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**NEW COMPLEXES OF Sm(III), Eu(III), Tb(III), Ho(III), Dy(III),  
AND Tm(III) WITH N-HYDROXYPHTHALIMIDE**

BY

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**Abstract.** The present work describes the synthesis and characterization of several lanthanide complexes with N-hydroxyphthalimide (HL). The main objectives of the present study aimed at finding the mechanisms of radiative transition taking place in the luminescence centers consisting in the trivalent cations of the considered lanthanides; establishing the combination ratios between lanthanide cations, such as Sm(III), Eu(III), Tb(III), Dy(III), Ho(III), Tm(III), and N-hydroxyphthalimide ligand; physical-chemical characterization of the obtained complexes; establishing the molecular structure of the obtained complexes; investigation of photoluminescence properties of the prepared complexes. The obtained lanthanide complexes were characterized by elemental chemical analysis, FTIR, TGA, EDX, SEM and fluorescence spectroscopy. Data show the formation of lanthanide complexes with N-hydroxyphthalimide ligand in 1:3 ratio.

**Key words:** lanthanide complexes; N-hydroxyphthalimide ligand; luminescence.

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## 1. Introduction

The identification of proper ligands able to complex lanthanides as central atoms in order to enhance the outstanding features of lanthanides has been of high interest due to their promising applications as optical materials or as tracing agents in biological or medical analyses (Armelaio *et al.*, 2010; Cotton, 2006). Various ligands have been investigated in order to obtain lanthanide complexes and further composites with photoluminescent properties (Lattuada *et al.*, 2011; Zhang *et al.*, 2015).

In the last decade a significant attention was given to the lanthanide complexes both from the perspectives of studying new lanthanide compounds but mainly due to their high application potential. The magnetic and optical properties of the lanthanide complexes are extensively studied for their potential applications ranging from medical imaging to optoelectronic devices or molecular magnetic compounds.  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+}$  or  $\text{Tm}^{3+}$  complexes with their radiative transitions located in the visible spectrum are also extensively studied for their applications in next generation optoelectronic devices like OLED, energy efficient light sources or even in medical investigation techniques (Ahmed & Iftikhan, 2014, Ilmi & Iftikhan, 2015; Kuriki *et al.*, 2002).

During the last years a growing interest was observed for the complex combinations of  $\text{Pr}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  which presents radiative transitions in the near infrared spectrum (NIR) for the high application potential in telecommunication and upconversion devices or medical diagnose (Hagan & Zuchner, 2011; Rabanal *et al.*, 2014; Zou *et al.*, 2011).

In our prior work, N-hydroxysuccinimide (Stan *et al.*, 2012) and maleimide (Stan *et al.*, 2014) ligands were tested using various lanthanide elements as central cation, a special attention being given to the photoluminescent properties which strongly depends on the efficient transfer of the excitation energy from the coordination site to the central lanthanide cation.

In the present work  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$  complexes with N-hydroxyphtalimide ligand are prepared and studied. A special attention is given to their photoluminescence properties of the obtained complexes. Also, the molecular structure of the obtained complexes is established.

## 2. Experimental

### 2.1. Materials

Chemicals used in the preparation of lanthanide complexes were of analytical grade or of high purity. N-hydroxyphtalimide (98%) was purchased from Merk Chemicals. Samarium chloride hexahydrate (99.99%), Europium chloride hexahydrate (99.9%), Terbium chloride hexahydrate (99.9%), Thulium chloride

hexahydrate (99.99%) and Dysprosium chloride hexahydrate (99.99%) were purchased from Alfa–Aesar. For the preparation of the lanthanide complexes and washing operations, absolute ethanol and high purity Milli-Q water were also used.

## 2.2. Preparation of N-Hydroxyphthalimide Complexes

Lanthanide complexes were prepared by classical methods as those described in literature (Armelaio *et al.*, 2010). However, these methods were adapted to the specific reagents, several stages were involved as follows: 1. reacting under stirring at a certain temperature the ligands and lanthanide chlorides in the suitable solvent; 2. solvent removal; 3. the obtained complexes were purified and dried to constant weight. In a first step, aqueous solutions of lanthanide chlorides were prepared for each studied complex by dissolving an amount of 10 mmol chloride in 10 mL of ultrapure water. To obtain complexes in the combination ratio of 1:3 and to avoid experimental errors, coordination and bound water of lanthanide chlorides was also taken into account for proper preparation of solutions. 10 mmol of N-hydroxyphthalimide ligand was dissolved in a water-ethanol mixture (1:2). For complete and fast dissolution of ligand, the mixture was heated up to 40–45°C under moderate stirring and sonication for approx. 10 min in an ultrasonic bath. The preparation of each studied complex was carried out by mixing the corresponding solutions of lanthanide chlorides with those of the ligand at a temperature of approx. 35°C, under continuous stirring, for 90 min. The chemical reaction that take place during the formation of the complexes are as follows:



where: Ln = Sm<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Tm<sup>3+</sup>.

In order to obtain high reaction yields, solutions of complexes were left in this state for about 48 h before any further operations to take place. Removal of the excess solvent was performed under vacuum using a Büchi Rotavap system at a temperature of approx. 40°C. Complexes obtained in solid state were subjected to purification operations by repeated washing with ultrapure water followed by drying. In order to obtain complexes with a proper degree of crystallinity, the removal of water is done through atmospheric evaporation. The final drying of the prepared complexes was performed in a vacuum oven at 40–45°C for approximately 72 h, till constant weight. The obtained complexes are slightly hygroscopic so they should be placed in sealed glass containers.

## 3. Results and Discussions

### 3.1. Characterization

First, the prepared lanthanide complexes were investigated by chemical elemental analysis. *Elemental chemical analysis* was performed on thermo

Fisher Scientific Flash EA- 1112 CHNS/O equipment provided with Eager 300 software. Samples of ligand and lanthanide complexes respectively were also analyzed by *IR spectroscopy* in the range of 400-4000  $\text{cm}^{-1}$  by means of FTIR 660 Plus spectrometer, according to KBr pellet method. *Thermal analysis* was performed using a Mettler Toledo TGA-SDTA851e equipment under  $\text{N}_2$  atmosphere at a flow rate of 20 mL/min, a heating speed of  $10^\circ/\text{min}$ , between 5-1000 $^\circ\text{C}$  and a sample weight range between 2.3-5.14 mg. The balance accuracy was set to 100,  $\beta$  heating rate was of  $10^\circ\text{C}/\text{min}$ ; the recording sensibility was of 500  $\mu\text{V}$  for T and TG modes, and 2.5 mV for DTG mode. The structural investigation of the newly obtained lanthanide complexes was performed by X-Ray Powder Diffraction. *The XRD* patterns were recorded in the  $2\theta$  range of  $20\text{-}60^\circ$  using Panalytical X'PertPro diffractometer provided with Cu-K $\alpha$  radiation source ( $\lambda = 0.15406$  nm) operated with the Panalytical X'Pert High Score Plus software. *SEM micrographs* were obtained by means of Hitachi TM-3000 operated at 15 KV accelerating voltage. Emission and excitation fluorescence spectra were recorded by Perking-Elmer LS-50B spectrometer. The excitations and emission slits were set at medium values (ex. slit = 10 and em. slit = 10) for each complex.

**Table 1**  
*Data Provided by Elemental Analysis in Case of Some Prepared Complexes*

| Complex  | Element      |             |              |             |              |             |              |             |
|--|--------------|-------------|--------------|-------------|--------------|-------------|--------------|-------------|
|  | C, [%]       |             | H, [%]       |             | N, [%]       |             | O, [%]       |             |
|  | <i>Pred.</i> | <i>Exp.</i> | <i>Pred.</i> | <i>Exp.</i> | <i>Pred.</i> | <i>Exp.</i> | <i>Pred.</i> | <i>Exp.</i> |
| [SmL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ](1) | 41.72        | 42.22       | 2.61         | 2.88        | 6.08         | 5.87        | 27.81        | 28.03       |
| [EuL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ](2) | 41.62        | 42.31       | 2.60         | 2.91        | 6.07         | 6.25        | 27.75        | 28.21       |
| [TbL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ](3) | 41.20        | 41.08       | 2.58         | 3.07        | 6.01         | 6.31        | 27.47        | 28.09       |
| [DyL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ](4) | 41.00        | 41.37       | 2.56         | 2.77        | 5.98         | 6.30        | 27.33        | 27.70       |
| [HoL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ](5) | 40.86        | 41.09       | 2.55         | 2.81        | 5.96         | 6.19        | 27.24        | 27.73       |
| [TmL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ](6) | 40.62        | 41.21       | 2.54         | 2.73        | 5.92         | 5.66        | 27.08        | 27.51       |

Data obtained by elemental analysis support the 1:3 metal to ligand ratio, which is in a good agreement with theoretically predicted results. The higher values determined experimentally for oxygen and hydrogen quantities are most probable due to the constitution, unbounded water present in the analyzed samples.

### 3.2. Chemical Analysis Through Energy Dispersive X-Ray Spectroscopy (EDX)

The chemical composition of the prepared complexes was also determined by energy dispersive X-Ray spectroscopy (EDX). The experimental results were compared with data obtained through theoretical calculations.

Table 2 presents the recorded data in case of several prepared complexes. A good agreement between recorded experimental data and predicted values can be noticed. Therefore, both investigation methods EDX and elemental analyses provided good results agreement between calculated and experimental values and confirm the 1:3 metal to ligand ratio for all the prepared complexes.

**Table 2**  
*Results Recorded by EDX Spectroscopy*

| Complex   | Element      |             |              |             |                 |             |              |             |
|---|--------------|-------------|--------------|-------------|-----------------|-------------|--------------|-------------|
|   | C, [%]       |             | N, [%]       |             | Lanthanide, [%] |             | O, [%]       |             |
|   | <i>Pred.</i> | <i>Exp.</i> | <i>Pred.</i> | <i>Exp.</i> | <i>Pred.</i>    | <i>Exp.</i> | <i>Pred.</i> | <i>Exp.</i> |
| [EuL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] | 41.62        | 42.17       | 6.07         | 6.40        | 21.96           | 21.40       | 27.75        | 30.03       |
| [TbL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] | 41.20        | 41.66       | 6.01         | 5.41        | 22.74           | 22.51       | 27.47        | 30.42       |
| [DyL <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] | 41.00        | 41.72       | 5.98         | 6.23        | 23.13           | 22.73       | 27.33        | 29.32       |

### 3.3. Thermal Analysis

Based on the recorded derivatograms, the thermal behavior of free ligand and prepared complexes were evaluated. Fig. 1 shows the recorded derivatograms for the ligand and also for one of the prepared complexes.

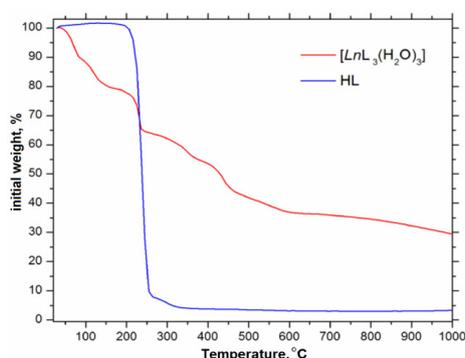


Fig. 1 – Recorded derivatograms for HL and [LnL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].

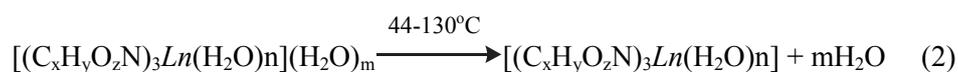
As may be noticed there is a significant difference between the thermal behavior of the ligand in comparison with that of the lanthanide complex. Thus, in case of the prepared complexes six decomposition stages were recorded while only two stages were recorded in case of the free ligand. The structural integrity of the free ligand is maintained until 175-210°C, at higher temperatures the ligand undergoing a fast decomposition. By complexation, all the newly prepared complexes gained a significantly higher thermal stability compared with that of the free ligand. Table 3 presents the results recorded by thermal analysis.

**Table 3**  
*Decomposition Stages for the Prepared Lanthanide Complexes*

| Complex | Initial Mass [mg] | Stage I          |          | Stage II         |          | Stage III        |          | Stage IV         |          | Stage V          |          | Stage VI         |          | Final mass [mg] |
|---------|-------------------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|-----------------|
|         |                   | Temp. range [°C] | mass [%] |                 |
| (1)     | 3.073             | 51.3<br>114.1    | 8.71     | 114.1<br>167.4   | 10.26    | 167.4<br>281.1   | 15.59    | 281.1<br>413.2   | 9.85     | 413.2<br>537.2   | 16.06    | 537.2<br>998.5   | 9.94     | 1.122           |
| (2)     | 3.753             | 58.4<br>109.3    | 8.14     | 109.3<br>157.9   | 11.46    | 157.9<br>228.7   | 16.62    | 228.7<br>401.7   | 9.21     | 401.7<br>556.9   | 15.58    | 556.9<br>998.5   | 10.70    | 1.088           |
| (3)     | 3.12              | 46.8<br>110.6    | 6.00     | 110.6<br>160.0   | 9.35     | 160.0<br>326.9   | 18.86    | 326.9<br>421.7   | 8.59     | 421.7<br>599.0   | 16.48    | 599.0<br>998.5   | 9.81     | 0.973           |
| (4)     | 4.805             | 54.5<br>113.9    | 4.98     | 113.9<br>186.1   | 9.32     | 186.1<br>254.1   | 15.47    | 254.1<br>440.8   | 16.19    | 440.7<br>565.4   | 13.16    | 565.4<br>998.5   | 8.96     | 1.523           |
| (5)     | 4.629             | 49.0<br>107.1    | 8.78     | 107.1<br>153.1   | 11.65    | 153.1<br>304.1   | 14.87    | 304.1<br>452.6   | 18.35    | 452.6<br>595.1   | 8.26     | 595.1<br>998.5   | 7.48     | 1.432           |
| (6)     | 3.561             | 55.1<br>115.3    | 6.61     | 115.3<br>141.8   | 10.09    | 141.8<br>279.1   | 13.21    | 279.1<br>406.1   | 17.52    | 406.1<br>543.1   | 11.31    | 543.1<br>998.5   | 8.34     | 1.178           |

For all the prepared complexes, the thermal decomposition starts with the elimination of various types of water (crystallization, structure, coordinative) in the first and second stages followed by the initiation of the complex destructure that further leads to unstable intermediary compounds. In the upper stages stable compounds are achieved, most probably lanthanide oxides. Therefore, the first and second decomposition stages are important to evaluate the number of water molecules bonded in the first coordination sphere. Also the elimination of the crystallization water is important due to the major influence in maintaining the structural integrity over the photoluminescent properties. Thus, the maximal temperature the complex can be safely expose to thermal attack might be determined. All the prepared complexes retain water when expose to ambient conditions. This weak bonded water starts to leave the system in the 50-70°C range, this process ending just above 100°C. This type of water is highlighted in IR spectra around 3500 cm<sup>-1</sup>.

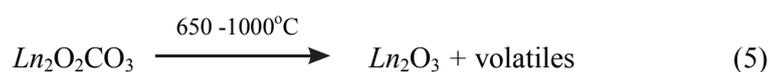
The weak bonded water leaving the system in the first decomposition stage is described by the following equations:



Strongly bonded coordination water leaves the system at higher temperatures, in the second stage:



In the upper decomposition stages, besides the volatile products, intermediate decomposition products like oxocarbonates ( $Ln_2O_2CO_3$ ) might form, which further decay to more stable compounds such as stable lanthanide oxides  $Ln_2O_3$ .



The formation of  $Ln_2O_3$  is confirmed by the study of Zhang *et al.* (2006) over some  $Dy^{3+}$  complexes by FT-IR analysis of the residue resulted from their thermal decomposition in the same temperature range used in this work. A similar conclusion regarding the final decomposition product was highlighted by Marques *et al.* (2003) in their study regarding some  $Dy^{3+}$ ,  $Ho^{3+}$ ,  $Tm^{3+}$  complexes by the data provided through P-XRD investigation.

### 3.4. IR Spectroscopy

Investigation of the recorded IR spectra revealed the interaction occurred between the N-hydroxyphthalimide ligand (HL) and the trivalent lanthanide cations. Fig. 2 presents the recorded spectra for the free ligand and some prepared complexes, for each case the significant absorption peaks were also included. The absorption bands were identified from the recorded spectrum of the free ligand for both categories of groups (involved and uninvolved in the complexes formation). The obtained results are in accordance with those presented by Krishnakumar *et al.* in their study regarding the structure of N-hydroxyphthalimide performed by FT-IR and DFT techniques (Krishnakumar *et al.*, 2009).

Table 4 presents several characteristic bond vibrations for the structure of the ligand which are of interest in the study of complexes formation. The spectral particularities due the existence of the aromatic ring are located in

3100-3000  $\text{cm}^{-1}$  range as low intensity multiple absorption bands specific for aromatic C-H bonds. C-C bonds are located in the 1860-1380  $\text{cm}^{-1}$  range, specific for skeletal vibrations. The O-H group attached at the nitrogen atom was identified at 3478  $\text{cm}^{-1}$ , this region being specific to the stretching vibration of this bond.

**Table 4**  
*Specific Vibrations of Bonds or Groups of N-Hydroxyphthalimide Ligand*

| Functional group/bond | Recorded peak<br>[ $\text{cm}^{-1}$ ] |
|-----------------------|---------------------------------------|
| O-H stretch           | 3478                                  |
| C-H stretch           | 3136                                  |
| C-C stretch           | 1856, 1607, 1383                      |
| C=O sim. Stretch      | 1788                                  |
| C=O asim. Stretch     | 1711                                  |
| C-H deformation       | 1607                                  |
| N-O stretch           | 1462, 473                             |
| C-H deformation       | 1341                                  |
| C-N stretch           | 1188, 519                             |
| N-OH deformation      | 1134                                  |
| C-H bend              | 972                                   |
| C=O deformation       | 878                                   |
| N-O twisting          | 642                                   |

Fig. 2 presents the spectra recorded for some of lanthanide complexes prepared with N-hydroxyphthalimide. Similar modifications are visible also for these complexes like the stretching of the carbonyl groups with the displacement of their characteristic wavenumber in the lower regions of the spectra, the initial peak appears split in two distinct peaks as a result of coordinative bond established by one of the two carbonyl groups which are present in the ligand molecule.

A major indication in favor of the formation of the complexes is the appearance of a absorption peak located in 437-429  $\text{cm}^{-1}$  range, which is specific to the covalent bonds established between lanthanide cation and the oxygen atom from the -OH group. Same correlation was noted between the specific vibration wavenumber of this bond and the placement of the cation in lanthanide series. Thus, with increasing of the atomic number the vibration wavelength of the Ln-O bond increases.

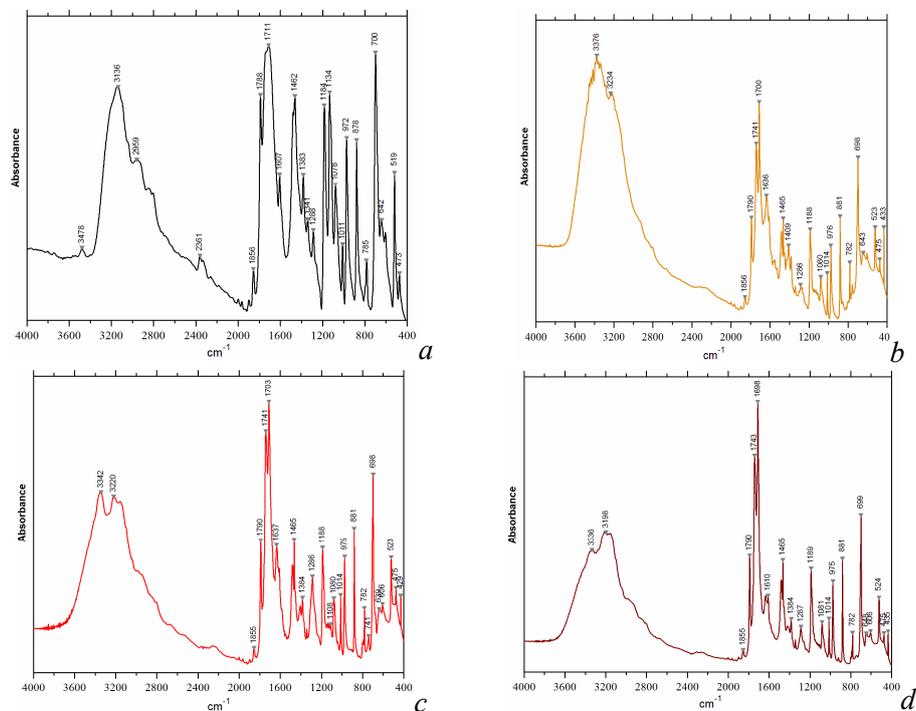


Fig. 2 – FT-IR spectra of N-hydroxyphthalimide (a) and lanthanide complexes with: (b)  $Dy^{3+}$ ; (c)  $Eu^{3+}$ ; (d)  $Ho^{3+}$ .

In Table 5 are presented some vibrations specific to bonds and groups recorded in the complexes prepared with the N-hydroxyphthalimide ligand as in the spectra of lanthanide complexes.

**Table 5**

*Specific Bonds and Groups Vibrations ( $cm^{-1}$ ) Recorded in the  $[LnL_3(H_2O)_3]$  Complexes*

| Functional group/bond                         | (1)       | (2)       | (3)       | (4)       | (5)       | (6)       |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| H <sub>2</sub> O crystalline (asim. Stretch.) | 3215      | 3220      | 3215      | 3234      | 3196      | 3231      |
| C-C stretch                                   | 1855/1384 | 1855/1384 | 1855/1384 | 1856/-    | 1856/1384 | 1856/1384 |
| C-H bend                                      | 975       | 975       | 975       | 976       | 975       | 976       |
| C=O sim. Stretch                              | 1790      | 1790      | 1790      | 1790      | 1790      | 1791      |
| C=O asim. Stretch                             | 1734/1707 | 1741/1703 | 1742/1698 | 1741/1700 | 1743/1698 | 1742/1699 |
| C=O deformation                               | 881       | 881       | 881       | 881       | 881       | 881       |
| N-O stretch                                   | 1465/475  | 1465/475  | 1465/475  | 1465/475  | 1465/475  | 1482/475  |
| N-O bend                                      | 640       | 639       | 641       | 643       | 648       | 638       |
| Ln-O  | 429       | 429       | 432       | 433       | 435       | 437       |

Cumulating the information provided by FTIR investigation it is concluded that the ligand have a bidentate behavior and the water in present in the first coordination sphere, therefore sustaining the proposed structure of the prepared complexes.

### 3.5. Powder X-Ray Diffraction (P-XRD)

The P-XRD investigation revealed the crystalline form of all prepared complexes with triclinic geometries in case of all complexes prepared with N-hydroxyphthalimide ligand whereas the crystalline form of the free ligand is orthorhombic. Table 6 presents the experimental results recorded for the free ligand and lanthanide complexes.

**Table 6**  
*Experimental Results Found for the Free Ligand and Lanthanide Complexes*

| Experimental unit cell parameters found for the ligands used in preparation of the lanthanide complexes |                 |                |                 |          |          |          |                             |                           |
|---|-----------------|----------------|-----------------|----------|----------|----------|-----------------------------|---------------------------|
| Ligand  | $\alpha$<br>[°] | $\beta$<br>[°] | $\gamma$<br>[°] | A<br>[Å] | b<br>[Å] | c<br>[Å] | Volume<br>[Å <sup>3</sup> ] | Crystallization<br>system |
| HL  | 90              | 90             | 90              | 14.6     | 9.15     | 6.88     | 919.86                      | Orthorhombic              |
| [Eu(L) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]   | 113.45          | 43.25          | 102.3           | 10.5     | 11.45    | 17.14    | 1287.49                     | Triclinic                 |
| [Tb(L) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]   | 44.78           | 86.83          | 92.71           | 6.49     | 11.27    | 21.08    | 1089.7                      | Triclinic                 |
| [Ho(L) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]   | 83.87           | 44.46          | 79.53           | 8.30     | 10.09    | 15.73    | 937.13                      | Triclinic                 |
| [Sm(L) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]   | 109.57          | 44.21          | 101.15          | 11.50    | 9.61     | 14.47    | 1317.8                      | Triclinic                 |
| [Dy(L) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]   | 84.23           | 66.46          | 106.1           | 15.66    | 9.20     | 8.69     | 1164.22                     | Triclinic                 |
| [Tm(L) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]   | 100.96          | 50.26          | 132.57          | 11.35    | 11.06    | 15.86    | 1019.44                     | Triclinic                 |

### 3.6. Scanning Electron Microscopy (SEM)

In case of prepared lanthanide complexes, SEM investigation sought to highlight both the crystalline structure and the possible morpho-structural differences among them. SEM images support the primary conclusions that the investigated complexes have a crystalline structure. The crystal structure of the complexes is particularly useful, as the photoluminescence properties of some of the prepared complexes occur only in solid phase and depend essentially on the existence of crystalline structures. The structural differences between complexes of lanthanides derived with N-hydroxyphthalimide ligand are minimal, which is explained by the similar behavior of lanthanides.

Fig. 4 shows the images obtained by SEM analyses in the case of complexes prepared with H-hydroxyphthalimide ligand where an elongated structure of the crystallites is observed. This preferential direction growth of crystallites is most likely due to the composition of the ligand molecule, which contains one aromatic ring. Dimensional characteristics and shape of crystallites

of the prepared complexes appear to have an insignificant role in differentiating photoluminescence properties of complexes. This observation is supported by the results of the investigation of complexes by spectrofluorometric techniques where it was noticed the presence or absence of these properties at complexes with similar geometry of the crystallites.

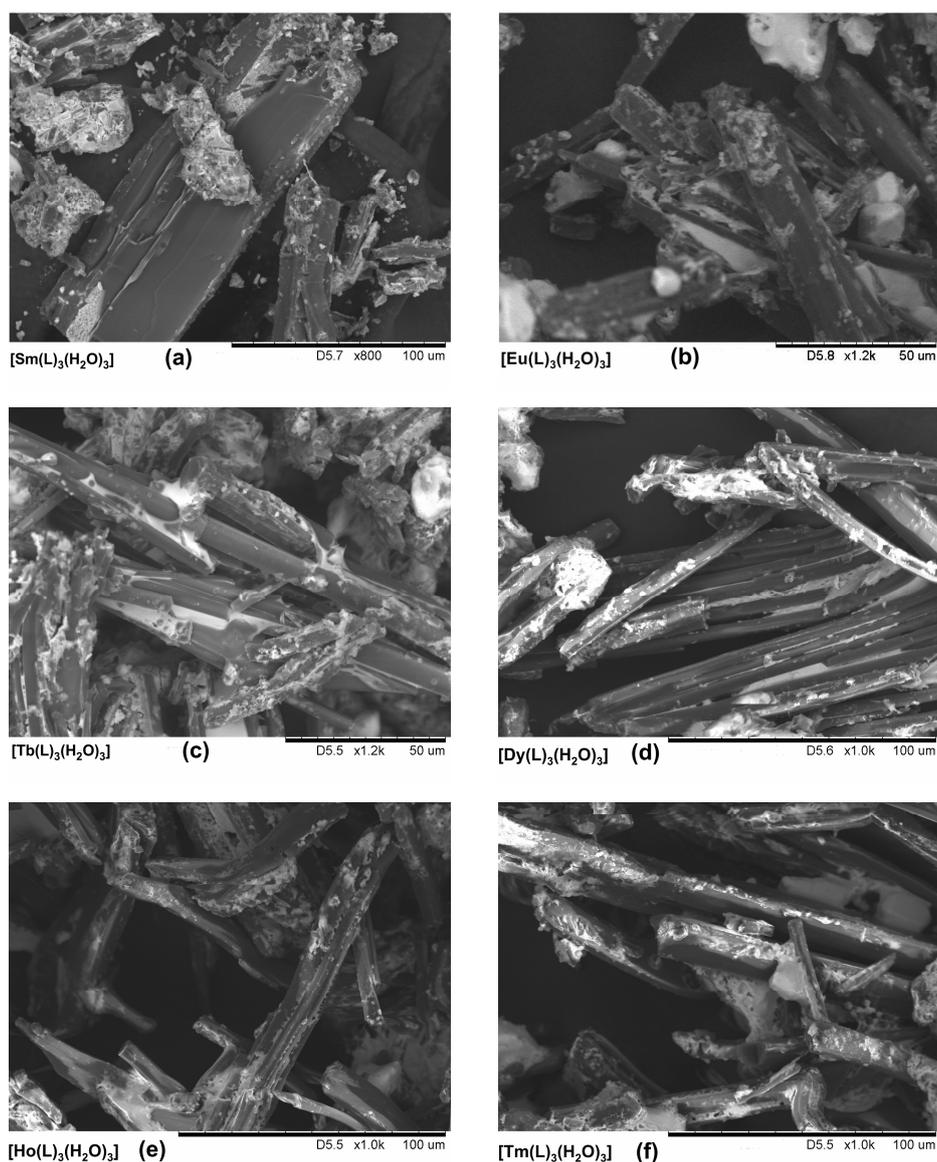


Fig. 3 – SEM images of lanthanide complexes prepared with N-hydroxyphthalimide: (a)  $\text{Sm}^{3+}$ ; (b)  $\text{Eu}^{3+}$ ; (c)  $\text{Tb}^{3+}$ ; (d)  $\text{Dy}^{3+}$ ; (e)  $\text{Ho}^{3+}$ ; (f)  $\text{Tm}^{3+}$ .

### 3.7. Fluorescence Analysis

In case of several prepared complexes the recorded excitation/emission spectra fluorescence revealed photoluminescent properties. In case of the prepared  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  complexes there were no evidence of any characteristic emission peaks. In their case, the emission spectra were recorded in the 300-400 nm excitation range. There were also investigated the potential anti-Stokes phonon assisted radiative transitions (Ronda, 2006; Auzel, 2004), through excitation with radiation located in NIR range (between 670 – 800 nm), because thulium ions allow obtaining of an emission peak centered at 476 nm due  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  transition through excitation of the  $^3\text{F}_{3,2}$  and  $^3\text{H}_4$  levels at 690 and 800 nm wavelengths (Su *et al.*, 2006).

The  $\text{Sm}^{3+}$  complex has no emission peaks, its emission spectrum (not shown here) being practically isolar. In case of  $[\text{Dy}(\text{L})_3(\text{H}_2\text{O})_3]$  complex (Fig. 4) the recorded excitation/emission spectra presents low intensity peaks located at 494 and 527 nm which are not specific to the lanthanide emissive center.

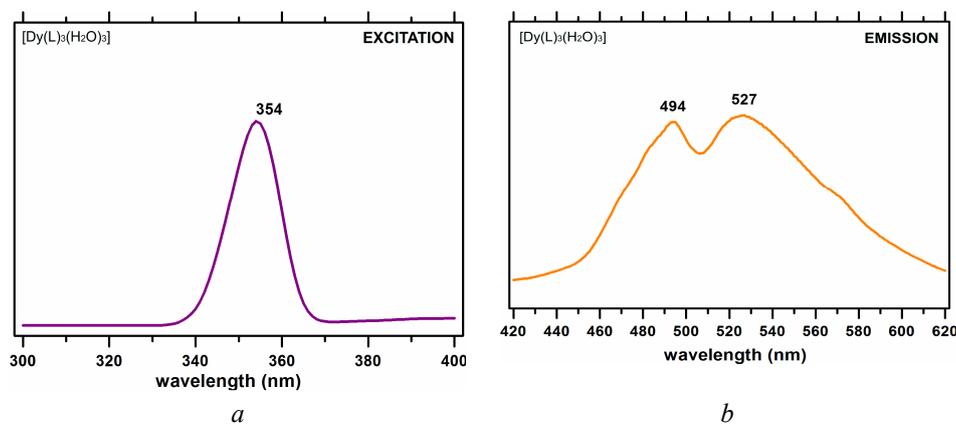


Fig. 4 – Excitation (a) and emission (b) spectra recorded for  $[\text{DyL}_3(\text{H}_2\text{O})_3]$ .

An interesting situation was observed in case of  $[\text{Eu}(\text{L})_3(\text{H}_2\text{O})_3]$  complex where besides the peaks at 493 and 521 nm that are due to radiative transitions occurred in the ligand (as recorded in case of  $[\text{DyL}_3(\text{H}_2\text{O})_3]$ ) also it can be observed specific  $\text{Eu}^{3+}$  peaks at 592 and 613 nm that are due to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  radiative transitions. In spite of the presence of these peaks, none of their emission could be visually detected.

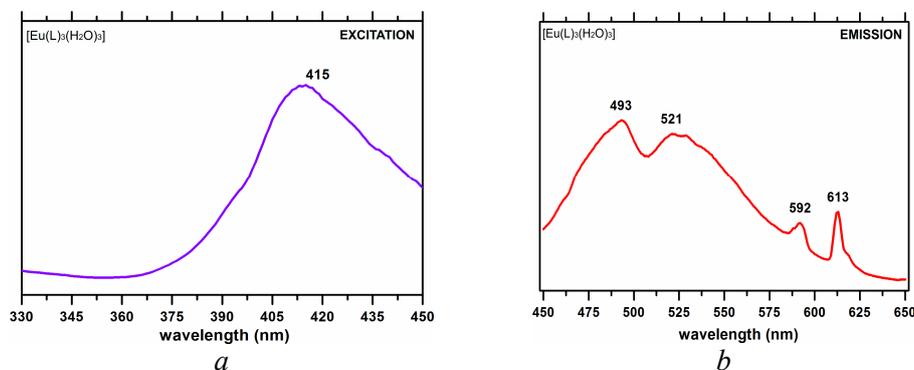


Fig. 5 – Excitation (a) and emission (b) spectra recorded for  $[\text{EuL}_3(\text{H}_2\text{O})_3]$ .

The most favorable situation was encountered in case of the complex prepared with  $\text{Tb}^{3+}$ , where characteristic emission peaks of  $\text{Tb}^{3+}$  cation were recorded. This is due to the low sensitivity of the  $\text{Tb}^{3+}$  radiative transitions to the surrounding crystalline field symmetry.

In case of  $[\text{Tb}(\text{L})_3(\text{H}_2\text{O})_3]$  complex the radiative transitions occurred in the ligand (as mentioned above) are not present either because their low intensity or being masked by the radiative peaks occurred in the central lanthanide cation. The excitation spectrum of this complex is presented in Fig. 6 (a) which reveals peaks centered at 393 nm.

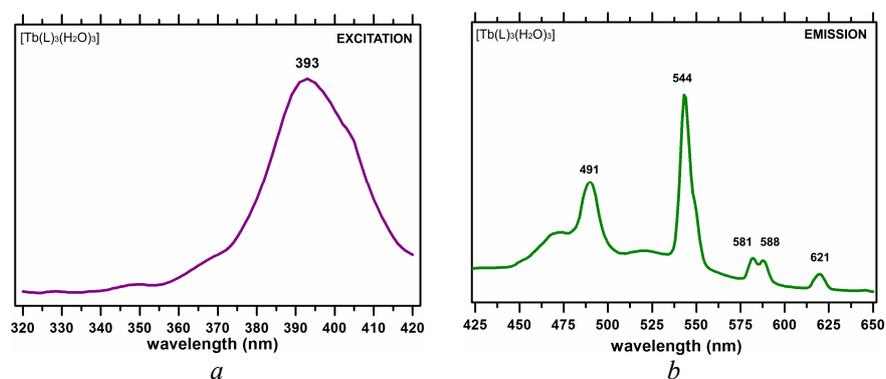


Fig. 6 – Excitation (a) and emission (b) spectra recorded for  $[\text{TbL}_3(\text{H}_2\text{O})_3]$ .

#### 4. Conclusion

The paper reports six new prepared lanthanide complexes with N-hydroxyphthalimide. In all cases the coordination number of the central cation is 9. A general molecular structure of the obtained lanthanide complexes was suggested based on elemental analysis, thermal analysis, FTIR analysis. Using XRD it was found that the crystallization is triclinic for all prepared lanthanide

complexes. Their photoluminescent properties were analyzed by fluorescence spectroscopy.  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes with N-Hydroxyphthalimide showed photoluminescent properties.

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NOI COMPLECȘI AI Sm(III), Eu(III), Tb(III), Ho(III), Dy(III)  
ȘI Tm(III) CU N-HIDROXIFTALIMIDA

(Rezumat)

Lucrarea de față prezintă sinteza și caracterizarea unor noi complecși ai metalelor tranziționale din blocul *f* cu N-hidroxiftalimida. S-au obținut astfel un număr de 6 complecși la un raport de combinare M/L de 1:3, care au fost investigați prin analiza chimică elementală, EDX, spectroscopia FT-IR, analiza termogravimetrică, spectroscopia de raze X, spectroscopia de fluorescență. Au fost remarcate proprietăți de fotoluminescență pentru complecșii preparați cu Eu<sup>3+</sup> și Tb<sup>3+</sup>.