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New Gd(III) complexes based on Succinimide, N- hydroxysuccinimide and N- hydroxyphtalimide with possible applications in optoelectronics and medical imaging

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This paper reports the synthesis and characterization of three new Gd(III) complexes with Succinimide, N-hydroxysuccinimide and N hydroxyphtalimide. Several investigation techniques were used for characterization of the new prepared complexes, as follows: Elemental chemical analysis, FT-IR, TG / DTA analysis, Powder X-ray diffraction, SEM and fluorescence spectroscopy. Data obtained through analysis revealed the formation of the Gd complexes with above mentioned ligands at 1:3, metal to ligand (M:L) molar ratio. The PL spectra revealed the fluorescent emission of the Gd - N-hydroxysuccinimide complex in the blue region of the visible spectrum, the peak emission being recorded at 423 nm which makes it particularly interesting for applications in optoelectronics and medical imaging.

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1. Introduction

In order to expand the studies over lanthanide complexes Succinimide [1], N-hydroxysuccinimide [2,3], N- hydroxyphtalimide [4,5] ligands were tested using Gd (III) as central atom. In the last years lanthanide complexes gained much attention not only for expanding the knowledge over their chemistry but, mainly because of their high application potential. Extensive research over Eu, Tb, Sm, Er, Dy or Yb complexes are in progress targeting various applications, among them, in cutting edge optoelectronic devices like OLED displays [6], NIR up conversion devices [7] or as assays in medical imaging. Gadolinium complexes are widely used as contrast agents in Magnetic Resonance Imaging (MRI) [8]. Also remarkable phosphorescence properties were observed in some gadolinium chelates [9].

In the present work a special attention was given on the photoluminescence (PL) since this property is highly dependent by the efficient energy transfer from the coordination site to the central lanthanide ion. An efficient radiative transition in the lanthanide ion can be triggered when its excited states are populated and the accompanying non-radiative deactivation processes are minimized [10]. To meet these conditions, efficient energy transfer from the surroundings is required, therefore the sensitization role of the coordination site is very important. The overall quantum yield of the radiative transition is additionally influenced by the efficient harvesting of the excitation energy by the coordination site [11,12].

2. Experimental

All chemicals used for Gd(III) complexes preparation were analytical grade or highest purity available. High purity Milli-Q water was used in preparation process. Succinimide (98%), N-hydroxysuccinimide (98%), N-hydroxyphtalimide (98%) were purchased from Merck Chemicals and Gadolinium(III) chloride hexahydrate (99,99%) was purchased from Sigma-Aldrich.

2.1. Preparation of the Gd(III) complexes

As stated above, three ligands were used in the complexation of the Gd (III) cation from $GdCl_3 \cdot 6H_2O$: Succinimide noted as HL^1, N-hydroxysuccinimide noted as HL^2, N-hydroxyphtalimide noted as HL^3.

From the reaction between succinimide and Gd(III), an aqueous solution of the complex is obtained at low acid pH, which is stable at room temperature.

First, 100 mL aqueous solutions of $GdCl_3 \cdot 6H_2O$ (0,1M) and 100 mL succinimide (0,3M) are prepared by dissolving the required quantities in high purity Milli-Q water. Preparation of the complex at molar ratio 1:3, central atom: ligand, was carried out by mixing the two prepared solutions and stirring for about 90 minutes, at room temperature. After evaporation at room temperature of the excess water, the complex is obtained in a white solid crystallized form. Then it was kept in an oven for drying, under vacuum, at 60^0C till constant weight. A similar procedure was used in the case of the other two complexes. The prepared complexes were also obtained in a white solid crystallized form. The reaction yield was between 99.3- 99.5 %, in every case.

2.2. Characterization

Samples of the prepared Gd(III) complexes were first investigated through chemical elemental analysis.

The IR absorption spectra of the ligands and respectively of the complexed compounds were recorded in the range of 400 - 4000 cm^{-1}, using the FT IR 660 Plus spectrometer, according to KBr pellet method.

The thermal stability of the prepared complexes was studied using a Q-1500D (MOM-Budapest) by simultaneous registering of the three curves (TG = weight loss, DTG = weight loss derivate and T = temperature). The sample was heated until 1000°C, the balance sensibility was 100; the heating rate β =10 °C/min.; the recording sensibility was 500 μV for mode T, 500 μV for mode TG and 2.5mV for mode DTG[13]. Fresh calcinated Al_2O_3 at 1200 °C was used as reference. Calibration of the derivatograph was made with CaC_2O_4. The samples weight range was 3.88-5.14 mg. The thermal decomposition included four phases at temperatures ranging from 60-65 °C to 1000 °C.

X-ray powder diffraction was used for the structural investigation of the prepared gadolinium complexes. The XRD patterns were recorded in the 20 - 60º 2θ range on a Panalytical X'PertPro diffractometer provided with a Cu-Kα radiation source (λ = 0,154060 nm). Unit cell parameters were further refined with the help of Panalytical X'Pert High Score Plus software being alternatively investigated through four indexing methods (Dicvol, McMaille, lto and Treor), only the highest values of figures of merit (FOM) being retained [14,15].

The SEM micrographs were recorded with a Hitachi TM-3000, working at 15 KV accelerating voltage.

The fluorescent emission and excitation spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer provided with the powder analysis kit. For each complex, the emission spectra were recorded in the same conditions, with the excitation and emissions slits initially adjusted at medium values (ex. slit:10, em. slit:10).

3. Results

From the experimental data obtained from elemental chemical analysis (Table 1) the following formulas are proposed: $[GdHL^1{}_3(H_2O)_3]Cl_3$, $[GdL^2{}_3(H_2O)_3]$, $[GdL^3{}_3(H_2O)_3]$.

Table 1. The elemental chemical analysis data of the prepared Gd(III) complexes.

The molecular formula of the studied complexes	The experimental values (%)				The calculated values (%)				
	Gd	C	H	N	Gd	C	H	N	Color
$[GdHL^1{}_3(H_2O)_3]Cl_3$	25,58	23,42	3,41	6,83	25,15	23,78	3,65	6,41	white
$[GdL^2{}_3(H_2O)_3]$	28,42	26,03	3,25	7,59	28,62	26,25	3,48	7,28	white
$[GdL^3{}_3(H_2O)_3]$	22,55	41,30	2,58	6,02	22,35	41,03	2,69	6,18	white

In Table 2 are presented the characteristic IR absorption bands significant for the formation of the studied complexes.

Table 2. Characteristic IR absorption bands of the studied complexes.

Gd(III)Complexes	**γ H_2O**	**γ C=O**	**γ Gd-O**	**γ Gd-N**
$[GdHL^1{}_3(H_2O)_3]Cl_3$	3420-3400	1680	420	650
$[GdL^2{}_3(H_2O)_3]$	3450-3500	1670	430	-
$[GdL^3{}_3(H_2O)_3]$	3400-3450	1675	450	-

Based on the derivatograms of the studied complexes, the characteristic temperature values of the thermal decomposition stages were established (Table 3).

Table 3. The thermal decomposition stages of the Gd(III) complexes.

Gd(III)Complexes	**The temperature of the beginning and ending of thermal decomposition (^{0}C)**	**Stage temperature range of the thermal decomposition, (^{0}C)**			
		Stage I	**Stage II**	**Stage III**	**Stage IV**
[GdHL$^1{}_3$(H$_2$O)$_3$]Cl$_3$	60-1000	60-163	163-486	486-847	847-1000
[GdL$^2{}_3$(H$_2$O)$_3$]	63-1000	63-170	170-490	490-850	850-1000
[GdL$^3{}_3$(H$_2$O)$_3$]	65-1000	65-175	175-503	503- 865	865- 1000

The obtained diffractograms for each of the three Gd complexes are presented in Fig. 1.

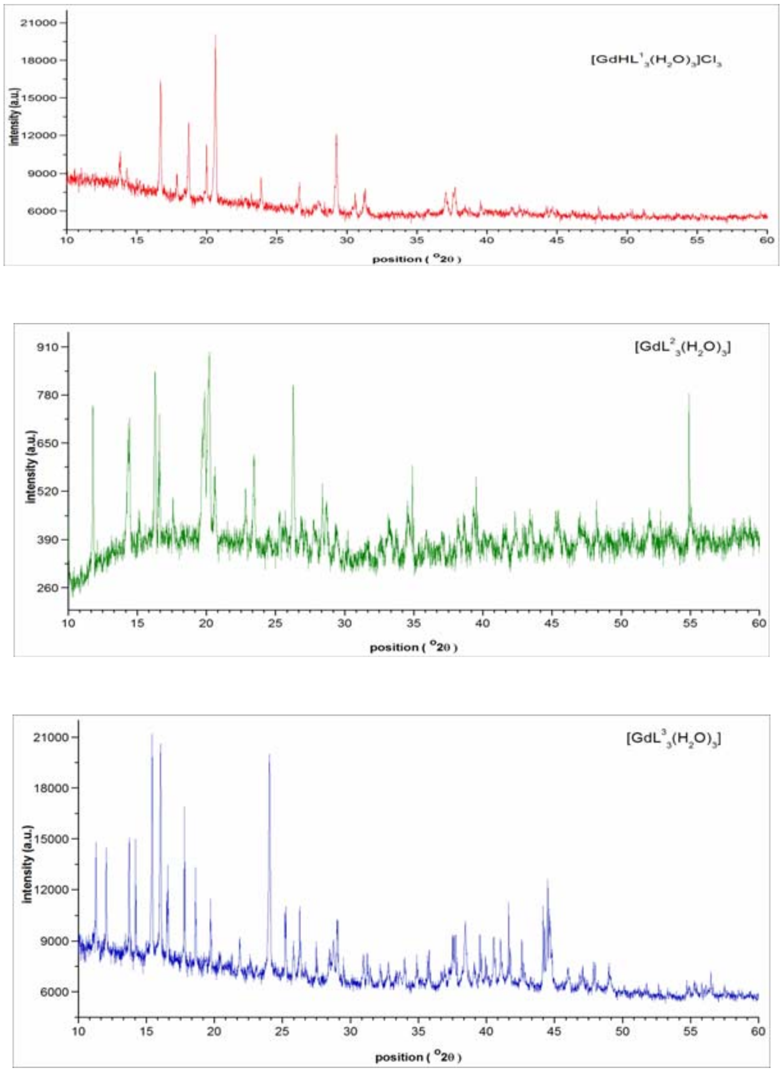


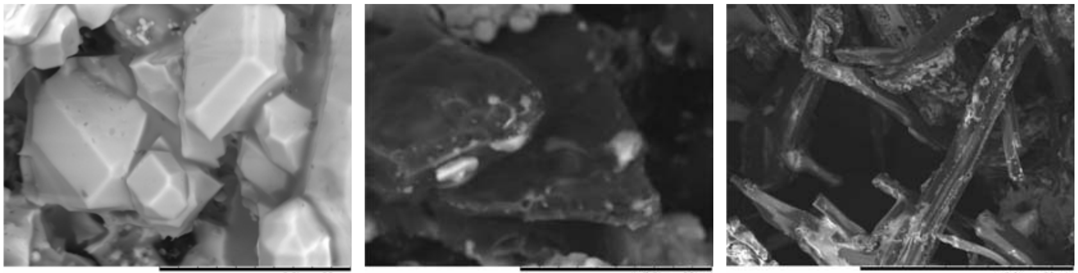
Fig. 1. Diffractograms of the new synthesized Gd(III) complexes.

The measured lattice parameters are presented in Table 4. For comparison, the lattice parameters of the ligands are also presented.

Table 4. Unit cell parameters of the prepared Gd complexes and corresponding free ligands.

Ligand/ Complex	**a** (Å)	**b** (Å)	**c** (Å)	**alpha** (°)	**beta** (°)	**gamma** (°)	**Cell volume** V/ 10^6 pm^3	**Crystallization system**
L^1	9,5577	6,4398	6,5393	90	102,492	90	392,963	monoclinic
L^2	7,4536	12,463	5,4163	90	90	90	503,14	orthorhombic
L^3	7,6697	15,158	6,063	102,245	101,86	77,968	664,035	triclinic
$[GdHL^1_3(H_2O)_3]Cl_3$	8,4651	21,6619	7,6974	96,889	94,137	81,418	1383,477	triclinic
$[GdL^2_3(H_2O)_3]$	18,5185	8,172	12,5839	90	93,2079	90	1901,381	monoclinic
$[GdL^3_3(H_2O)_3]$	24,034	7,8265	11,3968	90	117,1898	90	1906,872	monoclinic

SEM micrographs (Fig. 2) were recorded to highlight the crystalline structure and morpho-structural differences between prepared Gd(III) complexes.



$[GdHL^1_3(H_2O)_3]Cl_3$ $[GdL^2_3(H_2O)_3]$ $[GdL^3_3(H_2O)_3]$

Fig. 2. SEM images of the synthesized Gd complexes.

PL emission was investigated for each of the three Gd(III) complexes. Efficient sensitisation was found only in case of using the L_2 ligand which allows sufficient energy transfer to trigger the radiative transitions in the luminescent center (Gd^{3+} ion), therefore PL emission was observed only in case of $[GdL^2_3(H_2O)_3]$ complex. In Fig. 3 are presented the excitation and emission spectra of the synthesized $[GdL^2_3(H_2O)_3]$ complex.

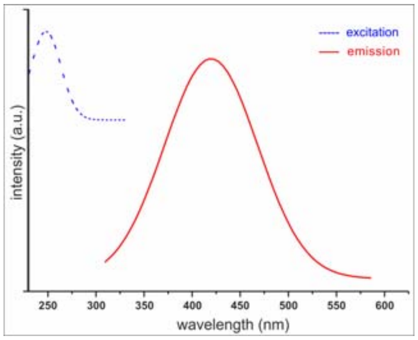


Fig. 3. Excitation and emission spectra of the $[GdL^2_3(H_2O)_3]$ complex.

The luminescent emission is placed in the blue region of the visible spectrum, the peak emission being recorded at 423 nm, under an excitation wavelength of 265 nm. The emission spectra is relatively broad, FWHM being approximately 100 nm.

4. Discussion

From the elemental chemical analysis results that the combination ratio between Gd(III) and HL^1, HL^2 and respectively HL^3 was 1:3 in all cases. The experimental data is in accordance with the proposed chemical formula for each prepared complex.

A special attention was given to the FT-IR absorption spectra of the studied complexes, especially in the regions corresponding to the Gd-O and Gd-N bonds resulted from the interaction of ligands functional groups with the central Gd(III) ion. As listed in Table 2, absorption lines corresponding to - OH , H_2O and

$Gd \leftarrow O = C<$ bonds, were observed.

In the low frequency IR spectrum (400 - 1500 cm^{-1}) valence vibration bands appeared to correspond to C-C , C-O, C-N bonds. No or insignificant changes were observed in the regions corresponding to the deformation vibrations of other bonds in the structure of the ligands after coordination of the central atoms with the corresponding ligand. The characteristic absorption bands of - OH groups initially observed in the free ligands HL^2 and HL^3 ligands at 1270-1290 cm^{-1}, are not present after the complexation process.

The stretching vibrations (valence) of carbonyls having an intense characteristic band with a maximum peak at 1725 cm^{-1} and a minimum one at 1665 cm^{-1} in case of the free HL^1, HL^2 and respectively HL^3 ligands, are shifted to 1426-1680 cm^{-1} in case of the prepared complexes, which is explained by the coordination bonds occurred between the central atom and oxygen atoms. In case of the complex containing succinimide (HL^1) the characteristic absorption band for Gd ← >N-H bond appears at 650 cm^{-1}.

The water molecules coordinated to the central atom were confirmed by symmetrical and asymmetrical stretching vibration at 3420 - 3400 cm^{-1} and from 1620-1625 cm^{-1}. The stretching vibration deformation was at 1600-1610 cm^{-1}.

According to thermal decomposition data, after the removal of the coordination water, the endothermic effects started, accompanied by thermal destruction. It was found that the final solid decomposition product, for all the studied complexes was Gd_2O_3. The most notable transformations occurred in the 200-500 ^oC temperature range where the endothermic effects were accompanied by exhaustion of volatile products.

XRD data accuracy of the provided results in case of the new prepared complexes was tested by the investigation in similar conditions and using same refinement methods of the known HL^1, HL^2, HL^3 ligands and then compared with the available data found in literature or XRD databases, the obtained results being in very good concordance.

The crystallization system is monoclinic for $[GdL^2_3(H_2O)_3]$ and $[GdL^3_3(H_2O)_3]$ complexes and triclinic in case of $[GdHL^1_3(H_2O)_3]Cl_3$ complex. The relative high volume of the unit cell for each of the studied complexes is explained by the contribution of the ligand at 1:3 combination ratio and also by the presence of the chemically bonded water, the obtained values being a further argument in favour of the proposed chemical structures of the new synthesized Gd complexes.

PL emission was observed only in case of $[GdL^2_3(H_2O)_3]$ complex. It is known that radiative transitions in case of lanthanide trivalent ions is achieved only in case of efficient energy transfer from the surrounding molecular site to the luminescent center and essentially depends by the energy gap (ΔE) between the lowest excited and highest excited multiplet sublevel states [10]. In case of the Gd^{3+} ions the energy gap is ΔE=14800 cm^{-1}, corresponding to $^5D_4 \rightarrow {}^7F_0$ transition [11]. For the other two Gd complexes ($[GdHL^1_3(H_2O)_3]Cl_3$and $[GdL^3_3(H_2O)_3]$) the conditions are not fulfilled since no PL emission was noted.

5. Conclusions

The paper presents the preparation and study of three new complexes resulted from the reactions between Gd(III) and Succinimide, N-hydroxysuccinimide, N-hydroxyphtalimide ligands. It was synthetised at 1:3 molar ratio, atom central: ligand, whose molecular formulas were confirmed by IR spectra analysis and elemental chemical analysis. From the recorded derivatograms it was found that thermal stability is quite similar for all three studied complexes, which is justified by the small structural differences of ligands and also by the same type of coordination of the central atom Gd (III).

The crystallization system is monoclinic for $[GdL^2_3(H_2O)_3]$ and $[GdL^3_3(H_2O)_3]$ complexes and triclinic in case of $[GdHL^1_3(H_2O)_3]Cl_3$ complex.

PL emission was observed only in case of $[GdL^2_3(H_2O)_3]$ complex. The PL emission is placed in the blue region of the visible spectrum, the peak emission being recorded at 423 nm under an excitation wavelength of 265 nm. Having the excitation peak situated in the short wave of the UV spectrum (UV-C) and the emission spectrum ranging from near UV to upper region of the visible spectrum the $[GdL^2_3(H_2O)_3]$ complex may be useful as conversion layer in various optoelectronic devices. Also due the low toxicity of the gadolinium complexes possible applications as tracing agents in bio analysis are targeted.

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