Synthesis and Characterization of New Luminescent Complex Compounds of Sm(III) with Acetylhydrazones and Heterocyclic Bases

MIRELA CALINESCU*[1], DANIELA MANEA[1], BOGDAN JURCA[2]

[1]University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 23 Dumbrava Roşie Str., 020462, Bucharest, Romania,

[2]University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry,1-3 Regina Elisabeta Str., 030018, Bucharest, Romania

New samarium(III) complex compounds with 2-aminobenzaldehyde acetylhydrazone (HL^a), 2-hydroxy-1-naphthaldehyde acetylhydrazone (H_2L^b), o-phenanthroline and α,α'-bipyridine as ligands have been synthesized and characterized by elemental and thermogravimetrical analyses, infrared, UV-Vis and luminescence spectroscopy. Based on these studies, the following formulae have been attributed to the complex compounds: $[Sm(L^a)_2(NO_3)]$, $[Sm(HL^b)_2(NO_3)]$, $[Sm(L^a)(o\text{-}phen)(NO_3)_2]$, $[Sm(HL^b)(o\text{-}phen)(NO_3)_2]$, $[Sm(L^a)(bipy)(NO_3)_2]$ and $[Sm(HL^b)(bipy)(NO_3)_2] . 2H_2O$, where the hydrazone ligands act as monobasic tridentate donors. The luminescence spectra of these complexes were recorded in solid state at room temperature. All the complexes show strong luminescent, characteristic of samarium(III) ion.

Keywords: Lanthanides, samarium, luminescence, hydrazone metal complexes.

Luminescent complex compounds of the trivalent rare earth ions, especially europium, terbium and samarium, have been intensively studied during the last years, due to their potential to be used as probes and labels in chemical and biological applications [1-3]. Thus, the luminescent measurements have been used to determine the symmetry around the metal ion or the number of coordinated water molecules, metal-metal distance and the nature of the metal-ligand bond [4,5].

The use of the lanthanide ions for sensitive and selective detection arises from their especially emission properties, including narrow band emission, very large Stokes shift and long lifetimes, that allow a very effective separation of the lanthanide luminescence from that of the background [6-8].

Since the lanthanide ions absorption in the visible region is very weak, it is necessary to obtain complex compounds with chromophoric ligands, which are able to absorb energy, efficiently transfer it to the cation and also protect the lanthanide ion from interaction with the solvent which leads to the quenching of the fluorescence [7,8].

Due to the theoretical importance and possible practical applications, we have prepared and characterized six complex compounds of Sm(III) with 2-aminobenzaldehyde acetylhydrazone (HL^a) and 2-hydroxy-1-naphthaldehyde acetylhydrazone (H_2L^b) as ligands. Four of the six complex compounds have mixed ligands in their coordination sphere : hydrazone with o-phenanthroline and hydrazone with α,α''-bipyridine.

Chemical properties of acetylhydrazones and their metal complexes have been subject of many studies, especially for their antibacterial and antifungal activities [9,10]. The most works were focus on the complexes with the first transition metal ions [10,11] and few studies included complex compounds of lanthanide ions with such ligands [12].

On the other hand, 1,10-phenanthroline and 2,2'-bipyridine have been extensively used last years as ligands for lanthanide ions [13,14]. Several lanthanide complexes with 1,10-phenanthroline and 2,2'-bipyridine or other ligands incorporating these heterocyclic nucleus possess a remarkable chemical stability, strong luminescence emission, long excited state lifetime and some of them, antitumor and anticancer activity [8,13,15].

Experimental part

All the chemicals used were of reagent grade and were purchased from Sigma-Aldrich and Merck.

Preparation of hydrazones

The hydrazone ligands were prepared according to the literature data, by the condensation reaction of acetohydrazide with the corresponding aldehyde, 2-aminobenzaldehyde (for the ligand HL^a) and 2-hydroxy-1-naphthaldehyde (for the ligand H_2L^b), in equimolecular ratio [16].

The mixtures of ethanolic solutions of acetohydrazide and aldehyde were placed in a round-bottomed flask and boiled under reflux for 2 h. The crystalline solids formed were filtered off, air dried and recrystallized from ethanol. HL^a, yellow, mp = 168 °C; H_2L^b, white, mp = 210 °C.

Preparation of metal complexes

$[Sm(L^a)_2(NO_3)]$ (**1**) and $[Sm(HL^b)_2(NO_3)]$ (**2**) were prepared in the following way: to a suspension of the ligand (1.77 g, 10 mmol for HL^a and 2.28 g, 10 mmol for H_2L^b) in hot ethanol (50 mL) was added dropwise with constant stirring a solution of hexahydrated samarium(III) nitrate (2.22 g, 5 mmol) in 10 mL ethanol. The *p*H was raised to 6 by addition of sodium hydroxide and the solutions were then stirred under reflux for 2 h. The precipitates obtained after cooling were filtered off, washed with ethanol and ether and dried in air.

Anal. Calcd. for $[Sm(L^a)_2(NO_3)]$ (%): C, 38.29; H, 3.54; N, 17.37; Sm, 26.59. Found: C, 38.02; H, 3.65; N, 16.98; Sm, 26.20. Yellow; mp > 280 °C (decomp).

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* *email: mirela_calinescu@hotmail.com; Tel.: 07263177237*

Anal. Calcd. for $[Sm(HL^b)_2(NO_3)]$ (%):C, 46.84; H, 3.30; N, 10.51; Sm, 22.52. Found: C, 46.65; H, 3.40; N, 10.28; Sm, 22.35. Yellow-greenish; mp > 260 °C (decomp).

Mixed ligand complexes **3**-**6** were prepared as follows: 5 mmol of the hydrazone ligand (0.885 g for HL^a and 1.14 g for H_2L^b) were mixed with 5 mmol of heterocyclic base (0.90 g *o*-phenanthroline, 0.78 g bipyridine, respectively) in 50 mL ethanol and the mixture was heated under reflux for 15 min. A solution of $Sm(NO_3)_3 \cdot 6H_2O$ (2.22 g, 5 mmol) in 10 mL ethanol was added to the mixture of the ligands and the *p*H was adjusted to 5.5 with sodium acetate. The clear solutions obtained were stirred under reflux for 2-3 h. After concentration and cooling, fine precipitates were formed. These were filtered off, washed with ethanol and ether and dried at air.

Anal. Calcd. for $[Sm(L^a)(o\text{-phen})(NO_3)_2]$ (**3**) (%): C, 40.00; H, 2.85; N, 15.55; Sm, 23.80. Found: C, 39.72; H, 2.90; N, 15.18; Sm, 23.57. White; mp = 315 °C (decomp).

Anal. Calcd. for $[Sm(HL^b)(o\text{-phen})(NO_3)_2]$ (**4**) (%): C, 44.05; H, 2.79; N, 12.33; Sm, 22.02. Found. C, 39.89; H, 2.92; N, 12.13; Sm, 21.95. Yellow; mp = 244 °C.

Anal. Calcd. for $[Sm(L^a)(bipy)(NO_3)_2]$ (**5**) (%): C, 37.62; H, 2.97; N, 16.17; Sm, 24.75. Found: C, 37.49; H, 2.94; N, 15.90; Sm, 24.58. Yellow; mp > 280 °C (decomp).

Anal. Calcd. for $[Sm(HL^b)(bipy)(NO_3)_2] \cdot 2H_2O$ (**6**) (%): C, 39.82; H, 3.31; N, 12.12; Sm, 21.64. Found: C, 39.60; H, 3.44; N, 12.00; Sm, 21.55. Orange; mp = 230 °C (decomp).

Analyses and physical measurements

Carbon, hydrogen and nitrogen were determined using a Carlo Erba 1180 analyzer. The metal content was determined gravimetrically, as oxide, Sm_2O_3. Thermogravimetric analysis was carried out in static air atmosphere, at a heating rate of 10 °C/min, using a STA 6000 Perkin Elmer 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.

Results and discussions

The results of elemental analysis and the spectral data are in agreement with the proposed formulae for the ligands and their metal complexes.

Infrared spectral studies

The important frequencies exhibited by the ligand HL^a and its complexes are listed in table 1 and those for the ligand H_2L^b and its complexes, in table 2.

Infrared spectra of free hydrazone ligands show a medium absorption band in the range 3183-3186 cm^{-1}, assigned to ν(NH) stretching vibration, indicating the existence of the ligands in keto form in solid state (fig. 1 and fig. 2) [9,17]. This band is also present in the IR spectra of the complexes **2**, **4** and **6**, which is a proof for the coordination of the ligand H_2L^b in the tautomeric keto form.

The IR spectra of the complexes **1**, **3** and **5** do not show band due to ν(NH), suggesting that the ligand HL^a passes in the tautomeric enol form **b** at the formation of its complexes.

The very strong IR bands at 1658 cm^{-1} for the ligand HL^a and 1677 cm^{-1} for the ligand H_2L^b were assigned to ν(C=O) mode of the carbonylic group [9,18,19]. In the IR spectra of the complexes **2**, **4** and **6** this band is shifted to lower wave numbers, indicating the coordination of the ligand

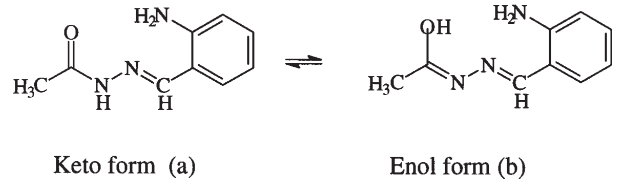


Fig. 1. Tautomeric forms of 2-aminobenzaldehyde acetylhydrazone (ligand HL^a)

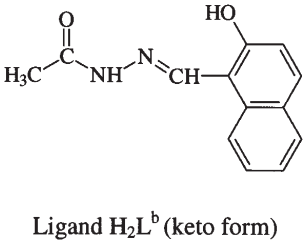


Fig. 2. Keto form of the ligand 2-hydroxy-1-naphthaldehyde acetylhydrazone (H_2L^b)

Table 1

CHARACTERISTIC BANDS IN THE IR SPECTRA OF THE LIGAND HL^a AND ITS SAMARIUM(III) COMPLEXES ($\tilde{\nu}_{max}$, cm^{-1})

Assignments	HL^a	(1)	(3)	(5)
$\nu_{as}(NH_2)$	3417 ms	3460 ms	3460 ms	3460 ms
$\nu_{sym}(NH_2)$	3320 m	3273 m	3300 m	3310 m
$\nu(NH_{sec})$	3183 m	-	-	-
ν(C=O) (amide I)	1658 vs	-	-	-
ν(C=N)	1623 s	1551 m	1550 m	1550 m
ν(C=N) uncomplexed	-	1620 s	1622 s	1620 s
δ(NH)+ν(CN) (amide II)	1580 m	-	-	-
$\nu(C_{arom}\text{-}N)$	1341 m	1384 m	1384 m	1368 m
δ(NH)+ν(CN) (amide III)	1310 m	-	-	-
$\nu(C\text{-}O_{enolic})$	-	1110 s	1106 s	1112 s
$\nu_1[\nu(NO)]$	-	1487 m	1485 s	1488 ms
$\nu_4[\nu(NO_2)]$	-	1319 m	1305 s	1319 m
ν_2 $[\nu(NO_2)]$	-	1030 m	1031 m	1035 m
ν_6 $[\nu(O_2NO)]$	-	820 w	863 w	860 w
ν(Sm-O)	-	657 m	656 m	659 m
ν(Sm-N)	-	630 w	639 w	620 w

Table 2
CHARACTERISTIC BANDS IN THE IR SPECTRA OF THE LIGAND H_2L^b AND ITS SAMARIUM (III) COMPLEXES ($\tilde{\nu}_{max}$, cm^{-1})

Assignments	H_2L^b	(2)	(4)	(6)
ν(OH)	3042 s	-	-	3410 m
$\nu(NH_{sec})$	3186 m	3197 m	3190 m	3197 m
ν(C=O) (amide I)	1677 vs	1605 vs	1621 s	1610 s
ν(C=N)	1644 s	1554 m	1549 m	1547 m
δ(NH)+ν(CN) (amide II)	1579 m	1580 m	1580 m	1580 m
δ(NH)+ν(CN) (amide III)	1324 s	1329 s	1335 s	1330 m
$\nu(C\text{-}O_{phenolic})$	1185 m	1191 m	1210 m	1193 m
ν_1[ν(NO)]	-	1509 m	1486 s	1462 s
$\nu_4[\nu(NO_2)]$	-	1300 s	1307 s	1310 m
ν_2 $[\nu(NO_2)]$	-	1035 m	1030 m	1026 m
ν_6 $[\nu(O_2NO)]$	-	855 w	843 w	832 w
ν(Sm-O)	-	634 w	639 w	643 m
ν(Sm-N)		585 w	573 w	590 w

H_2L^b to the metal ion through the carbonylic oxygen atom. This supposition is also supported by the presence, in the IR spectra of these complexes, of the bands due to the coupled vibrations δ(NH)+ν(CN) (amide II and amide III bands), which are slightly shifted from the position where they are in the infrared spectrum of the free ligand H_2L^b.

The absence of the bands due to ν(C=O) and δ(NH)+ν(CN) modes in the IR spectra of the complexes **1**, **3** and **5** are also in accordance with the coordination of the ligand HL^a to the metal ion in the tautomeric enol form [9,20].

The IR spectra of the hydrazone ligands show strong bands at 1623 cm^{-1} (HL^a) and 1644 cm^{-1} (H_2L^b), attributed to the stretching vibration of the azomethine group, ν(C=N) [9,17,20]. In the IR spectra of all the complexes this band is strongly shifted to lower wave numbers, indicating the involvement of the azomethinic nitrogen atom in coordination to the metal ion [9,17,20]. As result of the enolisation of the ligand HL^a, the strong band around 1620 cm^{-1} in the IR spectra of the complexes **1**, **3** and **5** may be assigned to uncomplexed >C=N- group, while the new strong band, at 1106-1112 cm^{-1} may be attributed to the enolic ν(C-O) stretching vibration of the C-O bond newly formed [9,20,21].

Other characteristic bands in the IR spectrum of the ligand HL^a are observed at 3417 cm^{-1} and 3320 cm^{-1}, attributed to $\nu_{as}(NH_2)$ and $\nu_{sym}(NH_2)$, respectively and at 1341 cm^{-1}, due to the stretching vibration of the $C_{aromatic}$-N bonding [22]. The shift of these bands towards higher frequencies is observed for all the three complexes with this ligand, indicating the coordination of the hydrazone ligand through the nitrogen atom of $-NH_2$ group.

In the case of the complexes **2**, **4** and **6**, the absence of the band due to $\nu(OH)_{phenolic}$ and the upward shift of the band assigned to the stretching vibration of $C\text{-}O_{phenolic}$ suggest the deprotonation of the phenolic group and the implication of phenolic oxygen atom in coordination to the metal ion [20]. Another large band, appearing in the IR spectrum of the complex (**6**) at 3410 cm^{-1} indicates the presence of crystalline water.

The IR spectra of all the complexes show the absorption bands assigned to the coordinated nitrate [23]. The separation of the highest frequency bands, ν_1 - ν_4 is about 200 cm^{-1}, in accordance with the participation of the nitrate as bidentate ligand [23].

Additional bands are observed in the IR spectra of the complexes with mixed ligands. These bands are associated with the stretching vibrations of >C=N- and >C=C< groups of 1,10-phenanthroline (1495 at 1426 cm^{-1}) and 2,2'-dipyridyl (1508-1511 at 1434 cm^{-1}) [15]. The positions of the bands attributed to >C=N- vibrations are shifted from those characteristic of 1,10-phenanthroline and 2,2'-dipyridyl, indicating the coordination of these ligands through imine nitrogen atoms [15].

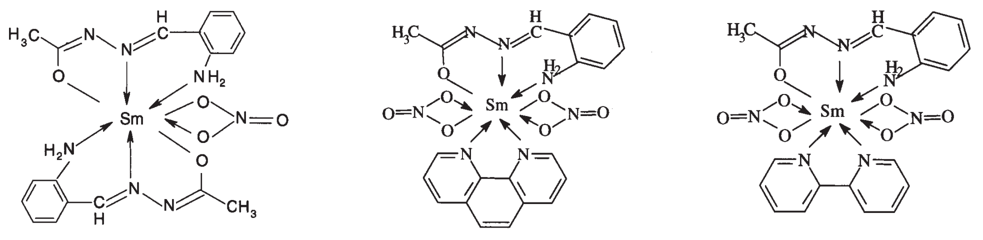
The bands with weak intensity, appearing in the IR spectra of the complexes at low wave numbers (550-660 cm^{-1}) may be assigned to the metal-donor atom vibrations: ν(M-O) and ν(M-N) [23].

On the base of the infrared spectra we can conclude that 2-aminobenzaldehyde acetylhydrazone (HL^a) is coordinated to the metal ion in the enolic form, through the aminic and azomethinic nitrogen atoms and enolic oxygen, as a monobasic tridentate NNO ligand. The ligand 2-hydroxy-1-naphthaldehyde acetylhydrazone is coordinated in keto form, as monobasic tridentate ONO donor, through the phenolic and ketone oxygen atoms and the azomethinic nitrogen. Because 1,10-phenanthroline and 2,2'-dipyridyl are neutral bidentate NN donors and taking into account of the presence of one or two bidentate nitrate, the coordinate number of samarium(III) ion is 8 in the complexes **1** and **2** and 9 in the complexes **3-6**.

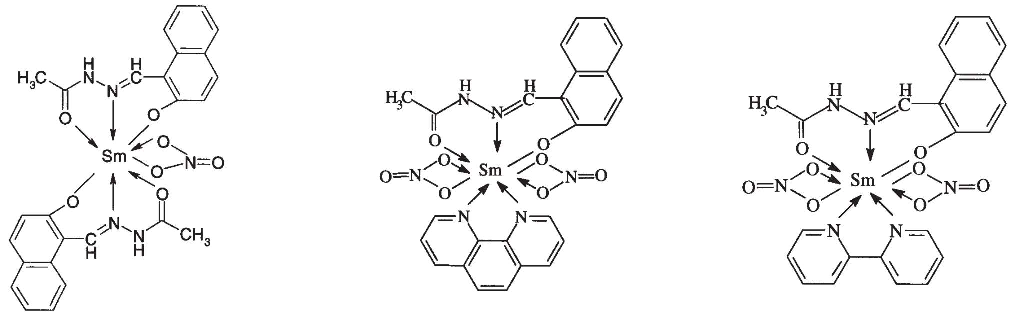
Thermogravimetric analysis

The observation of the TG curves of the complexes **1-5** indicates the absence of water molecules, either in or out the coordination sphere of the metal ion. These complexes are stable upon 280-300°C. For each of them the first weight loss lies in the temperature range 280-370 °C, due to the removal of coordination nitrate [24]. A further weight loss is observed in the range 380-650 °C, in a large exothermic process and corresponds to the fragmentation and elimination of the organic ligands [24-26]. The residue obtained after heating up to 900 °C is expected to be Sm_2O_3 and the metal percentages calculated from thermogravimetric curves correspond to the results of elemental analyses [18].

In the case of the complex **6** the first weight loss, in the range 100-130 °C, corresponds to the removal of crystalline water [25,26]. An endothermic process, with maximum at 295 °C, is due to the loss of coordinated nitrate, while the large and complex exothermic process, in the temperature range 380-900 °C, corresponds to the loss of organic ligands [24]. As in the case of the complexes **1-5**, the residue obtained at 900°C is Sm_2O_3 [18].



$[Sm(L^a)_2(NO_3)]$ **(1)** $[Sm(L^a)(o\text{-phen})(NO_3)_2]$ **(3)** $[Sm(L^a)(bipy)(NO_3)_2]$ **(5)**



$[Sm(HL^b)_2(NO_3)]$ **(2)** $[Sm(HL^b)(o\text{-phen})(NO_3)_2]$ **(4)** $[Sm(HL^b)(bipy)(NO_3)_2]\cdot 2H_2O$ **(6)**

Fig. 3. Proposed structural formulae for the complex compounds

Based on the presented data, the complex compounds are proposed to have the following the conformations shown in figure 3.

Ultraviolet-visible spectra

The UV-Vis spectra of the hydrazone ligands show a very strong absorption band in the ultraviolet region, with two maxima at 340 nm and 400 nm, due to the π→π* and n→π* transitions, respectively.

The electronic spectra of the complexes are dominated by the ligand bands, with a slight shift, due to the changes induced by the metal ion. Thus, the UV-Vis spectra of all the complexes show a strong band in the ultraviolet region, with a maximum peak at 340-430 nm. The shoulders observed in the spectra of the complexes with mixed ligands at 240-280 nm are due to the absorption of *o*-phenanthroline and 2,2'-bipyridine [27]. In addition, some absorption bands, in the visible region may be attributted to *f-f* transitions of Sm^{3+} [18,28].

The absorption maxima in the visible region for the complex compounds are summarized in table 3 and one representative spectrum is given in figure 4.

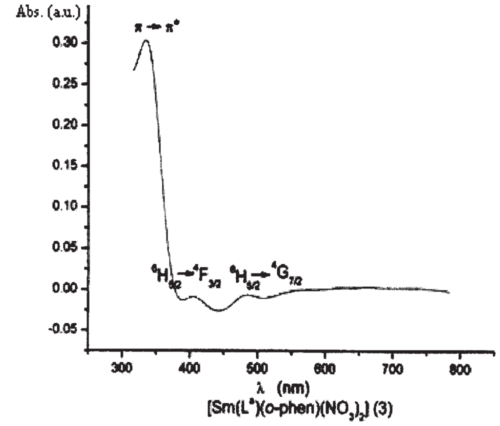


Fig. 4. UV-Vis absorption spectrum of the complex $[Sm(L^a)(o\text{-phen})(NO_3)_2]$

Luminescence studies

The emission luminescence spectra were recorded on solid sample, on a Jasco FP 6500 spectrofluorimeter. The excitation and the emission slit widths were 5 nm. The emission spectrum of 2-aminobenzaldehyde acetyl-

Table 3

ELECTRONIC TRANSITIONS (cm^{-1}) IN VISIBLE FOR SAMARIUM(III) COMPLEXES

Complex	Absorptions	Assignments
$[Sm(L^a)_2(NO_3)]$	16660	$^6H_{5/2} \rightarrow {}^4G_{5/2}$
$[Sm(HL^b)_2(NO_3)]$	15870	$^6H_{5/2} \rightarrow {}^4G_{5/2}$
$[Sm(L^a)(o\text{-phen})(NO_3)_2]$	13300 16600 20830 24400	$^6H_{5/2} \rightarrow {}^4F_{11/2}$ $^6H_{5/2} \rightarrow {}^6G_{5/2}$ $^6H_{5/2} \rightarrow {}^4G_{7/2}$ $^6H_{5/2} \rightarrow {}^4F_{3/2}$
$[Sm(HL^b)(o\text{-phen})(NO_3)_2]$	12900 16850	$^6H_{5/2} \rightarrow {}^4F_{11/2}$ $^6H_{5/2} \rightarrow {}^4G_{5/2}$
$[Sm(L^a)(bipy)(NO_3)_2]$	13200 16800	$^6H_{5/2} \rightarrow {}^4F_{11/2}$ $^6H_{5/2} \rightarrow {}^4G_{5/2}$
$[Sm(HL^b)(bipy)(NO_3)_2]\cdot 2H_2O$	13500 18180 23800	$^6H_{5/2} \rightarrow {}^4F_{11/2}$ $^6H_{5/2} \rightarrow {}^6G_{5/2}$ $^6H_{5/2} \rightarrow {}^4F_{3/2}$

Table 4
OBSERVED TRANSITIONS IN THE LUMINESCENCE SPECTRA OF SAMARIUM(III) COMPLEXES

Complex	λ_{exc} (nm)	$\lambda_{emission}$ (nm)	Assignments
$[Sm(L^a)_2(NO_3)]$	350	600	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
$[Sm(HL^b)_2(NO_3)]$	390	605	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
$[Sm(L^a)(o\text{-phen})(NO_3)_2]$	350	565 595 650	$^4G_{5/2} \rightarrow {}^6H_{5/2}$ $^4G_{5/2} \rightarrow {}^6H_{7/2}$ $^4G_{5/2} \rightarrow {}^6H_{9/2}$
$[Sm(HL^b)(o\text{-phen})(NO_3)_2]$	390	565 600 645	$^4G_{5/2} \rightarrow {}^6H_{5/2}$ $^4G_{5/2} \rightarrow {}^6H_{7/2}$ $^4G_{5/2} \rightarrow {}^6H_{9/2}$
$[Sm(L^a)(bipy)(NO_3)_2]$	370	610	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
$[Sm(HL^b)(bipy)(NO_3)_2]\cdot 2H_2O$	350	600	$^4G_{5/2} \rightarrow {}^6H_{7/2}$

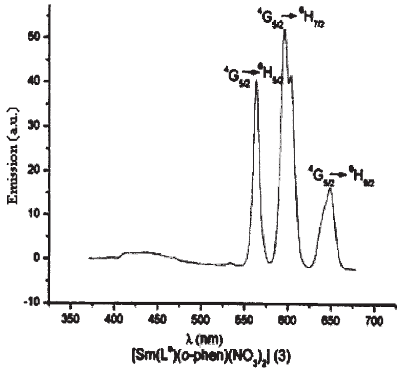


Fig. 5. Emission spectrum of $[Sm(L^a)(o\text{-phen})(NO_3)_2]$
(excitation at 350 nm)

hydrazone (HL^a), obtained by excitation at 350 nm, shows a large maximum from 420 to 470 nm and another peak at 550 nm. The ligand 2-hydroxy-1-naphthaldehyde acetylhydrazone shows a medium emission band, in the range 440-460 nm, with two maxima at 440 and 460 nm and a shoulder at 530 nm (excitation at 350 nm).

The fluorescence bands arising from Sm^{3+} emission in the complex compounds are listed in Table 4. The emission is due to the transitions from the resonant $^4G_{5/2}$ level to various ^6H_J levels [4,27-30].

Among the six complexes, only $[Sm(L^a)(o\text{-phen})(NO_3)_2]$ and $[Sm(HL^b)(o\text{-phen})(NO_3)_2]$ show tipically luminescence spectra for Sm^{3+} (fig. 5), with characteristic bands at 565, 595-600 and 650-645 nm, due to the transitions $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$, respectively [4,27-31]. No emission from the ligands can be observed in these cases. This fact indicates that a very efficient energy transfer occurs from the ligands to the central metal ion.

The luminescence spectra of the other four complexes show the main sharp emission band at 595-610 nm, arising from $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm^{3+} and a broad emission band, with one maximum at 450-500 nm, for the complexes **1** and **2** and two maxima for the complexes **5** and **6**, due to the emission from the ligands. We can suppose a poorly energy transfer from the ligands to the metal ion in these cases, so that the emissive state is characteristic of the ligand centered p-p* transition [31].

Conclusions

We have prepared six new complexes of samarium(III) with 2-aminobenzaldehyde acetylhydrazone (HL^a), 2-hydroxy-1-naphthaldehyde acetylhydrazone (H_2L), *o*-phenanthroline and α,α'-bipyridine as ligands, in view to obtain good luminescent lanthanide chelates.

Among the six complexes, satisfaction results have been obtained for the mixed ligand hydrazone-*o*-phenanthroline complexes, which show strong emission in solid state, characteristic for the samarium(III) ion. These complexes could be used as promising luminescent materials.

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