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Luminescence investigation of the Sm(III)-β-diketonates with sulfoxides, phosphine oxides and amides ligands

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Abstract

In this paper we report on a photoluminescent investigation of complexes involving Sm^{3+}-β-diketonates with sulfoxides, phosphine oxides and amides ligands. In the synthesis of the coordination compounds we used samarium tris(thenoyltrifluoroacetonate) dihydrated precursor with the following ligands (L): DBSO and PTSO sulfoxides; TPPO phosphine oxide and (PHA) *N*-phenylacetamide. They have shown high orange luminescence characteristic of the Sm^{3+} ion. The emission spectra of the Sm^{3+}-complexes present narrow bands arising from the $^4G_{5/2}\rightarrow{}^6H_J$ (J=5/2, 7/2, 9/2, 11/2) transitions with the hypersensitive $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition as a prominent group. It is observed an efficient intramolecular energy transfer from the triplet state (T) of the ligands to the emitting $^4G_{5/2}$ state of the Sm^{3+} ion. The experimental intensity parameters (η_{Sm} and η_{Eu}) for the Sm and Eu complexes have been determined and compared. The lifetimes (τ) of the emitting level $^4G_{5/2}$ of the Sm-complexes are approximately 10 times higher than in the precursor compound $[Sm(TTA)_3\cdot(H_2O)_2]$ indicating that radiative processes are operative in all the compounds due to the absence of multiphonon relaxation by coupling with the OH oscillators.

Keywords: Samarium; Luminescence; Thenoyltrifluoroacetonate; Sulfoxides and amides

1. Introduction

The application of compounds containing trivalent rare earth ions RE^{3+} is based mainly on their photoluminescence properties [1–6]. Luminescence investigation of RE^{3+}-β-diketonate complexes has increased in the last decade due to the higher efficiency of energy transfer from diketonate ligands to rare earth ions, which can be explained by the high absorption coefficient of the β-diketonate ligands [3–6]. The interest in the photoluminescent study of these complexes is the development of efficient light conversion molecular devices (LCMD) [7]. Among the rare earth ions the most investigated are those compounds with trivalent europium and terbium ions, owing to their intrinsic electronic spectroscopic properties. However, the Eu^{3+} ion has attracted more attention than the Tb^{3+} ion probably due to the facilities in the interpretation of its energy level structure, considering that the former has a non-degenerate emitting level ($^5D_0$) [8], while the Tb^{3+} ion has an emitting state ($^5D_4$) multi-degenerate. On the other hand, the compounds containing the Sm^{3+} ion have been less studied than those with Eu^{3+} and Tb^{3+} ions, taking into consideration that the trivalent samarium ion in general presents low luminescence intensity. The high luminescence of the rare earth tris-(thenoyltrifluoroacetonate) complexes depends on the energy level structure of the ligands and metal ion. For instance, the ligand triplet states are at higher energies than the $^5D_0$ and $^4G_{5/2}$ emitting states of the Eu^{3+} and Sm^{3+} ions, respectively (Fig. 1). On the other hand, the $[Tb(TTA)_3\cdot 2L]$ complexes do not show any luminescences at all owing to the fact that the T states are at lower energy than the emitting $^5D_4$ level.

The Sm^{3+} ion has an odd-electron configuration ($4f^5$) and, therefore, it is labeled as a Kramer ion due to its electronic states that are at least doubly degenerate for any crystal-field perturbation [9]. The maximum number of the Stark components for Kramer ions with $^{2S+1}L_J$ state is

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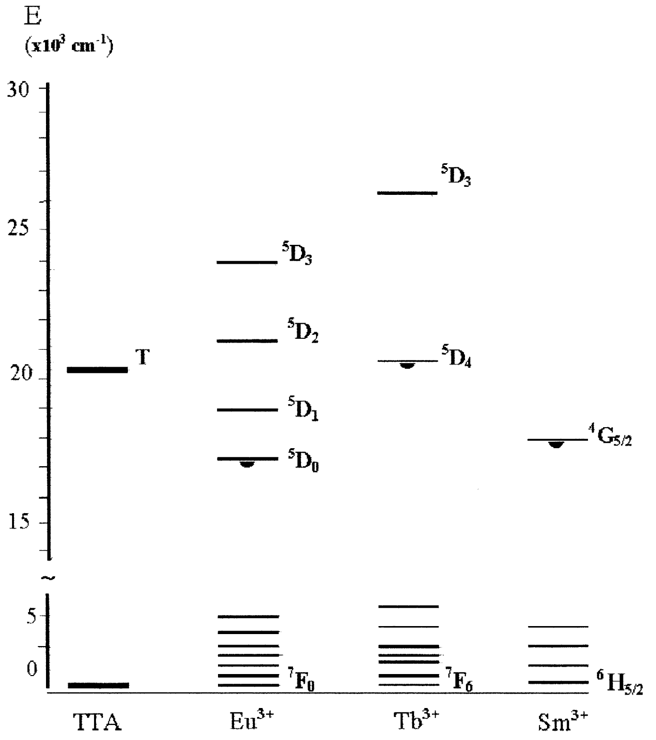

Fig. 1. Energy level diagram relating the triplet level (T) of the thenoyltrifluoroacetone counterion obtained from phosphorescence spectrum of [Gd(TTA)$_3$·2H$_2$O] [15] and some energy levels of the trivalent rare earth ion (Sm^{3+}, Eu^{3+} and Tb^{3+}).

$J+1/2$ for any symmetry lower than cubic [10]. The detailed analyses of the energy levels of Sm^{3+} in several hosts have been reported [11,12].

In this work we present a study on the unusual luminescence intensity in the new Sm^{3+}-β-diketonate compounds with sulfoxides, phosphine oxide and amide ligands. Our analysis is mainly dedicated to investigation about the influence of organic ligands in the energy transfer process to the metal ion. In addition, the Sm-ligand interaction will be studied via electronic spectroscopy based on the experimental intensity parameters η_{Sm}, and the lifetime of the emitting state ($^4G_{5/2}$).

2. Experimental details

2.1. Materials and procedures

Thenoyltrifluoroacetonate (TTA), dibenzyl sulphoxide (DBSO), *p*-tolyl sulfoxide (PTSO), triphenylphosphine oxide (TPPO) were purchased from Aldrich, while the *N*-phenylacetamide (PHA) ligand was synthesized by the method describe in Ref. [13]. The infrared spectra were measured at room temperature in a Perkin-Elmer 1750-FTIR spectrophotometer in the spectral range from 4000 to 400 cm^{-1}. The KBr plates and nujol mull suspension techniques for the compounds and films of the free ligand were applied. The TG curves were recorded with a thermobalance TGA 50 under dynamic nitrogen atmosphere (50 ml/min) and heating rate of 10 °C min^{-1} in the temperature range of 25 up to 900 °C. 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 this apparatus was fully controlled by a DM3000F spectroscopic computer. The lifetime data of the [Sm(TTA)$_3$·2L] complexes were obtained at room temperature, using the Phosphorimeter (SPEX 1934D) accessory coupled to the spectrofluorometer. The decay curves for the Sm-complexes at 298 K were recorded under excitation and emission around 377 and 648 nm, respectively.

2.2. Synthesis of the solid complexes

The precursor compound [Sm(TTA)$_3$·(H$_2$O)$_2$] was prepared by the method described by Charles and Ohlmann [14]. The only difference was that pentane was used instead of petroleum ether to remove the excess of chelating agent.

The trivalent samarium complexes were prepared by the method early described, for the compounds of europium with the sulfoxide ligands, by Malta et al. [15]. The trivalent samarium complexes were prepared by the dissolution of the crystals of [Sm(TTA)$_3$·(H$_2$O)$_2$] and sulfoxide, phosphine oxide and amide ligands in ethanol. The solutions were added in the molar ratio 1:2 (precursor compound:ligand) and allowed to stand together until the formation of the pale-yellow precipitated. The solid products were recrystallized from acetone and dried under vacuum over anhydrous calcium chloride in the desiccator at room temperature.

3. Results and discussion

3.1. Characterization

The samarium content was determined by complexometric titration with EDTA in methanol. The carbon, hydrogen and nitrogen contents were estimated by microanalytical procedures. The C, H, N and Sm^{3+} percentage values calculated/found for the complexes with the respective ligands are: hydrated compound (C: 33.92/33.85; H: 1.90/1.92; Sm^{3+}: 17.68/17.71), DBSO (C: 48.89/48.50; H: 3.39/3.15; Sm^{3+}: 11.77/11.53), PTSO (C: 48.99/48.49; H: 3.16/3.19; Sm^{3+}: 11.91/11.53), TPPO (C: 52.58/52.43; H: 3.09/3.39; Sm^{3+}: 10.97/10.39), and PHA (C: 44.25/43.45; H: 2.60/2.66; N: 2.58/2.71; Sm^{3+}: 13.89/13.82).

The IR spectra of Sm^{3+}-β-diketonate compounds with sulfoxides ligands 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. The displacement of the νC=O stretching from ~1680 cm^{-1} in the free TTA ligand to ~1607 cm^{-1} in the compounds suggesting that the coordination of the ligand to metal ion is occurring through the oxygen. In the case of the $[Sm(TTA)_3\cdot(TPPO)_2]$ complex it is observed a displacement of the νP=O stretching from 1191 cm^{-1} in the free TPPO ligand to 1172 cm^{-1} in complex, providing good evidence that the TPPO ligand is also coordinated through the oxygen atom. The IR spectrum of the $[Sm(TTA)_3\cdot(PHA)_2]$ complex shows a shift to lower frequency (1619 cm^{-1}) relative to the amide I band (νC=O) as compared with the free ligand (1660 cm^{-1}), suggesting that coordination of PHA ligand occurs through the oxygen of the amide group. The IR results show the absence of bands around 3500 cm^{-1}, which confirms that all the compounds are anhydrous.

The thermogravimetric curves of the complexes are shown in Fig. 2. The TG curve of the precursor $[Sm(TTA)_3\cdot(H_2O)_2]$ presents a weight loss in temperature range 80–120 °C that corresponds to release of water molecules. On the other hand, the TG curves of the complexes do not present any event in this region, showing the anhydrous character of these compounds. By comparing the thermal decomposition of the complexes it can be seen that the compound with the TPPO ligand presents the highest thermal stability.

3.2. Photoluminescence study

Fig. 3 shows the luminescence spectra of the $[Sm(TTA)_3\cdot 2L]$ complexes recorded in the range of 550–725 nm, at 77 K. The emission spectra were also recorded at room temperature (omitting figures), which present similar profile as well as that at low temperature, but less resolved. The emission spectra of the complexes consist of narrow bands assigned to the $^4G_{5/2}\rightarrow{}^6H_J$ transitions (where $J=5/2$, $7/2$, $9/2$ and $11/2$) of the Sm^{3+} ion. The electric dipole $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition presents the highest relative emission intensity around 648 nm. The emission spectra (Fig. 3) show that the transitions split in a

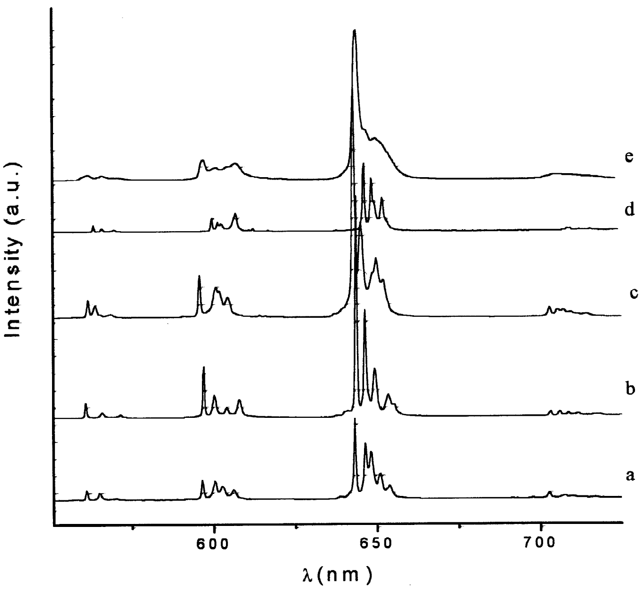

Fig. 3. Emission spectra of the $[Sm(TTA)_3\cdot 2L]$, at nitrogen liquid temperature, for the following ligands: (a) H_2O, (b) PHA, (c) TPPO, (d) DBSO, and (e) PTSO.

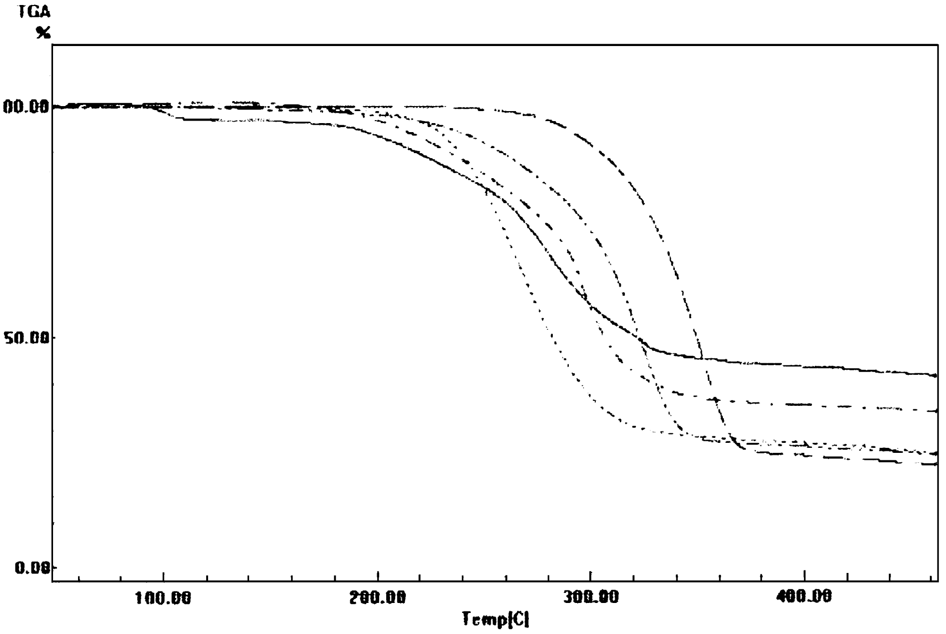

Fig. 2. TG curves of Sm^{3+} compounds containing the following ligands: H_2O (solid line); PHA (dash–dot line); TPPO (dash line); DBSO (dot) and PTSO (dash–dot–dot line) recorded in dynamic atmosphere of nitrogen (50 ml min^{-1}), and heating rate 10 °C min^{-1}.

Table 1
Energies of the $^4G_{5/2}\rightarrow{}^6H_{5/2-11/2}$ manifolds (cm^{-1}) observed in the emission spectra of [Sm(TTA)$_3$·2L], where L = H_2O, TPPO, PHA, DBSO and PTSO

Transitions	H_2O	TPPO	PHA	DBSO	PTSO
$^4G_{5/2}\rightarrow{}^6H_{5/2}$	17 825	17 806	17 832	17 749	17 806
	17 702	17 737	17 674	17 665	17 665
	17 544	17 593	17 495	17 553	17 525
$^4G_{5/2}\rightarrow{}^6H_{7/2}$	16 767	16 784	16 750	16 675	16 750
	16 658	16 644	16 661	16 625	16 642
	16 592	16 617	16 556	16 600	16 543
	16 502	16 545	16 453	16 477	16 485
$^4G_{5/2}\rightarrow{}^6H_{9/2}$	15 547	15 552	15 538	15 475	15 533
	15 475	15 504	15 470	15 425	15 468
	15 432	15 418	15 404	15 404	15 389
	15 361	15 389	15 305	15 347	15 361
	15 298	15 337	15 267	15 312	15 305
$^4G_{5/2}\rightarrow{}^6H_{11/2}$	14 337	14 229	14 221	14 142	14 190
	14 233	14 180	14 164	14 118	14 154
	14 160	14 144	14 112	14 100	14 094
	14 130	14 096	14 053	14 047	14 065
	14 094	14 053	13 951	14 017	13 999
	13 953	14 002	13 920	13 982	13 959

maximum number of $(J+1/2)$-components (Table 1) indicating that the Sm^{3+} ion occupies a site with low symmetry.

The transition $^4G_{5/2}\rightarrow{}^6H_{5/2}$(around 560 nm) is taken as the reference due to its predominant magnetic dipole character ($\Delta J=0$). On the other hand, the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition is magnetic-dipole forbidden and electric-dipole allowed. From this transition we determined the η_{Sm} intensity parameter, which is the ratio between the intensities of the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{5/2}$transitions for the Sm^{3+}-complexes [16].

The experimental intensity parameter η_{Sm} for the samarium complexes shows that the substitution of the two water molecules by the ligands increases the luminescence intensity in following order (Table 2): $H_2O<TPPO<PHA<DBSO<PTSO$, illustrating the hypersensitive behavior of the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition, indicating that the samarium ion is in a highly polarizable chemical environment. Table 2 shows also the η_{Eu} experimental intensity parameter for the [Eu(TTA)$_3$·2L] complexes (where L is the same ligands coordinated to the Sm-complexes). The η_{Eu} parameter is given by the ratio between the area under curves of the hypersensitive $^5D_0\rightarrow{}^7F_2$ transition allowed by electric-dipole and magnetic-dipole allowed $^5D_0\rightarrow{}^7F_1$ transition, $\eta_{Eu}={}^5D_0\rightarrow{}^7F_2/{}^5D_0\rightarrow{}^7F_1$. The η_{Eu} values show a behavior similar to that found for the Sm-complexes, corroborating with the electric-dipole character of the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition from H_2O to PTSO ligands. In addition, a higher polarizable chemical environment around the RE^{3+} ion is observed for the complexes (Sm and Eu) with sulfoxide ligands.

Table 2
Experimental intensity parameters and lifetime (τ) of $^4G_{5/2}$ emitting level (ms) for the [Sm(TTA)$_3$·2L] (where L = H_2O, TPPO, PHA, DBSO and PTSO), at room temperature

[Sm(TTA)$_3$·2L]	η_{Sm} [a]	Barycenter	η_{Eu} [a]	τ
H_2O	8.89	15 497	8.90	0.0042
DBSO	12.54	15 475	20.25	0.0677
PTSO	13.37	15 492	20.85	0.1114
TPPO	11.70	15 523	12.99	0.1298
PHA	12.15	15 507	15.50	0.0370

[a] Where the intensity parameters are ratio of intensities given by $\eta_{Sm}={}^4G_{5/2}\rightarrow{}^6H_{9/2}/{}^4G_{5/2}\rightarrow{}^6H_{5/2}$ and $\eta_{Eu}={}^5D_0\rightarrow{}^7F_2/{}^5D_0\rightarrow{}^7F_1$ for samarium and europium, respectively.

The energy of the triplet state (T) of the TTA ligand was obtained from the phosphorescence spectrum of the [Gd(TTA)$_3$·$(H_2O)_2$] complex recorded at 77 K under excitation at 337 nm in the spectral region from 400 to 700 nm (omitted figure). The triplet states were taken as the shortest wavelength from the phosphorescence bands due to 0–0 transition with energy level positions around of 21 280 cm^{-1} [15].

The luminescence decay curves of the $^4G_{5/2}$ emitting level of Sm-complexes were monitored in the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition [9]. The decay curves for the [Sm(TTA)$_3$·2L] (where L = H_2O, PHA, PTSO, DBSO and TPPO), at room temperature, were found to be a single exponential, indicating the existence of only one site symmetry around the Sm^{3+} ion. When we compare the lifetimes (Table 2) of all complexes it is observed that the [Sm(TTA)$_3$·$(H_2O)_2$] precursor ($\tau=0.0042$ ms) shows the smallest value, indicating that the water molecules play a role in the non-radiative processes in the Sm^{3+} complexes. It is also noted that the complex with the PHA ligand has a smaller value of lifetime than those containing sulfoxide and phosphine oxide ligands. This is probably due to the presence of N–H vibrations in the amide ligand that contribute to non-radiative deactivation of the $^4G_{5/2}$ emitting state of the Sm^{3+} ion [17].

4. Conclusion

The new [Sm(TTA)$_3$·2L] complexes (L = H_2O, TPPO, PHA, DBSO and PTSO) show strong orange luminescence when excited by ultraviolet radiation. The IR data show a shift of the stretching νX=O (where X = S, P and C) to smaller frequencies in the Sm^{3+}-complexes as compared with the free ligands, indicating that the coordination of the ligands to Sm^{3+} ion occur through the oxygen. The TG curves of the complexes do not show any event in the region up to 150 °C, indicating that the compounds are anhydrous. The emission spectra of the samarium complexes present bands corresponding to the $^4G_{5/2}\rightarrow{}^6H_J$ transitions, where $J=5/2$, $7/2$, $9/2$ and $11/2$, with the highest intensity band being the hypersensitive

$^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition. The Sm-complexes present lifetimes higher than the hydrated precursor, indicating the efficient luminescence quenching due to OH oscillators in the inner coordination sphere of Sm^{3+} ion in hydrated compound. The small value of the lifetime in the complex with the PHA ligand is probably due to N–H vibrations that can act as a channel of deactivation of the $^4G_{5/2}$ emitting level. The experimental intensity parameters (η_{Sm} and η_{Eu}) presented the same ligand order: $H_2O < TPPO < PHA < DBSO < PTSO$, showing the higher hypersensitive character of the transition $^4G_{5/2} \rightarrow {}^6H_{9/2}$ in the complex with the PTSO ligand. Based on these photoluminescence data we suggest that the Sm^{3+}-β-diketonate complexes are promising candidates as efficient light-converting device molecular (LCDM) similar to the respective Eu^{3+}-β-diketonate complexes.

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