



Luminescence of the films of europium (III) with thenoyltrifluoroacetate and macrocyclics

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Abstract

We discuss the syntheses, properties and the luminescence of the complexes, $\text{Eu}(\text{TTA})_3 \cdot 2\text{L} \cdot \text{H}_2\text{O}$, where TTA = thenoyltrifluoroacetate, L = 15C5 (1,4,7,10-tetraoxa-13-azacyclopentadecane,13-phenyl) and 18C6 (2,3,11,12-dicyclohexano-1,4,7,10,13,16-hexaoxacyclooctadecane). The film complexes with 15C5 and 18C6 ligands contain only one water molecule. The Ω_λ experimental intensity parameters ($\lambda = 2$ and 4) and the ratio between the intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions (R_{02}) were obtained for the compounds $\text{Eu}(\text{TTA})_3 \cdot 2(15\text{C}5) \cdot \text{H}_2\text{O}$ ($\Omega_2 = 39.5 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 8.9 \times 10^{-20} \text{ cm}^2$ and $R_{02} = 0.0087$) and $\text{Eu}(\text{TTA})_3 \cdot 2(18\text{C}6) \cdot \text{H}_2\text{O}$ ($\Omega_2 = 39.3 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 5.8 \times 10^{-20} \text{ cm}^2$ and $R_{02} = 0.0098$). The macrocyclic compounds, powder form, were also measured. The luminescence spectra of the $\text{Eu}(\text{TTA})_3 \cdot 2\text{L} \cdot \text{H}_2\text{O}$ films give the largest Ω_2 intensity parameter, due to the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition and indicating that the rare earth ion is in a polarizable chemical environment. The lifetimes of the macrocyclics complexes in the powder and film were measured. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Luminescent rare earth compounds, in particular with trivalent europium and terbium ions, have been studied because of their fluorescence efficiencies and emission spectra [1–5]. The photophysical properties of rare earth compounds with β -diketones and macrocyclic ligands such as crown ether [2] have been measured [6–8]. According to Lehn [9] such compounds could be used as light-conversion molecular devices (LCMD) called *antenna effect*, to indicate the ultraviolet-to-visible light conversion process involving distinct ligands and emitting components present in the

supramolecular species. In the case of the europium (III) ion the emitting and ground state levels are nondegenerate and cannot be split by the ligand field. Thus the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition can act as a probe [2]. If this transition, that is forbidden, has more than one peak around 578 nm then there is more than one chemical environment around the trivalent europium ion. As a consequence its luminescent properties can be used in many applications in areas such as biochemistry, optical devices, sensor, laser [1–5,10].

This work reports a preliminary study of these luminescent materials in the form of films. The luminescence measurements of these new species were compared with those of the salt precursor and 1:1 crown ether complexes [8]. The Ω_λ and R_{02} intensity parameters ($\lambda = 2$ and 4) [6] and lifetimes (τ) were also correlated.

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2. Experimental section

The rare earth oxides, diketone and 18-crown-6 reagents used in the preparations of the complexes were purchased (from Aldrich), and 15-crown-5 (from Merck) where, thenoyltrifluoroacetate (TTA), 1,4,7,10-Tetraoxa-13-azacyclopentadecane, 13-phenyl (15C5), and 2,3,11,12-Dicyclohexano-1,4,7,10,13,16-hexaoxacyclooctadecane (18C6). All the reagents were the purest commercially available. The infrared spectra were measured at room temperature in a FTIR spectrometer (Perkin–Elmer 1750) in the 4000 to 400 cm^{-1} spectral range on films deposited on CsI plates. The excitation and emission spectra at room temperature were collected at an angle of 22.5° (front face) in a spectrofluorometer (SPEX-Fluorolog 2) with double grating 0.22 m monochromators (SPEX 1680), a 450 W Xenon lamp as excitation source. This apparatus was controlled by a spectroscopy computer (DM3000F). The lifetime measurements were recorded at 298 K using the phosphorimeter (SPEX 1934D) accessory coupled with the spectrofluorometer.

3. Results

The complexes were prepared in the molar ratio 1:2 (salt:ligand) between the precursor rare earth salt and 18C6 and 15C5 macrocyclic ligands. First mixed ethanolic solutions of the reagents were, under stirring and at a temperature heating $\sim 50^\circ\text{C}$. Subsequently the solution volume was reduced until the film was deposited on the bottom of the beaker. The films were placed under vacuum in a desiccator, at room temperature, until the solvent was eliminated.

The europium percentage in the complexes was determined by complexometric titration with ethylenediaminetetraacetic acid disodium salt (EDTA) in methanol [11]. The carbon, hydrogen and nitrogen contents were determined by micro-analytical procedures. The C, H, N and Eu percentages found/calculated for the complexes with the respective ligands are: 15-crown-5 ether (C: 47.22/47.07; H: 4.53/4.50; N: 1.97/1.84 ; Eu^{3+} : 10.54/10.10) and 18-crown-6 ether [C: 48.70/48.74;

H: 5.49/5.14; Eu^{3+} : 9.63/9.29]. These data are consistent with the stoichiometries expected.

According to the results of IR spectroscopy the band around 3500 cm^{-1} confirms that both compounds were isolated in the hydrated form [8]. These data were reinforced by elementary analysis data which we suggest shows that the film compounds contain only one water molecule. The displacement of the C=O stretching mode from $\sim 1680\text{ cm}^{-1}$ in the free TTA ligand to $\sim 1607\text{ cm}^{-1}$ in the compounds is evidence that the metal ion is coordinated through the oxygens [6], indicated by the fact that the trivalent europium ion is a hard acid and has affinity for the oxygen of the ligands. In this work we noted the same hindrance as in Ref. [6] because there is not a precise assignment of the shift of the $\nu_{\text{as}}(\text{CCO})$ and $\nu_{\text{s}}(\text{CCO})$ stretching vibrational modes around 1100 cm^{-1} , due to the fact that the TTA vibrational transitions ($\nu_{\text{as}}\text{CF}_3$, $\nu_{\text{s}}\text{CF}_3$ and $\nu\text{C-F}$) mask these bands. In these compounds the same variations in the relative maximum amplitudes of the bands as in the ratio 1:1 in the powder form complexes [12–15] were observed.

Fig. 1 shows the excitation spectra of the precursor salt and films, in the range of 250–500 nm, by monitoring the emission at 611 nm, at room temperature.

Fig. 2 presents the luminescence spectra of the Eu^{3+} -films in the region of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions ($J=0-4$) with a property due to the widths of these bands when compared with the emission

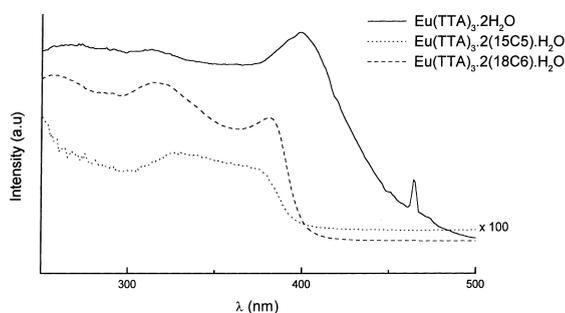


Fig. 1. Excitation spectra of the compounds $\text{Eu}(\text{TTA})_3 \cdot 2\text{L} \cdot \text{H}_2\text{O}$ (where $\text{L} = 18\text{-crown-6}$ and 15-crown-5 ligands) at room temperature monitoring at 611.4 nm and 611 to the 18C6 and 15C5 complexes, respectively.

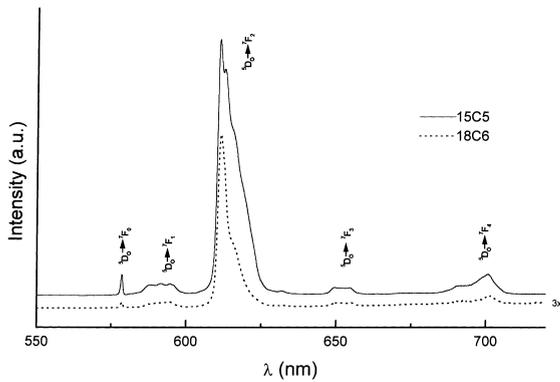


Fig. 2. Emission spectra of the compounds $\text{Eu}(\text{TTA})_3 \cdot 2\text{L} \cdot \text{H}_2\text{O}$ (where $\text{L} = 18\text{-crown-6}$ and 15-crown-5 ligands) at room temperature, under excitation at 374.8 and 384 nm to the 18C6 and 15C5 complexes respectively.

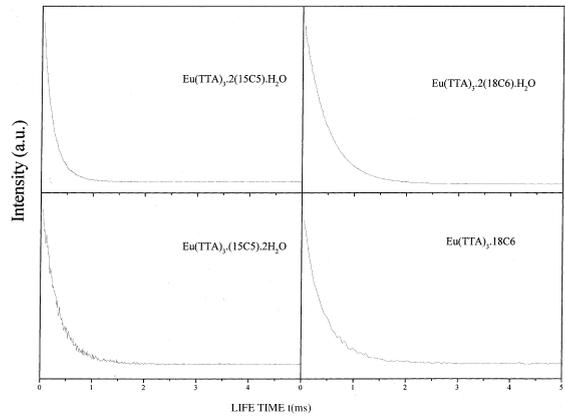


Fig. 3. Luminescence decay curves, at room temperature, of the $^5\text{D}_0$ emitting level in the powder and film compounds with general formula $\text{Eu}(\text{TTA})_3 \cdot x\text{L} \cdot y\text{H}_2\text{O}$ where $x = 0\text{--}2$ (where $\text{L} = 15\text{C5}$ and 18C6) and $y = 0\text{--}2$ (H_2O), monitored at 611 nm.

spectra of the 1:1 complexes, in powder form at room temperature [8].

The emission intensity, I , of a given transition is proportional to the surface, S , under the emission curve; $I = \hbar\omega AN$, where $\hbar\omega$ is the transition energy and N is the population of the emitting level ($^5\text{D}_0$). From the spontaneous emission spectra for the Eu^{3+} ion (Fig. 2) we have calculated the experimental intensity parameters, Ω_λ , where $\lambda = 2$ and 4 by using the $^5\text{D}_0 \rightarrow ^7\text{F}_{2,4}$ transitions. The Einstein spontaneous emission coefficient, A , is given by [6,8,16]

$$A = \frac{4e^2\omega^3}{3\hbar c^3} [2J + 1]^{-1} \chi \sum_{\lambda} \Omega_{\lambda} \langle ^7\text{F}_J \| U^{(\lambda)} \| ^5\text{D}_0 \rangle^2, \quad (1)$$

where $\chi = n_0(n_0^2 + 2)^2/9$ is a Lorentz local field correction, n_0 being the index of refraction of the medium. The magnetic dipole allowed $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition was taken as the reference. The squared reduced elements, $\langle ^7\text{F}_J \| U^{(\lambda)} \| ^5\text{D}_0 \rangle^2$, were taken

from Carnall et al. [17] and an average index of refraction equal to 1.5 was used [18].

The experimental intensity parameters, $\Omega_{2,4}$ (in units of 10^{-20} cm^2), and the ratio (R_{02}) are listed in the Table 1.

The lifetimes (τ , in ms) of the excited state, $^5\text{D}_0$, in the Eu^{3+} ion were measured for all complexes (Table 1) except the precursor salt. Its lifetimes were taken from Ref. [2]. Fig. 3 shows the luminescence decays that were collected by excitation of the 15C5 and 18C6 complexes at 374.8 and 384 nm, respectively.

4. Discussion

The films used for the luminescence data were obtained by adding drops of the respective complexes in dichloromethane solutions on a quartz

Table 1

Experimental intensity parameters Ω_2 , Ω_4 , R_{0-2} and $^5\text{D}_0$ lifetimes (τ) for the $\text{Eu}(\text{TTA})_3 \cdot x\text{L} \cdot y\text{H}_2\text{O}$ compounds, where $x = 0\text{--}2$ (where $\text{L} = 15\text{C5}$ and 18C6) and $y = 0\text{--}2$ (H_2O)

Compounds	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	R_{02}	τ^c (ms)	Ref
$\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}^a$	33.0	4.6	0.0130	0.260	6
$\text{Eu}(\text{TTA})_3 \cdot (15\text{C5}) \cdot 2\text{H}_2\text{O}^a$	37.1	11.7	0.0070	0.329	8
$\text{Eu}(\text{TTA})_3 \cdot 2(15\text{C5}) \cdot \text{H}_2\text{O}^b$	39.5	8.9	0.0087	0.229	*
$\text{Eu}(\text{TTA})_3 \cdot (18\text{C6})^a$	39.0	10.0	0.0009	0.412	8
$\text{Eu}(\text{TTA})_3 \cdot 2(18\text{C6}) \cdot \text{H}_2\text{O}^b$	39.3	5.8	0.0098	0.335	*

*This work, a = powder, b = film, c = Experimental error: $\pm 5\%$ on lifetimes.

slide. Film thickness varied because the dichloromethane solvent on the slide was evaporated in air to prepare the complex in the film form. The luminescence spectra were obtained only at room temperature because at liquid nitrogen temperature the film form becomes a powder. We observed that these materials turn again to the film when the system returns to room temperature.

The spectra in Fig. 1 are similar but are shifted to the blue in the case of 18-crown-6 (374 nm) and 15-crown-6 (385 nm) macrocyclic compounds, compared with the precursor salt (394 nm).

For the films the $^5D_0 \rightarrow ^7F_0$ transition (Fig. 2) is only one peak which we suggest is due to the presence of a single chemical environment around the rare earth ions, while this nondegenerate transition, split in the case of the $\text{Eu}(\text{TTA})_3 \cdot 18\text{C}6$ compound (1:1), indicates that there is more than one site occupied by the Eu^{3+} ion. In the film emission spectra, the forced electric dipole transition, $^5D_0 \rightarrow ^7F_2$, is the more intense transition indicating that Eu^{3+} is in a site without a center of inversion.

The intensity parameters can be related to a structural change in the chemical environment around the rare earth ion.

The results of the experimental intensity parameters, Ω_2 , for these films indicate that the coordination of the macrocyclic ligands to the metallic center increased the luminescence of the europium ion when compared with the luminescence of the precursor salt, while these numbers are similar to those of the compounds prepared in the molar ratio 1:1. All the powder and film complexes have a Ω_2 parameter indicative of the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition [6] and indicating that the europium ion is in a highly polarizable chemical environment [6–8].

We suggest, on the other hand, that the Ω_4 parameter for the film compounds are due to steric factors in which the TTA ligands prevent the macrocyclic ligands from getting closer to the europium ion, decreasing the Ω_4 [8] when compared with the 1:1 compounds. We suggest that these results show that the macrocyclic ligands act as antennas absorbing energy that is then transferred intramolecularly to the Eu^{3+} energy levels, which then emit their characteristic luminescence.

Table 1 presents the R_{02} s, an empirical intensity parameter, that is the ratio between the intensities of the $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_2$ transitions, for the powder and film compounds. The R_{02} parameter may give information about the J -mixing effect associated with the $^5D_0 \rightarrow ^7F_0$ transition. By comparison the following order was found: $18\text{C}6 (1:1) < 15\text{C}5 (1:1) < 15\text{C}5 (1:2) < 18\text{C}6 (1:2) < \text{precursor salt}$.

The luminescence decays, in Fig. 3, of the macrocyclic complexes can be fit with a single exponential, which we interpret, as indicating only one site symmetry from the Eu^{3+} ion.

The luminescence lifetimes of the emitting level, 5D_0 , in the Eu^{3+} ion are found in the following range [2]: (i) 0.1–1.0 ms in aqueous solution; (ii) to 2.5 ms in anhydrous solvent; (iii) ~ 4.5 ms in deuterated solvent; (iv) 3–6 ms in inorganic crystals. In the case of TTA-complexes [3], in the powder and film forms, they are between 0.26 and 0.80 ms. When we compare the lifetime of the precursor salt with those of systems containing macrocyclic ligands (Table 1) we observed an increase in the lifetimes of the complexes, except for the 15C5-complex film ($\tau = 0.229$ ms). This decrease is associated with the influence of the macrocyclic bulk [8] and the nonradiative decay channel due to vibronic coupling with the vibrations of the water molecule [2]. These data indicate greater luminescence efficiency in the anhydrous compound, $\text{Eu}(\text{TTA})_3 \cdot (18\text{C}6)$, as expected.

No transition from the 5D_1 and 5D_2 levels were observed in the 520–560 nm range.

5. Conclusion

In this study was observed that the Ω_2 intensity parameters in the film complexes are larger than those of the precursor salt because of the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition and indicating a structural change in the inner coordination sphere in the systems with macrocyclic ligands around Eu^{3+} ion. However, this parameter for the macrocyclic compounds are similar possibly due to the similarity in the first oxygens in the vicinity of the rare earth ion. In the case of the Ω_4 intensity parameter for the film compounds (ratio 1:2), it is smaller than for powder macrocyclic compounds

(ratio 1:1), suggesting that steric factors prevent that the crown-ether ligands get closer to the europium ion. The film complexes have a ${}^5D_0 \rightarrow {}^7F_0$ transition with only one peak indicating a single chemical environment around the trivalent europium ion. The larger lifetime of the 5D_0 level in $\text{Eu}(\text{TTA})_3 \cdot (18\text{C}6)$ is associated with the absence of the water molecule in this complex.

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