



SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF NEW COMPLEX COMPOUNDS OF EUROPIUM(III) AND TERBIUM(III) WITH 2-HYDROXY-1-NAPHTHALDEHYDE ACETYLHYDRAZONE AND HETEROCYCLIC BASES

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Six new europium(III) and terbium(III) complex compounds with 2-hydroxy-1-naphthaldehyde acetylhydrazone (HL), *o*-phenanthroline and α, α' -bipyridine as ligands have been prepared. The complexes have been characterized by elemental and thermal analysis, infrared, UV-VIS and luminescence spectroscopy. The complex compounds have the following formulas: $[\text{Tb}(\text{HL})_2(\text{H}_2\text{O})_2]\text{NO}_3$, $[\text{Eu}(\text{HL})_2(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$, $[\text{Tb}(\text{HL})(o\text{-phen})(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3$, $[\text{Eu}(\text{HL})(o\text{-phen})(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3$, $[\text{Tb}(\text{HL})(\alpha, \alpha'\text{-bipy})(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$ and $[\text{Eu}(\text{HL})(\alpha, \alpha'\text{-bipy})\text{Cl}_2] \cdot \text{H}_2\text{O}$, the hydrazone ligand acting as monobasic tridentate donor. The emission spectra in solid state for all the complexes show the characteristic bands of Eu^{3+} and Tb^{3+} respectively, while in ethanolic solution the emission is principally located on the ligands.

INTRODUCTION

The chemistry of luminescent lanthanide coordination compounds is the subject of increasing interest in the last years, due to the wide variety of their chemical and biological applications.^{1,2} Europium(III) and terbium(III) ions have the most important place in the biological studies, due to the suitable energy gap between the emissive excited state and the ground state and a large Stokes shift of emission, so there is unlikely to be any overlap of the emission bands with the absorption bands.^{3,4}

The lanthanide ions have yet low molar absorption coefficients in the visible and ultraviolet region. In the coordination chemistry, this drawback may be overcome using chromophoric ligands, which are able to absorb strongly energy at a suitable wavelength. The absorbed energy is transferred from excited singlet state of the ligand to the emitted state of the metal, such a mechanism being known as antenna effect.⁵⁻⁷

Recent developments in the coordination chemistry have allowed the design of ligands capable to generate kinetically inert complexes in solution and thus protect the metal ion from the chemical environment, to absorb efficiently energy and transfer it to the emitting center (metal).^{1,5}

Among the numerous types of organic ligands, the hydrazones have been widely used not only for their ability to form complexes with various structures, but also for their antibacterial, antifungal or antitumor activities.⁸ Acyl- and aroyl hydrazones, having oxygen and nitrogen as donor atoms show a remarkable capability to coordinate the lanthanide ions.⁹⁻¹²

On the other hand, 2,2'-bipyridine and 1,10-phenanthroline have been extensively used as ligands, due to their high chemical stability, redox properties and their good coordination capability. They are at the same time σ -donors and π -acceptors ligands.^{13,14} The lone pair of each nitrogen atom can generate a σ bond with the metal ion, while the aromatic ring can participate to π - π

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interactions. These ligands coordinate easily to metal ions forming a stable ring with five atoms. They can also be considered as diimines, contributing to the electron delocalization in the chelate ring.

This paper describes the synthesis and analytical and spectral characterization of six new complex compounds of europium(III) and terbium(III) with 2-hydroxy-1-naphthaldehyde acetylhydrazone as ligand. Four of these complexes have mixed ligands in the coordination sphere: hydrazone and *o*-phenanthroline, or hydrazone and α,α' -bipyridine, respectively.

RESULTS AND DISCUSSION

The hydrazone ligand (H₂L) (Figure 1) has been obtained by the condensation reaction of acetohydrazone with 2-hydroxynaphthaldehyde, in the presence of acetic acid.

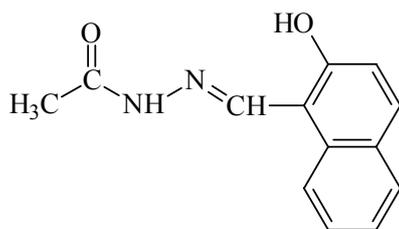


Fig. 1 – 2-hydroxy-1-naphthaldehyde acetylhydrazone.

Using this ligand and *o*-phenanthroline or α,α' -bipyridine six complex compounds of Tb(III) and Eu(III) have been obtained. Two of these complexes have been synthesized by the reaction of the hydrazone ligand with terbium nitrate and europium nitrate, respectively and correspond to the formulas [Tb(HL)₂(H₂O)₂]NO₃ (**1**) and [Eu(HL)₂(H₂O)₂]NO₃·H₂O (**2**). The other four complex compounds, with mixed ligands hydrazone-heterocyclic base, have been prepared by the reaction of a mixture of the hydrazone and *o*-phenanthroline or α,α' -bipyridine with the metal salt : terbium nitrate for the complexes [Tb(HL)(*o*-phen)(NO₃)(H₂O)]NO₃ (**3**) and [Tb(HL)(α,α' -bipy)(NO₃)(H₂O)]NO₃·H₂O (**5**), europium nitrate for the complex [Eu(HL)(*o*-phen)(NO₃)(H₂O)]NO₃ (**4**) and europium chlorure for the complex [Eu(HL)(α,α' -bipy)Cl₂]·H₂O (**6**).

The complex compounds have been characterized by elemental and thermogravimetric analyses, infrared, electronic and luminescence spectra.

Infrared spectra

The most important infrared bands for the hydrazone ligand and its complexes are reported in Table 1.

Table 1

Selected IR absorptions for the hydrazone ligand and its complexes (ν_{\max} , cm⁻¹)

H ₂ L	(1)	(2)	(3)	(4)	(5)	(6)	Assignments
-	3336 m	3317 m	3448 m	3449 m	3438 m	3330 m	ν (OH) (H ₂ O)
3046 m	-	-	-	-	-	-	ν (OH) (assoc)
3186 m	3197 m	3242 m	3222 m	3212 m	3227 m	3194 m	ν (NH _{sec})
1677 vs	1617 vs	1616 vs	1615 vs	1615 vs	1613 vs	1608 vs	ν (C=O) (amide I)
1644 vs	1564 s	1566 s	1583 m	1582 m	1581 m	1570 s	ν (C=N)
1622 s	-	-	-	-	-	-	δ (OH)
1579 m	1539 m	1537 m	1539 m	1539 m	1536 m	1540 m	δ (NH)+ ν (CN) (amide II)
1324 s	1326 m	1326 m	1330 m	1343 m	1362 m	1364 m	δ (NH)+ ν (CN) (amide III)
1241 m	1244 s	1241 m	1243 m	1238 m	1238 m	1237 m	ν (C _{aliph} -N)
1185 ms	1190 ms	1190 m	1191 m	1192 m	1189 m	1193 m	ν (C-O _{phenolic})
-	1385 vs	1388 vs	1384 vs	1388 s	1387 s	-	ν_3 [ν (NO ₃)]
-	833 w	836 w	828 w	831 w	830 w	-	δ (NO ₃)
-	-	-	1459 m	1459 m	1470 s	-	ν_1 [ν (NO)]
-	-	-	1295 s	1291 s	1290 s	-	ν_4 [ν (NO ₂)]
-	-	-	1029 m	1030 m	1030 w	-	ν_2 [ν (NO ₂)]
994 m	1008 m	1003 w	1005 w	1004 w	1018 m	999 m	ν (NN)
-	636 w	638 w	639 w	639 w	647 w	640 w	ν (Ln-O)
-	500 w	494 w	490 w	495 w	496 w	490 w	ν (Ln-N)

The infrared spectrum of 2-hydroxy-1-naphthaldehyde acetylhydrazone (H₂L) shows a very strong band at 1677 cm⁻¹, due to the stretching vibration of the carbonyl group, $\nu(\text{C}=\text{O})$ (amide I band) and another medium band, at 3186 cm⁻¹, assigned to the bonding vibration of NH secondary amine group, in accordance with the existence of the ligand, in solid state, in the cetonic form.¹⁵⁻¹⁷

In the IR spectra of all the complexes the band due to NH stretching vibration is also present, shifted comparatively with the position in the spectrum of the ligand, indicating the coordination of the hydrazone in the cetonic form.¹⁵

The very strong band occurring at 1677 cm⁻¹ for the hydrazone ligand shifts significantly to the lower wave numbers in the IR spectra of all the complexes, in accordance to the coordination of the ligand through the carbonylic oxygen atom.^{15,16} Further proof for the coordination of the hydrazone through the ketonic oxygen atom is the shift of the bands arising from the combined vibrations $\delta(\text{NH})+\nu(\text{CN})$ (amide II and amide III), observed in the spectrum of the ligand at 1579 cm⁻¹ and 1324 cm⁻¹, respectively: the amide II band is shifted to lower frequencies, while the amide III band is shifted to higher frequencies.^{15,18}

Another important band, very strong, observed in the IR spectrum of the hydrazone ligand at 1644 cm⁻¹, may be attributed to the stretching vibration of the azomethine group, $\nu(\text{C}=\text{N})$.^{17,19-21} In the spectra of all the complexes this band is shifted to lower wave numbers, indicating the involvement of the iminic nitrogen atom in coordination. This supposition is also supported by the positive shift of the vibration $\nu(\text{NN})$ in the IR spectra of the complexes.²²

The characteristic bands for the aromatic ring vibrations occur in the 1400-1600 cm⁻¹ range and are insignificantly shifted in the spectra of the complexes comparatively with that of the ligand.¹⁵

The IR spectra of the complexes (1) – (5) show two new bands, one very strong, at 1384-1388 cm⁻¹ and another of medium intensity, around 830-840 cm⁻¹, due to the vibrations of ionic nitrate.²³ Moreover, the apparition of other three bands, in the range 1459-1470 cm⁻¹ (ν_1), 1290-1295 cm⁻¹ (ν_4) and 1030 cm⁻¹ (ν_2), in the IR spectra of the complexes (3) – (5), indicates the presence of coordinated nitrate.²³ The separation of two highest frequency bands, $\nu_1 - \nu_4$ is approximatively 170-180 cm⁻¹, in accordance with the participation of the nitrate as bidentate ligand.²³

IR spectrum of the hydrazone ligand shows also a medium band at 3046 cm⁻¹, due to the stretching vibration of hydrogen bonding associated OH, $\nu(\text{OH})$ and a strong sharp band, at 1622 cm⁻¹, attributed to the in-plane bending vibration of OH group, $\delta(\text{OH})$.^{15,22} The loss of the proton as consequence of coordination to the metal ion is indicated by the absence of these bands in the IR spectra of all the complexes. Another large band, appearing in the IR spectra of all the complexes around 3300-3400 cm⁻¹ indicates the presence of crystalline or coordinated water.²²

The coordination of the ligand through the phenolic oxygen is also supported by the shift of the band due to the stretching vibration of C-O bond (1185 cm⁻¹ in the IR spectrum of the ligand) to higher wave numbers for all the complexes.^{15,22}

The infrared spectra of the complexes (3) – (6) show also characteristic bands assigned to the stretching vibrations of $>\text{C}=\text{N}-$ and $>\text{C}=\text{C}<$ of *o*-phenanthroline or 2,2'-bipyridine. These are the strong bands at 1495/ 1426 cm⁻¹ for the complexes [Tb(HL)(*o*-phen)(NO₃)(H₂O)]NO₃ (3) and [Eu(HL)(*o*-phen)(NO₃)(H₂O)]NO₃ (4), and 1508-1511/1434 cm⁻¹ for [Tb(HL)(α,α' -bipy)(NO₃)(H₂O)]NO₃·H₂O (5) and [Eu(HL)(α,α' -bipy)Cl₂]·H₂O (6), respectively. All these bands show important shifts from their position in the infrared spectra of *o*-phenanthroline and 2,2'-bipyridine, indicating the coordination of the nitrogen atoms to the metal ions.¹⁴

In the far-IR spectra, the complex compounds show weak absorption bands (Table 1), which may be assigned to $\nu(\text{Ln}-\text{O})$ and $\nu(\text{Ln}-\text{N})$.^{14,23}

Thermal analyses

In the TG curves of [Eu(HL)₂(H₂O)₂](NO₃)·H₂O (2), [Tb(HL)(α,α' -bipy)(NO₃)(H₂O)]NO₃·H₂O (5) and [Eu(HL)(α,α' -bipy)Cl₂]·H₂O (6) the first weight loss at 100-110 °C corresponds to the elimination of the crystalline water.²⁴ For all the complexes, excepting [Eu(HL)(α,α' -bipy)Cl₂]·H₂O (6), the endothermic peak at 240-250 °C is due to the loss of coordinated water.²⁴

All the compounds (except 6) show a large exothermic process, between 320 - 600 °C, corresponding to the decomposition of the anionic and coordinated nitrate and the organic ligand.²⁵ In all the cases, the final decomposition product is the oxide, M₂O₃ (M = Eu, Tb).²⁶

Based on the results presented above we can conclude that the hydrazone acts as monobasic

tridentate ligand, coordinating through azomethinic nitrogen, carbonylic and phenolic oxygen atoms; *o*-phenanthroline and α,α' -bipyridine are neutral bidentate NN donors. Based on these data, the complex compounds are proposed to have the conformations shown in Figure 2:

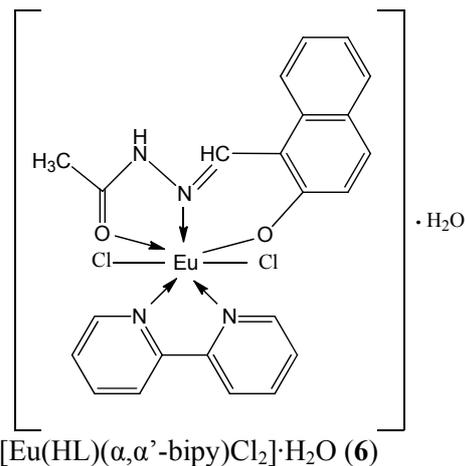
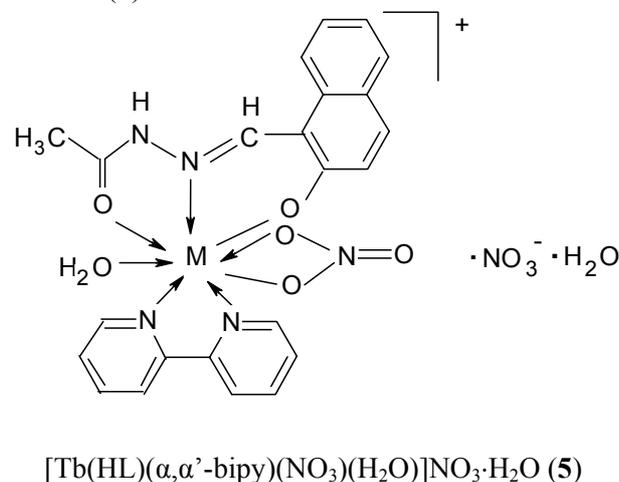
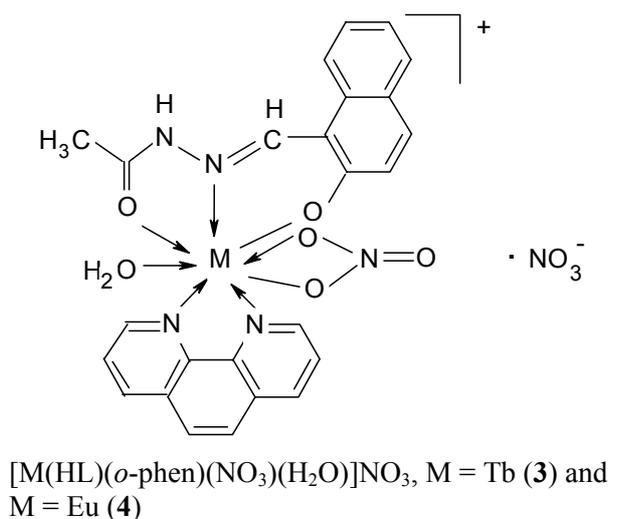
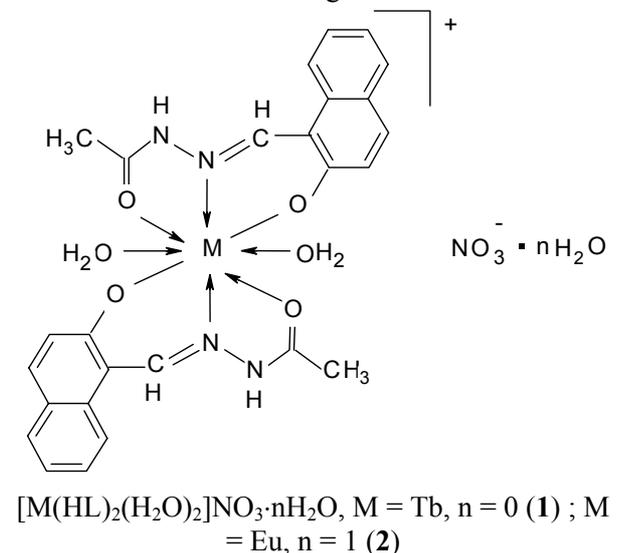


Fig. 2 – Proposed structures for the complex compounds.

Luminescence studies

Prior to the luminescence studies, we have registered the ultraviolet-visible diffuse reflectance spectra for the hydrazone ligand and its metal complexes. The ligand shows a very strong absorption band in the ultraviolet region, with two maxima, at 350 and 400 nm, due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively.

The effect of the complexation is the bathochrome shift of the low energy band to 420-430 nm in the UV-VIS spectra of the complexes. In addition, some weak absorption bands, appearing in the visible region, may be attributed to $f-f$ transitions of lanthanide ions.

The emission luminescence spectra were recorded on solid sample and, for comparison, in ethanolic solution, 10^{-4} M.

The ligand 2-hydroxy-1-naphthaldehyde acetylhydrazone shows a relative strong emission band, in the range 440-460 nm, with two maxima at 440 and 460 nm and a shoulder at 550 nm (excitation at 400 nm).

Terbium(III) complexes. [Tb(HL)₂(H₂O)₂][NO₃] displays a large fluorescence emission, from 450 to 650 nm, with maxima characteristic to $^5D_4 \rightarrow ^7F_J$ ($J = 3-6$) transitions of Tb³⁺ ion (Figure 3).

The most intensive band lies at 540 nm and may be attributed to the transition $^5D_4 \rightarrow ^7F_5$, while the medium emission band with maximum at 480 nm and the other, with low intensity, at 625 nm can be attributed to $^5D_4 \rightarrow ^7F_6$ and $^5D_4 \rightarrow ^7F_3$ transitions, respectively.²⁸⁻³⁰ The $^5D_4 \rightarrow ^7F_4$ transition is less visible, appearing as a shoulder at 565 nm.²⁷⁻²⁹

The emission spectrum for the same complex, but in ethanolic solution, shows important changes comparatively with the spectrum in solid state. The strongest band, at 540 nm, characteristic to the green emission of Tb^{3+} appears as a shoulder of a large band, with maximum at 470 nm. This fact could be explained by the non-radiative deactivations due to the interaction with high energy vibrations groups O-H of the solvent. We can suppose that the ligand don't assign a good protection against the chemical environment; in this case the luminescence spectrum is dominated by the emission of the ligand.

The same situation is observed for the other two complexes of terbium: while in solid state the emission spectra display bands at 495 and 540 nm for $[Tb(HL)(o\text{-phen})(NO_3)(H_2O)]NO_3$ and at 475 and 535 nm for $[Tb(HL)(\alpha,\alpha'\text{-bipy})(NO_3)(H_2O)]NO_3 \cdot H_2O$, due to ${}^5D_4 \rightarrow {}^7F_6$ and ${}^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+} , in ethanolic solution the emission is located on the ligands. Thus, two emission maxima can be observed in ethanolic solution: one, around 400 nm, due to the emission of *o*-phenanthroline or 2,2'-bipyridine and another at 460 nm, due to the emission of the hydrazone ligand.

Europium(III) complexes. The luminescence spectra of europium(III) complexes in solid state are dominated by a sharp strong emission band, at 600 nm, due to the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} (excitation at 400 nm).²⁷⁻³⁰ Other emission bands, with lower intensity, are also observed: at 560 nm (due to the ${}^5D_0 \rightarrow {}^7F_0$ transition), at 535 nm, 460 nm (these two bands being characteristic of the hydrazone ligand) and at 430 nm (characteristic of the emission of *o*-phenanthroline or 2,2'-bipyridine) (Figure 4).

It is known that the characteristic emission of Eu^{3+} appears in the range 560-680 nm, due to the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions.^{1,5,30} The presence of the bands under 560 nm indicates either an emission from the 5D_1 level due to a triplet ${}^3\pi\pi^*$ state of the ligand with higher energy than 5D_0 level of europium(III), or a less efficace ligand→metal energy transfer than in the case of terbium(III) complexes. In ethanolic solution, the emission is that characteristic of the ligands for all the three europium(III) complexes.

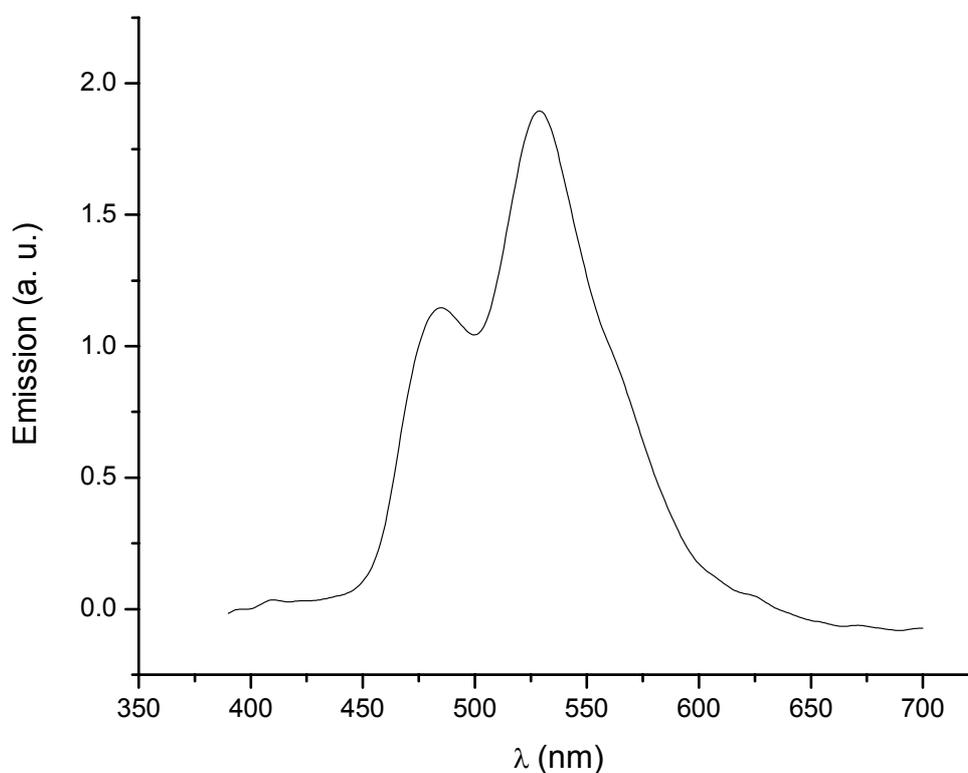


Fig. 3 – The emission spectrum of $[Tb(HL)_2(H_2O)_2]NO_3$ in solid state and at room temperature (excitation at 390 nm).

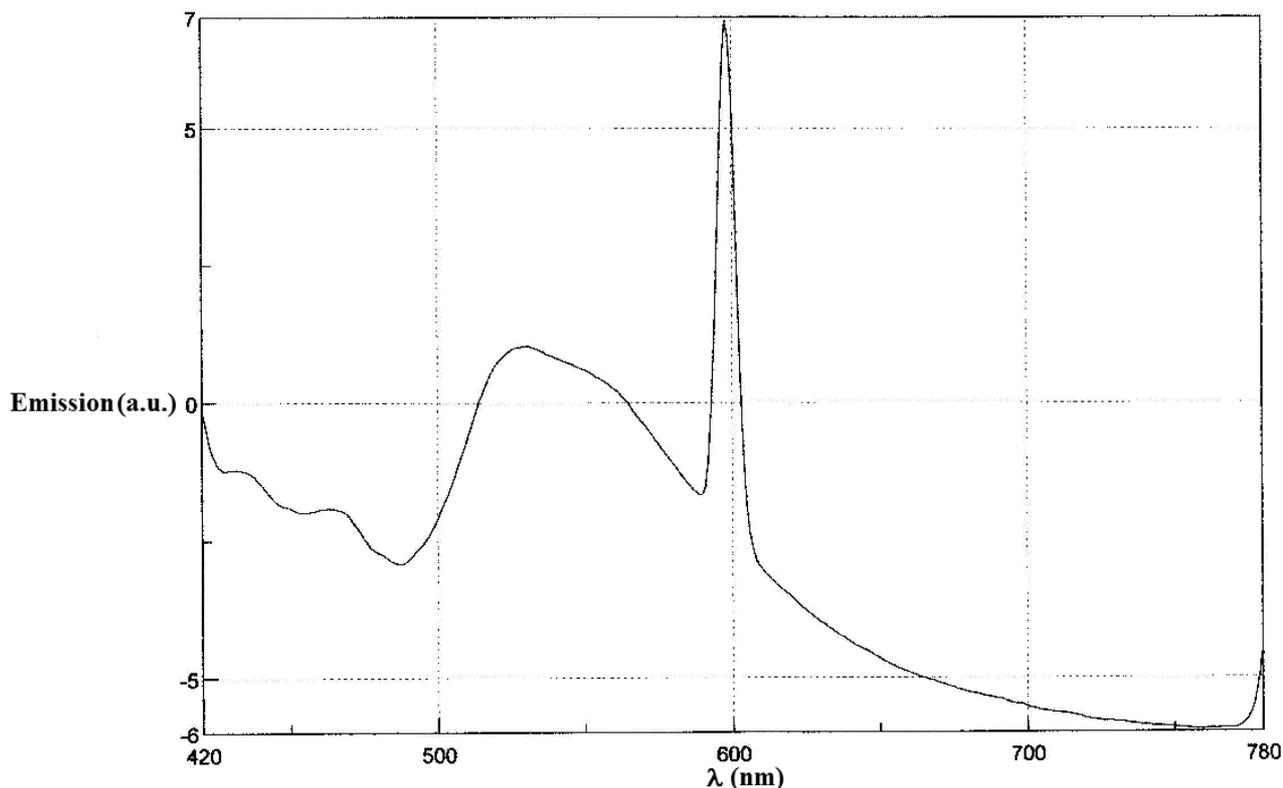


Fig. 4 – The emission spectrum in solid state and at room temperature of $[\text{Eu}(\text{HL})_2(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (excitation at 400 nm).

EXPERIMENTAL

All the chemicals were purchased from Aldrich and Merck and were used without further purification.

Synthesis of the ligand

The hydrazone ligand was prepared by the condensation reaction of acetohydrazide with 2-hydroxy-1-naphthaldehyde, as follow: 10 mmol of acetohydrazide dissolved in methanol was refluxed for 2 h with a methanolic solution of 2-hydroxy-1-naphthaldehyde (10 mmol), in the presence of few drops of glacial acetic acid. The light-yellow solid product formed was filtered off, washed with methanol and ether and dried at air. The compound was recrystallised from methanol. M.p. = 210 °C.

Synthesis of the complexes

The complex $[\text{Tb}(\text{HL})_2(\text{H}_2\text{O})_2]\text{NO}_3$ (**1**), diaqua bis(2-hydroxy-1-naphthaldehyde acetylhydrazone) terbium(III) nitrate, was prepared by the following method: 0.228 g (0.001 mol) of the ligand H_2L were dissolved in 30 mL ethanol by refluxing, with continuous stirring. To this solution were added 0.2175 g (0.0005 mol) of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, dissolved in a minimal amount of ethanol. The pH was then raised to 5.5 by the addition of sodium acetate. The resulting solution was heated under reflux for 1 h and the solid formed was filtered off, washed with ethanol and dried at air.

Analytical data: exp.%: C: 43.20; H: 3.35; N: 10.02; Tb: 22.12; calc.%: C: 43.88; H: 3.65; N: 9.84; Tb: 22.36. P.f. > 250 °C (decomposition).

The synthesis of $[\text{Eu}(\text{HL})_2(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**2**), diaqua bis(2-hydroxy-1-naphthaldehyde acetylhydrazone) europium(III) nitrate monohydrate : to a quantity of 0.228 g (0.001 mol) of the ligand H_2L dissolved in 35 mL ethanol with heating, 0.223 g (0.0005 mol) of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol were added. The resulted solution was refluxed for 1-2 h and then cooled to room temperature, when a yellow solid product separated out. This was filtered off, washed with ethanol and dried at air.

Analytical data: exp.%: C: 43.01; H: 3.31; N: 9.94; Eu: 21.00; calc.%: C: 43.21; H: 3.87; N: 9.69; Eu: 21.05. P.f. > 280 °C (decomposition).

The complexes $[\text{Tb}(\text{HL})(o\text{-phen})(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3$ (**3**), aqua nitro(*o*-phenanthroline)(2-hydroxy-1-naphthaldehyde acetylhydrazone)terbium(III) nitrate and $[\text{Eu}(\text{HL})(o\text{-phen})(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3$ (**4**), aqua nitro(*o*-phenanthroline)(2-hydroxy-1-naphthaldehyde acetylhydrazone) europium(III) nitrate have been prepared by the following method : 0.228 g (0.001 mol) of the ligand H_2L and 0.198 g (0.001 mol) of *o*-phenanthroline were dissolved together in ethanol, under reflux. A yellow-greenish solution was obtained (pH = 6). To this solution the metal salt dissolved in ethanol was added: 0.435 g (0.001 mol) of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.446 g (0.001 mol) of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, respectively. The clear solutions obtained were stirred under reflux for 2 h. After concentration and cooling, colored precipitates were formed: orange for the complex (**3**) and yellow-orange for the complex (**4**). These were filtered off, washed with ethanol and ether and dried at air.

Analytical data: Complex (**3**) exp.%: C: 41.01; H: 2.70; N: 11.24; Tb: 21.32; calc.%: C: 41.32; H: 2.61; N: 11.57; Tb: 21.90. M.p. \approx 240 °C (decomp).

Complex (**4**) exp.%: C: 41.35; H: 2.73; N: 11.54; Eu: 20.98; calc.%: C: 41.72; H: 2.64; N: 11.68; Eu: 21.14. M.p. \approx 250 °C (decomp).

The complex [Tb(HL)(α,α' -bipy)(NO₃)(H₂O)]NO₃·H₂O (**5**), aqua nitro(α,α' -bipyridine)(2-hydroxy-1-naphthaldehyde acetylhydrazone)terbium(III) nitrate monohydrate has been prepared by mixing together equimolar amounts of the ligand H₂L (0.028 g – 0.001 mol), α,α' -bipyridine (0.156 g – 0.001 mol) and terbium nitrate pentahydrate (0.435 g – 0.001 mol) in ethanol. The mixture was stirred under reflux for 2 h and the obtained solution at heating is then cooled at room temperature. We have obtained a yellow precipitate, which was filtered off, washed with ethanol and ether and dried at air.

Analytical data: exp. %: C: 39.02; H: 2.81; N: 11.71; Tb: 22.38; calc. %: C: 39.31; H: 2.70; N: 11.96; Tb: 22.64. M.p. \approx 230 °C (decomp).

(6) The complex [Eu(HL)(α,α' -bipy)Cl₂]·H₂O, dichloro(α,α' -bipyridine)(2-hydroxy-1-naphthaldehyde acetylhydrazone)europium(III) monohydrate has been prepared in the same way as the complex [Tb(HL)(α,α' -bipy)(NO₃)(H₂O)]NO₃·H₂O, using in this case the europium trichloride hexahydrate (0.366 g – 0.001 mol). By addition of the metal salt to the ethanolic solution of the ligands, the colour changes from light-yellow to orange. The resulted solution was refluxed for 2h and then cooled to room temperature, when a yellow solid product separated out. It has been separated, washed and dried as above.

Analytical data: exp. %: C: 43.90; H: 3.12; N: 8.74; Eu: 24.02; calc. %: C: 44.23; H: 3.04; N: 8.97; Eu: 24.35. M.p. \approx 260 °C (decomp).

Carbon, hydrogen and nitrogen were determined using a Carlo Erba 1180 analyzer. The metal content was determined gravimetrically, as oxide, M₂O₃. Thermogravimetric analysis was carried out in static air atmosphere, at a heating rate of 10 °C/min, using a MOM Q-1500 derivatograph. Infrared spectra (in KBr pellets) were recorded on a BIORAD FTIR 135 spectrophotometer, in the range 4000-400 cm⁻¹. UV-VIS diffuse reflectance spectra were measured on a UV-VIS Jasco 650 spectrophotometer, in the range 200-900 nm. Fluorescence measurements were made on a Jasco FP 6500 spectrofluorimeter, on solid sample and in ethanolic solution. The excitation and emission slit widths were 5 nm.

CONCLUSION

The six new complex compounds of europium(III) and terbium(III) with 2-hydroxy-1-naphthaldehyde acetylhydrazone (H₂L), *o*-phenanthroline and α,α' -bipyridine as ligands displayed a good stability in solid state and strong luminescent emission, characteristic of these lanthanide cations. In ethanolic solution, the complexes showed a large fluorescence band, with maxima bellow 550 nm, due to the non-radiative losses caused by the interactions with molecules of the solvent. Despite these problems, the synthesized complexes could be used as luminescent materials in solid state.

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