

Luminescence Properties of Divalent Europium Complexes with 15-Crown-5 Derivatives

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Abstract

Luminescence of divalent europium complexes with 15-crown-5 and its derivatives has been studied. Structure of the Eu^{2+} -15-crown-5 complex in methanol is determined by the use of the emission intensity molar ratio method and of proton NMR of the Sr^{2+} analogues. Luminescence intensities are generally very large, and the most intense emission is given by a methanol solution of Eu^{2+} -15-crown-5 complex whose ligand has no side chain. Luminescence lifetimes and quantum yields have been measured for the complexes.

Introduction

It is well known that certain polyoxymacrocyclic ligands can form stable complexes with lanthanide ions [1–4]. Photochemical properties of divalent europium complexes of the ligands ‘crown ethers’ have attracted much interest because of practical applications related to lasers [5].

Adachi *et al.* [6, 7] have reported that the most intense fluorescence is produced by the 15-crown-5 complex of Eu^{2+} . Sabbatini *et al.* [8, 9] have illustrated the absorption and emission properties of Eu^{2+} cryptate in aqueous solution. However, the chemical structure of the emitting complex has been ambiguous.

This paper details results obtained by the use of low temperature PMR to elucidate the structure of the complex in methanol solution and describes effects of a side chain attached to a 15-crown-5 ring on emission properties.

Experimental

Materials

Ligands used are illustrated in Fig. 1. 15-C-5 was purchased from Wako, Japan. Other polyethers were kindly supplied by Professors T. Shono, M. Okahara,

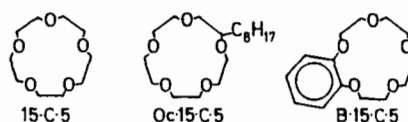


Fig. 1. Schematic representation of the ligands used.

K. Kimura and Y. Nakatsuji of Osaka University. EuCl_2 was prepared from 99.99% Eu_2O_3 , which was mixed with excess NH_4Cl and then was heated at 700°C for 2 h under a 99.99% hydrogen atmosphere. Methanol (a SG product from Wako) was completely degassed by freeze-pump-thaw cycles on a high vacuum line. All other compounds were at least reagent grade and used as supplied.

Instrumentation and Procedures

Emission and excitation spectra were taken on a Shimadzu Absolute Spectrofluorophotometer, Model RF-502, using the Automatic Compensation and pre-calibration system for the instrumental factors [6, 7, 10]. Emission spectra were measured at the maximum peak wavelength of the excitation spectra of the complexes. The emission intensity was calculated from the area of the emission band recorded.

Fluorescence quantum yields were determined by comparison with that of a 1×10^{-5} M quinine bisulfate–0.1 N H_2SO_4 solution ($\phi = 0.55$) [11, 12]. The excitation wavelength for the standard quinine solution was 365 nm.

Fluorescence lifetimes of the complexes were measured by the use of a Horiba Time-resolved Spectrofluorometer NAES-1100 equipped with a high pressure hydrogen lamp (pressure 1 MPa, half-width 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).

Fluorescence decay was analyzed by deconvolution using a built-in-microcomputer (Intel 8085). Lifetimes were obtained by averaging several measurements, the scattering being less than 10%.

TABLE I. Absorption and Emission Spectra of Eu^{2+} Complexes

Complex	Eu:ligand	Absorption		Emission $\lambda_{\text{max}}^{\text{em}}$ (cm^{-1})
		$\lambda_{\text{max}}^{\text{abs}}$ (cm^{-1})	($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)	
15-C-5	1:3	40320(1325)	31450(450)	23150
Oc15-C-5	—	40000(1650)	31250(638)	23640
B15-C-5	—	37450(3250)	30580(480)	23980
EuCl_2		40320(1150)	30490(494)	20450

The PMR spectra were obtained using a JEOL LMN-PS-100 spectrometer (100 MHz, sweep width 1080 Hz).

All the measurements were carried out on freshly prepared samples.

Results and Discussion

Luminescence and Absorption Spectra of the Complexes

Spectroscopic data of the title complexes of Eu^{2+} are summarized in Table I. Figure 2 illustrates emission and absorption spectra of the Eu^{2+} -15-C-5 complex, as well as those of EuCl_2 .

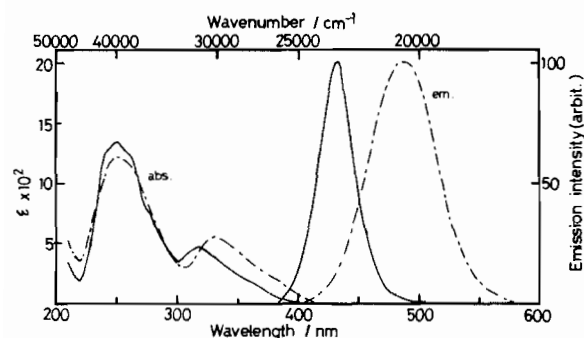


Fig. 2. Emission and absorption spectra of Eu^{2+} -15-C-5 (—) and EuCl_2 (---).

The lowest energy electron configuration of the Eu^{2+} ion is $4f^7$ and the ground state is ${}^8S_{7/2}$ [13]. The first excited configuration for Eu^{2+} is $4f^65d$. For EuCl_2 and the Eu^{2+} -15-C-5 complex, absorption is due to direct excitation of Eu^{2+} , namely $4f^7 \rightarrow 4f^65d$. For Eu^{2+} -B15-C-5 and Eu^{2+} -BB15-C-5 complexes, two or three additional absorption bands owing to aromatic double bonds of the ligands are observed. The wavelengths of the absorption are 227 nm for the Eu^{2+} -B15-C-5 complex and 210 and 232 nm for the Eu^{2+} -BB15-C-5 complex.

The molar absorption coefficient of the absorption at 276 nm is extraordinarily great because the absorption of the aromatic bonds overlaps with that of

Eu^{2+} . The emission of Eu^{2+} takes place from the $4f^65d$ level; the peak wavelength of the emission appears at around 420–430 nm for the complexes and 489 nm for EuCl_2 . The Stokes shift between the maxima of the corresponding absorption and emission bands is $\geq 6500 \text{ cm}^{-1}$.

Emission due to the aromatic double bonds of B15-C-5, which would appear at $\approx 330 \text{ nm}$, was observed if the concentration of the complex ($\text{L}:\text{Eu}^{2+} = 1:1$) was in a range of $1 \times 10^{-4} \approx 2 \times 10^{-3} \text{ M}$ or $8 \times 10^{-3} \approx 8 \times 10^{-2} \text{ M}$, while at concentration of $4 \times 10^{-3} \text{ M}$ the emission of the aromatic ligand disappeared completely and the intensity of the emission from Eu^{2+} reached a maximum value. Details of this phenomenon will be given elsewhere.

Stoichiometry of the Complexes

The establishment of stoichiometry of the complexes was attempted by means of the molar ratio method using emission intensities of the complexes. For the Eu^{2+} -15-C-5 complex, the ligand-to- Eu^{2+} ratio was found to be 3:1 [6, 7]. The ratio is, however, unusual in the crown complexes. Therefore, a PMR measurement was undertaken to clarify the structure of the complexes. Crown complexes of Sr^{2+} were used instead of the corresponding Eu^{2+} complexes because the paramagnetic Eu^{2+} ion of the latter would result in line broadening. A Sr^{2+} ion has the same charge and an almost equal radius [14].

Figure 3 shows the relation between the proton resonance shift for hydrogen in the 15-C-5 and the metal-to-ligand ratio. (The abscissa of Fig. 3 is represented by the reciprocal to that mentioned the previous paragraph.) Again, the shift levels off at the 3:1 ratio.

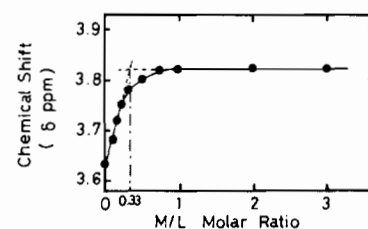


Fig. 3. Chemical shift vs. molar ratio (M/L) for Sr^{2+} -15-C-5.

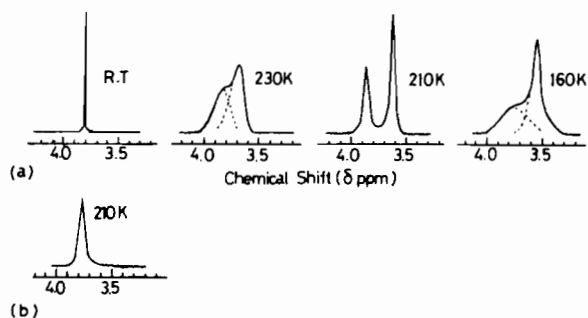


Fig. 4. Changes in the PMR spectra of the Sr^{2+} -15-C-5 complex at low temperatures. (a) M:L = 1:3 (b) M:L = 1:1.

Figure 4 illustrates changes in the PMR spectra of Sr^{2+} complexes at low temperatures. The signal which is singlet at room temperature has split into a doublet structure, indicating that the hydrogen in the complex is in two different circumstances. A peak at 3.8 ppm is assigned to the hydrogen of the 15-C-5 ligand coordinating to Sr^{2+} ; the other peak is assigned to the hydrogen located at a slightly remote position because the former peak has grown broader at 160 K. The peak intensity ratio observed is 1:2, suggesting that one 15-C-5 ring coordinates Sr^{2+} ; that is, a 1:1 complex is actually formed. A sample prepared by mixing Sr^{2+} with 15-C-5 at a 1:1 ratio gave only one resonance peak even at 210 K (Fig. 4b). These findings lead to a structural model of the complex in which a Eu^{2+} ion is capped with one crown and enclosed by two crowns located far from the central ion (Fig. 5).

Stoichiometries of complexes with other 15-C-5 derivatives have not been determined because the

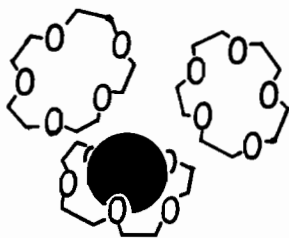


Fig. 5. A model of the Eu^{2+} -15-C-5 complex.

TABLE II. Luminescence Properties of Eu^{2+} Complexes

Complex	Eu:ligand	ϕ (%) ^a	τ (ns) ^b	$k/10^5$ (s ⁻¹) ^c	$k^*/10^5$ (s ⁻¹) ^d	I^e
15-C-5	1:3	28	800	3.5	9.0	690
Oc15-C-5	—	21	761	2.8	12	690
B15-C-5	—	1.5	143, 824 ^f	1.2	69	95
EuCl_2		0.04	20	0.18	420	1.0

^aLuminescence quantum yield. ^bLuminescence lifetime. ^cRadiative rate constant. ^dNon-radiative rate constant. ^eIntensity of emission ($\text{EuCl}_2 = 1.0$). ^fSee text.

molar ratio plots of their emission intensities give some extraordinary values, such as $\text{Eu}^{2+}:\text{L} = 1:7$, or the intensities have increased uniformly with the ratio of the ligands. It is well known that the luminescent properties of Eu^{3+} and Tb^{3+} ions in solution are sensitive to the environment of the first coordination sphere surrounding the ions [15]. However, in some Eu^{2+} -crown ether methanol systems, an outer sphere may also be responsible for the emission intensities.

Luminescence Intensities and Quantum Yields

The observed emission intensities of the complexes are generally very large. Of the 15-C-5 derivative complexes examined, the most intense fluorescence is given by methanol solutions of 15-C-5 and of Oc15-C-5 with Eu^{2+} , the intensity of which is 690 times greater than that given by a EuCl_2 -methanol solution of the same Eu^{2+} concentration (Table II). Concentration of the Eu^{2+} ion in the complex solutions was maintained at 4.0×10^{-3} M.

Reasons for the intensity increase are: (1) the ligand 15-C-5 substitutes completely methanol molecules coordinated to a Eu^{2+} ion and (2) the attached ligand protect the central Eu^{2+} ion from collisions with solvent molecules of methanol. Methanol has an OH group in its structure and acts as a very effective quencher of excited energy.

A side chain in Oc15-C-5 impairs the quantum yield slightly; an aromatic ring in B15-C-5 impairs the quantum yield heavily. The latter cannot form a cage structure around the Eu^{2+} ion, as 15-C-5 does, because of steric hindrance. The aromatic group also exhibits luminescence at 337 nm by the UV irradiation. Details will be given elsewhere.

Lifetimes of Luminescence

Lifetimes of luminescence for the complexes are listed in Table II. The values for the complexes are considerably larger than that for EuCl_2 .

Figure 6 shows a decay curve of the B15-C-5 complex. It seems to have two components ($\tau = 143$ ns and $\tau = 824$ ns), indicating the existence of two kinds of complexes. The complex having a longer lifetime is probably similar in structure to the 15-C-5

TABLE III. Luminescence Properties of EuBr_2 -crown Complexes in Various Solvents

Sample	Solvent	ϕ (%) ^a	τ (ns) ^b	$k/10^5$ (s ⁻¹) ^c	$k^*/10^5$ (s ⁻¹) ^d	I^e
EuBr ₂	MeOH	0.03	1.5	2.0	6600	1.0
	EtOH	0.07	3.5	2.0	2900	2.0
	PrOH	0.07	3.7	1.9	2700	2.5
Eu(II)-15-C-5	MeOH	24	8.3×10^2	2.9	9	690
	EtOH	23	6.5×10^2	3.6	12	680
	PrOH	23	7.5×10^2	3.1	10	660
Eu(II) 18-C-6	MeOH	6.7	20.0×10^1	3.3	46	160
	EtOH	2.2	6.3×10^1	3.5	150	69
	PrOH	1.3	4.4×10^1	3.0	220	38

^aQuantum yield. ^bLuminescence lifetime. ^cRadiative rate constant. ^dNon-radiative rate constant. ^eEmission intensity ($\text{EuCl}_2 = 1.0$).

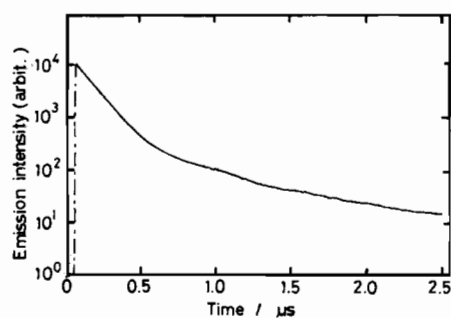


Fig. 6. Luminescence lifetime of the B15-C-5 complex.

complex. The one with the shorter lifetime seems to be from a coexisting 1:1 or 1:2 complex.

Radiative and non-radiative rate constants were derived from the quantum yields, and the lifetimes were obtained. The latter becomes greater on going from 15-C-5 to B15-C-5, while the former has almost the same value. This is because the protection of Eu^{2+} in the 15-C-5 complex from solvent molecules is superb.

Table III lists luminescence properties of EuBr_2 -crown complexes in various solvents. For 15-C-5 complexes, lifetimes and quantum yields do not exhibit any differences in different solvents, while, in 18-C-6 complexes, these values decrease with increase in molecular weight of the solvent. The metal-to-ligand ratio of the 18-C-6 complex is 1:1 [16], and the complex has an equatorial-surrounded structure whose top and bottom are open. Thus, the solvent molecules can collide with or even coordinate to the central Eu^{2+} ion and can consume the excited energy of Eu^{2+} .

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