

Synthesis and Photoluminescent Properties of Lanthanides Acetoacetanilide Complexes

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Abstract This work reports on the photoluminescent properties of three new lanthanide complexes with acetoacetanilide (aaa), a β -diketonate ligand. The complexes have the general molecular formulae $[\text{RE}(\text{aaa})_3(\text{H}_2\text{O})]$, they are soluble in organic solvents such as ethanol and chloroform and insoluble in water. The energy of the triplet state was determined at about $4,700\text{ cm}^{-1}$ higher than the $^5\text{D}_4$ emitting level of the Tb (III) ion, leading to an absolute quantum yield of 22 % for the $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ complex. The photoluminescent properties were studied and the luminescence parameters of the $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$ complex were experimentally determined. The photostabilities of the complexes under continuous UV irradiation were measured and the data indicate low stability of the $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ complex when the system is excited at the band attributed to energy transfer from the ligand to terbium(III) ion. However, its photostability is significantly improved under inert atmosphere.

Keywords Luminescence · Beta-diketone complexes · Terbium(III) · Europium(III)

Introduction

Research about photoluminescent rare earth (RE) complexes has attracted significant attention since the discovery of antenna effect [1] by Weissman that has allowed the use of RE in many different potential applications such as photoluminescence [2], electroluminescence [3] and in

immunoassays [4]. The rare earth β -diketonate complexes are widely studied mainly due to their photoluminescent behaviors. The most common complex of this family is the diaqua-tris(thenoyltrifluoroacetate)europium(III) - $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ that presents a quantum efficiency of the $^5\text{D}_0$ level around 29 %, a quantum yield of 23 % and an energy transfer from the triplet state of the ligand to the europium(III) levels known as antenna effect [5, 6].

Beyond 2-thenoyltrifluoroacetone (Htta), other β -diketonate ligands, such as dibenzoylmethane (Hdbm) [7] and acetylacetonate (Hacac) [8] have been studied due to their potential photoluminescent properties. In these complexes the energy transfer from the ligand states to lanthanide ions depends on the energy difference between the triplet state (T_1) of the ligand and the levels of the RE(III) ion [9] and the specific selection rules [10]. It is important to point out that the emission quantum yield of the RE(III) complexes depends, among other factors, on the molar absorption coefficient of the ligand, the energy of its triplet state, the rates of energy transfer and back transfer between the ligand states and the lanthanide ion levels, the energy and the radiative and non-radiative rates of the lanthanide emitting state [11].

Acetoacetanilide (Haaa) is a β -diketonate ligand commonly used for preparation of transition metal complexes [12–16], however, up to now there are no examples of rare earth complexes using this ligand. Acetoacetanilide has an amide group [17] that provides higher electronic density in the quasi-aromatic ring of the formed complexes. On the other hand, it makes the proton of the beta carbon of the β -diketonate group less acidic leading to extra care to prepare the salt of this ligand using specific acid–base reactions, since the LUMO orbital is predominantly over the β -diketonate group [18]. In its neutral form, the molecule is

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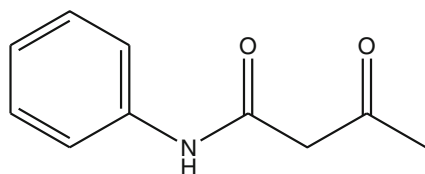


Fig. 1 Molecular structure of the acetoacetanilide (Haaa) ligand

not planar, due to the presence of intramolecular hydrogen bonds between carbonyl and amine groups [19].

Based on the lack of information about the preparation and characterization of rare earth- acetoacetanilide complexes, the present work reports on the preparation of new complexes of europium(III), gadolinium(III) and terbium(III) with acetoacetanilide (Haaa) ligand and their photoluminescent characterization. The emission lifetimes, the Judd-Ofelt intensity parameters, the quantum efficiencies of the emitting states, the absolute quantum yields as well as the photo stabilities of the europium(III) and terbium(III) complexes were determined.

Experimental Details

The reagents (rare earth oxides Eu_2O_3 , Gd_2O_3 and Tb_4O_7 and the ligand Haaa) were purchased from Aldrich and used without further purification. The rare earth chlorides RECl_3 were prepared by reaction with HCl , dried and maintained under vacuum. The complexes were precipitated using 6 mmol acetoacetanilide (Fig. 1) and 6 mmol KOH , dissolved in 20 mL of water at room temperature. Then 2 mmol of RECl_3 ($\text{RE}=\text{Eu(III)}$, Gd(III) and Tb(III)) in 10 mL of water were added dropwise to the ligand solution under stirring. The complexes were immediately precipitated (Eu^{3+} complex: pale yellow; Gd^{3+} and Tb^{3+} complexes: white) and after 2 h

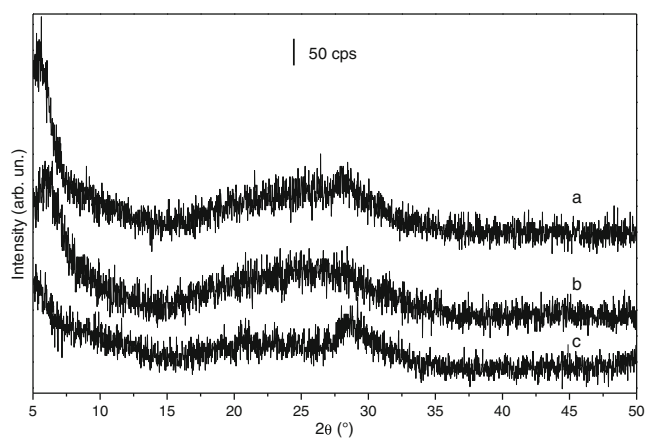


Fig. 3 Powder X-ray diffraction of the complexes **a** $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$; **b** $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$; **c** $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$

of stirring, each solid was filtered, washed with water and dried under vacuum. The complexes have high solubility in many organic solvents, such as acetone, methanol, ethanol and chloroform, and they are insoluble in water. The yields of the reactions are: $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$ 55 %; $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$ 73 %; $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ 91 %.

The chemical formulas of the complexes were suggested by complexometric titration of lanthanide(III) ions using a standard 0.01 mol L^{-1} ethylenediaminetetraacetic acid (edta) solution and by thermogravimetric analyses that were obtained using a TA SDT Q600 from 27°C up to 900°C with $10^\circ\text{C}/\text{min}$ as a heating rate under a synthetic air flow of $50 \text{ mL}/\text{min}$. The X-ray diffractograms (XRD) were obtained with a Shimadzu XRD-700 diffractometer, in the range 2θ from 5 to 50° , at $2.0^\circ/\text{min}$, using 1 mm slit and $\text{CuK}\alpha$ radiation. The infrared spectra were carried out with a Bomem MB – Series model B 100 FTIR spectrometer, with a resolution equal to 4 cm^{-1} and 32 scans per spectrum, in KBr pellets.

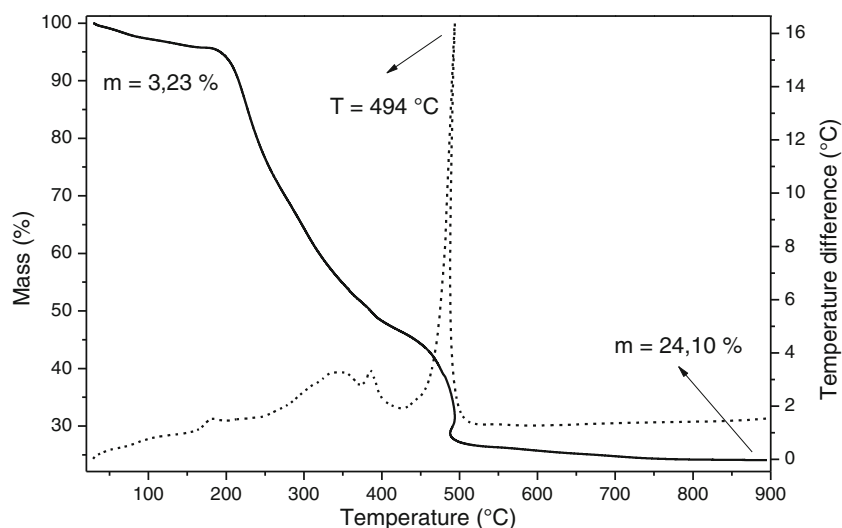


Fig. 2 TG and DTA curves of the $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$ complex

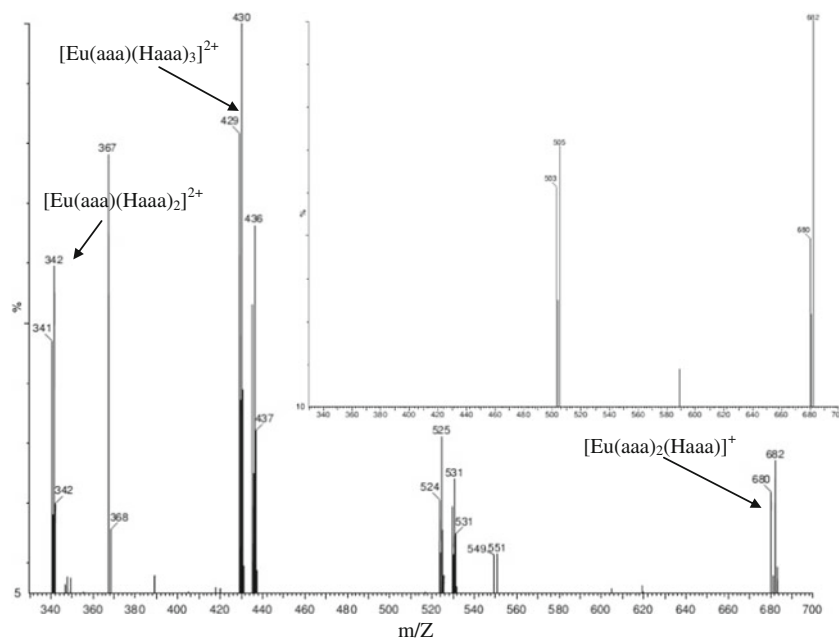


Fig. 4 Mass spectrometry of the $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$ complex. The inset corresponds to the MS/MS analysis of the signal at $m/z=680$

The mass spectrometry was carried out in a XEVO QTOF Waters spectrometer in the ESI MS and MS/MS modes and positive acquisition. The fragments were generated using electric potentials between 1 and 15 eV. In order to perform this analysis 1 mg of the complex was dissolved in 1 mL of ethanol. Then 1 μL of the ethanolic complex solution was acidified with 1 mL of 1 % v/v aqueous formic acid.

The photoluminescent data were obtained in a Fluorolog-3 spectrofluorometer (Horiba FL3-22-iHR320), with double-gratings (1200 gr/mm, 330 nm blaze) in the excitation monochromator and double-gratings (1200 gr/mm, 500 nm blaze) in the emission monochromator with a Xenon lamp ozone free

450 W (Ushio) as radiation source. The excitation spectra were obtained between 200 and 600 nm and corrected in real time according to the lamp intensity and optical system of the excitation monochromator using a silicon diode as a reference. The emission spectra were carried out between 350 and 720 nm using the front face mode at 22.5° in order to obtain the best relation between high signal and low scattering of the radiations' source. All of them were corrected according to the optical system of the emission monochromator and the photomultiplier (Hamamatsu R928P) response. The time resolved emission spectra were measured using a multichannel system (FluoroHub-B) with a delay of 5.333 μs , in order to attribute the band emissions from triplet and singlet states of the gadolinium complex. The emission decay curves were obtained with a pulsed 150 W Xenon lamp using the multichannel system and 1024 channels. The absolute quantum yields were measured using a Quanta- ϕ (Horiba F-309) integrating sphere equipped with an optical-fibers bundle (NA = 0.22 - Horiba- FL-3000/FM4-3000). The photostability of the complexes against UV radiation were performed for 12 h at 300 K using pettier sample cooler (Horiba F-3004) system. The emission intensities were continually recorded using a kinetic acquisition mode of the spectrofluorimeter system.

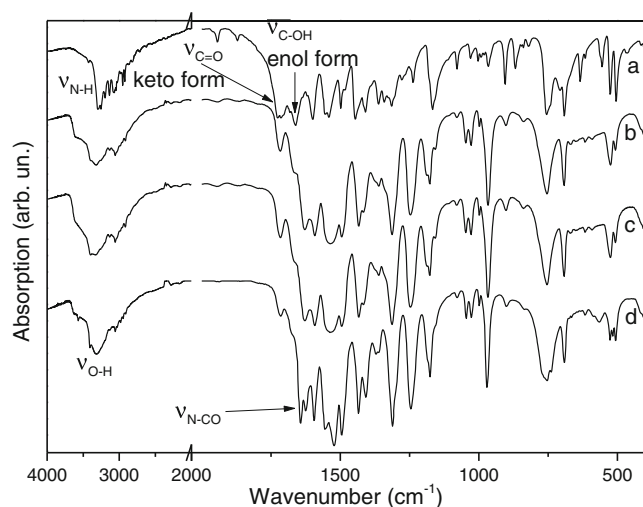


Fig. 5 FT-IR spectra, **a** acetoacetanilide (Haaa), **b** $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$, **c** $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$, **d**: $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$

Results and Discussion

Characterization

The molecular formulae of the complexes were proposed according to the percentages of the rare earth(III) ions

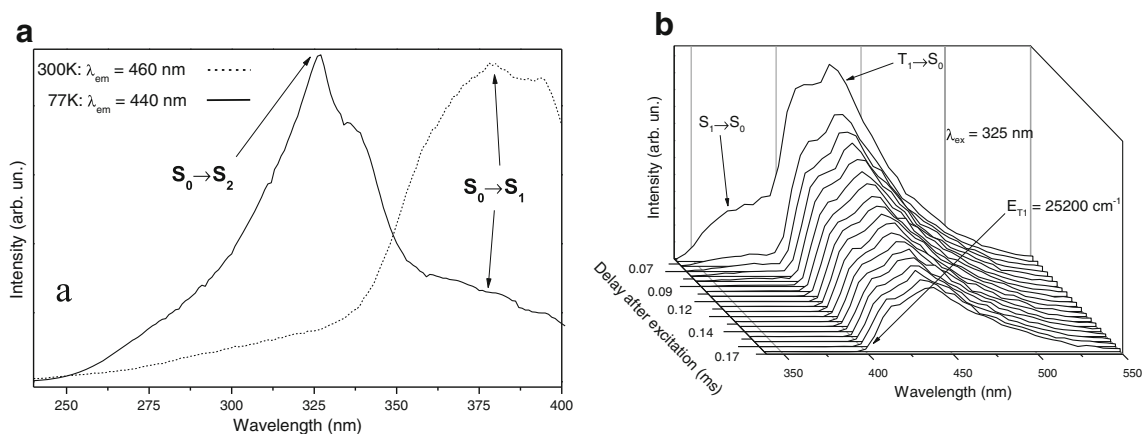


Fig. 6 **a** Excitation spectra of the $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$ complex obtained at 77 K and 300 K and **(b)** time resolved emission spectra of $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$ complex obtained at 77 K

obtained by complexometric titration. % RE(calc./exp.): $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$ (21.8/21.5), $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$ (22.3/22.6), $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ (22.5/23.4) and by thermogravimetric analysis. The thermogravimetric curve (Fig. 2) of the $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$ complex show three main events. The first one, up to 160 °C, is due to the loss of one non-coordinated water molecule, % H_2O (calc 2.56/exp 3.23). The water molecule is supposed to be non-coordinated because there is no endothermic event in this range of the DTA curve. The next events are correlated to progressive loss of the ligand species resulting in the respective rare earth oxide, % Gd_2O_3 (calc 25.75/exp 24.10).

XRD patterns of the rare earth complexes are similar to each other (Fig. 3). All of them show a non-crystalline halo centered at 22° (2 θ). Also, one may observe low intensity and broad diffraction peaks at 5.5 and 28.5° (2 θ). The XRD data suggest that the complexes are non-crystalline however they may present low degree of organization at short distances.

The mass spectrometry analysis was performed to determine the molecular mass of the rare earth acetoacetanilide complexes. The MS analysis of the europium(III) complex (Fig. 4) indicates the formation of the $[\text{Eu}(\text{aaa})_3]$ specie. According to the isotopic pattern of the Eu^{3+} ion it is possible to identify the m/z signals due to Eu^{3+} -containing fragments. The peaks attributed to the complex are a doublet with m/z ratios equal to 680 and 682, corresponding to the $[\text{Eu}(\text{aaa})_2(\text{Haaa})]^+$ and $[\text{Eu}(\text{aaa})_2(\text{Haaa})]^+$ ions, respectively. The fragments at $m/z=341$ and 342 are attributed to the doubly charged species $[\text{Eu}(\text{aaa})(\text{Haaa})_2]^{2+}$ and $[\text{Eu}(\text{aaa})(\text{Haaa})_2]^{2+}$. The signals at m/z 429 and 430 are attributed to the doubly charged tetrakis complex, $[\text{Eu}(\text{aaa})(\text{Haaa})_3]^{2+}$ and $[\text{Eu}(\text{aaa})(\text{Haaa})_3]^{2+}$. The MS/MS analysis of the complex $m/z=680$ (Fig. 4 - inset), generate signals at $m/z=503$ and 505, corresponding to the $[\text{Eu}(\text{aaa})_2]^+$ ion and peaks at m/z 587 and 589 that may be attributed to the complex minus a $\text{C}_6\text{H}_5\text{-NH}$ fragment.

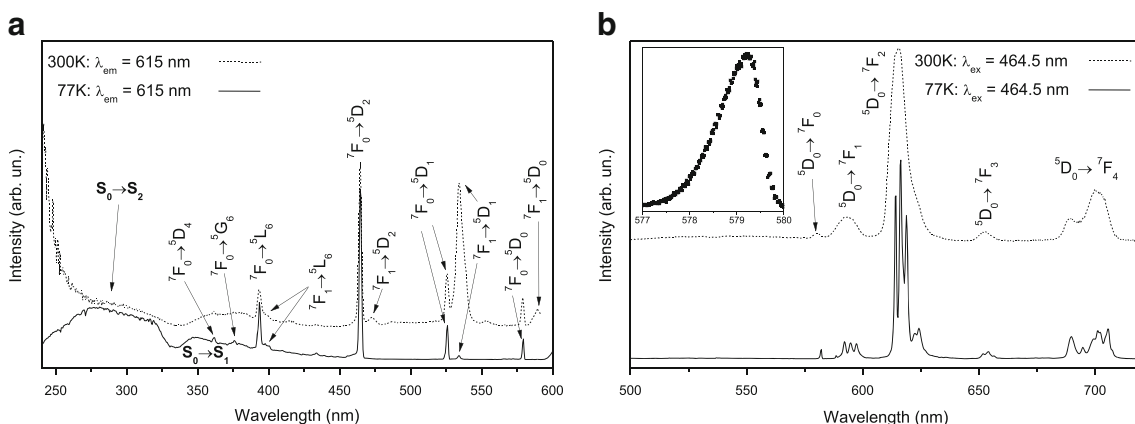


Fig. 7 Excitation **(a)** and emission **(b)** spectra of the $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$ complex obtained at 77 and 300 K. The inset shows the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ emission spectrum obtained at 77 K

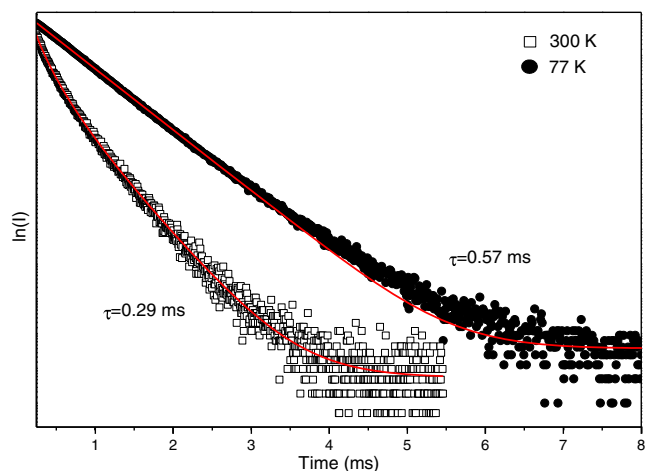


Fig. 8 Emission decay curves of 5D_0 level of the $[Eu(aaa)_3(H_2O)]$ complex obtained at 77 K and 300 K, by excitation at 464.5 nm with emission monitored at 615 nm

The infrared spectra (FT-IR) of the $[RE(aaa)_3(H_2O)]$ complexes (Fig. 5) show bands attributed to the same normal modes of vibration with differences of 2 or 3 cm^{-1} between them, indicating the same coordination modes. It is possible to verify, in the FT-IR spectra of the complexes (Fig. 5), that the asymmetric (1726 cm^{-1}) and symmetric (1714 cm^{-1}) stretching modes of the carbonyl groups of the Haaa ligand (Fig. 5a) are displaced to 1594 and 1524 cm^{-1} , respectively [20], indicating that the rare earth ions are coordinated by the β -diketone group of the ligand, forming a quasi-aromatic ring [21]. Furthermore, the C–H and N–H stretching bands, shown by the ligand spectrum at 3070 cm^{-1} and 3425 cm^{-1} , respectively, are not quite visible in the spectra of the complexes due to the broad and intense O–H stretching band of the water molecules. The bands at 1079 and 999 cm^{-1} are attributed to the in plane bending of the aromatic C–H bonds and the bands at 755 and 1871 cm^{-1} are attributed to the out of plane bending of the aromatic C–H bonds. These bands do not change their spectral position after coordination to rare earth ions. The band around 400 cm^{-1} in the spectra of the complexes can be attributed to the bonding between the RE^{3+} ion and C=O groups of the aaa^- ligands [15].

Photoluminescent Properties

The emission spectrum of the $[Gd(aaa)_3(H_2O)]$ complex (Fig. 6), obtained at liquid nitrogen temperature (77 K), shows that the phosphorescence band of the ligand starts at 395 nm , meaning that the non-phonon energy of the triplet (T_1) state of the aaa^- ligand is approximately at $25,300\text{ cm}^{-1}$. It is interesting to note (Fig. 6a) that the higher energy excitation band attributed to $S_0 \rightarrow S_2$ is more intense than the $S_0 \rightarrow S_1$ band in the spectra obtained at 77 K, while the inverse is observed when the excitation spectrum is carried out at 300 K (Fig. 6a). At low temperature the phosphorescence band is more intense than the fluorescence one (Fig. 6b) probably because the intersystem crossing process is more efficient at 77 K. The fluorescence and phosphorescence bands (Fig. 6b) were discriminated by their different emission lifetimes. The $S_1 \rightarrow S_0$ transition present emission lifetime shorter than $5\text{ }\mu\text{s}$ and the $T_1 \rightarrow S_1$ transition present emission lifetime equal to $167\text{ }\mu\text{s}$.

The excitation spectra of the $[Eu(aaa)_3(H_2O)]$ complex (Fig. 7a) indicate that the bands attributed to $^7F_0 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5D_1$ and $^7F_0 \rightarrow ^5D_0$ transitions of the Eu^{3+} ion are quite intense compared to the ligand excitation band, being the $^7F_0 \rightarrow ^5D_2$ excitation band the most intense one (Fig. 7a). That data indicates that in this complex the 5D_0 level of $Eu(III)$ ion is not efficiently populated by energy transfer either from the $T \rightarrow ^5D_0$ or the $T \rightarrow ^5D_1 \rightarrow ^5D_0$ mechanisms. This probably happens because of the large energy difference between the triplet state of the ligand and the 5D_0 or 5D_1 levels of the $Eu(III)$ ion. The energy difference between the triplet state and the 5D_0 level is around $8,000\text{ cm}^{-1}$. That difference makes difficult an efficient ligand-metal energy transfer. The emission bands of the $Eu(III)$ complex in the spectrum obtained at 77 K (Fig. 7b) are well defined and some Stark levels are distinguishable. The $^5D_0 \rightarrow ^7F_0$ emission band (Fig. 7b – inset) is unfolded but this transition is asymmetric and relatively broad (about 36 cm^{-1}) indicating that the $Eu(III)$ ions are located in similar chemical environments. The emission spectrum obtained at 300 K shows low intensity phosphorescence band around 500 to 550 nm , corresponding to the transition $T_1 \rightarrow S_0$ of the ligand. The presence of this low intensity phosphorescence band is due

Table 1 Judd-Ofelt intensity parameters (Ω_λ), ratio of the $^5D_0 \rightarrow ^7F_0 / ^5D_0 \rightarrow ^7F_2$ areas, emission lifetime values of the 5D_0 level (τ), emission coefficients (A), quantum efficiency (η) and absolute quantum yield (Φ) of europium(III) complexes

Complexes	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	R_{02} (10^{-3})	τ (300 K) (ms)	τ (77 K) (ms)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	η (%)	Φ (%)
$[Eu(aaa)_3(H_2O)]$	9.7	11.7	21	0.29	0.57	518	2931	3449	15	1
$[Eu(btfa)_3(H_2O)_2]$ [5]	20.6	3.5	–	0.17	–	349	2283	2632	13	22
$[Eu(tta)_3(H_2O)_2]$ [5]	33	4.6	–	0.26	–	1110	2740	3850	29	23

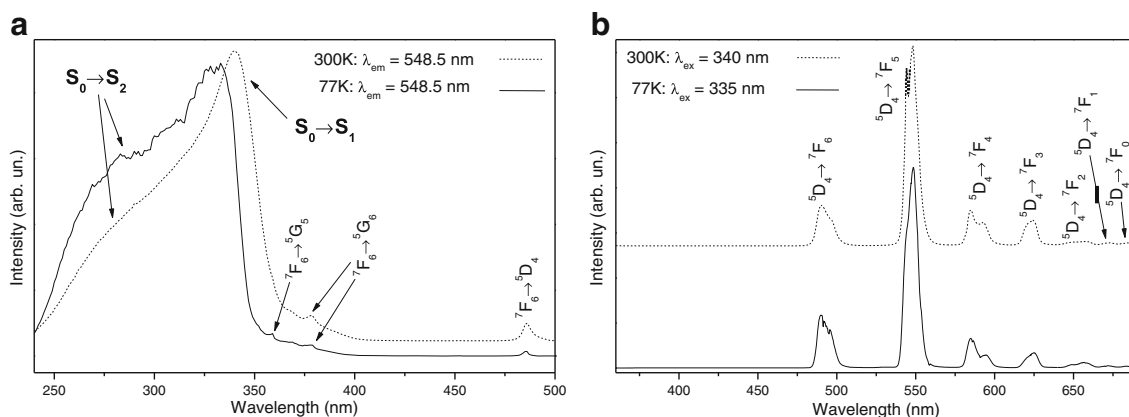


Fig. 9 Excitation (a) and emission (b) spectra of [Tb(aaa)₃(H₂O)] complex obtained at 77 and 300 K

to the large energy difference between the T₁ state of the ligand and the ⁵D₀₋₁ levels of the Eu(III) ion.

The emission decay curve of the [Eu(aaa)₃(H₂O)] complex was measured (Fig. 8) and it can be fitted to a first order exponential decay indicating that the europium(III) ions are located in similar chemical environments. The emission lifetime of the ⁵D₀ level of the Eu³⁺ ion in the complex is equal to 0.29 ms at 300 K, but at 77 K the emission lifetime increases to 0.57 ms. This difference indicates that at 300 K the emission of the Eu³⁺ ion is suppressed by vibrational couplings, attributed mainly to the O–H and N–H oscillators. The total emission coefficient A_{tot} is given by the sum of radiative (A_{rad}) and non-radiative (A_{nrad}) coefficients. The high value of A_{nrad}, 3448 s⁻¹, leads to a lower quantum efficiency value (15 %) (Table 1).

The intensities parameters Ω₂ and Ω₄ were also experimentally measured from the emission spectrum at 300 K and the values are presented in Table 1. One may note that

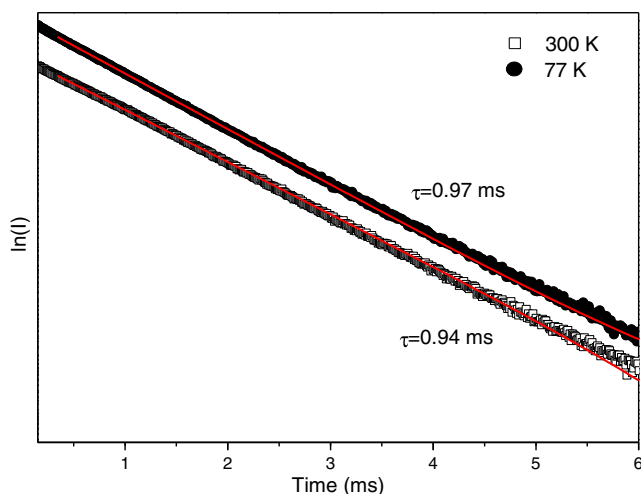


Fig. 10 Emission decay curves of ⁵D₄ level of the [Tb(aaa)₃(H₂O)] complex obtained at 77 K and 300 K, by excitation at 340 nm with emission monitored at 548.5 nm

the Ω₂ value is lower than other beta-diketones [5], probably because the chemical environments are less polarizable than the sites occupied by europium(III) ions in the beta-diketone complexes related on Table 1. The results also indicate that europium(III) ions are located in the chemical environment with no inversion center that may be distorted in direction to a centro symmetric one, as verified by the intensity ratio between the transitions ⁵D₀→⁷F₂/⁵D₀→⁷F₄ (Fig. 7b). [22, 23].

The absolute quantum yield of the [Eu(aaa)₃(H₂O)] complex was obtained by excitation at 464 nm (⁷F₀→⁵D₂ transition) since the complex does not present an energy transfer ligand-europium(III) band. Even under direct excitation, the [Eu(aaa)₃(H₂O)] complex show a low absolute quantum yield indicating that the emission of the Eu³⁺ ions is strongly suppressed by non-radiative routes, probably due to O–H and N–H oscillators, that may efficiently couple with the ⁵D₀ emitting level [24, 25]. As reported previously in the literature [5], if the energy of the triplet state T₁ is higher

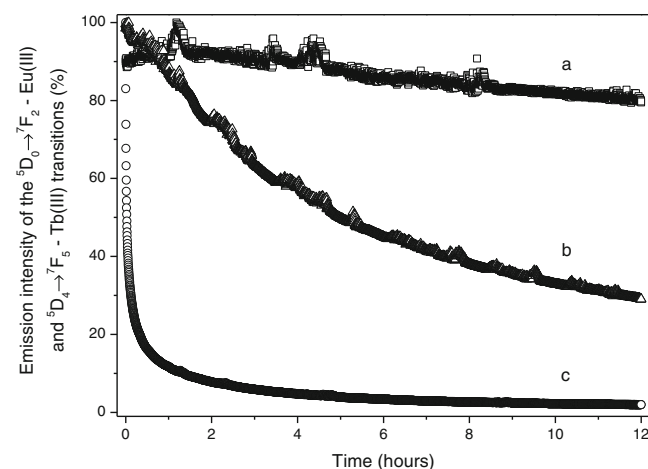


Fig. 11 Photo-stability curves obtained at 300 K: **a** [Eu(aaa)₃(H₂O)] (λ_{exc}=464 nm, air); **b** [Tb(aaa)₃(H₂O)] (λ_{exc}=340 nm, N₂ atmosphere); **c** [Tb(aaa)₃(H₂O)] (λ_{exc}=340 nm, air atmosphere)

than $22,000\text{ cm}^{-1}$ the energy transfer from ligand to Eu^{3+} ion is not efficient due to the high energy difference between T_1 state and 5D_1 level, as in the case of hydrated europium (III) squarate complex ($\Phi < 1\%$), that is lower than its analogue terbium(III) complex ($\Phi = 25\%$) [26]. As the energy of the T_1 state of the $[\text{Gd}(\text{aaa})_3(\text{H}_2\text{O})]$ complex was determined as $25,300\text{ cm}^{-1}$, it is possible to explain the low emission quantum yield of the $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$ complex. Also in this situation, the back energy transfer rates maybe higher from the energy levels 5D_4 and 5G_6 of Eu^{3+} ion than from 5D_0 level [27].

The excitation spectra of the $[\text{Tb}(\text{aaa})_3\text{H}_2\text{O}]$ complex obtained at 300 K and 77 K (Fig. 9) exhibits the excitation bands of the ligand more intense than the transitions of the terbium(III) ion which are almost overlapped by the intense excitation band of the ligand. The high intensity of the ligand excitation band and the absence of ligand emission (phosphorescence), unlike what happens to the europium(III) complex (Fig. 7b), suggest that the energy transfer from the triplet state to the 5D_4 level of the terbium(III) ion is more effective leading to an absolute quantum yield of 22%, when the system is excited at the ligand (330 nm).

The energy of the triplet T_1 state of the aaa^- ligand ($25,300\text{ cm}^{-1}$) suggests that the energy transfer from the triplet state of the ligand to the rare earth ions probably is more efficient for terbium(III) ion than for europium (III) ion due to the higher energy of the 5D_4 emitting level of the terbium(III) ion [28]. If the energy difference between T_1 state and 5D_4 emitting level of Tb^{3+} ion is less than $2,000\text{ cm}^{-1}$ the back energy transfer rate may be considerably high, changing the electronic population of the 5D_4 level of the Tb^{3+} ion [29]. However, the triplet state of the aaa^- ligand is $4,700\text{ cm}^{-1}$ higher than the 5D_4 level of the terbium(III) ion, that is high enough to minimize the back energy transfer rate from the 5D_4 level to triplet state of the ligand [30].

The emission band ${}^5D_4 \rightarrow {}^7F_5$ of the terbium(III) ion in the $[\text{Tb}(\text{aaa})_3\text{H}_2\text{O}]$ complex was monitored to evaluate the emission decay curve (Fig. 10). The emission lifetime of the 5D_4 level of the Tb(III) ion was measured to be equal to 0.94 ms at 300 K. Terbium(III) ion usually has longer emission lifetimes than those exhibited by europium(III) ions [31]. The energy difference between emitting and fundamental levels in Tb(III) ion decreases the vibronic coupling of the 5D_4 level to the O-H oscillator of the water molecules, which increases the probability of the radiative process [32]. The emission decay curve of the complex obtained at 77 K (Fig. 10) can also be fitted to a single order exponential decay function indicating that the Tb(III) ion is localized in similar chemical environments. The emission lifetime at 77 K (0.97 ms) is practically equal to that obtained at room temperature indicating that the

vibronic coupling of the Tb(III) with the thermal and O-H vibration mode does not constitute an efficient non-radiative route.

Although $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ complex present non-coordinated water molecule like its analogue $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$, the O-H oscillator does not effectively quenches 5D_4 level of Tb^{3+} ion due to low probability of coupling seven vibronic modes of the O-H oscillator. This non-radiative route is observed for Eu^{3+} complexes due to the lower energy of its 5D_0 emitting level, which may couples with five vibrational modes of the O-H oscillator. Therefore, the radiative decay rate from the europium(III) 5D_0 level is usually more affected by temperature and by vibronic modes than the radiative decay rate of the terbium(III) 5D_4 level, in the case of hydrated systems [33].

The photo-stability measurements of the Eu^{3+} and Tb^{3+} complexes are shown in Fig. 11. In the case of the $[\text{Eu}(\text{aaa})_3\text{H}_2\text{O}]$ complex (Fig. 11, curve a), the europium(III) ion is directly excited (${}^7F_0 \rightarrow {}^5D_2$) leading to a low decrease of the emission intensity as a function of time. On other hand, when the $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ complex is excited at 340 nm, under air atmosphere (Fig. 11, curve c), its emission intensity decreases to low levels at the first hour probably due to the decomposition of the complex. After 12 h under continuous irradiation the emission intensity is equal to 2% of the initial intensity. This emission intensity profile is not observed when the photo-stability measurement is performed under nitrogen atmosphere (Fig. 11- curve b), indicating that the reaction of the oxygen with the triplet state has a great influence on the ligand degradation and perhaps specific devices may be constructed if the terbium complex is properly encapsulated under vacuum and/or nitrogen atmospheres.

Conclusion

Three new rare earth β -diketonate complexes were synthesized by a relatively simple chemical route and were chemically and spectroscopically characterized. The energy of the triplet state of the ligand was measured to be at $25,300\text{ cm}^{-1}$ according to the non-phonon transition of the time-resolved emission spectrum of the Gd(III) complex obtained at 77 K. The photostability of the $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$ and $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ complexes shows that despite the degradation of the Tb^{3+} complex at irradiation under air atmosphere the degree of photo degradation maybe decreased if the complexes are encapsulated in an oxygen-free atmosphere package. The absolute quantum yields were measured showing a quantum yield around 20% for $[\text{Tb}(\text{aaa})_3(\text{H}_2\text{O})]$ complexes and around 1% for the $[\text{Eu}(\text{aaa})_3(\text{H}_2\text{O})]$.

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