Luminescence of Divalent Europium Complexes with 18-Crown-6 Derivatives

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Abstract

The luminescence of divalent europium complexes with 18-crown-6 and its derivatives has been studied. The quantum yields and lifetimes of the emission were determined by conventional methods. The observed intensity of the luminescence is generally very large and the most intense luminescence is given by a methanol solution of 18-crown-6 complex with Eu^{2+} the intensity of which is 150 times greater than that given by a $EuCl_2$–methanol solution of the same Eu^{2+} concentration.

Radiative and non-radiative rate constants for the excited states of the complexes have been estimated from emission lifetimes and quantum yields. The emission intensity enhancement on complex formation with crown ethers seems to be due to the insulation of the Eu^{2+} ion from the close approach of solvent molecules resulting in non-radiative energy losses.

Introduction

Complexes of lanthanide ions with multidentate macrocyclic ligands have attracted considerable interest [1–11]. The thermodynamic and spectroscopic properties of the complexes of some divalent lanthanide ions such as Sm^{2+}, Eu^{2+} and Yb^{2+} in solution have also been studied intensively [12, 13].

On the contrary, the emission properties of the complexes of the divalent lanthanides have received little attention [14–17].

Adachi *et al.* [14, 15] showed that the most intense fluorescence is given by a methanol solution of 15-crown-5 complex with Eu^{2+}. Sabbatini *et al.* [6, 7] have reported absorption and emission properties of an Eu^{2+} cryptate in aqueous solution.

A divalent europium ion known as a $4f^6 5d \rightarrow 4f^7$ broad band emitter has been used for X-ray intensifying screens BaFCl: Eu [12] as well as for lamp phosphors [18]. The ground state of Eu^{2+} is $^8S_{7/2}$ with the 4f configuration. The lowest lying excited configuration is $4f^6 5d$. The 4f electrons are shielded from the surrounding lattice or ligands by 5s and 5p electrons and thus are affected only weakly by changes in the environment. The energy of the promoted 5d electrons, however, is strongly·perturbed by its surroundings; changes in this level are responsible for the effects of the ligand field on the optical properties of Eu^{2+} compounds.

This paper presents the results obtained on the measurement of the luminescence properties of the Eu^{2+} complexes formed in reactions between anhydrous $EuCl_2$ and 18-crown-6 derivatives in methanol.

Experimental

Materials

The ligands used are illustrated in Fig. 1. 18-C-6 and DCH18-C-6 were kindly offered by Nippon Soda Co., Tokyo, Japan. B18-C-6 and BB18-C-6 (n = 5) were prepared in a similar manner to that described elsewhere [19].

$EuCl_2$ was prepared from 99.99% Eu_2O_3, which was mixed with excess NH_4Cl and then 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. This process was essential to prevent the oxidation of Eu^{2+} in the complexes to Eu^{3+}

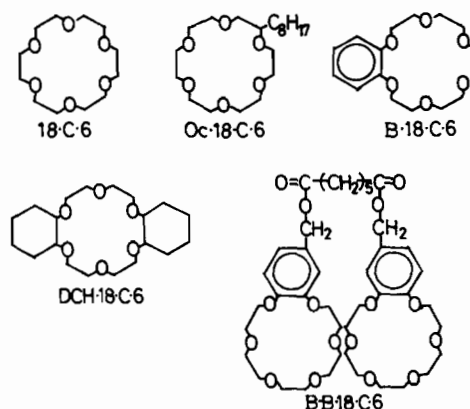All other compounds were at least reagent grade and used as supplied.

Fig. 1. Schematic representation of ligands used.

Instrumental and Procedures

Emission and excitation spectra were determined on a Shimadzu Absolute Spectrofluorophotometer, Model RF-502, using the automatic Compensation and pre-calibration system for the instrumental factors [14, 15, 20]. Emission spectra were taken 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 ($\phi = 0.55$) [21, 22]. The excitation wavelength for the standard quinine solution was 365 nm.

Fluorescence lifetimes of the complexes were measured using a Horiba Time-resolved Spectrofluorometer NAES-1000 equipped with a high pressure hydrogen lamp (pressure 1 MPa, half-width of the pulse < 2ns). The emission was monitored using a Hamamatsu 1P28 photomultiplier (for a starting pulse) and a Hamamatsu R928P photomultiplier (for a stop pulse).

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

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

The spectroscopic data obtained for the title complexes of Eu^{2+} are summarized in Table I. Figure 2 illustrates emission and absorption spectra of the Eu^{2+} 18-C-6 complex, as well as those of $EuCl_2$. All the emissions obtained peaked at 22300–22700 cm^{-1}. The absorption spectrum patterns of the complexes consist of two bands attributed to Eu^{2+} (36200–38900 cm^{-1} and 30400–31400 cm^{-1}) and
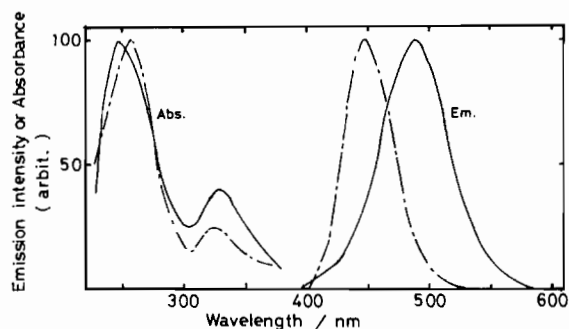

Fig. 2. Emission and absorption spectra of Eu^{2+} complexes in methanol: $EuCl_2$ ——— , 18-C-6 complex —·—·—.

some other bands due to aromatic conjugated double bonds of ligands (48500, 43100 and 36200 cm^{-1} for B18-C-6 and 47600, 36200 and 35800 cm^{-1} for BB18-C-6). The absorptions of Eu^{2+} are attributable to the 4f → 5d transitions [23].

The emission spectra are composed of broad bands due to transitions between the $^8S_{7/2}$ state and the crystal field components of the $4f^6 5d$ configuration if the lowest $4f^6 5d$ component is situated below the $^6P_{7/2}$ state of the $4f^7$ configuration and this is the case. Detailed arguments of the energy levels of Eu^{2+} have been described elsewhere [17, 27].

When the complexes are formed, the emission wavelength moves to a shorter wavelength and becomes significantly stronger compared with the methanol solvated $EuCl_2$.

Stoichiometry of the Complexes

The gradual addition of 18-C-6 to a methanol solution of $EuCl_2$ resulted in an increase in emission intensity, which reached a maximum after approximately 1 equivalent of the ligand had been added (Fig. 3). The stoichiometry of the complex was, therefore, found to be 1:1 (Eu:ligand). The situation was the same for other ligands except for BB18-C-6, which has a 2:1 ratio.

The cavity size of 18-C-6 is approximately 0.14 nm [26] and is enough to accommodate one Eu^{2+} ion in its ring. These stoichiometries were confirmed by means of PMR measurements.

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

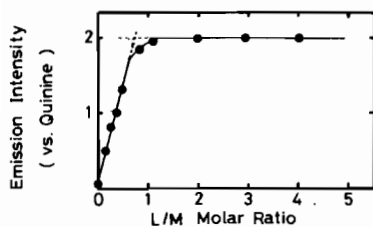| Complex	(Eu:ligand)	Absorption				Emission
		λ_{max}^{abs}, cm^{-1}		$(\epsilon, M^{-1} cm^{-1})$		λ_{max}^{em}, cm^{-1}
18-C-6	(1:1)	38910	(1237)	30770	(338)	22420
Oc18-C-6	(1:1)	38760	(2025)	30860	(555)	22470
DCH18-C-6	(1:1)	38910	(1900)	31450	(345)	22730
B18-C-6	(1:1)	37310	(3260)	30490	(388)	22370
BB18-C-6	(2:1)	36230	(3538)	30680	(562)	22320
EuCl₂		40320	(1150)	30490	(494)	20450

Fig. 3. Molar ratio (L/M) *vs.* emission intensity plot for Eu^{2+} 18-C-6 complex.

Crown complexes of Sr^{2+} were used instead of the corresponding Eu^{2+} complexes because the latter would shift the signals and because Sr^{2+} has the same charge and almost the same radius as Eu^{2+} [24]. A peak on a PMR spectrum for the Sr^{2+} 18-C-6 complex was found at 3.8 ppm while protons of the uncomplexed 18-C-6 appeared at 3.6 ppm.
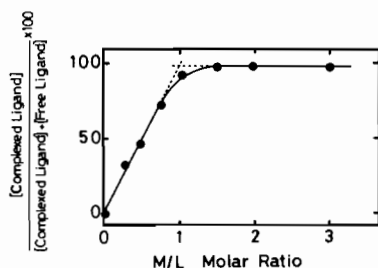

Fig. 4. Variation of proton NMR signal as a function of molar ratio (M/L) for Sr^{2+} 18-C-6 complex.

Figure 4 illustrates the relation of molar ratios (Sr^{2+}/18-C-6) *vs.* peak intensity ratios of the protons of the complex to the sum of peak intensities of the protons of the complex and of the uncomplexed ligands. The result also indicates that the complex is a 1:1 ratio. Similar results were obtained for complexes of Oc18-C-6 and DCH18-C-6.

For B18-C-6 and BB18-C-6, the proton exchange between the complexed and uncomplexed ligands was considerably faster at room temperature, so that only one peak appeared at a weighted mean position in the shift of the complexed and uncomplexed ligands.

Figure 5 shows a molar ratio plot for the Sr^{2+} B18-C-6 complex, indicating the presence of a 1:1
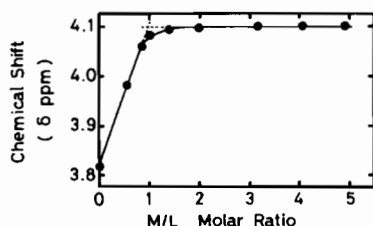

Fig. 5. Chemical shift *vs.* molar ratio (M/L) for Sr^{2+} B18-C-6.

complex. For the Sr^{2+} BB18-C-6 complex, a 2:1 complex was found, that is, each crown ring contains one metal ion in its cavity hole. All the ratios were confirmed for Eu^{2+} complexes by the emission intensity molar ratio method.

Luminescence Intensities and Quantum Yields

The observed intensity of the fluorescence was generally very large; of the 18-C-6 derivative complexes examined, the most intense fluorescence was given by a methanol solution of 18-C-6 complex with Eu^{2+}, the intensity of which was 150 times greater than that given by a EuCl$_2$–methanol solution of the same Eu^{2+} concentration. The concentration of Eu^{2+} ion in the complex solutions was maintained at 4.0 × 10^{-3} M.

Crown ethers having an aromatic ring exhibit an emission at $\simeq$300 nm ($\simeq$33000 cm^{-1}) which overlaps with an Eu^{2+} absorption band. The excitation energy obtained with the ligand, therefore, could migrate to an Eu^{2+} ion in the complex.

In the Eu^{2+} BB18-C-6 complex, the emission intensity from the double bonds decreased with the complexation of Eu^{2+} ions by a factor of about 20, suggesting the existence of the energy transfer.

No little surprise is occasioned by the result that the complexes of ligands having an aromatic ring give a weak emission. The aromatic group does not act as an intramolecular sensitizer. The substitute hinders the formation of a stable complex because the aromatic ring decreases the flexibility of the 18-C-6 ring.

Cyclohexane rings also reduce the emission intensity for the same reason as that described above, though the extent of clamping of the carbon–carbon bond is not great.

Stability constants of Sr^{2+} analogues estimated from the data in Figs. 3, 4 and 5 decrease with substitution with a side chain or a cyclic or aromatic group though the extent of the decrease is small. This finding coincides with the fact that the emission intensity decreases with the substitution.

Luminescence quantum yields obtained from absorption and emission intensities are also tabulated in Table II.

Possible quenching processes for the luminescence of the complexes are (1) an interaction of solvent molecules with the complexes, *i.e.*, the collision of methanol molecules with the complexes, (2) the vibration of solvated methanol and (3) the vibration of coordinated ligands. For a solution of EuCl$_2$ methanol, process (2) seems to be predominant.

The central Eu^{2+} active site in 18-C-6 is effectively protected by the ligands from collision with solvent molecules and the fitting of the Eu^{2+} ion to the hole of this ligand is very good so that the non-radiative deactivation processes such as (2) and (3) are minimal among several 18-C-6 derivatives. For the Oc18-C-6

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

Complex	(Eu:ligand)	ϕ (%)[a]	τ (ns)[b]	k (s/10^5)[c]	k^*(s/10^5)[d]	I[e]	log K_{Sr}[f]
18-C-6	(1:1)	9.4	142	6.6	64	150	3.76
Oc18-C-6	(1:1)	6.7	143	4.7	66	120	3.74
DCH18-C-6	(1:1)	3.8	89	4.3	110	87	3.68
B18-C-6	(1:1)	0.20	28	0.72	360	9.2	3.62
BB18-C-6	(2:1)	0.05	g	g	g	2.2	3.57
EuCl$_2$		0.04	20	0.18	420	1.0	−

[a] Luminescence quantum yield.   [b] Luminescence lifetime.   [c] Radiative Rate constant.   [d] Non-radiative rate constant.
[e] Intensity of emission (EuCl$_2$ = 1.0).   [f] Stability constant of Sr^{2+} analogue.   [g] Not available.

complex, an octyl group vibrates fairly freely letting the excitation energy loose slightly.

The complexes of B18-C-6 and BB18-C-6 have shown very poor quantum yields. A plausible explanation for this is given above (see intensities section).
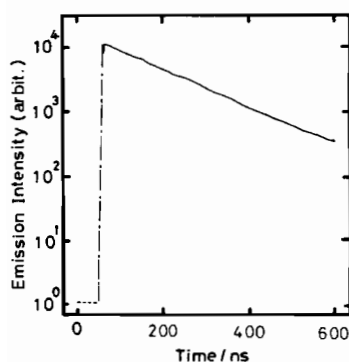

Fig. 6. Intensity of emission *vs.* time for Eu^{2+} 18-C-6 complex.

Lifetimes of Luminescence

Figure 6 illustrates emission intensities *vs.* time for the 18-C-6 complex. Lifetimes obtained are listed in Table II. The value for the BB18-C-6 complex was less than 10 ns.

The lifetimes are relatively short, but the emission is typical of $4f^6 5d \rightarrow 4f^7$ transitions.

One can estimate the values of the radiative rate constants k and the non-radiative rate constant k^* from eqns. (1) and (2).

$$\phi = k\tau \qquad (1)$$

$$\tau = \frac{1}{k + k^*} \qquad (2)$$

The radiative rate constants k obtained are almost constant except for the B18-C-6 complex, while k^* becomes larger for the DCH18-C-6 complex.

The luminescence enhancement owing to complexation is, therefore, not due to an increase in the k values, but due to a decrease in the k^* values.

Acknowledgements

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