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Luminescence behavior of Eu^{3+} with thenoyltrifluoroacetonate, sulfoxides and macrocyclics

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Abstract

In this work we present a study of the luminescence intensity of $Eu(TTA)_3 \cdot xL$, where TTA=thenoyltrifluoroacetonate (L denotes DBSO and PTSO sulfoxides, and derivatives of 15C5 and 18C6 macrocyclics). The complexes with 15-crown-5 ether ligand contain two H_2O molecules. The complexes were characterized by a microanalytical procedure, IR spectroscopy and molar conductance. They show high luminescence mainly in the red region. The characteristic emission spectra of Eu^{3+} in these compounds show uncommonly high values of the Ω_2 intensity parameters, reflecting the hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition and indicating that the rare earth ion is in a highly polarizable chemical environment. The $^5D_0 \rightarrow {}^7F_0$ transition splitting, in the case of $Eu(TTA)_3 \cdot 18C6$, indicates more than one site of symmetry occupied by Eu^{3+}. © 1998 Elsevier Science S.A.

Keywords: Europium; Luminescence; Macrocyclics; Sulfoxides; Thenoyltrifluoroacetonate

1. Introduction

The study of luminescent compounds containing rare earth ions is an important field of investigation because it opens up the possibility of designing efficient light-converting molecular devices (LCMD). The 4f–4f luminescence intensity in these compounds is the result of a balance among strong absorption by the ligands, ligand–rare earth ion energy transfer rates, nonradiative decays and radiative emission rates.

When irradiated with ultraviolet light, several rare earth β-diketone compounds show strong luminescence in their electronic spectra [1,2]. The 4f–4f intraconfigurational transitions exhibit narrow line emissions. This is a direct consequence of the fact that the 4f orbitals are well shielded from the chemical environment by the closed 5s5p external orbitals. These properties enable them to be extremely sensitive as luminescent probes that can give information about small perturbations surrounding the rare earth ion.

In this work we present the syntheses and study of the luminescence properties of new and highly luminescent Eu^{3+} compounds, namely $Eu(TTA)_3 \cdot xL$, where TTA=thenoyltrifluoroacetonate (L denotes DBSO=dibenzyl sulfoxide, PTSO=*p*-tolyl sulfoxide, 15C5=1,4,7,10-tetraoxa-13-azacyclopentadecane,13-phenyl and 18C6=2,3,11,12-dicyclohexano-1,4,7,10,13,16-hexaoxacyclo-octadecane). The complexes with the 15C5 ligand contain two H_2O molecules.

The luminescence properties of macrocyclic complexes of the rare earths have been studied extensively in the last two decades [3–6] and recently we have considered in a systematic way some rare earth complexes derived from cyclic sulfoxides [2]. The association between Eu^{3+}–β-diketonates with sulfoxides and macrocyclic ligands shows luminescence enhancement as a consequence of the efficient antenna effect of the ligands. In investigations of the luminescence of Eu^{3+} in the solid state the phenomenological intensity parameters Ω_2 and Ω_4 were calculated. The R_{0-2} parameter, which gives the ratio between the $^5D_0 \rightarrow {}^7F_0$ and the $^5D_0 \rightarrow {}^7F_2$ transitions, was also determined.

2. Experimental details

2.1. Materials and procedures

Thenoyltrifluoroacetonate (TTA), dibenzyl sulfoxide (DBSO), *p*-tolyl sulfoxide (PTSO), 1,4,7,10-tetraoxa-13-

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azacyclopentadecane,13-phenyl (15C5) and 2,3,11,12-dicyclohexano-1,4,7,10,13,16-hexaoxacyclo-octadecane (18C6) were used as received. The infrared spectra were measured at room temperature in a Perkin-Elmer 1750-FTIR spectrophotometer in the 4000–400 cm^{-1} spectral range. The KBr plates and nujol mull suspension techniques for the compounds and films of the free ligands were applied. The excitation and emission spectra were recorded in a spectrofluorometer SPEX-Fluorolog 2 with double grating 0.22 m SPEX 1680 monochromators, a 450 W xenon lamp as excitation source and the apparatus was fully controlled by a DM3000F spectroscopic computer.

2.2. Synthesis and characterization of the solid complexes

Crystals of $\mathrm{Eu(TTA)_3{\cdot}2H_2O}$ were prepared by the method described by Charles and Ohlmann [7]. The only difference was that pentane was used instead of petroleum ether to remove the excess of chelating agent. The trivalent europium complexes with the ligands DBSO and PTSO were prepared by a similar method where the crystals of $\mathrm{Eu(TTA)_3{\cdot}2H_2O}$ and sulfoxide ligands were dissolved in ethanol. The solutions were added in the molar ratio 1:2 (salt/ligand) and allowed to stand together until the formation of a pale-yellow precipitate. The solid product was recrystallized from acetone and dried under vacuum over anhydrous calcium chloride in a desiccator at room temperature overnight [2].

The 15-crown-5 and 18-crown-6 macrocyclic complexes were obtained by mixing $\mathrm{Eu(TTA)_3{\cdot}2H_2O}$ ethanolic solution and the ligands in the same solvent, followed by stirring. The solution was allowed to stand overnight under stirring and heating (50°C). The solid compounds were dried under vacuum over anhydrous calcium chloride in a desiccator at room temperature overnight.

The europium content was determined by complexometric titration with EDTA [8] in methanol. The carbon, hydrogen and nitrogen contents were estimated by microanalytical procedures. The C, H, N and Ln percentage values found/calculated for the complexes with the respective ligands are: PTSO (C, 47.42/48.90; H, 3.24/3.16; $\mathrm{Eu^{3+}}$, 11.92/11.98), 15-crown-5 ether (C, 41.90/41.89; H, 3.43/3.60; N, 1.21/1.24; $\mathrm{Eu^{3+}}$, 13.58/13.25) and 18-crown-6 ether (C, 43.68/43.82; H, 4.10/4.18; $\mathrm{Eu^{3+}}$, 12.04/12.60). These percentage values for the complexes with the $\mathrm{H_2O}$ and DBSO ligands are reported in Ref. [2].

The IR spectra show the displacement of the S=O stretching from 1033 and 1039 cm^{-1} in the free DBSO and PTSO ligands to ~1007 and 1006 cm^{-1} in the compounds, respectively, and the displacement of the C=O stretching from ~1680 cm^{-1} in the free TTA ligand to ~1607 cm^{-1} in the compounds provides good evidence that the metal ion is coordinated through the oxygens [2,9]. The absence of bands around 3500 cm^{-1} confirms that the compounds with DBSO and PTSO are anhydrous. This is also observed for the 18C6 complex, although in the case of the 15C5 complex a band around 3500 cm^{-1} reinforces the elemental analysis results that suggest a compound with two water molecules. A precise assignment of the shift of the ν_{as}(CCO) and ν_s(CCO) stretching vibrational modes about 1100 cm^{-1} is difficult because in this spectral range the TTA vibrational transitions ($\nu_{as}\mathrm{CF_3}$, $\nu_s\mathrm{CF_3}$ and νC–F) mask these attributes. However, upon complexation, we observe a variation in the shape and relative intensity of the bands [10–13].

3. Experimental intensity parameters

It is very important to obtain the phenomenological intensity parameters because it is possible to obtain information about the chemical environment around the metal ion. The emission intensity, *I*, of a given transition is proportional to the surface, *S*, under the emission curve

$$I = \hbar\omega AN \propto S \tag{1}$$

In Eq. (1) $\hbar\omega$ is the transition energy and N is the population of the emitting level ($^5\mathrm{D}_0$). From the emission spectra for $\mathrm{Eu^{3+}}$ (Fig. 1) we have determined the experimental intensity parameters Ω_2 and Ω_4 by using the $^5\mathrm{D}_0\rightarrow{}^7\mathrm{F}_2$ and $^5\mathrm{D}_0\rightarrow{}^7\mathrm{F}_4$ transitions, respectively. The Einstein coefficient, *A*, is given by [2,14]

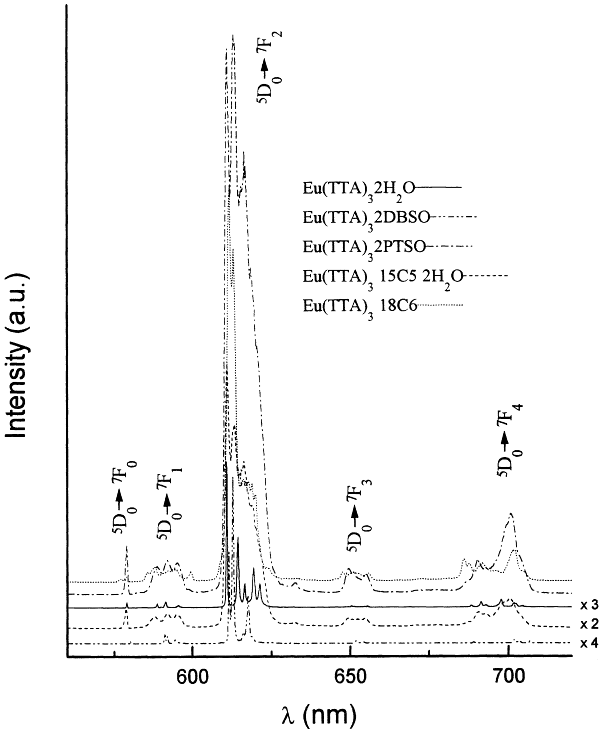

Fig. 1. Emission spectra of the compounds $\mathrm{Eu(TTA)_3{\cdot}}x\mathrm{L}{\cdot}y\mathrm{H_2O}$, at 77 K, under excitation at 394 nm.

$$A = \frac{4e^2\omega^3}{3\hbar c^3}\frac{1}{2J+1}\left[\frac{n_0(n_0^2+2)^2}{9}\right]\sum_{\lambda}\Omega_{\lambda}\langle {}^7\mathrm{F}_J \| U^{(\lambda)} \| {}^5\mathrm{D}_0\rangle^2 \tag{2}$$

where $n_0(n_0^2+2)^2/9$ is a Lorentz local field correction, n_0 being the index of refraction of the medium. The magnetic dipole allowed ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$ transition was taken as the reference. The reduced matrix elements in Eq. (2) were taken from Ref. [15] and an average index of refraction of 1.5 was used. The Ω_6 intensity parameter was not included in this study since the ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_6$ transition could not be observed and this transition presents, in general, an extremely low intensity [6].

4. Results and discussion

The emission spectra of the compounds show transitions from the lowest excited ${}^5\mathrm{D}_0$ state. Fig. 1 shows that the ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_J$ transitions are represented in the spectra by sharp emission lines in the spectral range from 560 to 720 nm. The ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_0$ nondegenerate transition appears in all the spectra measured here, indicating that the europium ion is in an environment of low symmetry.

Table 1 shows the observed ${}^7\mathrm{F}_J$ ($J=0$, 1, 2, 3 and 4) energy sublevels for the compounds studied. Except for the Eu–β-diketone with 18-crown-6 ether all the other compounds studied in this work present spectral lines consistent with the maximum number of components $(2J+1)$,

Table 1
Energies of the ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_{0-4}$ manifolds (cm^{-1}) observed in the emission spectra of Eu(TTA)$_3\cdot x$L (where L = H_2O, DBSO, PTSO and 18C6) and Eu(TTA)$_3\cdot$15C5$\cdot 2H_2O$ at 77 K

Transitions	H_2O	DBSO	PTSO	15C5	18C6
${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_0$	17 268	17 241	17 274	17 277	17 337
					17 409
					17 271
${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$	16 984	16 915	16 984	17 012	17 077
	16 906	16 892	16 898	16 892	17 018
	16 793	16 818	16 906	16 807	17 007
					16 932
					16 898
					16 886
					16 835
					16 807
					16 683
${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$	16 369	16 350	16 367	16 367	16 345
	16 279	16 318	16 310	16 303	16 313
	16 221	16 228	16 223	16 224	16 249
	16 149	16 192	16 152	16 160	16 239
	16 097	16 160	16 113	16 129	16 228
					16 213
					16 192
					16 160
					16 134
${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_3$	15 513	15 361	14 401	15 399	15 442
	15 418	15 342	15 356	15 351	15 399
	15 399	15 286	15 328	15 328	15 384
	15 377	15 253	15 265	15 272	15 370
	15 359	15 230			15 361
	15 309				15 319
	15 255				15 253
					15 244
${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_4$	14 528	14 514	14 552	16 404	15 179
	14 463	14 497	14 488	14 447	14 543
	14 430	14 249	14 333	14 426	14 484
	14 333	14 221	14 302	14 306	14 468
	14 251	14 163	14 265	14 245	14 455
	14 238			14 217	14 438
	14 196				14 422
					14 355
					14 367
					14 257
					14 245
					14 204
					14 188

Table 2
Experimental intensity parameters Ω_2, Ω_4 and R_{0-2} for $Eu(TTA)_3 \cdot xL$ (L = DBSO, PTSO, and 18C6) and $Eu(TTA)_3 \cdot 15C5 \cdot 2H_2O$ compounds

Compound	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	R_{0-2}
$Eu(TTA)_3 \cdot 2H_2O$	33.0	4.6	0.0130
$Eu(TTA)_3 \cdot 2DBSO$	29.0	4.7	0.0050
$Eu(TTA)_3 \cdot 2PTSO$	54.5	38.2	0.0038
$Eu(TTA)_3 \cdot 15C5 \cdot 2H_2O$	37.1	11.7	0.0070
$Eu(TTA)_3 \cdot 18C6$	39.0	10.0	0.0009

where the $^5D_0 \rightarrow {}^7F_2$ transition is the most intense, pointing to a site symmetry without center of inversion. In the case of the 18-crown-6 complex the $^5D_0 \rightarrow {}^7F_J$ transitions present more than one, three, five and nine lines, for $J = 0$, 1, 2 and 4, respectively, indicating that the europium ion is located in more than one chemical environment.

Table 2 presents the experimental intensity parameters R_{0-2}, Ω_2 and Ω_4. For the sake of comparison the hydrated compound, $Eu(TTA)_3 \cdot 2H_2O$, was also studied [2].

The strong luminescence of $Eu(TTA)_3 \cdot 2H_2O$ can be explained by the more effective interaction between the rare earth ion and the bulky hydrophobic substituents of the β-diketonates (thienyl and trifluoromethyl groups), indicating a smaller contribution of the O–H vibrational deactivation. Moreover, the thenoyltrifluoroacetonate anions behave as absorbing groups suitable for the antenna effect. In the case of the complexes $Eu(TTA)_3 \cdot 2L$ (L = DBSO, PTSO and 18C6), where the two water molecules are substituted by the ligands L, an increase in the luminescence is observed as a consequence of the decrease in the possibility of luminescence quenching. Although $Eu(TTA)_3 \cdot 15C5 \cdot 2H_2O$ is hydrated it presents a strong luminescence, therefore indicating that the europium ion is found in a chemical environment effectively shielded from interaction with the two water molecules.

From the emission spectra of Eu^{3+}, for all the compounds, high values of the Ω_2 intensity parameter were obtained, reflecting the hypersensitive character of the $^5D_0 \rightarrow {}^7F_2$ transition and indicating that Eu^{3+} is in a highly polarizable chemical environment. These results suggest that the short distance effects are dominant. On the other hand, the PTSO complex shows a higher value for the Ω_4 parameter (Table 2) which is probably due to the bulky effects at longer distance experienced by the rare earth ion, perhaps as a consequence of the difference in the basicity of the oxygen donor ligand.

The R_{0-2} experimental intensity parameter may give information about the J-mixing effect associated with the $^5D_0 \rightarrow {}^7F_0$ transition, following the order: 18C6 < PTSO < DBSO < 15C5 < H_2O.

5. Conclusions

The strong luminescence of the salt $Eu(TTA)_3 \cdot 2H_2O$ is, in part, due to the protection of the rare earth ion from the interaction with vibrational deactivation provided by the bulky hydrophobic substituents of the β-diketone because of thienyl and trifluoromethyl groups. The $Eu(TTA)_3 \cdot 2L$ compounds (L = DBSO, PTSO and 18C6) present a stronger luminescence, when compared with the precursor salt, because the water molecules are substituted by the sulfoxides and 18-crown-6 macrocyclic ligands. The presence of the 15-crown-5 ether ligands in the complex $Eu(TTA)_3 \cdot 15C5 \cdot 2H_2O$ also contributes to the decrease in the luminescence quenching induced by the OH group. These ligands behave as absorbing groups suitable for an efficient antenna effect. The unusual high values of the intensity parameters in these compounds indicate a coordination geometry of rather low symmetry and a chemical environment around the rare earth ion which is highly polarizable.

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