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Luminescence of divalent europium complexes with N-pivot lariat azacrown ethers

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Abstract

The luminescence and absorption spectra and emission lifetimes of divalent europium complexes with 10-(2-methoxyethyl)-1,4,7-trioxa-10-azacyclododecane (MEN12C4) and 13-(2-methoxyethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (MEN15C5) have been investigated. The stoichiometry of the Eu^{2+} N-pivot lariat monoazacrown ether complexes in methanol was determined by the use of the emission intensity molar ratio method and by monitoring the shift and splitting of the proton magnetic resonances for the Sr^{2+} analogs. These results indicated the formation of the strongly bound 1:1 Eu^{2+} complex with MEN15C5. It was also found that the 1:2 Eu^{2+}–MEN12C4 complex was formed in the presence of excess ligand and that the 1:1 complex was predominantly formed for the ratio of MEN12C4:$Eu^{2+} \leqslant 1$. Furthermore it was revealed that the oxygen atom in the 2-methoxyethyl group also coordinated to the Eu^{2+} ion. Luminescence intensity was enhanced by the complexation, compared with that for the Eu^{2+} ion solvated by methanol. The luminescence intensities for both the 1:2 Eu^{2+}–MEN12C4 and the 1:1 Eu^{2+}–MEN15C5 complex were 410 and 13 times greater than that given by a methanolic $EuCl_2$ solution of the same Eu^{2+} concentration (4×10^{-3} M), respectively. The emission intensity for the Eu^{2+}–MEN12C4 complex was larger than that obtained for any other Eu^{2+} macrocyclic ligand complex having nitrogen as coordinating atoms.

Introduction

A divalent europium ion emits blue luminescence by a 4f–5d transition under UV excitation, in general. Since such a 4f–5d transition is allowed for the absorption and emission of electric-dipole radiation, the Eu^{2+} ion strongly absorbs the light of appropriate wavelengths for itself.

When complexes are formed between Eu^{2+} and optical non-absorbing crown ethers or cryptands, the luminescence intensity is enhanced by the encapsulation of the central emitting Eu^{2+} ion [1–8]. For the Eu^{2+} complexes with ligands including the nitrogen atom, the emission peak is located at a longer wavelength side than that for a Eu^{2+} oxygen coordinating crown ether complex, but the obtained luminescence intensity is a modest one [2].

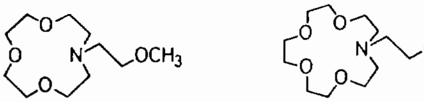
In this paper, we prepare the Eu^{2+} complexes with N-pivot lariat monoazacrown ethers, and have investigated their fluorescence properties. It is also elucidated that the emission characteristics of the complexes are associated with the stoichiometries and local symmetries around the central Eu^{2+} ion of the complexes.

Experimental

Materials

The ligands used were 10-(2-methoxyethyl)-1,4,7-trioxa-10-azacyclododecane (MEN12C4) and 13-(2-methoxyethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (MEN15C5), as illustrated in Fig. 1. They were synthesized by a method similar to that in ref. 9. The purity was confirmed by NMR, mass spectra and the obtained compounds also gave C, H and N combustion analysis (±0.3%).

The sample solutions of divalent europium azacrown ether complexes were prepared by dissolving anhydrous $EuCl_2$ and azacrown ethers in anhydrous degassed methanol. $EuCl_2$ was prepared from Eu_2O_3 (99.99%) mixed with an excess of NH_4Cl and then heated at 300 °C for 1 h, 400 °C for 2 h, 500 °C for 1 h and 700 °C for 2 h in a hydrogen atmosphere.



MEN12C4 MEN15C5

Fig. 1. Schematic representation of ligands used.

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Measurement and instrumentation

Absorption spectra were obtained by means of a Shimadzu double beam spectrophotometer, model UV 180. Emission and excitation spectra were recorded on a Hitachi 850 fluorescence spectrophotometer, using an appropriate emission filter. Emission intensity was recorded on the sample solution which has the same Eu^{2+} concentration of 4×10^{-3} M, except for that in the Job's method of continuous variations.

Fluorescence quantum yields were determined by comparison with that of a 1×10^{-5} M quinine sulfate -0.1 M H_2SO_4 ($\Phi=0.55$). The excitation wavelength for the standard quinine solution was 365 nm.

Luminescence lifetimes were determined using a Horiba time-resolved spectrofluorometer NAES-1100, equipped with a high pressure hydrogen lamp; (pressure 1 MPa, half-width of the pulse <2 ns). Fluorescence decays were analysed by deconvolution using a built-in-microcomputer. All the measurements were carried out on freshly prepared samples.

^1H NMR spectra (in $CDCl_3$ or methanol-d_4) for the Sr^{2+} title monoazacrown ether complexes were recorded on a JEOL JNM-GSX-400 (400 MHz NMR). The ligand concentration was held constant in this measurement. Mass spectra were obtained on a JEOL JMS-DX303 instrument.

Results and discussion

Absorption and luminescence spectra of the complexes

Emission and absorption spectra of the title Eu^{2+} complexes, as well as that of $EuCl_2$, are illustrated in Fig. 2. The ground state of Eu^{2+} is $^8S_{7/2}$ ($4f^7$) [10, 11] and the lowest excited configuration is $4f^65d$ in this case. Their absorption peaks in the near-UV region mainly consisted of two broad bands ascribed to the transition from the $4f^7$ level to the split $4f^65d$ levels of Eu^{2+} [12].

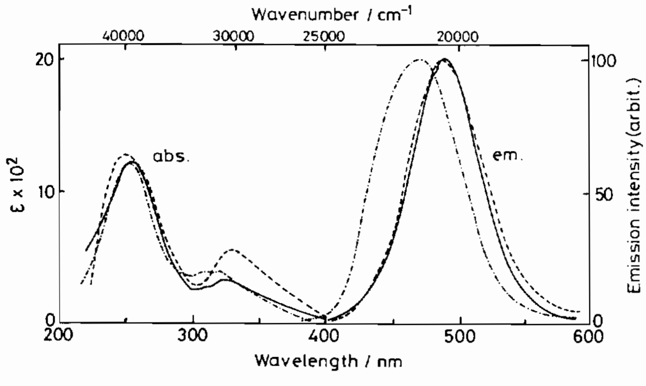

Fig. 2. Absorption and emission spectra of Eu^{2+}–MEN12C4 (——), Eu^{2+}–MEN15C5 (–·–) for a methanolic solution containing 1:1 Eu^{2+}:ligand, and $EuCl_2$ (– – –) in methanol.

The absorption maxima and the corresponding extinction coefficients are summarized in Table 1, where the data for Eu^{2+}–12-crown-4(12C4) and Eu^{2+}–15-crown-5(15C5) are also given for the purpose of comparison. The most intense absorption appeared at 257 and 252 nm for Eu^{2+}–MEN12C4 and Eu^{2+}–MEN15C5, respectively. The maximum molar extinction coefficient was *c.* 10^3 dm^3 mol^{-1} cm^{-1} in each case. The magnitude of this order indicates that the absorption peak is due to an electric-dipole allowed transition. When the complexes of Eu^{2+} with the title azacrown ethers are formed, the splitting widths of the two peaks, i.e. the crystal-field splittings of the excited 5d levels, become narrower and a slight splitting of the peak appearing at *c.* 320 nm is observed (see Table 1). These phenomena could be caused by the lower symmetry of the title azacrown ethers' environment around Eu^{2+}.

The radiative emission of Eu^{2+} originates from the transition from the lowest energy component of the 5d levels to the ground state of $4f^7$. The peak of each emission was located at 488 nm for Eu^{2+}–MEN12C4 and at 472 nm for Eu^{2+}–MEN15C5. They appeared at the longer wavelength side as they do for Eu^{2+}–15C5 (432 nm) and Eu^{2+}–18C6 (436 nm). This finding was similar to the results obtained in the studies on the fluorescence spectra for the Eu^{2+}–diazacrown ether and cryptand complexes [2]. For Eu^{2+}–MEN12C4, the half-width of the emission band (*c.* 2100 cm^{-1}) is smaller than that of $EuCl_2$ (*c.* 2800 cm^{-1}), while the half-width (*c.* 3400 cm^{-1}) for Eu^{2+}–MEN15C5 is much larger. The Eu^{2+}–MEN12C4 complex exhibited a Stokes shift of about 10 800 cm^{-1} and that of the Eu^{2+}–MEN15C5 complex was 10 100 cm^{-1}. The values of the Stokes shifts are almost equal to that of $EuCl_2$ (10 000 cm^{-1}). These results may be considered by the notion that the cohesion energies in the ground and excited states and the symmetry of the complex influence such a 5d–4f transition of Eu^{2+}.

Stoichiometry and luminescence intensity of the complexes

Addition of MEN12C4 to a methanol solution of $EuCl_2$ results in the enhancement of the fluorescence intensity of the complex (Fig. 3). The position of the curve-bend generally gives the stoichiometry of the complex. In this case, however, the observed curve-bend was not sharp. It can be interpreted as the notion that the stability of the Eu^{2+} complex with MEN12C4 is extremely low. Determination of the stoichiometry of the complex will be discussed later in detail with the data of both NMR for the Sr^{2+} analog and the Job's method of continuous variation using the emission intensity.

The emission intensity also increased by portion-wise addition of MEN15C5 to Eu^{2+} (Fig. 4). It reached a

TABLE 1. Absorption and emission properties of Eu^{2+} complexes

Complex	Absorption maxima[a] (cm^{-1})	Split[b] (10^3 cm^{-1})	Emission maximum (cm^{-1})	Stokes shift (10^3 cm^{-1})
Eu^{2+}-12C4	39680(—), 31060(—)	8.6	20490	10.6
Eu^{2+}-15C5	40320(1325), 31450(450)	8.9	23150	8.3
Eu^{2+}-MEN12C4	38910(1238), 32680(300), 31250(263)	6.2, 1.4	20490	10.8
Eu^{2+}-MEN15C5	39680(1217), 33260(300), 31250(389)	6.4, 2.0	21190	10.1
$EuCl_2$	40320(1258), 30490(558)	9.8	20490	10.0

[a] Extinction coefficient ϵ (mol^{-1} cm^{-1}) given in parentheses. [b] Crystal-field splitting of the excited 5d level.

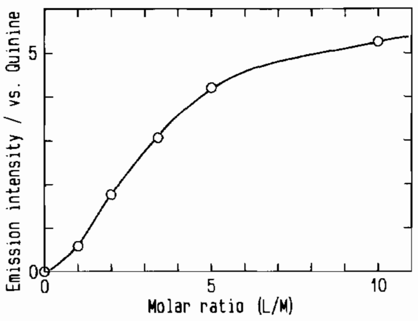

Fig. 3. Molar ratio of ligand:metal (L/M) vs. emission intensity plot for Eu^{2+}-MEN12C4 complex in methanol.

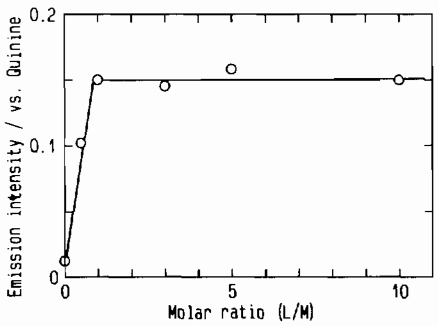

Fig. 4. Molar ratio of ligand:metal (L/M) vs. emission intensity plot for Eu^{2+}-MEN15C5 complex in methanol.

maximum after *c.* 1 equiv. of the ligand had been added to Eu^{2+}. The sharp curve-bend indicates that the MEN15C5 ligand easily forms the complex with Eu^{2+} and that the stoichiometry of the complex is 1:1 (ligand:Eu). This result is different from the ligand-to-Eu^{2+} ratio (3:1) for the Eu^{2+}-15C5 complex, which has been established in refs. 2 and 7. One ring of the MEN15C5 ligand fails to accommodate one Eu^{2+} ion completely, since the cavity size of the 15C5 ring (approximately 1.7–2.2 Å) [13] is smaller than the diameter of the Eu^{2+} ion (2.34–2.7 Å) [14] as the eight-coordinated site. Therefore, the formation of the Eu^{2+}-MEN15C5 complex must be affected by the 2-methoxyethyl group in the ligand.

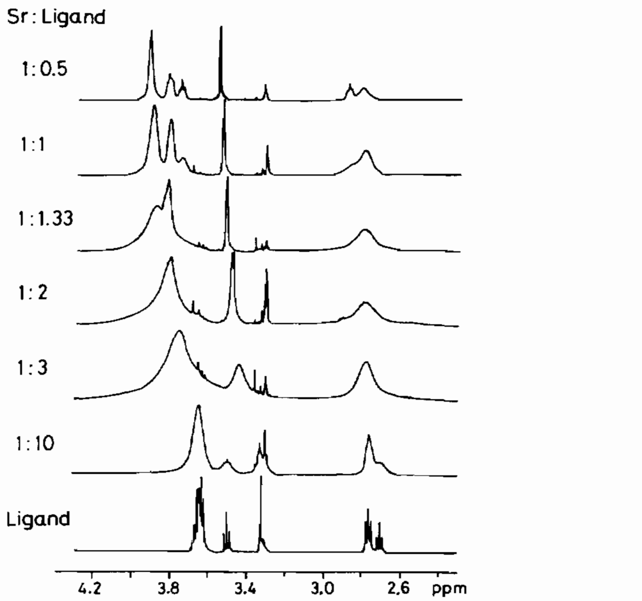

Fig. 5. ^1H NMR spectra for Sr^{2+}-MEN12C4 complex in methanol-d_4 at 26 °C.

NMR measurements were undertaken to clarify the stoichiometry of Eu^{2+}-MEN12C4. Figure 5 shows ^1H NMR spectra for the Sr^{2+}-MEN12C4 complex in methanol-d_4 at 26 °C. The Sr^{2+} complex was used instead of the Eu^{2+} one, because the paramagnetic Eu^{2+} ion would result in broadening and shifting of the resonances. The Sr^{2+} ion has the same charge and an almost equal radius [14]. The highly resolved resonances of the uncomplexed MEN12C4 are easily assigned, as follows. The chemical shift, δ, for protons of $-CH_2O-$ in the ring is 3.60–3.67 (multiplet) ppm. The protons of $-CH_2N-$ in the ring and of $-CH_2N-$ in the side chain are found at 2.76 (triplet) and 2.70 (triplet) ppm, respectively. The protons of $-CH_2O-$ and CH_3O- groups in the side chain appear at 3.50 (triplet) and 3.32 (singlet) ppm, respectively. On addition of $SrCl_2$ to a methanol-d_4 solution of MEN12C4, almost all of the protons were downfield shifted and most of them collapsed into a broad resonance. As $SrCl_2$ is added, the resonances change gradually. The resonances obtained in the range of azacrown:salt$\geqslant$2 would be ascribed to one complex, and the resonances appearing for azacrown:salt$\leqslant$1 to another complex. In order to get further information, ^{1}H NMR measurement of the same solution was performed at a lower temperature (−23 °C) (Fig. 6). The well-resolved resonances given by slowing down the rate of ligand exchange reveal the formation of two kinds of complexes, that is, the resonances for azacrown:salt ratios between 10:1 and 1:1 are quite different from those for the ratios between 1:1 and 1:0.5. The two kinds of the resonances will be explained in terms of the formation of the 1:1 and 1:2 Sr^{2+}:azacrown complex. It can be also seen in Fig. 7(a) and (b), which depicts the chemical shifts for the protons of $-CH_2O-$ in the side chain and of $-CH_2N-$ in the azacrown ring versus the molar ratio at 26 °C, respectively, that a curve-bend appears at the ratio of Sr^{2+}:azacrown = 1:2. Therefore we can conclude that a 1:1 Eu^{2+}:azacrown complex is formed for azacrown:salt $\leqslant 1$ and that a 1:2 one is formed for azacrown:salt $\geqslant 2$. Furthermore the non-sharp bend in Fig. 7(a) indicates that the oxygen atom in the 2-methoxyethyl group weakly coordinates to Eu^{2+}.

^{1}H NMR spectra for the Sr^{2+}–MEN15C5 complex in methanol-d_4 at 26 °C are illustrated in Fig. 8. The resonances for the protons of the complexed ligand have been shifted downfield and appear separately from those of the uncomplexed ligand in this case. Judging from the change of the resonances versus the molar ratio, all of the resonances can be attributed to either a uncomplexed ligand or a strongly bound 1:1 Eu^{2+}:MEN15C5 complex. The formation of the only 1:1 metal:MEN15C5 complex is consistent with the data of the emission intensity molar ratio method described above.

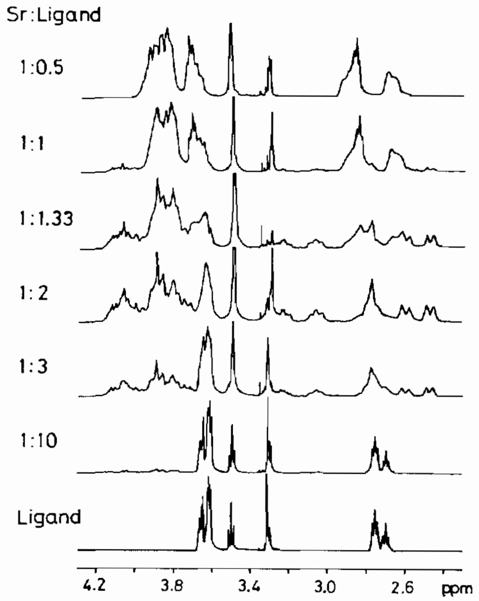

Fig. 6. ^{1}H NMR spectra for Sr^{2+}–MEN12C4 complex in methanol-d_4 at −23 °C.

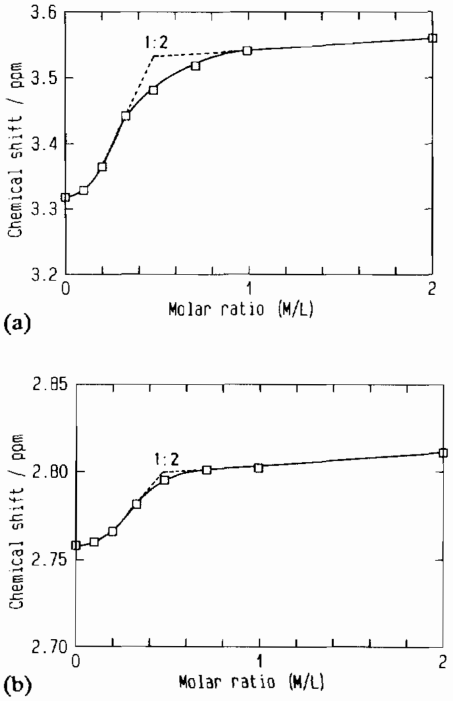

Fig. 7. Chemical shift vs. molar ratio of metal:ligand (M/L) for Sr^{2+}–MEN12C4 at 26 °C; (a) $-OCH_3$ in the side chain, (b) $-CH_2N-$ in the ring.

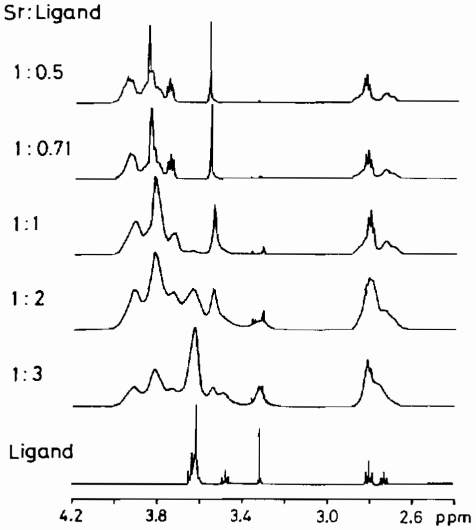

Fig. 8. ^{1}H NMR spectra for Sr^{2+}–MEN15C5 complex in methanol-d_4 at 26 °C.

The Job's method of continuous variations using the emission intensity was applied to elucidate the stoichiometry of the Eu^{2+} complexes. For Eu^{2+}–MEN12C4, a peak deviated from the position of M/(L+M) = 0.5, i.e. L/M = 1, and it appeared at M/(L+M) = 0.25, which means M:L = 1:3, as shown in Fig. 9. However, it does not indicate that the stoichiometry of the complex is 3:1 (ligand:Eu^{2+}), because it was judged from the result of the molar ratio method that the stability of the Eu^{2+}

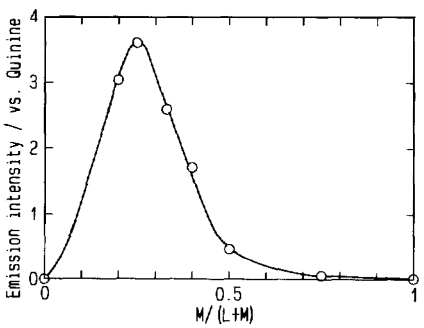

Fig. 9. Continuous variation method of emission intensity for Eu^{2+}–MEN12C4 in methanol.

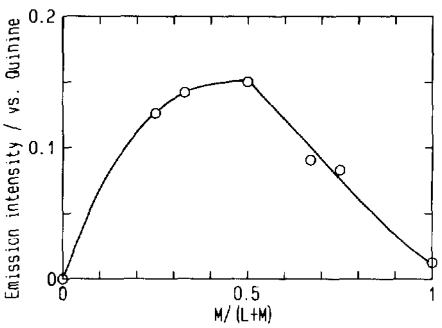

Fig. 10. Continuous variation method of emission intensity for Eu^{2+}–MEN15C5 in methanol.

complex with MEN12C4 was very low. This result, therefore, will be explained in terms of the formation of the 1:2 Eu^{2+}–MEN12C4 complex, which is supported by the NMR data.

As the M/(L+M) ratio decreases, the emission intensity increases to only a small extent for the ratios between 0.5 and 1 (Fig. 9). The rapid increase of the emission intensity can be also seen as the M/(L+M) ratio becomes less than OS. These findings indicate that the 1:1 complex formed in the presence of an excess of the Eu^{2+} ion has a low luminescence quantum yield and that the 1:2 Eu^{2+}:MEN12C4 complex has a considerably high quantum yield.

The Job's plot applied to the emission intensity of Eu^{2+}–MEN15C5 suggested the 1:1 complex to be the only complex present (Fig. 10). This conclusion is consistent with both the data of the molar ratio method and the NMR data.

The luminescence intensity obtained for the 1:2 Eu^{2+}–MEN12C4 complex was 410 times larger than that given by a EuCl$_2$–methanol solution of the same Eu^{2+} concentration (4 X 10^{-3} M). It was 13 times larger than that for the 1:1 Eu^{2+}–MEN15C5 complex. The wavelengths of the maximum fluorescence and the emission intensity for the Eu^{2+} complexes with the various macrocyclic ligands having nitrogen are collected in Table 2. The Eu^{2+}–MEN12C4 complex exhibited the most intense emission and the longest wavelength of the emission.

TABLE 2. Luminescence properties of Eu^{2+} complexes with the various macrocyclic ligands including the nitrogen atom

Complex	Emission maximum (nm)	I” (%)
Eu^{2+}–MEN12C4	488	410
Eu^{2+}–MEN15C5	472	13
Eu^{2+}–N15C5(2,1)^{b,d}	460	130
Eu^{2+}–N18C6(2,2)^{c,d}	469	6.8
Eu^{2+}–Cryp.(2,1,1)^{d}	445	1.0
Eu^{2+}–Cryp.(2,2,1)^{d}	445	29
Eu^{2+}–Cryp.(2,2,2)^{d}	468	270
EuCl$_2$	488	1.0

“Emission intensity (vs. EuCl$_2$). [b]1,4,7-Trioxa-7,13-diazacyclopentadecane. [c]1,4,7,13-Tetraoxa-1,10-diazacyclooctadecane. [d]Ref. 2.

Photophysical properties

Luminescence quantum yields and luminescence lifetimes are summarized in Table 3. The emission intensity obtained for these Eu^{2+} complexes is larger than that for EuCl$_2$.

Radiative and non-radiative rate constants are derived from the equations

$$\phi = k\tau$$

$$\tau = 1/(k + k^*)$$

where k and k^* are the radiative and non-radiative rate constants, respectively. The radiative constant k is almost the same value of the order of 10^5 and its value can be ascribed to the electric-dipole allowed and partly spin-forbidden 5d–4f transition of Eu^{2+}, while k^* changes from 10^5 to 10^8 s^{-1}. The enhancement of the emission intensity is due to a decrease in the k^* value. The excited Eu^{2+} ion is non-radiatively deactivated by being coordinated with some methanol molecules, because the OH groups having a high vibration energy ($\nu = 3600\ \mathrm{cm}^{-1}$) and effectively quench the excited energy from the Eu^{2+} ion. The magnitude of k^* will, therefore, be strongly dependent on the number of methanol molecules coordinated to Eu^{2+}. As its number of methanol molecules decreases, the value of k^* decreases and the luminescence quantum yield becomes larger.

The formation of the Eu^{2+} complex with a macrocyclic ligand leads to the elimination of some solvent molecules from the coordination sphere of the central Eu^{2+} ion. Such an encapsulation effect would increase as the ratio of ligand:Eu^{2+} increases in the stoichiometry of the complex. For the 1:2 Eu^{2+}:MEN12C4 complex, the k^* value was relatively small (11 x 10^{-5} s^{-1}). On the other hand, the 1:1 Eu^{2+}:MEN15C5 complex gave a greater k^* value (620×10^5 s^{-1}).

TABLE 3. Luminescence properties of Eu^{2+} complexes

Complex	Eu:ligand	ϕ[a] (%)	τ[b] (ns)	k[c] (10^5 s^{-1})	k^*[d] (10^5 s^{-1})	I[e] (%)
Eu^{2+}–12C4		3.6	300	1.2	32	93
Eu^{2+}–15C5	1:3	28	800	3.5	9.0	690
Eu^{2+}–MEN12C4	1:2	14	810	1.7	11	410
Eu^{2+}–MEN15C5	1:1	0.31	16	1.9	620	13
$EuCl_2$		0.036	1.7	2.1	5900	1.0

[a]Luminescence quantum yield. [b]Luminescence lifetime. [c]Radiative rate constant. [d]Non-radiative rate constant. [e]Emission intensity (vs. $EuCl_2$).

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