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

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New samarium(III) complex compounds with 2-aminobenzaldehyde acetylhydrazone (HLα), 2-hydroxy-1-naphthaldehyde acetylhydrazone (H2Lβ), α-phenanthroline and α,α’-bipyridine as ligands have been synthetized and characterized by elemental and thermogravimetric analyses, infrared, UV-Vis and luminescence spectroscopy. Based on these studies, the following formulae have been attributed to the complex compounds: [Sm(Lα)2(NO3)]2, [Sm(HLβ)2(NO3)]2, [Sm(Lα)(o-phen)(NO3)2], [Sm(HLβ)(o-phen)(NO3)2], [Sm(Lβ)(bipy)(NO3)2] and [Sm(HLβ)(bipy)(NO3)2]. 2H2O, 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 (H2Lβ) and 2-hydroxy-1-naphthaldehyde acetylhydrazone (H2Lα) 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 focused 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 hydrazones ligands were prepared according to the literature data, by the condensation reaction of aceto-hydrazide with the corresponding aldehyde, 2-aminobenzaldehyde (for the ligand HLα) and 2-hydroxy-1-naphthaldehyde (for the ligand H2Lβ), 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.

H2Lα, yellow, mp = 168 °C; H2Lβ, white, mp = 210 °C.

Preparation of metal complexes
[Sm(Lα)(NO3)]2 (1) and [Sm(HLβ)(NO3)]2 (2) were prepared in the following way: to a suspension of the ligand (1.77 g, 10 mmol for H2Lα and 2.28 g, 10 mmol for H2Lβ) 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 pH 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(Lα)(NO3)]2 (%): 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).
Anal. Calcd. for [Sm(HL\textsubscript{a})(\textit{o-phen})(NO\textsubscript{3})\textsubscript{2}] (3) (%): C, 40.00; H, 2.79; N, 15.55; Sm, 23.80. Found: C, 39.72; H, 2.92; N, 15.13; Sm, 21.95. White; mp = 315 °C (decomp).

Anal. Calcd. for [Sm(HL\textsubscript{b})(\textit{o-phen})(NO\textsubscript{3})\textsubscript{2}] (4) (%): C, 44.05; H, 2.79; N, 16.17; Sm, 24.58. Yellow; mp > 280 °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\textsubscript{2}O\textsubscript{3}. Thermo-gravimetric 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\textsuperscript{-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 spectrophotometer, 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 HLa and its complexes are listed in table 1 and those for the ligand H\textsubscript{2}Lb and its complexes, in table 2.

Infrared spectra of free hydrazone ligands show a medium absorption band in the range 3183-3186 cm\textsuperscript{-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\textsubscript{2}Lb\textsuperscript{2+} 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 HLa passes in the tautomeric enol form at the formation of its complexes.

The very strong IR bands at 1658 cm\textsuperscript{-1} for the ligand HLa and 1677 cm\textsuperscript{-1} for the ligand H\textsubscript{2}Lb 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
Enolisation of the ligand HLa, the strong band around 1620 cm⁻¹, confirms coordination to the metal ion \[9,17,20\]. As a result of the involvement of the azomethinic nitrogen atom in the stretching vibration of the azomethine group, \(\nu(C=N)\), bands are slightly shifted from the position where they are in the infrared spectrum of the free ligand H₂Lb.

The absence of the bands due to \(\nu(C=O)\) and \(\delta(NH)\) of the complexes 1, 3 and 5 is in accordance with the coordination of the ligand HLa 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 (HLa) and 1644 cm⁻¹ (H₂Lb), attributed to the stretching vibration of the azomethine group, \(\nu(C=N)\) \[9,17,20\]. In the IR spectra of the complexes, the bands due to the stretching vibration of the azomethine group are present.

The bands with weak intensity, appearing in the IR spectra of the complexes at low wave numbers (350-660 cm⁻¹), may be assigned to the metal-donor atom vibrations: \(\nu(M-O)\) and \(\nu(M-N)\) \[23\].

On the base of the infrared spectra we can conclude that 2-aminobenzaldehyde acetylhydrazone (HLa) is coordinated to the metal ion in the enolic form, through the phenolic and ketone oxygen atoms and the azomethinic nitrogen, as a monobasic tridentate NNO ligand. The ligand 2-hydroxy-1-naphthaldehyde acetylhydrazone is coordinated to the metal ion in the keto form, as a monobasic tridentate NO2 ligand.

**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 380-900 °C, corresponds to the fragmentation and elimination of the organic ligands \[24-26\]. The residue obtained after heating up to 900 °C is Sm₂O₃ \[18\].

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 range 380-900 °C, corresponds to the loss of organic ligands \[24\].

<table>
<thead>
<tr>
<th>Assignments</th>
<th>H₂Lb</th>
<th>(2)</th>
<th>(4)</th>
<th>(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu(OH))</td>
<td>3042 s</td>
<td>-</td>
<td>-</td>
<td>3410 m</td>
</tr>
<tr>
<td>(\nu(NH_{ase}))</td>
<td>3186 m</td>
<td>3197 m</td>
<td>3190 m</td>
<td>3197 m</td>
</tr>
<tr>
<td>(\nu(C=O)) (amide I)</td>
<td>1677 vs</td>
<td>1605 vs</td>
<td>1621 s</td>
<td>1610 s</td>
</tr>
<tr>
<td>(\nu(C=N))</td>
<td>1644 s</td>
<td>1554 m</td>
<td>1549 m</td>
<td>1547 m</td>
</tr>
<tr>
<td>(\nu(NH)+\nu(CN)) (amide II)</td>
<td>1579 m</td>
<td>1580 m</td>
<td>1580 m</td>
<td>1580 m</td>
</tr>
<tr>
<td>(\nu(NH)+\nu(CN)) (amide III)</td>
<td>1324 s</td>
<td>1329 s</td>
<td>1335 s</td>
<td>1330 m</td>
</tr>
<tr>
<td>(\nu(C-O)_{phenolic})</td>
<td>1185 m</td>
<td>1191 m</td>
<td>1210 m</td>
<td>1193 m</td>
</tr>
<tr>
<td>(\nu(C-O)) of nitrate</td>
<td>-</td>
<td>1509 m</td>
<td>1486 s</td>
<td>1462 s</td>
</tr>
<tr>
<td>(\nu(C-O)) of nitrate</td>
<td>-</td>
<td>1300 s</td>
<td>1307 s</td>
<td>1310 m</td>
</tr>
<tr>
<td>(\nu(C-O)) of nitrate</td>
<td>-</td>
<td>1035 m</td>
<td>1030 m</td>
<td>1026 m</td>
</tr>
<tr>
<td>(\nu(C-O)) of nitrate</td>
<td>-</td>
<td>855 w</td>
<td>843 w</td>
<td>832 w</td>
</tr>
<tr>
<td>(\nu(C-O)) of nitrate</td>
<td>-</td>
<td>634 w</td>
<td>639 w</td>
<td>643 m</td>
</tr>
<tr>
<td>(\nu(Sm-O))</td>
<td>-</td>
<td>585 w</td>
<td>573 w</td>
<td>590 w</td>
</tr>
</tbody>
</table>

| Characteristic bands in the IR spectra of the ligand H₂Lb and its samarium (III) complexes (\(\nu_{max}\) cm⁻¹) |
|---|---|---|---|
| \(\nu(C=O)\) | >1450 cm⁻¹ | \(\nu(C=O)\) of nitrate | >1450 cm⁻¹ |
| \(\nu(C-N)\) | >1600 cm⁻¹ | \(\nu(C-N)\) | >1600 cm⁻¹ |
| \(\nu(C-O)\) of nitrate | >1500 cm⁻¹ | \(\nu(C-O)\) of nitrate | >1500 cm⁻¹ |
| \(\nu(C-O)\) of nitrate | >1400 cm⁻¹ | \(\nu(C-O)\) of nitrate | >1400 cm⁻¹ |
| \(\nu(C-O)\) of nitrate | >1300 cm⁻¹ | \(\nu(C-O)\) of nitrate | >1300 cm⁻¹ |
| \(\nu(C-O)\) of nitrate | >1200 cm⁻¹ | \(\nu(C-O)\) of nitrate | >1200 cm⁻¹ |

H₂Lb 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 of \(\nu(NH) + \nu(CN)\) (amide II and amide III bands), which are shifted from the position where they are in the infrared spectrum of the free ligand H₂Lb.

Additional bands are observed in the IR spectra of the complexes with mixed ligands. These bands are associated with the stretching vibrations of \(\nu(C=O)\) and \(\nu(NH)\) groups of 1,10-phenanthroline (1495 cm⁻¹) and 2,2'-dipyridyl (1508-1511 cm⁻¹) \[15\]. The IR spectra of all the complexes show the absorption bands due to the stretching vibration of the azomethine group, \(\nu(C=N)\), attributed to the stretching vibration of the \(\nu(C=O)\) band newly formed.

Other characteristic bands in the IR spectrum of the ligand HLa are observed at 3417 cm⁻¹ and 3320 cm⁻¹, attributed to the stretching vibration of the \(\nu(NH)_{ase}\) and \(\nu(NH)\), respectively and at 1341 cm⁻¹, due to the stretching vibration of the \(\nu(C-N)\) 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 \(\nu(C=O)\) \(\nu(C=O)_{phenolic}\) 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, \(\nu_{\text{upper}}\), of about 200 cm⁻¹, in accordance with the participation of the nitrate as bidentate ligand \[25\].
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 $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ 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 attributed 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. 3. Proposed structural formulae for the complex compounds](image)

**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-
hydrazine (HL), 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 Sm³⁺ emission in the complex compounds are listed in Table 4. The emission is due to the transitions from the resonant ⁴G₅/₂ level to various ⁴H levels [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 ⁴G₅/₂ → ⁴H⁷/₂ transition of Sm³⁺ 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 poor 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 acetylhydrazine (HL), 2-hydroxy-1-naphthaldehyde acetylhydrazone (HL), 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 hydrazine-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.

References


Fig. 5. Emission spectrum of [Sm(L')-o-phen](NO₃)₃ (excitation at 350 nm)