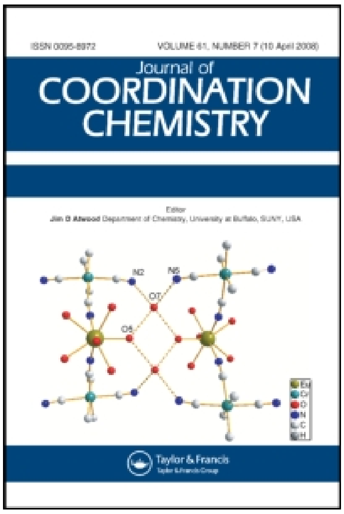

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Luminescence Investigations on Eu(III) Thenoyltrifluoroacetonate Complexes with Amide Ligands

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LUMINESCENCE INVESTIGATIONS ON Eu(III) THENOYLTRIFLUOROACETONATE COMPLEXES WITH AMIDE LIGANDS

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The influence of amide ligands on the photoluminescent behavior of tris(thenoyltrifluoroacetonate)-europium(III) in the solid state is reported. Elemental analysis showed that these compounds have the following formulas $[Eu(TTA)_3 \cdot (ANL)_2]$ and $[Eu(TTA)_3 \cdot PZA]$, where ANL = acetanilide and PZA = pyrazinamide. The photoluminescence spectra of the complexes recorded in the range 420–720 nm at 77 K show narrow bands arising from the $^5D_0 \rightarrow {}^7F_J$ transitions (where $J = 0$–4), under excitation at 394 nm. Based on the emission spectra and luminescence decay curves the intensity parameters (Ω_λ), lifetime (τ) and emission quantum efficiency (η) were determined. The Ω_2 values indicate that the Eu^{3+} ion in these complexes is in a highly polarizable chemical environment. The higher value of η (60%) obtained for the complex with the ANL ligand, in comparison with the complex with the PZA ligand (30%), indicates a more efficient deactivation of the Eu^{3+} ion in the $[Eu(TTA)_3 \cdot PZA]$ complex.

Keywords: Trivalent europium; Luminescence; Thenoyltrifluoroacetonate; Amides

INTRODUCTION

The chemical nature of the solid state of compounds forming β-diketonate chelates with trivalent europium (Eu^{3+}) continues to be extensively studied [1–5]. The main properties of these compounds are that they exhibit narrow emission bands with high luminescence intensity in the visible red region of the spectrum, presenting large Stokes shifts and long lifetimes of the $^{2S+1}L_J$ emitting level [5–7]. Based on these properties the

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Eu^{3+}-β-diketonate complexes have been examined as light conversion molecular devices (LCMDs) in the study of photo- and electroluminescent compounds [7–10].

Among the β-diketonate ligands, 2-thenoyltrifluoroacetone (TTA) has been shown to be an efficient "antenna" in the energy transfer processes from the ligand to the rare earth ion. Its hydrated complex with the Eu^{3+} ion is generally used as a precursor to synthesize highly luminescent complexes where the water molecules, which act as a luminescence quencher, are substituted by sulfoxides, phosphine oxide and heterocyclic organic ligands [5–7]. These compounds present higher emission quantum yields and lifetimes of the emitting level compared to the europium hydrated complex (Fig. 1a).

The special attention given to the Eu^{3+} ion is due mainly to facility in interpretation of the spectral data and to the high luminescence intensity in the visible region of the spectra presented by its complexes. The main emitting level of this ion, $^5D_0$, is non-degenerate, which facilitates interpretation of the $^5D_0 \rightarrow {}^7F_J$ transitions. Consequently, the spectral data can help in identification of the site symmetry around the Eu^{3+} ion. In addition, the allowed forced electric-dipole $^5D_0 \rightarrow {}^7F_2$ transition is hypersensitive to the chemical environment around the ion and its intensity can give information about the covalent character of the metal–ligand bonds. Furthermore, the allowed magnetic-dipole $^5D_0 \rightarrow {}^7F_1$ transition is almost insensitive to the chemical environment, and is generally taken as the reference transition [11]. Additionally, the $^5D_0 \rightarrow {}^7F_0$ transition can be used as a probe in identification of the number of sites occupied by the Eu^{3+} ion.

The luminescence of the excited state is generally quenched by vibrational energy transfer to high-energy oscillators such as OH, NH and CH belonging to the ligand donor groups or to solvent molecules [12,13]. Salama and Richardson [14] showed that the contribution of NH oscillators to non-radiative deactivation of the emitting state of the RE^{3+} ion is less efficient than the contribution of OH oscillators. The luminescence quenching decreases as the distance between the oscillators and the metal ion increases and consequently, the luminescence efficiency is higher in systems where the oscillators are not bound to the RE^{3+} ion [15].

Amide ligands are potentially useful in a variety of applications, including as complexing agents for selective extraction of f-elements and precious metals, and as improved ligands for magnetic resonance imaging (MRI) agents [16–18]. Because of

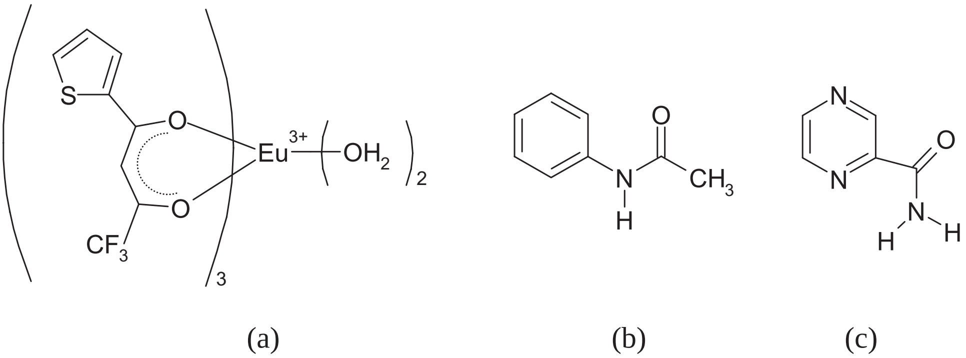

FIGURE 1 Molecular structure of: (a) The $[Eu(TTA)_3 \cdot (H_2O)_2]$ complex; (b) acetanilide and (c) pyrazinamide.

the hard acid character of the trivalent rare earth ions, coordination of amides to these metal ions generally occurs through the oxygen of the amide group [19].

The objective of this work is to prepare and characterize the solid-state complexes ([Eu(TTA)$_3$ · (ANL)$_2$] and [Eu(TTA)$_3$ · PZA]), where ANL = acetanilide (Fig. 1b) and PZA = pyrazinamide (Fig. 1c), to analyze the influence of the amide ligands on the photoluminescence of the europium ion, and to elucidate the parameters governing the emission quantum efficiency (η). The luminescence properties have been studied based on the Judd–Ofelt intensity parameters (Ω_λ), radiative (A_{rad}) and non-radiative (A_{nrad}) rates, and lifetimes of the emitting $^5D_0$ level (τ).

EXPERIMENTAL

Materials and Measurements

All solvents were of reagent grade and used without further purification. Aniline, acetic anhydride and sodium bicarbonate were purchased from Merck, while PZA ligand was purchased from Aldrich Co.

The carbon and hydrogen content were determined by the usual microanalytical procedures using an elemental analyzer model CHN 2400 (Perkin-Elmer, USA) while the Eu^{3+} content was obtained by complexometric titration with EDTA using xylenol orange as indicator.

The infrared spectra of the samples were used to provide information about the nature of coordination of the PZA and ANL ligands to the RE^{3+} ions. These spectra were recorded in the range from 4000 to 400 cm^{-1} in KBr pellets, using a Bomem model MB102 FTIR spectrophotometer. TG analysis was performed with a TG-50 thermobalance (Shimadzu) using platinum crucibles with 2 mg of the sample, under a dynamic nitrogen atmosphere (50 mL min^{-1}) and a heating rate of 10°C min^{-1}.

The excitation spectra of the complexes in the solid state were obtained in the spectral range 250–500 nm by monitoring the intensity of the $^5D_0 \rightarrow {}^7F_2$ band at 612 nm, while the emission spectra were obtained in the range 560–720 nm from excitation at 394 nm. The phosphorescence spectra of the Gd^{3+}-complexes were recorded in the range 420–720 nm under excitation at 377 nm. The luminescence decay curve of the $^5D_0$ emitting level was measured using a phosphorimeter SPEX 1934D accessory coupled with the spectrofluorometer. These luminescence instruments were fully controlled by a computer with the DM3000F spectroscopic program and the spectral intensities were automatically corrected for the photomultiplier response.

Synthesis of Acetanilide and Rare Earth Complexes

Acetanilide ligand (ANL) was synthesized in a reaction mixture of aniline (0.07 mol, 6.52 g) and acetic anhydride (0.08 mol, 8.17 g), which was stirred for 1 h. After addition of 20 mL of water to hydrolyze the excess acetic anhydride the product mixture was reacted with 20 mL aqueous solution of NaHCO$_3$ (0.5 M). The ligand was extracted from the reaction solution using chloroform, yielding 6.67 g (~60%) of a colorless solid product that was purified by recrystallization from ether (20 mL).

The hydrated complexes [RE(TTA)$_3$ · (H$_2$O)$_2$] (where RE = Eu^{3+} and Gd^{3+}), were synthesized as described [4]. The complexes with amide ligands were synthesized by reaction between the RE^{3+}-TTA hydrated complex (1.17×10^{-3} mol, 1 g) and PZA (3.50×10^{-3} mol, 0.41 g) or ANL (3.50×10^{-3} mol, 0.47 g) dissolved in acetone (molar ratio of precursor complex:ligand of 1:3). The mixture was stirred for 2 h at room temperature and the solid products were washed with water to remove excess amide ligand.

RESULTS AND DISCUSSION

Characterization

The chemical composition of the RE^{3+}-complexes determined by CHN elemental analysis and the RE^{3+} content in percentages found (calculated) obtained by complexometric titration with EDTA in methanol solution for the Eu-complexes with the respective ligands were: PZA (C: 37.15 (37.10); H: 1.85 (1.82); N: 4.36 (4.47); Eu^{3+}: 16.09 (16.18) and ANL (C: 44.27 (44.24); H: 2.65 (2.62); N: 2.72 (2.58); Eu^{3+}: 13.94 (13.98). For the Gd-complexes with the respective ligands the values were: PZA (C: 37.01 (36.89); H: 2.67 (2.76); N: 3.05 (2.97); Gd^{3+}: 16.75 (16.66) and ANL (C: 43.90 (44.02); H: 3.63 (3.58); N: 2.53 (2.56); Gd^{3+}: 14.30 (14.42). These results agree with the formulas; $[RE(TTA)_3 \cdot (ANL)_2]$ and $[RE(TTA)_3 \cdot PZA]$.

The IR spectra of the complexes with PZA and ANL ligands as compared with those of the hydrated precursors (figures not shown) show the absence of the large band around 3500 cm^{-1} which is assigned to the O–H stretching of the H_2O molecules, indicating substitution of the water molecules by the amide ligands in the first coordination sphere of the rare earth ion. A comparison of the IR spectra of the free PZA and ANL ligands with those obtained from the complexes show a downward shift of the amide I band ν(C=O) from 1719 and 1663 cm^{-1} to 1680 and 1620 cm^{-1}, respectively. The IR data suggest that bonding of the amide ligands to the RE^{3+} ion is occurring through the oxygen of the amide group. The coordination numbers of the metal ions in the complexes with PZA and ANL are thus seven and eight, respectively.

The TG curves of the hydrated complexes (figures not shown) give the first mass loss event (4.3 and 4.2%, for $[Eu(TTA)_3 \cdot (H_2O)_2]$ and $[Gd(TTA)_3 \cdot (H_2O)_2]$, respectively) around 90–120°C, in agreement with the loss of two water molecules. In contrast, the TG curves for the complexes with the amide ligands showed that they are stable up to 210°C without any weight loss, corroborating the elemental analysis and IR spectral data. Above these temperatures decomposition of the organic part of the complexes takes place.

Luminescence Study

Phosphorescence spectra of the Gd^{3+} complexes at 77 K under excitation at 377 nm are presented in Fig. 2. The spectral data were used to obtain information about the triplet state (T) of the ligands, since energy transfer from these levels to the excited state of the Gd^{3+} ion is not observed owing to the large energy gap in this ion. The hydrated and ANL complexes present a similar spectral profile, except that the latter is shifted to lower energy, probably because of the steric effects of the acetanilide around the RE^{3+} ion. The broad band associated with TTA in the complexes

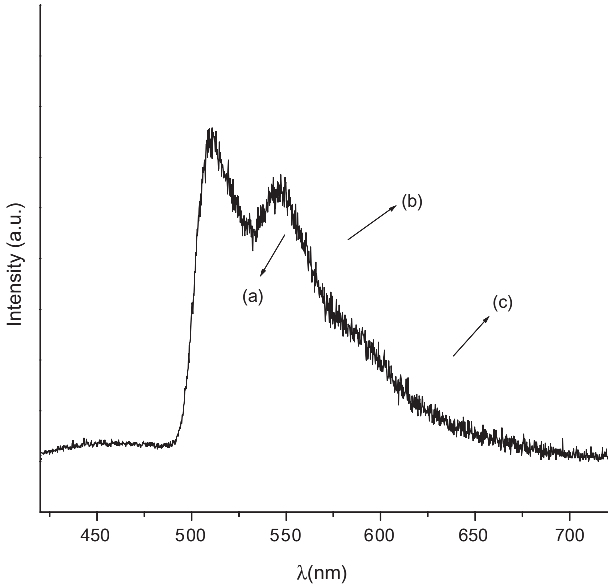

FIGURE 2 Phosphorescence spectra of Gd^{3+}-TTA complexes in the solid state, under excitation at 377 nm, at 77 K: (a) H_2O (solid); (b) ANL (dash dot) and (c) PZA (dot).

containing the H_2O, PZA and ANL ligands is located at 492, 494 and 500 nm, respectively. The attributions of these transitions were taken as the zero-phonon transition (smallest wavelength).

The phosphorescence lifetimes for $[Gd(TTA)_3 \cdot (ANL)_2]$ and $[Gd(TTA)_3 \cdot PZA]$ are 4.7 and 3.7 ms, respectively. These τ values are considerably higher than the values 0.5 and 0.4 ms observed for the emitting $^5D_0$ level in the europium complexes, indicating that emission in the Gd complexes arises from a ligand triplet state.

Figure 3 shows the excitation spectra of the Eu^{3+}-complexes recorded in the range of 250 to 560 nm monitoring the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (around 612 nm), at 77 K. The spectra essentially consist of two bands around 350 and 394 nm, which are assigned to the band from the TTA ligand that overlaps the $4f^6$-intraconfigurational $^7F_0 \rightarrow {}^5G_6$, $^5H_4$ and $^5L_6$ transitions. A narrow and weak band around 464 nm arising from the intraconfigurational $^7F_0 \rightarrow {}^5D_2$ transition is also observed.

The emission spectra of the Eu^{3+}-complexes recorded in the spectral range from 560 to 720 nm, at 77 K are presented in Figs. 4(a)–(c). They consist of sharp lines that are attributed to the $^5D_0 \rightarrow {}^7F_J$ (where $J = 0$–4) transitions. All the complexes show the $^5D_0 \rightarrow {}^7F_2$ transition as the most intense. The $^5D_0 \rightarrow {}^7F_0$ transition in both complexes is not split, indicating one chemical environment around the Eu^{3+} ion, with C_{nv}, C_n or C_s point symmetry. In addition, the observed $^5D_0 \rightarrow {}^7F_J$ transitions are split into $(2J+1)$ components (Table I), indicating that the Eu^{3+} ion is in a chemical environment of low symmetry. It is important to note the absence, in the spectral range 420–560 nm, of the broad phosphorescence band from the TTA ligand, (figure not shown), showing that the ligand-to-europium energy transfer process is quite efficient.

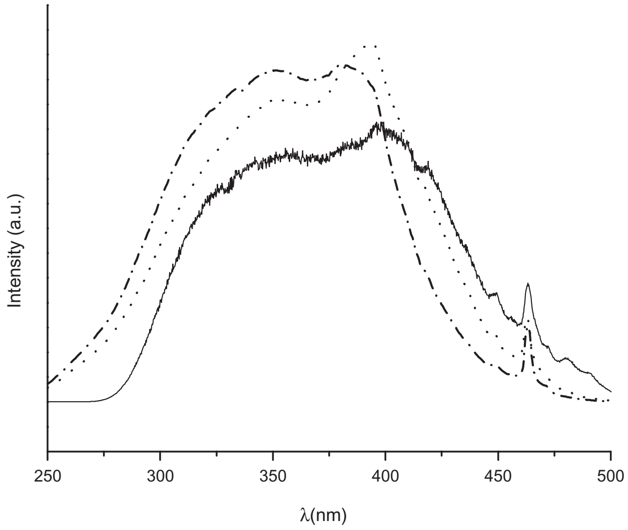

FIGURE 3 Excitation spectra of Eu^{3+}-TTA complexes in the solid state, with emission monitored at 612 nm, at 77 K: H_2O (solid), ANL (dash dot) and PZA (dot).

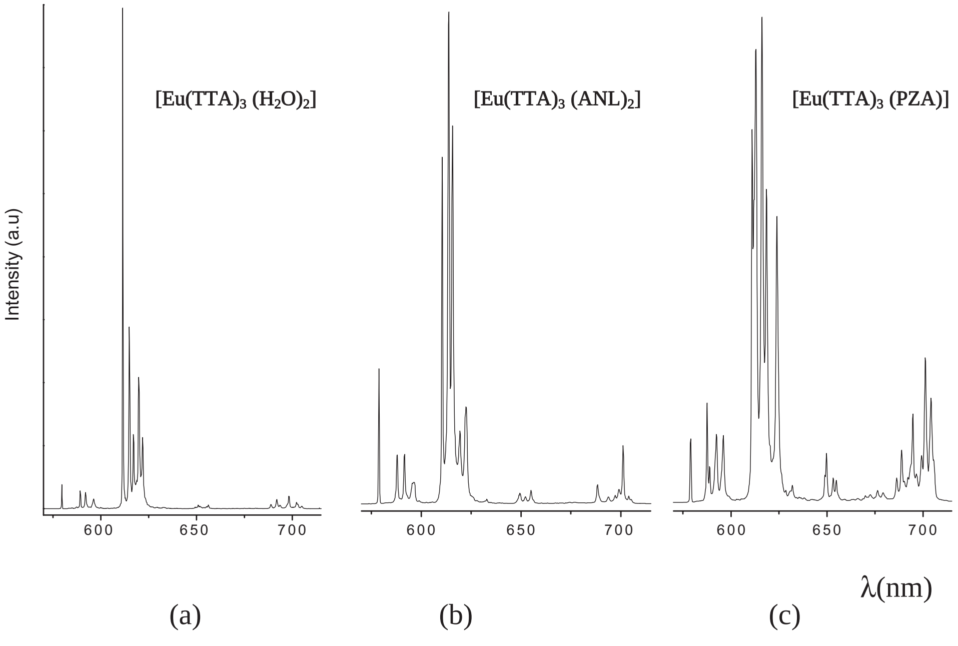

FIGURE 4 Emission spectra of europium complexes in the solid state, under excitation at 394 nm, at 77 K: (a) $[Eu(TTA)_3 \cdot (H_2O)_2]$; (b) $[Eu(TTA)_3 \cdot (ANL)_2]$ and (c) $[Eu(TTA)_3 \cdot (PZA)]$.

In the standard theory of 4f–4f intensities, the Ω_λ intensity parameters contain the contributions from the forced electric dipole and dynamic coupling mechanisms [5]. These parameters can be estimated theoretically from structural data or determined experimentally from absorption or emission spectra. The experimental intensity

TABLE I Energy levels of the $^5D_0 \rightarrow {}^7F_{0\text{–}4}$ transitions (cm^{-1}) observed from the emission spectra of the [Eu(TTA)$_3$ · (H$_2$O)$_2$], [Eu(TTA)$_3$ · (ANL)$_2$] and [Eu(TTA)$_3$ · PZA] complexes

Transition	*[Eu(TTA)$_3$ · (H$_2$O)$_2$]*	*[Eu(TTA)$_3$ · (ANL)$_2$]*	*[Eu(TTA)$_3$ · PZA]*
$^5D_0 \rightarrow {}^7F_0$	17283	17277	17271
$^5D_0 \rightarrow {}^7F_1$	16995	17007	17018
	16926	16903	16880
	16790	16779	16779
$^5D_0 \rightarrow {}^7F_2$	16377	16383	16366
	16276	16292	16313
	16228	16244	16228
	16145	16145	16170
	16119	16062	16026
$^5D_0 \rightarrow {}^7F_4$	14522	14526	14569
	14510	14505	14514
	14459	14426	14447
	14451	14413	14393
	14397	14343	14355
	14372	14306	14298
	14249	14261	14261
	14217	14205	14201
	14205	14180	14172

parameters Ω_2 and Ω_4 for the [Eu(TTA)$_3$ · (ANL)$_2$] and [Eu(TTA)$_3$ · PZA] complexes were determined from the expression

$$\Omega_\lambda = \frac{3\hbar c^3 A_{0-\lambda}}{4e^2\omega^3\chi\langle {}^5D_0 \| U^{(\lambda)} \| {}^7F_J\rangle^2} \tag{1}$$

where $\chi = n_0(n_0^2 + 2)^2/9$ is a Lorentz local field correction. The squared reduced matrix elements are $\langle {}^5D_0 \| U^{(2)} \| {}^7F_2\rangle^2 = 0.0032$ and $\langle {}^5D_0 \| U^{(4)} \| {}^7F_4\rangle^2 = 0.0023$, and an average index of refraction equal to 1.5 was used. The radiative rates of spontaneous emission A$_{0-\lambda}$, where $\lambda = 2$ and 4, were determined from the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. The $^5D_0 \rightarrow {}^7F_1$ transition was taken as the reference. The $A_{0-\lambda}$ values were obtained by using the relation [5]

$$A_{0-\lambda} = A_{0-1}\frac{S_{0-\lambda}}{S_{0-1}}\frac{\sigma_\lambda}{\sigma_1}, \tag{2}$$

where $S_{0-\lambda}$ is the area under the curve related to the $^5D_0 \rightarrow {}^7F_\lambda$ transition obtained from the spectral data, and σ_λ is the energy barycenter of the transition. The Ω_6 intensity parameter was not determined since the $^5D_0 \rightarrow {}^7F_6$ electronic transition presented a very weak intensity (Fig. 4).

The experimental intensity parameters Ω_2 and Ω_4 are presented in Table II. The higher value of the Ω_2 parameter for the [Eu(TTA)$_3$ · (ANL)$_2$] complex indicates a more polarizable chemical environment in this compound and suggests a metal–ligand bond with a higher covalent character.

Table II also shows the values of emission quantum efficiency (η), which were determined by the equation

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}}, \tag{3}$$

TABLE II Experimental intensity parameters and lifetimes of emitting $^5D_0$ level for the $[Eu(TTA)_3 \cdot (H_2O)_2]$, $[Eu(TTA)_3 \cdot (ANL)_2]$ and $[Eu(TTA)_3 \cdot PZA]$ complexes

Complex	$\Omega_2 \times 10^{20}$ (cm^2)	$\Omega_4 \times 10^{20}$ (cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$[Eu(TTA)_3 \cdot (H_2O)_2]$	33.0	4.6	1110	2736	3846	0.3	29
$[Eu(TTA)_3 \cdot (ANL)_2]$	34.9	10.5	1256	705	1961	0.5	64
$[Eu(TTA)_3 \cdot PZA]$	19.2	8.6	752	1667	2419	0.4	31

where A_{rad} is the radiative emission rate which is given by $A_{rad} = \sum_J A_{0J}$ and A_{nrad} is the non-radiative decay rate of the emitting $^5D_0$ level [5]. The total decay rate is experimentally determined from the reciprocal of its lifetime $\tau^{-1} = A_{tot} = A_{rad} + A_{nrad}$. The highest value of the η parameter was obtained for the $[Eu(TTA)_3 \cdot (ANL)_2]$ complex, owing to a significant decrease in the non-radiative rate ($A_{nrad} = 750\,s^{-1}$) as compared to the hydrated complex ($A_{nrad} = 2736\,s^{-1}$). On the other hand, the η value for the $[Eu(TTA)_3 \cdot (PZA)]$ complex is similar to the value for the hydrated compound, from similar contributions of both non-radiative and radiative rates. The higher value of emission quantum efficiency (η) for the complex with ANL is possibly due to lower efficiency of the luminescence quenching by the N–H oscillators of the ANL ligand. These results indicate that the complex with ANL ligand presents a value of η as high as those obtained for TTA-complexes with sulfoxide, phosphine oxide and heterocyclic organic ligands [5–7]. Based on these results the Eu^{3+}-β-diketonate complex with acetanilide ligand can be employed in light conversion molecular devices (LCMDs).

CONCLUSIONS

New complexes having the formulas $[RE(TTA)_3 \cdot (PZA)]$ and $[RE(TTA)_3 \cdot (ANL)_2]$ (where $RE^{3+} = Eu$ and Gd) were synthesized and characterized by elemental analysis, thermogravimetric analysis (TG) and IR spectroscopy. Photophysical properties of these compounds have also been studied. The absence of the broad phosphorescence band from the TTA ligand shows that energy transfer processes from the ligand-to-europium ion are quite efficient. The higher value of the Ω_2 intensity parameter for the $[Eu(TTA)_3 \cdot (ANL)_2]$ complex reflects a more polarizable chemical environment for the Eu^{3+} ion and suggests a metal–ligand bond with higher covalent character. The highest value of η was obtained for the $[Eu(TTA)_3 \cdot (ANL)_2]$ complex, owing to a significant decrease in the non-radiative decay rate from the $^5D_0$ level compared to the hydrated complex.

Acknowledgments

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