ORIGINAL PAPER

Synthesis and Study of the Photophysical Properties of a New Eu^{3+} Complex with 3-Hydroxypicolinamide

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Abstract This work reports on the synthesis and characterization of a new complex of Eu^{3+} with the 3-hydroxypicolinamide ligand (Hhpa). Here we present an approach for obtaining bis[2-carbamoyl(κO)pyridin-3-olato (κO')] lanthanide complexes, which were characterized through elemental analysis, thermal analysis, infrared and photoluminescence spectroscopies (emission, excitation, luminescence lifetimes, quantum efficiencies, Judd-Ofelt parameters and quantum yields). Although hpa can act as a bidentate ligand in different conformations, the results attest for the occurrence of a unique coordination site of low symmetry for the Eu^{3+} ions, in which two anionic hpa ligands coordinate the cations through an O/O chelating system. The phosphorescence of the synthesized gadolinium complex provides the energy of the triplet state, which is determined to be at 20,830 cm^{-1} over the ground state. This makes the Hhpa ligand very adequate for sensitizing the Eu^{3+} luminescence, which leads to a very efficient antenna effect and opens a wide range of applications for the complex in light emitting organic-inorganic devices.

Keywords Europium · 3-hydroxypicolinamide · Luminescence · Lanthanide · Coordination compounds

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Introduction

Luminescent rare earth complexes have been subject of several studies due to their important properties and applications. Since these compounds can be applied as phosphors and as starting materials with laser properties, their luminescence behavior has become an important area of research [1, 2]. The possibility of design novel photoluminescent materials has impelled numerous investigations dealing with new lanthanide complexes. The optical and photoluminescent properties of lanthanide(III) complexes with different kind of aromatic ambidentate ligands were already reported by several authors [3–5]. Moreover, a series of europium compounds having different coordination numbers was also studied through its photoluminescent and optical properties, which were correlated to their structures [1, 6–11]. Luminescent complexes bearing Eu^{3+} ions are very special for the coordination chemistry of the rare earth metals, once these cation present unique spectroscopic properties within the trivalent lanthanides. The understanding of this special luminescent behavior can provide much valuable information about the structural (site symmetry, coordination geometry) and electronic (nephelauxetic and crystal field parameters, energy transfer mechanisms) properties of the complexes [1, 2, 6, 7].

Lanthanide ions have *f-f* intraconfigurational transitions which are Laporte forbidden and, consequently, present low absorption intensities. The interest in rare earth compounds having aromatic ambidental ligands has increased since it was found that they can act as light collectors (antenna effect), thus by-passing the weak absorption of the lanthanides and resulting in highly efficient phosphors. So, in this process, the emission intensity of the metal may be considerably enhanced by populating the lanthanide emitting levels through excitation on proper aromatic chromophores able to performing energy transfer [7, 12–14].
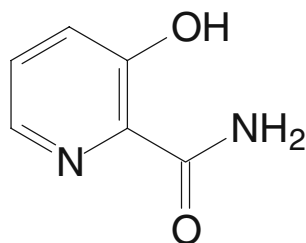
The 3-hydroxypicolinamide compound (Hhpa), which molecular structure is shown in Fig. 1, is an aromatic ligand whose molecular structure is a model compound of the virginiamycin S (VS), an hexapeptide which is considered as an antibiotic for blocking the protein synthesis at the bacterial ribosome [15]. The 3-hydroxypicolinyl residue is a light absorbing group, which is also responsible for complexing properties and proton-transfer action of VS. With regard to its chelation properties, it is believed that the complexation of the hpa species (deprotonated ligand) with alkaline earth ions occurs through the phenolate oxygen with the participation of the amide carboxyl group [15]. The study on the photophysical properties of a Zn^{2+} complex with this ligand was also reported [16], but, at the best of our knowledge, there are no data about the photophysical properties of complexes having this ligand bonded to the rare earth ions. Thus, in this work we report, for the first time, on the synthesis and characterization of an europium (III) complex with the hpa ligand. The evaluation of the photophysical properties of the synthesized complex allows a better understanding of the electronic and structural properties of the Hhpa as a ligand for lanthanide(III) ions, which is very important for the development of new organic-inorganic luminescent materials for many applications.

Experimental Procedure

Synthesis of the Eu^{3+} Complex

An $EuCl_3$ aqueous solution in a concentration of 0.10 mol L^{-1} was prepared through the dissolution of the previously calcinated europium oxide (Eu_2O_3, Aldrich, 99.99%) at 900 °C for 2 h in concentrated hydrochloric acid. The final pH of this solution was evaluated as 5.0–6.0. For the complex synthesis, an appropriate amount of the previously prepared Eu^{3+} aqueous solution has its solvent exchanged for ethanol (through continuous additions of ethanol, EtOH, under mild heating), having its volume reduced to few milliliters (0.5–1.0 mol L^{-1}). In the mean time, an ethanolic solution of potassium 2-carbamoylpyridin-3-olate (Khpa) (0.1 mol L^{-1}) was prepared through the dissolution of an equimolar amount of 3-hydroxypicolinamide (Hhpa, Aldrich, 98%) and potassium hydroxide in ethanol under mild heating, in order to obtain an Eu^{3+}/hpa molar ratio of 1/3. The ethanolic europium chloride solution was then poured over the yellowish limpid Khpa solution, which readily yields a pale yellow precipitate. The system was kept under magnetic stirring at room temperature for 2 h, and after that it was reserved in a closed flask at ~0 °C overnight. The precipitate was filtered and thoroughly washed with lots of portions of ethanol, warm water, and again with ethanol. The solid was finally dried under vacuum over silica and was maintained in this closed system. For the determination of the energy of the first triplet excited state of the ligand, the gadolinium complex with hpa was also prepared. For this intention, the same procedure was followed, except for the replacement of the $EuCl_3$ solution by a similar $GdCl_3$ solution (0.1 mol L^{-1}, pH 5-6), prepared through the dissolution of the correspondent previously calcinated oxide (Gd_2O_3, Strem Chemicals, 99.99%).

Complex Characterization

The composition of the obtained Eu^{3+}/hpa complex was determined through elemental analysis (C, H, N) in a Carlo Erba Instrument EA 1110. The Eu^{3+} percentage was determined through chelatometry [17]. For this, different amounts of the complex were dissolved in hydrochloric acid solutions and after titrated with a standard edta solution using xylenol orange as indicator (the pH of the titrated solutions was previously adjusted to 5.8 with the addition of an ammonium hydroxide solution). The Eu^{3+} percentage was confirmed through thermal analysis (thermogravimetry –TGA, derivative thermogravimetry—DTG, and differential thermal analysis, DTA), which was carried out in a Thermal Analyst Instrument SDT 2960 Simultaneous DTA/TGA, operating under a synthetic air atmosphere (with a 100 mL min^{-1} flux), with a heating rate of 10 °C min^{-1} up to 1000 °C. The Fourier Transform Infrared Spectra (FT-IR) of the ligand and the obtained Eu^{3+}/hpa complex were recorded at room temperature in the 400–4000 cm^{-1} range in a Bruker Equinox 55 equipment, using KBr pellets (~1% wt.). The ligand UV-Vis absorption spectrum (in EtOH solution) was obtained in an HP Diode Array 8453A spectrophotometer. The complex UV-Vis

Fig. 1 Molecular structure of the 3-hydroxypicolinamide (Hhpa) ligand

emission and excitation spectra were obtained in a Horiba-Jobin Yvon SPEX Triax 550 FluoroLog 3 spectrofluorometer, using a 450 W xenon arc lamp as excitation source and a Hamamatsu R928P photomultiplier for the detection. The spectra were corrected for the lamp intensity and for the photomultiplier sensitivity in the monitored wavelength range using the apparatus software. Luminescence lifetime measurements were performed by coupling the phosphorometer apparatus (SPEX 1934 D) to the spectrofluorometer, using a 150 W pulsed xenon lamp as excitation source. The measurements were carried out at room temperature (300 K) and 77 K (liquid N_2, using a quartz Dewar flask).

Results and Discussion

The elemental analysis data of the obtained complex provided the following percentages (exp./calc.): C–32.59/33.12%, H–3.09/3.18%, N–11.85/11.04%. These results support the occurrence of two anionic hpa groups in the complex, besides an ethanol molecule and a chloride anion, thus providing a Eu^{3+}:hpa:Cl:EtOH molar proportion of 1:2:1:1. The edta complexometric titration results attest for a $28\pm2\%$ Eu^{3+} percentage (calc.: 29.93%) in the complex, which is, within the experimental error, in agreement with the proposed formula. It was not possible to form single crystals of this new complex, since it was insoluble in a large amount of solvents. For the same reason, it was not to perform conductivity experiments in order to elucidate the role of the chloride anions (as ligands or counter ions). So, the employed characterizations were not capable to define if the true form of the complex is [EuCl(hpa)$_2$(EtOH)] (chloridoethanolbis[2-carbamoyl(κO)pyridin-3-olato(κO')] europium(III)) or [Eu(hpa)$_2$(EtOH)]Cl (ethanolbis[2-carbamoyl(κO)pyridin-3-olato(κO')]europium(III) chloride).

The thermal analysis data (TGA, DTG, DTA) of the synthesized complex depict a decomposition profile that is coherent with the expected composition (Fig. 2). The first decomposition step occurs at ~78 °C (DTG peak), corresponding to a weight loss of 6.57%. This step, which is of endothermic nature (indicated by the negative peak in the DTA curve), can be ascribed to the loss of the coordinated EtOH molecules. The following stage of thermal decomposition occurs as a set of many individual steps from 300 to 550 °C. Only the first of these steps (centered at ~330 °C) presents an endothermic character, which can be associated to a melting/partial decomposition of the complex. The other steps are of exothermic nature and correspond to the total oxidation of the organic fractions of the complex, thus yielding an inorganic residue of 33.68% of Eu_2O_3. Based on these results, the experimental europium percentage in the complex was determined as 29.09%, in agreement with the expected for the
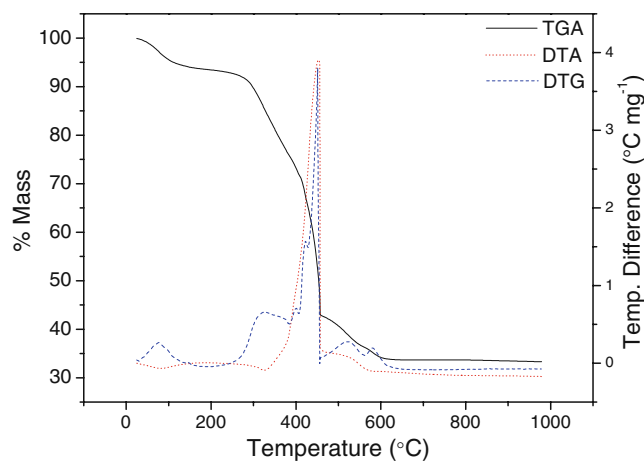

Fig. 2 Thermal analysis curves (TGA, DTG, and DTA) of the synthesized Eu^{3+}/hpa complex

proposed complex formula as well as with the percentage calculated from titration measurements. As a consequence of the presence of chloride anions in the complex, little amounts of the solid may be not fully decomposed at 900 °C due to the formation of europium(III) oxychloride (EuOCl), which has a lower Eu^{3+} percentage than Eu_2O_3, which contributes to a negative deviation from the expected value.

Figure 3 displays FT-IR spectra of both Hhpa ligand and prepared Eu^{3+} complex. In the ligand spectrum (Fig. 3a), the characteristic bands of the present groups are observed: hydrogen-bonded OH and NH_2 groups (3500 to 3000 cm^{-1}), aromatic overtone combinations of the pyridine system (1800–2000 cm^{-1}), C=O stretching of the amide carbonyl group (1693 cm^{-1}), deformation movements in the NH_2 groups and C=C and C=N stretchings in the pyridine ring (1616 and 1597 cm^{-1}), C–N stretching in primary amide groups (1454 cm^{-1}), and NH_2 and N–C=O deformation (777 and 650 cm^{-1}) [18]. In the Eu^{3+} complex spectrum (Fig. 3b), the "fingerprint region" of the spectrum at around 1350 to1100 cm^{-1} is deeply changed in comparison to the free ligand, as a consequence of the coordination of the enolate groups, whose characteristic C–O stretching bands appear in this range. The coordination of the carbonyl groups through the oxygen atoms is supported by the broadening of the C=O stretching band and also by its shifting for lower energies (1634 cm^{-1}) when compared to the free ligand, as a consequence of the decrease of the C=O bond force constant due to the coordination with the Eu^{3+} ion. Moreover, the N–C=O deformation band is also shifted for lower energies (627 cm^{-1}). The alterations on the other bands can be treated as a consequence of the chelation through the oxygen carbonyl, which also affects the NH_2 amide group movements (e.g. shift of the C–N stretching for lower energies and lowering and shift of the NH_2 wag band, which occurs as a shoulder at 750 cm^{-1}).

Fig. 3 FT-IR spectra of the 3-hydroxypicolinamide ligand (Hhpa) **a**, and of its Eu³⁺ complex (Eu(hpa)₂Cl(EtOH)) **b**
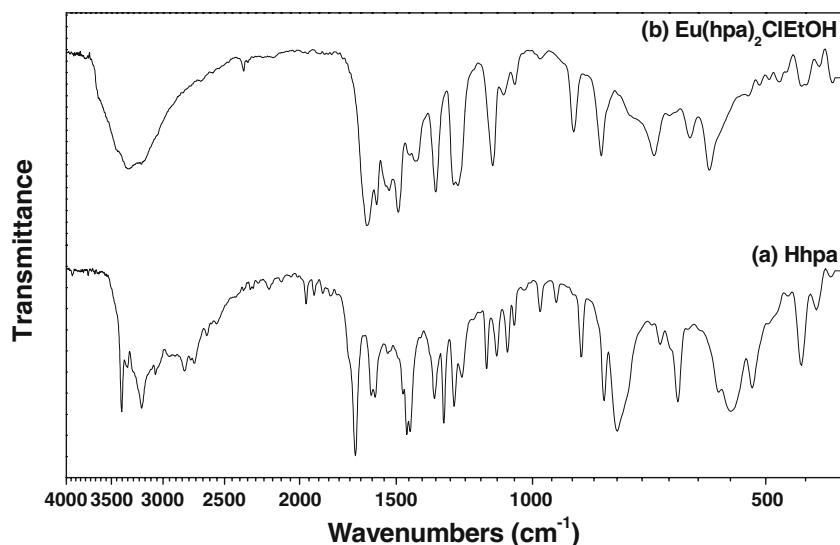
Thus, the results confirm the ambidentate nature of the hpa ligand, which has the ability to form two kinds of chelates, with an O/N coordinated or an O/O coordinated system. In the Eu^{3+} complex case, as both carbonyl and NH_2 groups have characteristics of hard ligands, both coordination systems are acceptable with regard to the established ligand-metal bonds. Nevertheless, the O/O coordination may be preferred due to steric and electronic stability factors. When the coordination occurs through the carbonyl amide groups, there is the establishment of hydrogen bonds between the hydrogen atoms of the NH_2 group and the nitrogen atom of the pyridine ring, forming a pseudo-five member ring system as illustrated in Fig. 4. Thus, when the oxygen atoms are in a "cis" conformation in order to form the O/O chelate, an additional stabilization is acquired due to the establishment of hydrogen bonds, which does not occur in the same magnitude as in the O/N chelate. The other factor that favors the O/O coordination is the electron resonance occurring between the enolate and
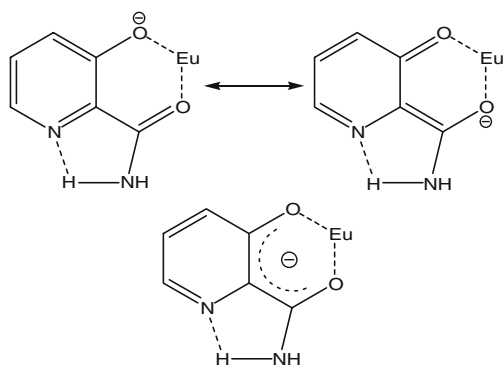
the amide carbonyl groups, in a very similar system as those observed for the β-diketonates (Fig. 4) [19, 20]. The coordination through the oxygen atoms of the hpa ligand leads to the formation of a six-member ring, which presents a strong resonance stabilization due to the π-electron delocalization.

Figure 5 depicts the excitation profile of the synthesized Eu^{3+} complex at room temperature and 77 K, besides a comparison with the absorption spectra of the Hhpa and hpa in ethanolic solutions, where hpa was obtained dissolving the ligand in a 0.01 mol L^{-1} ethanolic KOH solution. The absorption spectra consist of two broad bands being the lower energy one ascribed to the $S_1 \leftarrow S_0$ $(\pi\pi^*)$ absorption, while the other set of bands is related to the
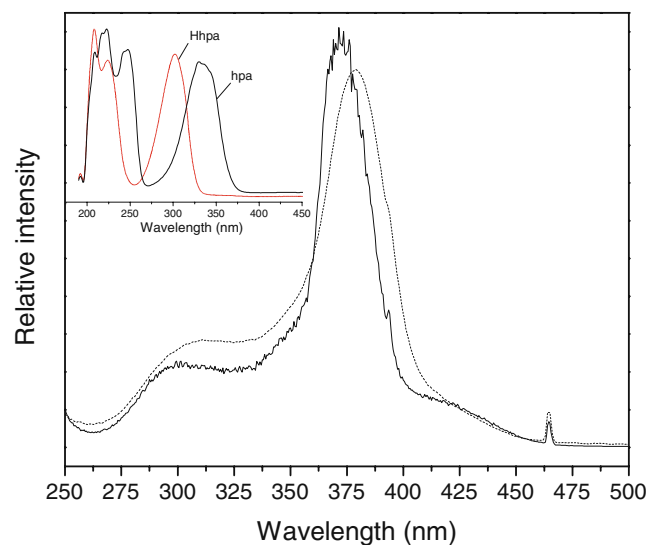

Fig. 4 Steric and electronic factors that favor the occurrence of the O/O coordination for the hpa ligand in the obtained complex: the establishment of intramolecular hydrogen bond and the π-electron resonance between the oxygen atoms

Fig. 5 Excitation spectra of the Eu^{3+}/hpa complex (monitoring the $^5D_0 \rightarrow ^7F_2$ transition, $\lambda_{em}=612$ nm) at 77 K (solid line) and at room temperature (dashed line). (Inset: absorption spectra of the Hhpa and hpa species in ethanolic solution)

$S_1 \leftarrow S_0$ ($n\pi^*$) absorption. The Eu^{3+} excitation in the synthesized complex is practically independent of the temperature, once both excitation spectra present essentially the same profile. The only intraconfigurational Eu^{3+} f-f absorptions that can be noticed are the $^5L_6 \leftarrow ^7F_0$ and the $^5D_2 \leftarrow ^7F_0$ transitions at 394 and 464 nm, respectively. The other excitation lines expected within the Eu^{3+} f^6 configuration are overcome by the strong ligand absorptions, which are followed by the energy transfer for the metal center (antenna effect). In comparison with the free ligand or with its anionic form in ethanolic solution, the excitation bands ascribed to the ligand absorptions are shifted to lower energies as a consequence of the coordination of the hpa groups with the Eu^{3+} ions. This fact can be due to the effect of the high π-electron delocalization in the complex, which increases the ligand absorptivity, stabilizes the bonds in the complex, and decreases the energies of the ligand excited states.

In this case, although the population of the Eu^{3+} emitting states can occur through direct transfer from the ligand excited singlet state to the higher ^5D_J levels, the mechanism involving energy transfer from the ligand triplet, which is populated through the intersystem crossing to the metal may be predominant. The determination of the energy of the ligand first triplet state can be accomplished by measuring the ligand phosphorescence ($T_1 \rightarrow S_0$ transitions) in its Gd^{3+} complex [7]. Although various differences between the gadolinium complexes and the other lanthanide complexes can be pointed (e.g. thermodynamic stability, bond length and magnetic effects), the Gd^{3+} complexes are proper for this determination due to the high energy gap between the ground and excited levels within the $4f^7$ configuration ($\sim 32,000$ cm^{-1}, between the $^8S_{7/2}$ and ^6P_J levels), which avoids energy transfer from the ligand triplet to the metal excited levels. Moreover, in the presence of Gd^{3+} (and other lanthanide ions), the rate of population of the triplet state is increased, once the paramagnetic and "heavy ion" effects favor the mixing between singlet and triplet states increasing the rate of the intersystem crossing [20].

Figure 6 displays the phosphorescence spectrum of the synthesized gadolinium complex under ligand excitation ($\lambda_{exc}=375$ nm). This measurement was performed at 77 K in order to avoid the non-radiative deactivation of the triplet state.

The spectrum shows a weak band centered at ~ 415 nm, which can be ascribed to the normally Stokes shifted singlet emission, in agreement with the literature [21]. The intense triplet emission band starts at ~ 480 nm and is centered at ~ 530 nm, indicating that the triplet state lies at $\sim 20,830$ cm^{-1} of the ground state. This triplet energy is comparable to the well-known β-diketonates ones, which are very proper for sensitizing the Eu^{3+} luminescence,
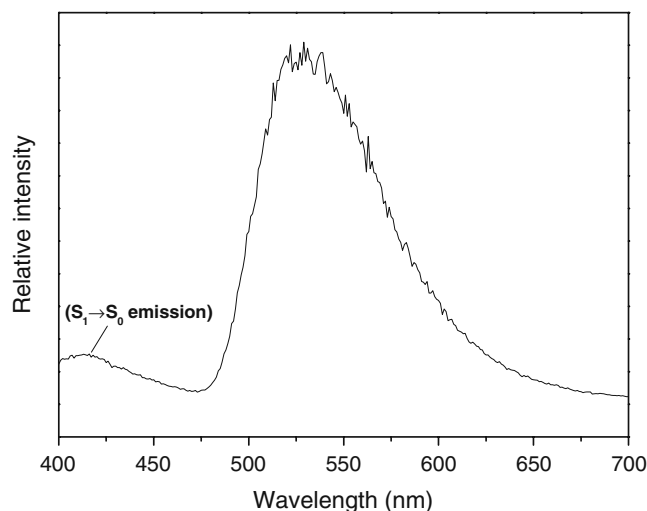

Fig. 6 Phosphorescence spectrum of the Gd^{3+}/hpa complex at 77 K under ligand excitation (λexc=380 nm) for the determination of the triplet state energy

such as thenoyltrifluoroacetonate (ttfa, $T_1 \sim 20,300$ cm^{-1}) and 1,3-diphenylpropane-1,3-dionate, also known as dibenzoylmethane, dbm, $T_1 \sim 20,660$ cm^{-1} [20]. So, the high emission intensity observed for the Eu^{3+}/hpa complex can be explained by an efficient antenna effect of the hpa ligand, which is schematized in the diagram of Fig. 7. Besides, for having a triplet state at this energy, we can suggest that the hpa ligand is able to efficiently sensitize the luminescence of other lanthanides, such as Sm^{3+} ($^4G_{5/2}$), Tb^{3+} ($^5D_4$), Ho^{3+} ($^5S_2$) and Er^{3+} ($^4S_{3/2}$).

The emission spectrum at 77 K of the Eu^{3+}/hpa complex (Fig. 8) exhibits the characteristic $^5D_0 \rightarrow ^7F_J$ ($J=0$–4) Eu^{3+} emissions. The spectrum recorded at room temperature (not shown) presents essentially the same emission profile, although a higher resolution of the emission bands is observed at 77 K. This occurs because at 77 K the higher vibrational levels of the ligand are depopulated, thus
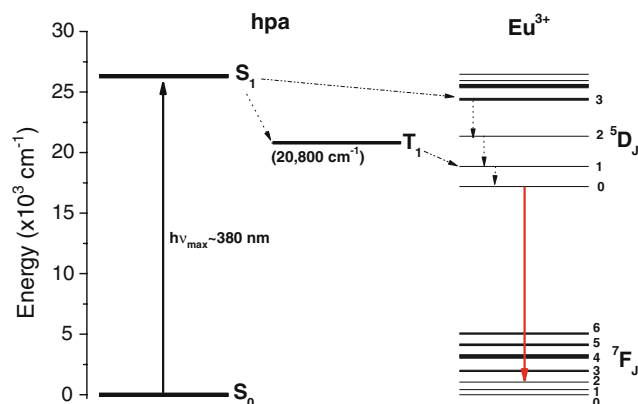

Fig. 7 Simplified energy level diagram representing the involved energy transfer processes and transitions in the luminescence of the Eu^{3+}/hpa complex
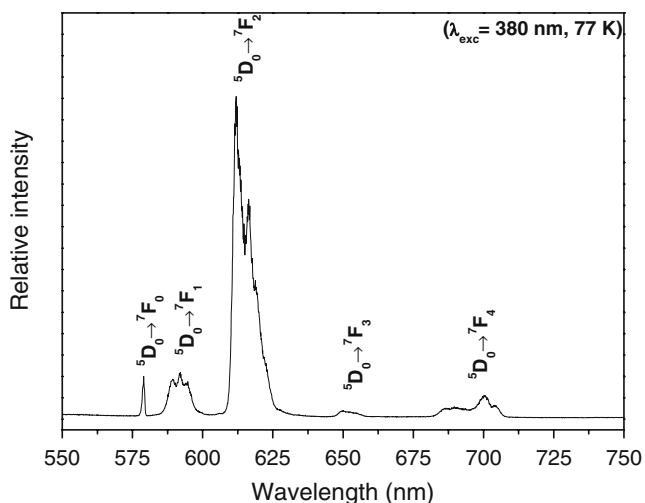
Fig. 8 Emission spectrum of the Eu^{3+}/hpa complex under $\lambda_{exc}=$ 380 nm excitation at liquid nitrogen temperature (77 K)

Fig. 9 Luminescence decay curves ($^5D_0$ level) of the Eu^{3+}/hpa complex at 300 and 77 K (monitoring the $^5D_0 \rightarrow ^7F_2$ transition, $\lambda_{em}=$ 612 nm)

resulting in a less intense vibronic coupling between the ligand vibrational modes and the metal electronic states. The hypersensitive $^5D_0 \rightarrow ^7F_2$ transition is the predominant, indicating that the Eu^{3+} ions occupy sites of low symmetry without inversion center [1, 2]. Moreover, the $^5D_0 \rightarrow ^7F_0$ transition occurs as a single band, and the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions present, respectively, three and five observable components. These facts can be related to the occupation of a single site of C_1, C_s, C_2, or C_{2v} symmetries [22]. Emissions of the higher ^5D_J levels are only weakly observed, and even at 77 K no ligand triplet phosphorescence is noticed, thus indicating an efficient depopulation of the T_1 state through the antenna effect.

The $^5D_0$ luminescence decay curves were acquired at room temperature and 77 K by measuring the decrease of the emission intensity against the time. It is known that the deactivation of an excited state may correspond to a first order kinetic process. In the absence of energy transfer processes, the registration of the radiative deactivation of each emitting species may originate a monoexponential curve [2]. In the Eu^{3+}/hpa case, as shown in Fig. 9, both at 77 and 300 K, the plot of the logarithm of the intensity against the time results in a linear relation that attests for the occurrence of a single coordination site for the Eu^{3+} ions. Because in the measurement obtained at 300 K after 3 ms the signal/noise ratio became very low, resulting in an "artificial" deviation of the linear behavior, such data were discharged. The lifetime values (Table 1) were obtained by fitting the experimental data for monoexponential decay curves. The relatively short lifetime determined for the Eu^{3+}/hpa complex at room temperature ($\tau=$ 0.42 ms) is a consequence of the large number of high energy vibrational oscillators around the Eu^{3+} ions, mainly the amide NH_2 groups and ethanol OH groups (both with ν_{max} ~3500 cm^{-1}). These groups, which strongly contrib-
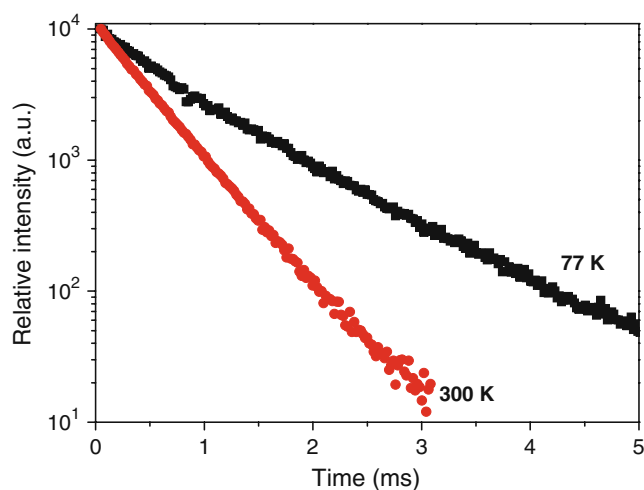
ute for the multiphonon deactivation for the $^5D_0$ level, have their higher vibrational levels depopulated at 77 K, lowering the rate of vibronic coupling, and resulting in an increase of the Eu^{3+} luminescence lifetime ($\tau=0.76$ ms).

The Eu^{3+} luminescent behavior of the synthesized complex was also evaluated through the calculation of the radiative (A_{RAD}) and non-radiative (A_{NRAD}) decay rates for the determination of the emission quantum efficiency (η), besides the calculation of the Judd-Ofelt intensity parameters (Ω_λ) for the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions from the experimental data [7, 23]. The Judd-Ofelt intensity parameters contain the contributions of the forced electric dipole and the dynamic coupling mechanisms of the *f-f* electronic transitions, being dependent on the nature of the lanthanide cation and the occupied chemical environment. Its value can be experimentally determined from the Einstein spontaneous emission coefficient of the considered transition (A_{0-J}) through:

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

where e is the elemental charge, ω is the angular frequency of the $^5D_0 \rightarrow ^7F_J$ transition, $\hbar$ is the Planck's constant over 2π, χ is a Lorentz local field correction of the material refractive index ($\chi=n(n^2+2)^2/9$, $n \approx 1.5$), and $\left\langle ^5D_0 \left\| U^{(2)} \right\| ^7F_2 \right\rangle^2$ and $\left\langle ^5D_0 \left\| U^{(4)} \right\| ^7F_4 \right\rangle^2$ are the square reduced matrix elements, which have tabulated values of 0.0032 and 0.0023 for the $^5D_0 \rightarrow ^7F_2$ and the $^5D_0 \rightarrow ^7F_4$ transitions, respectively. The A_{0-J} values can be determined for each $^5D_0 \rightarrow ^7F_J$ transition by taking the $^5D_0 \rightarrow ^7F_1$ transition, which is magnetic dipole allowed and thus presents a radiative decay rate that is almost independent

Table 1 Luminescence lifetimes, radiative and non-radiative decay rates, emission quantum efficiencies of the $^5D_0$ level, Judd-Ofelt intensity parameters, $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensity ratios, and exper- imental quantum yields calculated for the synthesized Eu^{3+}/hpa complex at 300 and 77 K

	τ (ms)	A_{RAD} (s^{-1})	A_{NRAD} (s^{-1})	η (%)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	I_{02}/I_{01}	q_{exp} (%)
300 K	0.42	559	1821	24	15	3.1	8.5	30
77 K	0.76	542	773	41	14	3.8	8.1	*

* Not performed due to experimental impossibilities

** The calculated parameters are accurate within 10%; luminescence lifetimes are accurate within 5%

on the ligand field as reference, being $A_{0-1} \approx 50$ s^{-1}. So, the A_{0-J} values are calculated through:

$$A_{0-J} = A_{0-1} \frac{S_{0-J}\sigma_{0-1}}{S_{0-1}\sigma_{0-J}} \qquad (2)$$

where S_{0-J} is the area corresponding to the $^5D_0 \rightarrow {}^7F_J$ transition and σ_{0-J} is the energy barycentre of the ^7F_J level, both determined from the emission spectrum. The A_{RAD} value is obtained by summing the A_{0-J} values of all $^5D_0 \rightarrow {}^7F_J$ transitions. Finally, the A_{NRAD} value is deter- mined by using the A_{RAD} and τ values, once:

$$A_{RAD} + A_{NRAD} = \tau^{-1} \qquad (3)$$

and the emission quantum efficiency is determined from:

$$\eta = \frac{A_{RAD}}{A_{RAD} + A_{NRAD}} \qquad (4)$$

As it is seen in Table 1, the A_{RAD} values are practically independent of the temperature, while a very large lowering in the rate of non-radiative deactivation (A_{NRAD}) is observed. This is a consequence, as previously discussed, of the lowering of the ligand vibrational influence. The large diminution in the A_{NRAD} results in a high increase of the excited state quantum efficiency, which becomes almost two times greater. Nevertheless, although the complex presents a very high emission intensity, their quantum efficiencies are low when compared to other well known complexes such as [Eu(ttfa)$_3$(dbso)$_2$] ($\eta \approx 70$%), [Eu(ttfa)$_3$(tppo)$_2$] ($\eta \approx 72$%), and [Eu(dbm)$_3$(dbso)] ($\eta \approx 67$%) [20] (where dbso and tppo denote, respectively, the dibenzyl sulphoxide and triphenyl- phosphine oxide ligands). In these cases, however, there are no groups in the ligand molecules which strongly contribute for the excited state quenching, such as OH and NH$_2$ in our case.

As shown in Table 1, the Ω_λ intensity parameters also are, as expected, practically independent of the temperature, since they are related to the radiative rate of excited state deactivation of the considered transitions. The Ω_2 value, which depends on the degree of covalence experienced by the metal (higher Ω_2 values correspond to higher cova- lences), although being lower than the usually found for

europium β-diketonates [7, 20], attests for a highly covalent character for the bonds established in the complex. In the $Eu^{3+/}$hpa complex, the predominance of the Ω_2 parameter over the Ω_4 one ($\Omega_2 > \Omega_4$) is an indication that the distribution of the ligands around the metal center leads to a predominance of the lower rank crystal field components over the higher rank ones, which can be correlated to a site with low centrosymmetric character for Eu^{3+} [7, 23]. Moreover, the low value of the Ω_4 parameter indicates a low hypersensitive behavior for the $^5D_0 \rightarrow {}^7F_4$ transition. Another observation is that the ratio between the integrated areas of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions indicate that the Eu^{3+} ions occupy non-centrosymmetric sites in the complex, once, in these situations, the $^5D_0 \rightarrow {}^7F_2$ transition is intensified through vibronic coupling mechanisms and relaxation of the Laporte's rule. The obtained values are relatively low when compared with other Eu^{3+} complexes [19]. This corresponds to the occupation of more symmetric chemical environments and can be explained by taking in account the low coordination number (CN=6) and the occurrence of two hpa ligands, which confer to the complex a higher structural rigidity and a more symmetric coordi- nation geometry.

Finally, the quantum yield (q_{exp}) was also experimen- tally determined [7, 19] for the Eu^{3+}/hpa complex as shown in Table 1. The quantum yield is defined as the ratio between the number of photons emitted and the number of photons absorbed by the sample. The attainment of its value can be performed through absolute measurements or through comparisons with standard phosphors, by applying Eq. 5:

$$q_{exp} = \left(\frac{1 - r_{ST}}{1 - r_x} \right) \left(\frac{\Delta\Phi_x}{\Delta\Phi_{ST}} \right) q_{ST} \qquad (5)$$

where r_{st} and r_x are the amount of reflected radiation by the standard and the sample, respectively. These values are obtained by comparing the diffuse reflectance of the sample and the value of the standard phosphor with a reflectance standard. In this case, magnesium oxide ($r = 90$% in the UV- Vis range) was utilized. $\Delta\Phi_x$ and $\Delta\Phi_{st}$ are the integrated photon flux calculated from the emission spectra obtained

at the same experimental conditions as the sample and the standard, respectively. q_{st} is the quantum yield of the standard phosphor; it was utilized here the standard phosphor easily obtainable sodium salicylate (q_{st}=60% at room temperature). The quantum yield value found for the Eu^{3+}/hpa complex was evaluated as 30%, which is in agreement with the typical values found for complexes that have vibronic-deactivating groups in their structures [7, 20]. For example, taking the $[Eu(ttfa)_3(H_2O)_2]$ (q_{exp}=23%) and $[Eu(dbm)_3(H_2O)]$ (q_{exp}=1%) [20] for comparison, the quantum yield found was relatively high. This attests that, even in the presence of only two light absorbing species, there is an efficient antenna effect, which makes the hpa a very proper ligand for Eu^{3+} ions to improve their luminescent properties.

Conclusion

The 3-hydroxypicolinamide was proved to be a good aromatic ambidentate ligand for lanthanide ions. The employed synthetic methodology yielded a bis[2-carba-moyl(κO)pyridin-3-olato(κO')] complex, in which the hpa ligand forms an O/O chelate. This result is supported by the infrared and luminescence spectroscopy results, which respectively attest the chelation through the carbonyl and enolate oxygen atoms and the occurrence of a unique coordination site for the Eu^{3+} ions. The hpa triplet level was determined to be at ~20,830 cm^{-1}, which makes this pyridinic amide a very proper ligand for sensitizing the Eu^{3+} luminescence, besides being capable to act as a light collector for other lanthanide ions, such as Sm^{3+}, Tb^{3+}, Ho^{3+} and Er^{3+}. A highly intense luminescence is observed in the Eu^{3+}/hpa complex, with a characteristic emission profile of europium(III) occupying low symmetry sites without inversion center and with a highly covalent character. The emissions of the Eu^{3+} $^5D_0$ level are, however, partially quenched due to the presence of the OH and NH_2 groups, which contribute for the multiphonon deactivation of the metal excited states, reducing the emission quantum efficiencies (η=24% at 300 K, and η=41% at 77 K). Nevertheless, the experimental quantum yield is relatively high (q_{exp}=30%), as a result of a high ligand absorptivity and an efficient antenna effect. The elucidation of the luminescence properties of the synthesized complex and the hpa ligand ability of coordinating lanthanide ions allows carrying out studies comprising the comprehension of the binding sites in the potential antibiotic virginiamycin S by applying Eu^{3+} ions as a probe. Moreover, the hpa ligand is also potentially applicable in the development of functional luminescent devices, such as organic-inorganic thin films, and compounds for luminescent labeling.

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