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Luminescent properties of diketonates of trivalent europium with dimethyl sulfoxide

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Abstract

Photoluminescent properties of the tris(thenoyltrifluoroacetonate)europium(III) dihydrate with dimethyl sulfoxide (DMSO), in the solid state, are reported. The compound $Eu(TTA)_3 \cdot 2DMSO$ and the precursor salt were characterized by IR spectroscopy, differential scanning calorimetry and elemental analysis. The emission data indicate that the substitution of the two water molecules by DMSO ligand in the complex causes an intensification of luminescence corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions associated with one of the site symmetries. Large values of the Ω_2 intensity parameter (35.2×10^{-20} cm^2) were obtained, reflecting the hypersensitive character of the $^5D_0 \rightarrow {}^7F_2$ transition and indicating that Eu^{3+} ion is in a highly polarizable chemical environment. This is consistent with systems containing sulfoxide ligands DBSO and PTSO. The DMSO complex also shows a higher value for the Ω_4 parameter (6.8×10^{-20} cm^2) as a consequence of the difference in the basicity of the oxygen donor ligand. Lifetime measurements ($\tau = 0.72$ ms) confirm that the Eu^{3+} luminescence has a higher efficiency than in the case of the hydrated compound.

Keywords: Europium; Photoluminescence; Thenoyltrifluoroacetonate; Dimethyl sulfoxide

1. Introduction

The luminescent properties of trivalent rare earth (RE^{3+}) complexes of β-diketonate and other organic ligands have been systematically investigated in our laboratory [1–3]. This interest is mainly due to their potential uses as fluorescent sensors in natural, medical, analytical and bioinorganic sciences, and probes with Sm^{3+}, Eu^{3+} and Tb^{3+} are of special interest because of the particularly suitable spectroscopic properties of these 4f ions [4,5].

The rare earth ions are classified as ‘‘hard’’ acids with a strong preference for negatively charged donor groups (hard base), in the order O>N>S. The rare earth ions show a strong tendency to bind water, carboxylates, diketonates, sulfoxides, 1,10-phenanthroline *N*-oxide, etc. [5].

Dimethyl sulfoxide (DMSO), a by-product of the wood industry, has been in use as a commercial solvent since 1953. It is also one of the most studied but least understood pharmaceutical agents [6–8].

Of all the rare earth ions, Eu^{3+} is the most famous for its luminescent properties. The main advantage of using Eu^{3+} as a luminescence probe to study the composition of the first coordination sphere is the non-degeneracy of the $^5D_0$ and $^7F_0$ levels resulting from their totally symmetric shape. As a consequence, the number of signals into which the $^5D_0 \rightarrow {}^7F_0$ transition is subdivided corresponds to the number of different species present with low symmetry (Cs, Cn, Cnv). Moreover, the emission spectra of Eu^{3+} are relatively uncomplicated, even when it is complexed by ligands with low symmetry.

2. Experimental

The following compounds were prepared: $RE(TTA)_3 \cdot 2L$ (where $RE = Eu^{3+}$, Gd^{3+} and $L = H_2O$, DMSO). The hydrated compounds were prepared by the method described by Charles and Ohlmann [9]. In this synthesis pentane was used instead of petroleum ether to remove the excess thenoyltrifluoroacetone [1].

The precursor salts $RE(TTA)_3 \cdot 2H_2O$ were dissolved in excess DMSO ligand. This solution was stirred until the formation of a yellow precipitate. The complexes were dried under vacuum over anhydrous calcium chloride at

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room temperature overnight to remove the excess of sulfoxide ligand.

The photoluminescent data of the complexes, in the solid state, were obtained with a Spex Fluorolog spectrofluorometer, Model FL212 system, double grating 0.22 m Spex 1680 monochromators, and a 450 W xenon lamp as excitation source using the front face mode. This apparatus was fully controlled by a DM3000F spectroscopic computer. The lifetime measurements were recorded at room and liquid nitrogen temperature using a phosphorimeter (SPEX 1934D) accessory coupled to the spectrofluorometer.

The RE^{3+} content was estimated by complexometric titration with EDTA, where the complexes were dissolved in methanol using xylenol orange as an indicator. The carbon and hydrogen percentages were determined by microanalytical procedures. The percentage values found/calculated for the europium and gadolinium complexes were: C, 33.67/33.97; H, 2.48/2.44; Eu^{3+}, 15.12/15.35 and C, 33.80/33.70; H, 2.43/2.25; Gd^{3+}, 15.65/15.80, respectively.

The IR spectra were recorded at room temperature using a Perkin-Elmer 1750-FTIR spectrometer in the 4000–400 cm^{-1} range with nujol mull suspension techniques. Fig. 1a shows the characteristic bands of the hydrated complex, $Eu(TTA)_3 \cdot 2H_2O$, in the 3500–3200 cm^{-1} range (antisymmetric and symmetric OH stretching) and at 1630–1600 cm^{-1} (HOH bending) [10]. These bands vanish in the $Eu(TTA)_3 \cdot 2DMSO$ spectra. Fig. 1b confirms that this is the anhydrous form. The displacement of the S=O stretching from 1033 cm^{-1} in the free DMSO ligand to ~1015 cm^{-1} in the compounds, and the displacement of the C=O stretching from 1680 cm^{-1} in HTTA to 1612 cm^{-1} in the compounds, provide good evidence that the metal ion is coordinated through the oxygens.

The TG/DTG curves were obtained with a Shimadzu TG50 thermobalance in an air dynamic atmosphere of 40 ml min^{-1}, under 10°C min^{-1} heating rate and with samples weighing about 5 mg. This technique was used to confirm that the compound with DMSO ligand is anhydrous. The thermogravimetric data show that the hydrated compound contains two water molecules and they also show that the $Eu(TTA)_3 \cdot 2DMSO$ compound is more stable than the hydrated compound in the temperature range 25–120°C [1].

3. Results and discussion

The emission spectrum of $Eu(TTA)_3 \cdot 2DMSO$ (Fig. 2) at low temperature does not present the peaks corresponding to the triplet state (T) of the β-diketone ligand. On the other hand, the T state is observed in the phosphorescence spectra of the hydrated compounds [1] and $Gd(TTA)_3 \cdot 2DMSO$ (Fig. 3), indicating that energy transfer from the triplet to the Eu^{3+} ion is very efficient.

In the $Gd(TTA)_3 \cdot 2DMSO$ compound a very weak band was detected (~400 nm) similar to the TTA complexes with H_2O, DBSO (benzyl sulfoxide) and PTSO (*p*-tolyl sulfoxide), which is associated with the fluorescence from excited singlet states (S) of the ligands. This indicates that internal conversion and intersystem crossing to the lowest T in the β-diketonate are operative.

The excitation spectra of the europium compound were recorded in the range 250–500 nm by monitoring the emission at 614 nm at 298 and 77 K.

The luminescence spectra of $Eu(TTA)_3 \cdot 2DMSO$ were recorded in the region of the $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0$–4) in the range 550–720 nm.

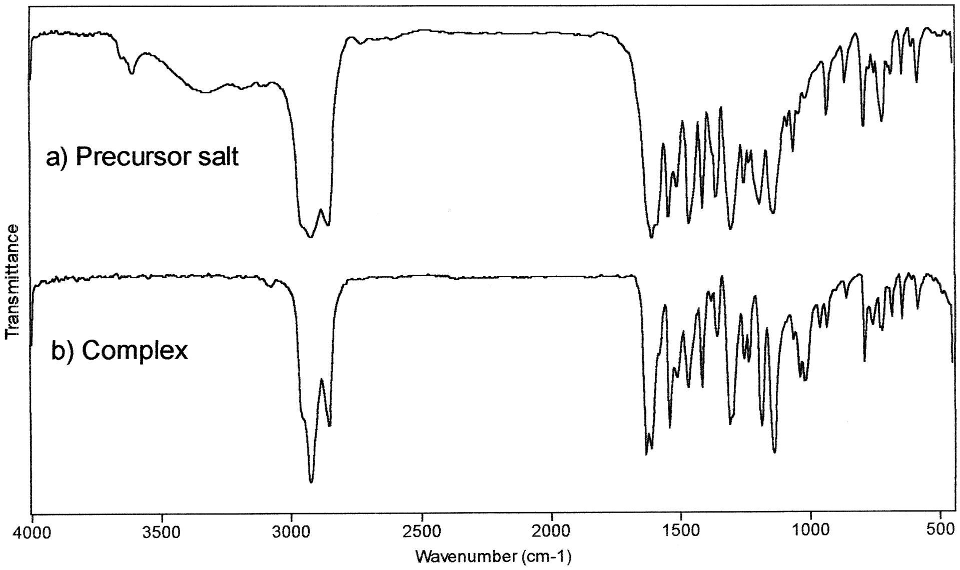

Fig. 1. Infrared spectra of (a) the hydrated compounds and (b) compounds $Eu(TTA)_3 \cdot 2DMSO$.

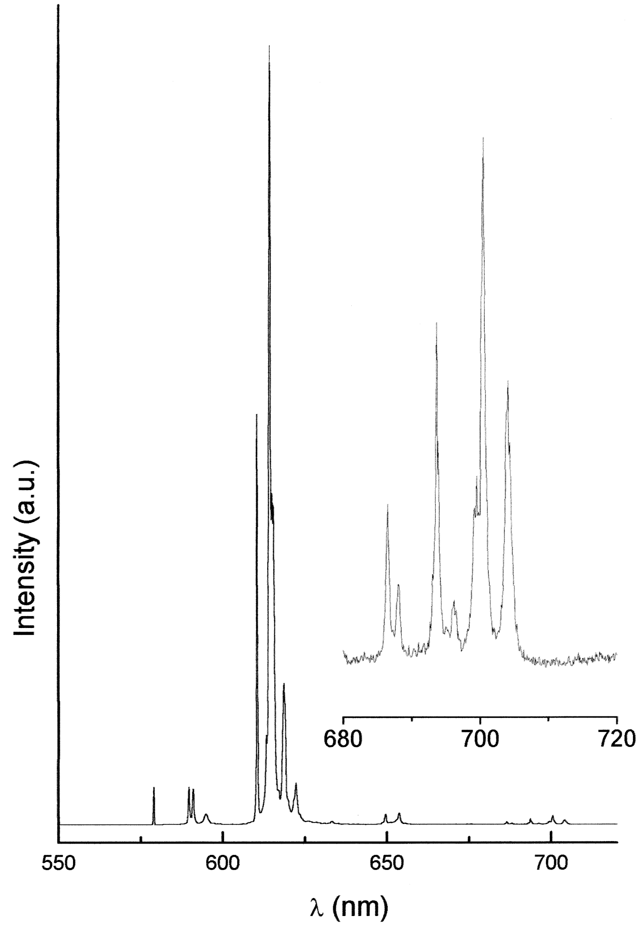

Fig. 2. Emission spectrum of the compound Eu(TTA)$_3$·2DMSO at 77 K with excitation at 394 nm, in the solid state. The $^5D_0 \rightarrow {}^7F_4$ transition in the range 680–710 nm is shown in the inset.

The presence of the $^5D_0 \rightarrow {}^7F_0$ transition serves as a good diagnostic of the crystallinity and purity of the compounds. Since the band is unsplit by the ligand field effect, any splitting observed is necessarily due to a multiplicity of Eu^{3+} sites. However, a single symmetrical peak is observed (Fig. 2), indicating that only one Eu^{3+} species is present in the sample, since for this compound any species is expected to have very low symmetry as in the case of the compound Eu(TTA)$_3$·2DBSO studied in Ref. [2]. In the emission spectrum, 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 [11,12].

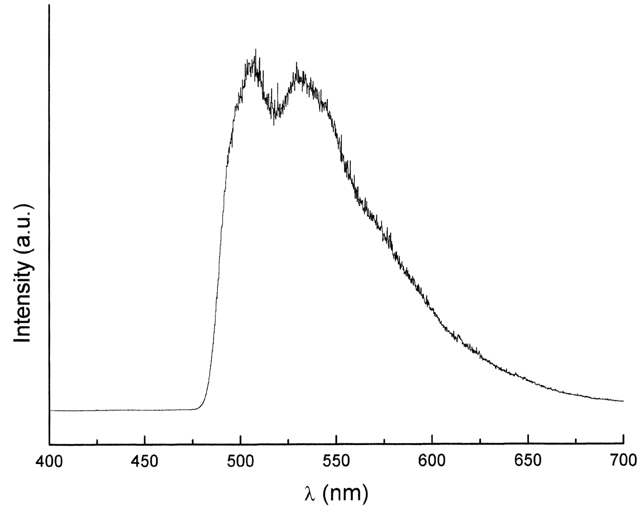

Fig. 3. Luminescence spectrum of the compound Gd(TTA)$_3$·2DMSO at 77 K under excitation at 370 nm, in the solid state.

The emission intensity, I, of a given transition is proportional to the surface, S, under the emission curve: $I = \hbar\omega A N$, where $\hbar\omega$ is the transition energy, A is the spontaneous emission coefficient and N is the population of the emitting level ($^5D_0$). From the emission spectra for the Eu^{3+} ion (Fig. 2) we have calculated the experimental intensity parameters, Ω_λ [13], where $\lambda = 2$ and 4, by using the $^5D_0 \rightarrow {}^7F_{2,4}$ transitions and the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole allowed transition as the reference [14]. The equation for the Einstein spontaneous emission coefficient is given by [15]

$$A = \frac{4e^2\omega^3}{3\hbar c^3}\frac{1}{2J+1}\chi\sum_{\lambda}\Omega_\lambda\langle {}^5D_0\|U^{(2)}\|{}^7F_\lambda\rangle^2 \qquad (1)$$

where $\chi = n_0(n_0+2)^2/9$ is a Lorentz local field correction, n_0 being the index of refraction of the medium. $\langle {}^5D_0\|U^{(2)}\|{}^7F_\lambda\rangle^2$ is the reduced matrix element and an average index of refraction equal to 1.5 was used.

The obtained experimental intensity parameter Ω_2 for the DMSO complex shows that the coordination of the sulfoxide ligand to the rare earth ion increases the luminescence intensity of the europium ion when compared with the hydrated compound. The Ω_2 values follow the order DBSO<DMSO<PTSO, indicative of the hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition and showing that the europium ion is in a highly polarizable chemical environment.

The Ω_4 parameter for this compound (Table 1) presents an intermediate value between the DBSO and PTSO complexes due to steric factors in which the TTA ligands prevent the sulfoxide ligands from approaching closer to the europium ion in the order DBSO<DMSO<PTSO.

The R_{02} intensity parameter, shown in Table 1, is the ratio between the intensities of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transitions for the DMSO complex. The R_{02} parameter may give information on the J-mixing effect associated with the $^5D_0 \rightarrow {}^7F_0$ transition as described in detail in Refs. [15,16]. In this case, this effect is mainly due to the mixing between the $^7F_2$ manifold and the $^7F_0$ level through the rank two components of the ligand field [16]. By comparison, the following order was found: DBSO<PTSO<DMSO<H$_2$O.

Table 1 also presents the lifetimes (τ) of the excited state, $^5D_0$, in the Eu^{3+} ion measured for the DMSO and PTSO complexes. The decay curves of the complexes can be fit with a single exponential, suggesting that no other

Table 1
Experimental intensity parameters Ω_2, Ω_4, R_{02} and lifetimes for the $Eu(TTA)_3 \cdot 2L$ compounds, where L = DBSO, DMSO, PTSO and H_2O, obtained at room temperature

$Eu(TTA)_3 \cdot 2L$	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	R_{02}	τ (ms)	Ref.
H_2O	33.0	4.6	0.0130	0.26	[1]
DBSO	29.0	4.7	0.0050	0.74	[1]
DMSO	35.2	6.8	0.0110	0.72	This work
PTSO	36.4	11.4	0.0080	0.60	This work

depopulation channel for the $^5D_0$ level, such as cross relaxation between Eu^{3+} ions, is operative.

In earlier work [1] we obtained luminescence lifetimes of complexes with water and DBSO ligands of 0.26 and 0.74 ms, respectively (Table 1). When we compare the lifetime of the precursor salt with those of systems containing different sulfoxide ligands (Table 1) we observe an increase in the lifetimes of these complexes, as indeed expected, from the nonradiative decay channel due to vibronic coupling with the vibrations of the two water molecules.

4. Conclusion

The optical luminescence spectra and intensity parameter analysis of the DMSO complex shows a higher Ω_2 value than those of the hydrated salt, reflecting the hypersensitive character of the $^5D_0 \rightarrow {}^7F_2$ transition and indicating a structural change in the inner coordination sphere in the environment around the Eu^{3+} ion. However, if we compare this parameter value among the sulfoxide compounds (Table 1) they are very similar, possibly due to the similar chemical properties of these ligands.

In the case of the Ω_4 intensity parameter for the DBSO compound, it is smaller than for DMSO and PTSO, suggesting that steric factors prevent this ligand getting closer to the europium ion. The complex exhibits the $^5D_0 \rightarrow {}^7F_0$ transition with only one peak, suggesting the presence of a single chemical environment around the trivalent europium ion. The longer lifetime of the $^5D_0$ level in $Eu(TTA)_3 \cdot 2DMSO$ is associated with the absence of water molecules. Based on these luminescence characteristics we believe that this compound is a promising candidate as a very luminescent material for photoluminescent applications.

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References

[1] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves e Silva, S. Alves Jr., F.S. Farias Jr., A.V.M. de Andrade, J. Lumin. 75 (3) (1997) 255.

[2] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves e Silva, C.M. Donega, S. Alves, Chem. Phys. Lett. 282 (3/4) (1998) 233.

[3] H.F. Brito, O.L. Malta, L.R. Souza, R. Ferraz, C.A.A. Carvalho, J.F.S. Menezes, J. Alloys Comp. 275–277 (1998) 254.

[4] F.S. Richardson, Chem. Rev. 82 (1982) 541.

[5] J-C.G. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences — Theory and Practice, Elsevier, Amsterdam, 1989, Chapter 7.

[6] L. Santos, P.G. Tipping, Immunol. Cell Biol. 72 (1994) 406.

[7] M.S. Evans, K.H. Reid, J.B. Sharp, Neurosci. Lett. 150 (1993) 145.

[8] L. Lubredo, M.S. Barrie, J. Surg. Res. 53 (1992) 62.

[9] R.G. Charles, R.C. Ohlmann, J. Inorg. Nucl. Chem. 27 (1965) 255.

[10] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, 1986.

[11] G.F. Buono-Core, H. Li, B. Marciniak, Coord. Chem. Rev. 99 (1990) 55.

[12] J.M. Lehn, Angew. Chem. Int. Engl. 29 (1990) 1304.

[13] R.D. Peacock, Structure and Bonding 22 (1975) 83.

[14] O.L. Malta, M.A. Couto dos Santos, L.C. Thompson, N.K. Ito, J. Lumin. 69 (1996) 77.

[15] O.L. Malta, Mol. Phys. 42 (1) (1981) 65.

[16] O.L. Malta, W.M. de Azevedo, E.G. de Araújo, G.F. de Sá, J. Lumin. 26 (1982) 337.