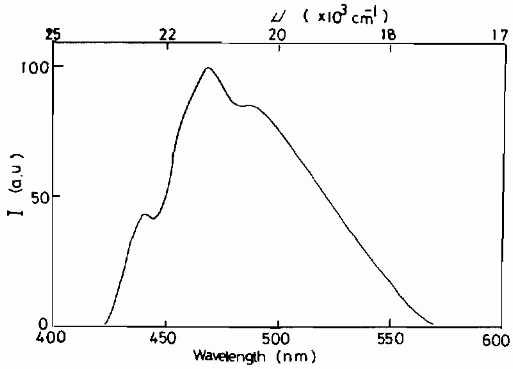

Fig. 5. Phosphorescence spectrum at LN for Ce(III)–bpy complexes.

(ii) Rate constants for intramolecular energy transfer

The decay time of the emission of the ligand in the absence of Ce(III) was about 1.10 ns, which is about 6 orders shorter than the usual phosphorescence lifetime. Addition of $CeCl_3$ into a methanol solution of bpy results in a decrease in the lifetime, which reaches 0.53 ns. The short lifetime for the Ce(III)–bpy complex shows that the radiative transition probability of the bpy ligand is lowered as complex formation between $CeCl_3$ and bpy occurs, and there would be some energy transfer from bpy to the Ce(III) ion. The energy transfer was recognized as a non-radiative process because no overlap between the excitation spectrum of bpy and the emission spectrum of Ce(III) was observed, and the lifetime of the bpy·ligand was shortened. The rate constant k_{et} of the intramolecular energy transfer may be calculated according to ref. 23, where τ_1 is the lifetime of the

$$\begin{aligned} 1/\tau_1 &= 1/\tau_2 + k_{et} \\ k_{et} &= 1/\tau_1 - 1/\tau_2 \end{aligned} \tag{1}$$

340 nm band of bpy in the complex (i.e., 0.53 ns), τ_2 is the lifetime of bpy with another metal such as Y with which no energy transfer can take place (about

TABLE I. Luminescence Properties of bpy Ligands

Sample	Φ^a (%)	τ^b (ns)	$k_{10}{}^c$ $\times 10^7$ (s^{-1})	$k^*_{10}{}^d$ $\times 10^8$ (s^{-1})	$k_{et}{}^e$ $\times 10^8$ (s^{-1})
bpy	0.019	1.10	1.70	9.0	
Y(III)–bpy	0.50	0.88	1.67	10.0	
Ce(III)–bpy		0.53	very small	18.0	7.5

[a] Φ, quantum yield. [b] τ, lifetime. [c] k_{10}, radiation transition rate constant. [d] k^*_{10}, radiation-less transition rate constant. [e] k_{et}, energy transfer rate constant.

$k_{et} = 7.5 \times 10^8\ s^{-1}$

0.88 ns). Thus, there is a relationship between the rate constants and the lifetime [23, 24], namely,

$$\tau = 1/(k_{10} + k^*_{10}) \tag{2}$$

where k_{10} refers to the rate constant for the fluorescence of the transition from S_1 to S_0, and k^*_{10} is a radiation-less rate constant of the transition. The quantum yield of the fluorescence is related to several rate constants in the following way [17b, 24]

$$\phi = k_{10}/(k_{10} + k^*_{10}) \tag{3}$$

where ϕ is the quantum yield of the bpy ligand. The results from eqns. (2) and (3) are shown in Table I. Because of the large energy transfer rate constant, it is suggested that the energy transfer from bpy to the Ce(III) in the complex is easily brought about.

(iii) T–S emission spectra

Two-dimensional T–S emission spectra of the Ce(III)–bpy complex in methanol at room temperature are shown in Fig. 6. The complex shows emission spectra strongly dependent on the delay time. The emission maximum of the complex at 340 nm shifts to 365 nm and the decay also changes from about 9.6 ns to 13.6 ns. In comparison of the emission spectra with em_1 and em_2, we assign the peaks at 340 nm and 365 nm to bpy and Ce(III) ion in the complex system, respectively. In the T–S emission spectra, at about 9.6 ns delay after the pulse trigger, fluorescence of the bpy ligand becomes much stronger than that of the Ce(III) which hardly appears at this stage. At 13.6 ns delay, however, the latter becomes stronger. The emission from the Ce(III) continues to grow, and reaches its maximum at about 14.4 ns after the flash, and thereafter decays (see curve (6) and (7) of Fig. 6). Thus, the energy transfer process from the bpy ligand to the Ce(III) is directly observed in the T–S emission spectra. The T–S emission spectra of $CeCl_3$ in methanol under indentical condition are displayed in Fig. 7, for comparison. It is apparent from Fig. 7 that the Ce(III) emission steadily increases its intensity with time elapsed. This implies that the emission of $CeCl_3$ in the absence of the bpy ligand is due to the direct excitation of Ce(III) ion rather than to the energy transfer. Thus, bpy seems to play an important role as an 'intermediary' of the energy transfer in the complex.

Intramolecular energy transfer in lanthanide complexes can occur through different paths depending on the nature of the ligand. The dominant mechanism of intramolecular energy transfer is from the triplet state to the resonance level of a lanthanide, for instance, Eu(III) and Tb(III) ions, which are of a spin-forbidden type, and the role of the triplet state is enormously important [12–14]. On the contrary, we propose here that energy transfer proceeds through

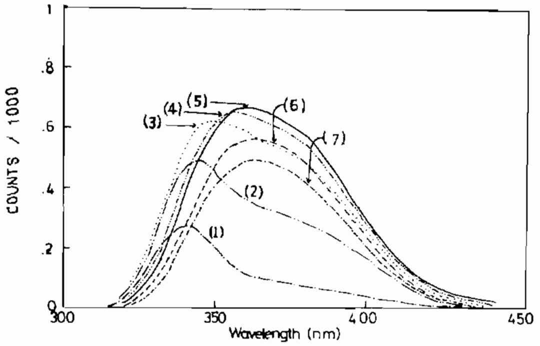

Fig. 6. Two-dimensional spectrum at LN for Ce(III)–bpy complexes. (1) 9.6 ns, (2) 11.2 ns, (3) 12.8 ns, (4) 13.6 ns, (5) 14.4 ns, (6) 22.8 ns, (7) 26.8 ns.

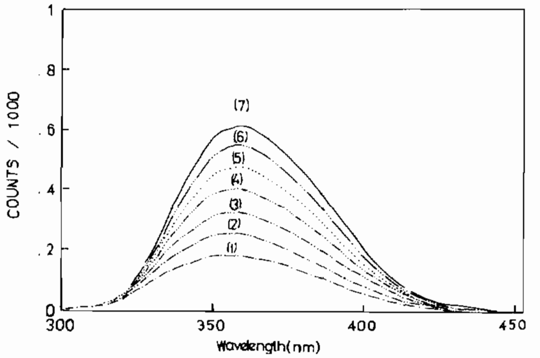

Fig. 7. Two-dimensional T–S emission spectra for $CeCl_3$ in methanol solution: (1) 1.6 ns; (2) 2.0 ns; (3) 2.4 ns; (4) 3.0 ns; (5) 3.6 ns; (6) 4.2 ns; (7) 4.8 ns.

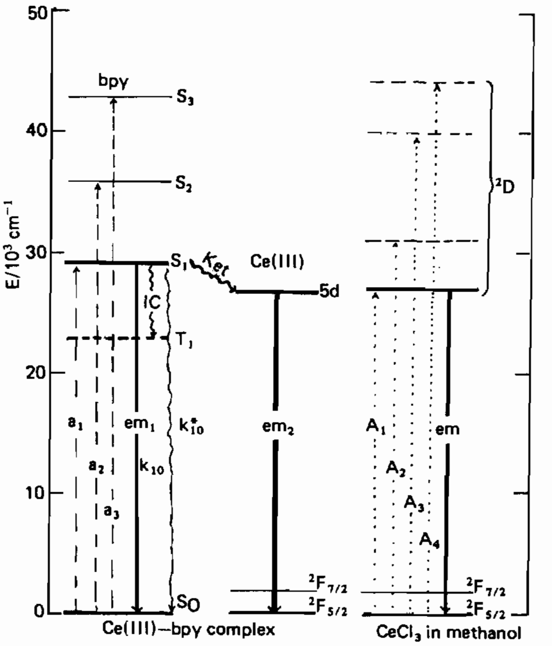

Fig. 8. Energy-level diagram and possible paths of energy transfer for the Ce(III)–bpy complex methanol system. For comparison, energy-level diagram of $CeCl_3$ in methanol is shown. a_1–a_3 and A_1–A_4 correspond to the absorption of S_0–S_{1-3} of bpy in the Ce(III)–bpy complex and $^2F_{5/2}$–^2D level of $CeCl_3$ in methanol, respectively. em_1 and em_2 transferred from S_1–S_0 of the bpy ligand and from 5d–4f of the Ce(III) complexed with bpy, and em is the transition from ^2D to the 4f level of $CeCl_3$ in methanol. k_{10} and k^*_{10} indicate radiation and radiation-less rate constants, and k_{et} is energy transfer rate constant from S_1 to the 5d level of the Ce(III) in the complex. IC is S_1–T_1 intersystem crossing.

the lowest excited singlet state of the complex rather than the lowest triplet state, if the RE ion is Ce(III) having an f–d transition. On the other hand, the phosphorescence at LN provides evidence that the position of the lowest triplet state T_1 is at 22.8×10^3 cm^{-1}, as shown in Fig. 8. From the results and shorter lifetime (0.53 ns) of the ligand, we consider that the emission band with maximum at 340 nm of the bpy ligand (see em_1 in Fig. 3) is fluorescence transferred from the lowest excited singlet state S_1 to the ground state S_0. The S_1–S_0 fluorescence occurs when the singlet state is excited at first and then the energy transfers to the 5d level of the Ce(III) ion. The Ce(III) ion emits a fluorescence band at 365 nm from the 5d–4f transition, as shown in Fig. 8. The radiation-less S_1–T_1 intersystem crossing is also expressed. Although the singlet energies may be quenched partly by the intersystem crossing to the triplet T_1 which lies below a 5d level of the Ce(III) ion, the luminescence from the 5d level of the Ce(III) ion in the complex was clearly observed.

Conclusions

(1) The bpy ligand complexed with Ce(III) plays an important role in the energy transfer.

(2) The triplet state T_1 is lower than the 5d level of the Ce(III) ion, and phosphorescence is only observed at LN.

(3) Energy transfer to the Ce(III) ion takes place through the lowest excited singlet state S_1 of the ligand.

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