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Dinuclear lanthanide(III) complexes with Schiff bases ligands derived from carbonohydrazide. Synthesis, spectroscopic studies and structural characterization.

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Abstract. The ligand *N'*-(2-hydroxy-3-methoxybenzylidene)nicotinohydrazide (H₂L) was prepared by reaction of nicotinohydrazide with 2-hydroxy-3-methoxybenzaldehyde in a reflux ethanol solution. The lanthanide complexes were prepared by reaction of the ligand with the lanthanide nitrate. These complexes are well characterized by elemental analysis, IR, UV spectroscopies, conductance and room temperature magnetic moment measurement. The structure of the complexes was determined by single X-ray diffraction technique. The complexes of Gd and Tb are isostructural and are formulated as $\{[Ln(HL)(H_2O)_2(NO_3)]_2 \cdot (NO_3)_2 \cdot (H_2O)_2\}$. In these structures, each Ln atom is nine coordinated. In the crystal of the dinuclear complex $\{[Eu_2(HL)_2(H_2O)_2(NO_3)_3] \cdot (NO_3) \cdot (H_2O)_2\}$ one Eu(III) center is nine-coordinated and the other one is ten-coordinated. One nitrate anion acts in η^2 -coordination mode and as μ_2 -mode bridge between the two Eu(III) centers. In all the complexes, the ligand acts as bridge in tetradentate fashion. The nitrogen and the oxygen atoms of the hydrazino moiety are coordinated to one Ln(III) center and the oxygen atom of the methoxy group is coordinated to the other Ln(III) center. The phenolate oxygen atom bridges the two Ln(III) centers. One nitrate group acts in bidentate manner to each Ln(III). Two nitrate groups remain uncoordinated. In both Gd and Tb dinuclear complexes the coordination polyhedra are best described as a tricapped trigonal prism for each of the two centers. In the dinuclear complex of Eu, the polyhedron of the ten-coordinated Eu can be regarded as a 1333 stacking pattern while the polyhedron of the nine-coordinated Eu is best described as a monocapped square antiprism. The molecules are linked together in each case by multiple hydrogen bond interaction resulting in a three-dimensional network.

Keywords: Nicotinic hydrazide, Gadolinium, Terbium, Europium, Complex, X-ray diffraction.

I. Introduction

Lanthanide complexes with Schiff bases continue to be an attractive field research owing to numerous potential applications. Trivalent cations with 4f electrons are known as hard acid character [1]. They preferably interact with Schiff bases ligand containing donor atoms with hard basic character such as oxygen or nitrogen. According to these considerations it is expected that the hydrazone type ligands will coordinate the Ln(III) ion through its oxygen and nitrogen atoms. Generally, the bond of lanthanide to Schiff base involves displacement of proton from the free ligand molecule. Consequently, the spectroscopic properties of the resulting complexes are determined by the symmetry of the ligand [2,3]. Lanthanide complexes are known having luminescence [4,5], magnetic [6,7], catalytic [8,9] and biological properties [10,11]. Antifungal [12,13], antibacterial [14,15] and anticancer [15,16] activities of lanthanide complexes have been reported in the literature. Owing to their possible luminescent, phosphorescent and nuclear magnetic properties, lanthanide complexes have been reported as diagnostic tool [17] in medical field. Our research group has considerable interest in the preparation of polydentate ligands containing different hard and/or soft donor sites [18-20]. Indeed, these ligands are capable of producing various topological structures [3,21,22]. It is possible to design according to well-defined synthesis strategy ligand molecules with particular conformations to coordinate metal ions in various modes, giving rise to specific architectures. By use of an acyclic Schiff base, which presents two inner hard donor atoms it is possible to prepare dinuclear lanthanide complexes. Herein we report the synthesis, characterization, and X-ray structures of gadolinium(III), terbium(III) and europium(III) complexes derived from *N'*-(2-hydroxy-3-methoxybenzylidene)nicotinohydrazide (H₂L). H₂L is an organic ligand molecule bearing hard donor sites such as oxygen and nitrogen atoms containing two open coordination cavities (ONO and OO), which can host ions with large size such as lanthanides. Each lanthanide ion is linked to one of the two ligand molecules by ONO site and by OO site to the second ligand molecule. The nitrate group adopts several modes of coordination (scheme 1).



Scheme 1. Chemical structure of the ligand and schematic drawing of his coordination mode.

II. Experimental

2.1. Material and Physical measurement

All chemicals and solvents were of analytical reagent grade and were used directly without further purification. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on an FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400 cm^{-1} region. The UV-Visible spectra was recorded on a Perkin Elmer Lambda UV-Vis spectrophotometer. The molar conductance of $1 \times 10^{-3} \text{M}$ in DMSO solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: $\text{Hg}[\text{Co}(\text{SCN})_4]$).

2.2. Synthesis of the ligand N'-(2-hydroxy-3-methoxybenzylidene)nicotinohydrazide (H2L)

To a solution of o-vanillin (3.0 g, 0.197 mmol) in 20 mL ethanol was added dropwise a solution of nicotinic hydrazide (2.702 g, 0.197 mmol) in 20 mL of ethanol. The mixture was stirred under reflux for 2 hours. On cooling, the yellow precipitate was isolated by filtration and successively washed with 2 x 10 mL of ethanol and dried in air. Yield: 81.2%. M.P. 190 °C. Analytical for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3$: Calc (found) %C = 61.99 (62.03); %H = 4.83 (4.80); %N = 15.49 (15.44). IR (cm^{-1}): 3333 (NH); 3200 (OH); 1654 (C=O); 1603 (C=N); 1570; 1474; 1420 (C=C) arom., 1300 (C-O phénolique); 1242 (C-O éther); 1075 (N-N); 890; 833; 777; 721; 706 (CH) arom. UV-vis (Solution, DMF, nm): 273; 337; 372. NMR 1H (DMSO- d_6 , δ (ppm)): 12.21 (s, OH); 10.78 (s, NH); 9.09 (s, HC=N); [8.29-6.80] (m, Harom); 3.82 (s, OCH₃). NMR 13C (DMSO- d_6 , δ (ppm)): 161.33 (C=O); 152.38 (C=N); 148.56 (C-O phénolique); 148.24 (C-O éther); [147.88; 147.04; 135.40; 128.57; 120.60; 120.39; 119.03; 113.75] (Carom.); 55.74 (OCH₃).

2.3. Synthesis of the complexes of the ligand H2L.

To a suspension of H2L (0.1 g, 0.369 mmol) in 10 ml of ethanol was added a solution $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (0.369 mmol) in 10 mL of ethanol. The resulting yellowish mixture was stirred for 60 min at room temperature. The resulting suspension was filtered, and the filtrate was left at room temperature. On standing for one-week crystals suitable for X-ray analysis were isolated for Gd, Tb and Eu complexes. $\{[\text{Gd}(\text{HL})(\text{H}_2\text{O})_2(\text{NO}_3)]_2 \cdot (\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2\}$ (**1**). Yield: 42.37 (%). Analytical for $\text{C}_{28}\text{H}_{36}\text{Gd}_2\text{N}_{10}\text{O}_{24}$: Calc (found) %C = 27.77 (27.75); %H = 3.00 (2.98); %N = 11.56 (11.53). UV-vis (Solution, DMF, nm): 257; 283; 303; 360; 376; 402. $\mu_{\text{eff}} = 3.81 \mu\text{B}$. Λ (Ω - $1.\text{cm}^2.\text{mol}^{-1}$, DMF): 147. $\{[\text{Tb}(\text{HL})(\text{H}_2\text{O})_2(\text{NO}_3)]_2 \cdot (\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2\}$ (**2**). Yield: 40.50 (%). Analytical for $\text{C}_{28}\text{H}_{36}\text{Tb}_2\text{N}_{10}\text{O}_{24}$: Calc (found) %C = 27.69 (27.65); %H = 2.99 (2.96); %N = 11.53 (11.49). UV-vis (Solution, DMF, nm): 256; 283; 304; 345; 385; 402. $\mu_{\text{eff}} = 4.91 \mu\text{B}$. Λ (Ω - $1.\text{cm}^2.\text{mol}^{-1}$, DMF): 146. $\{[\text{Eu}_2(\text{HL})_2(\text{H}_2\text{O})_2(\text{NO}_3)_3] \cdot (\text{NO}_3) \cdot (\text{H}_2\text{O})_2\}$ (**3**). Yield: 40.54 (%). Analytical for $\text{C}_{28}\text{H}_{32}\text{Eu}_2\text{N}_{10}\text{O}_{22}$: Calc (found) %C, 28.88 (28.85); %H, 2.77 (2.78); %N, 12.03 (12.00). UV-vis (Solution, DMF, nm): 256; 285; 302; 322; 376; 402. $\mu_{\text{eff}} = 2.48 \mu\text{B}$. Λ (Ω - $1.\text{cm}^2.\text{mol}^{-1}$, DMF): 137.

2.4. X-ray data collection, structure determination and refinement

Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [23]. Structure solution and refinement were performed using SHELXT [24] and SHELXL-2014/7 [25]. All hydrogen atoms were added in calculated positions and refined in riding mode on the parent atom. Molecular graphics were generated using ORTEP-3 [26].

Table 1 Main infrared and UV data for Gd³⁺, Tb³⁺ and Eu³⁺ complexes.

Complex	Infrared (ν (cm ⁻¹))								
	$\nu_{C=O}$	ν_{C-N}	ν_{C-O}	ν_{O-CH_3}	NO ₂				$\Delta\nu$
					ν_1	ν_5	ν_2	ν_3	
H₂L	1654	1603	1242	1160	-	-	-	-	-
1	1604	1559	1212	1103	1437	1263	1047	1389	174
2	1610	1560	1216	1104	1453	1280	1081	1387	173
3	1607	1560	1216	1101	1457	1282	1082	1385	175
UV (λ_{max} (nm))									
H₂L	273, 337, 372 [pH 7], 287 [pH 13], 319								
1	257, 283, 303, 360, 376, 402								
2	256, 283, 304, 345, 385, 402								
3	256, 285, 302, 322, 376, 402								

Table 2 Crystallographic data for Gd³⁺, Tb³⁺ and Eu³⁺ complexes.

Chemical formula	C ₂₈ H ₃₂ N ₄ O ₁₆ Gd ₂ ·2(N O ₃)·2(H ₂ O)	C ₂₈ H ₃₂ N ₄ O ₁₆ Tb ₂ ·2(NO ₃)·2(H ₂ O)	C ₂₈ H ₃₂ N ₄ O ₁₆ Eu ₂ ·2(NO ₃)·2(H ₂ O)
<i>M</i> (g/mol)	1211.17	1214.51	1164.54
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Temperature (K)	173 K	173 K	173 K
Form and color	Prismatic, yellow	Prismatic, yellow	Prismatic, orange
Crystal size (mm)	0.13 × 0.12 × 0.12	0.10 × 0.10 × 0.09	0.11 × 0.11 × 0.10
<i>a</i> (Å)	9.4391 (4)	9.3958 (5)	9.9829 (7)
<i>b</i> (Å)	10.6653(3)	10.6152 (5)	14.3478 (9)
<i>c</i> (Å)	12.2983 (4)	12.2812 (6)	14.8546 (10)
α (°)	66.410 (1)	66.587 (1)	69.357 (2)
β (°)	69.597 (1)	69.692 (1)	78.733 (2)
γ (°)	74.388 (1)	74.701 (1)	82.710 (2)
<i>V</i> (Å ³)	1051.26 (6)	1042.83 (9)	1948.8 (2)
<i>Z</i>	1	1	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
<i>D</i> _{calc} (g/cm ³)	1.913	1.934	1.981
μ (mm ⁻¹)	3.23	3.46	3.29
<i>F</i> (000)	594	596	1144
<i>h</i> , <i>k</i> , <i>l</i>	-13 ≤ <i>h</i> ≤ 13 -13 ≤ <i>k</i> ≤ 14 -17 ≤ <i>l</i> ≤ 17	-13 ≤ <i>h</i> ≤ 13 -14 ≤ <i>k</i> ≤ 12 -17 ≤ <i>l</i> ≤ 16	-12 ≤ <i>h</i> ≤ 12 -11 ≤ <i>k</i> ≤ 12 -19 ≤ <i>l</i> ≤ 19
No. of measured reflections	13130	24652	28640
Independent reflections	5671	5583	7766
Data/parameters/restraints	5095/9/308	4807/9/308	5413/0/573
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.026	0.030	0.062
<i>wR</i> (<i>F</i> ²)	0.059	0.065	0.139
Rint	0.035	0.046	0.063
GOF	1.03	1.03	1.06
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.76, -0.60	1.61, -1.52	3.25, -3.34

Table 3 Selected distances (Å), bond angles (°) for Gd³⁺, Tb³⁺ and Eu³⁺ complexes.

Gd1—O1	2.2953 (17)	Tb1—O2	2.2824 (17)	Eu1—O2	2.337 (6)
Gd1—O3	2.3713 (18)	Tb1—O1	2.3570 (19)	Eu1—O5	2.463 (7)
Gd1—O5	2.385 (2)	Tb1—O5	2.3685 (19)	Eu1—O12	2.554 (7)
Gd1—O4	2.409 (2)	Tb1—O4	2.395 (2)	Eu1—O7W	2.466 (8)
Gd1—O1 ⁱ	2.4241 (18)	Tb1—O2 ^h	2.410 (2)	Eu1—O13	2.661 (7)
Gd1—O2 ⁱ	2.5135 (19)	Tb1—O6	2.498 (2)	Eu1—O1	2.490 (7)
Gd1—O6	2.514 (2)	Tb1—O3 ^h	2.5106 (19)	Eu1—O9	2.540 (8)
Gd1—N1	2.546 (2)	Tb1—N3	2.524 (2)	Eu1—N2	2.511 (8)
Gd1—O7	2.567 (2)	Tb1—O7	2.567 (2)	Eu2—O2	2.444 (6)
O2—Gd ⁱ	2.5135 (19)	O1—Tb1 ^h	2.410 (2)	Eu2—O5	2.339 (6)
O1—Gd1 ⁱ	2.4241 (18)	O3—Tb1 ^h	2.52106(19)	Eu2—O4	2.340 (7)
Gd1—Gd1 ⁱ	3.7721 (3)	Tb1—Tb1 ⁱⁱ	3.7558 (3)	Eu2—O8W	2.386 (8)
O1—Gd1—O3	137.92 (6)	O2—Tb1—O1	138.55 (7)	Eu2—O13	2.513 (8)

O1—Gd1—O5	83.36 (7)	O2—Tb1—O5	83.77 (7)	Eu2—O3	2.489 (6)
O3—Gd1—O5	83.18 (7)	O1—Tb1—O5	83.39 (7)	Eu2—O15	2.528 (7)
O1—Gd1—O4	77.04 (7)	O2—Tb1—O4	77.46 (7)	Eu2—N4	2.537 (8)
O3—Gd1—O4	88.81 (7)	O1—Tb1—O4	88.05 (7)	Eu1—Eu2	3.681
O5—Gd1—O4	140.47 (8)	O5—Tb1—O4	140.40 (8)	O2—Eu1—O6	137.3 (2)
O1—Gd1—O1 ⁱ	73.91 (7)	O2—Tb1—O2 ⁱⁱ	73.68 (7)	O2—Eu1—O1	129.3 (2)
O3—Gd1—O1 ⁱ	140.33 (7)	O1—Tb1—O2 ⁱⁱ	140.49 (7)	O5—Eu1—O7W	73.5 (3)
O5—Gd1—O1 ⁱ	77.70 (7)	O5—Tb1—O2 ⁱⁱ	78.07 (7)	O2—Eu1—O7W	76.9 (3)
O4—Gd1—O1 ⁱ	127.27 (6)	O4—Tb1—O2 ⁱⁱ	127.58 (7)	O6—Eu1—N2	131.6 (2)
O1—Gd1—O2 ⁱ	132.90 (7)	O2—Tb1—O6	140.60 (6)	O5—Eu1—N2	141.1 (3)
Gd1—O1—Gd1 ⁱ	106.09 (7)	O1—Tb1—O6	68.72 (7)	O1—Eu1—N2	63.1 (3)
O3—Gd1—O2 ⁱ	77.28 (6)	O5—Tb1—O6	134.19 (7)	O6—Eu1—O5	64.8 (2)
O4—Gd1—O2 ⁱ	145.92 (7)	O2 ⁱⁱ —Tb1—O6	100.69 (7)	O4—Eu2—O2	137.1 (2)
O1i—Gd1—O2 ⁱ	63.53 (6)	O2—Tb1—O3 ⁱⁱ	132.96 (7)	O5—Eu2—O4	136.1 (2)
O1—Gd1—N1	73.82 (6)	O1—Tb1—O3 ⁱⁱ	77.06 (7)	O5—Eu2—O8W	87.8 (3)
O3—Gd1—N1	64.14 (7)	O5—Tb1—O3 ⁱⁱ	69.07 (7)	O4—Eu2—O8W	78.1 (3)
O5—Gd1—N1	68.56 (8)	O2—Tb1—N3	74.18 (7)	O4—Eu2—N4	72.1 (3)
O4—Gd1—N1	73.11 (8)	O2 ⁱⁱ —Tb1—N3	135.50 (7)	O5—Eu2—N4	64.4 (3)
O1—Gd1—N3	118.27 (6)	O6—Tb1—N3	123.62 (7)	O3—Eu2—N4	138.1 (3)
O3—Gd1—N3	93.93 (6)	O3 ⁱⁱ —Tb1—N3	124.78 (7)	Eu1—O5—Eu2	100.1 (2)
O5—Gd1—N3	146.18 (7)	Tb1—O2—Tb1 ⁱⁱ	106.32 (7)	Eu1—O13—Eu2	90.7 (2)

Symmetry code: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$.

III. Results And Discussion

3.1. General studies

The element analyses results are in accordance with the formulae. The infrared spectrum of the ligand H₂L present a sharp and intense band at 3543 cm⁻¹ which is attributed to the vibration of the phenolic group of the molecule ligand. Additional bands at 3333 cm⁻¹ and 3068 cm⁻¹ are pointed and assigned respectively to N—H and C—H. The absorption of the C=O is pointed as a strong band 1654 cm⁻¹ while the medium band at 1603 cm⁻¹ represents the vibration of the C=N function. The medium intensity band at 1075 cm⁻¹ is attributed to the vibration of the N—N bond. The ¹H and ¹³C NMR spectra of the ligand are recorded in d₆-dms_o. The broad singlet signal at 12.21 ppm is attributed to the phenolic hydrogen atom. The singlets at 10.78 ppm and 9.09 ppm are respectively attributed to the N—H, and H—C=N. The aromatic hydrogen atoms are revealed in the 6.82-8.78 ppm region. The signal of the CH₃O— group is pointed as a singlet at 3.82 ppm. The ¹³C NMR reveals two characteristic signals at 161.33 ppm and 152.38 ppm attributed respectively to the C=O and C=N functions. The signals of the aromatic carbon atoms are in the range 113.75-148.52 ppm. The signal of the CH₃O— group is pointed as a singlet at 55.75 ppm. Upon coordination the intense band of the C=O is strongly shifted to low frequencies. The medium intensity band of C=N is slightly shifted to low frequencies. These facts are indicative of the involvement of the carbonyl oxygen and the imino nitrogen atoms in the coordination to the Ln (III) ion. In the infrared spectra of all the complexes an intense and sharp band is pointed in the range 1385-1389 cm⁻¹. This band is characteristic of the presence of uncoordinated nitrate group. The presence of a coordinated nitrate group in the complexes is evidenced by the presence of bands attributed to $\nu(\text{N}=\text{O})$ (ν_1) 1437cm⁻¹(Gd³⁺), 1453cm⁻¹(Tb³⁺), 1437cm⁻¹(Eu³⁺), $\nu_{\text{as}}(\text{NO}_2)$ (ν_5) 1263cm⁻¹(Gd³⁺), 1280cm⁻¹(Tb³⁺), 1282 cm⁻¹(Eu³⁺), $\nu_{\text{s}}(\text{NO}_2)$ (ν_2) 1047cm⁻¹(Gd³⁺), 1081cm⁻¹(Tb³⁺), 1082cm⁻¹(Eu³⁺) (**Table 1**). The magnitude $\Delta\nu = \nu_1 - \nu_5$ is indicative of the mode of coordination. The $\Delta\nu$ values in the range 173-175 cm⁻¹ are indicative of the presence of bidentate bridging nitrate group. These observations are in

accordance with the structure determined by crystallographic diffraction study. Freshly millimolar prepared dimethylformamide (dmf) solutions of the complexes are used for the molar electrical conductivity measurement. After standing for two weeks, the values of the conductivity are quite constant for three lanthanides complexes. No substitution of a coordinated site by dmf molecules was observed. The Λ_M values (**Table 1**) of the complexes **1**, **2** and **3** are higher than the expected value for a 2:1 [27]. All the three binuclear complexes are paramagnetic in nature. The μ_{eff} values of 3.81, 4.91 and 2.48 μ_B are due respectively to the gadolinium **1**, the terbium **2** and the europium **3** complexes. These values are consistent with the presence of unpaired 4f electrons in the three lanthanide ions which are not involved in the bond formation. These observed values are strongly different of the values for the free lanthanide ions [28][Gd: 7.94 μ_B ; Tb: 9.72 μ_B and Eu: 9.58 μ_B]. These observations are suggestive of the presence of magnetic interactions between the two metal centers and/or strong influence of the ligand field on the magnetic moment [29]. The main bands of the electronic spectral data of the ligand H₃L and his lanthanide complexes recorded in dmf are listed in **Table 1**. According to literature data the attribution of these bands is done. The ligand H₂L shows an intense absorption band at 273 nm at pH = 7. When the pH is increased to 13 the λ_{max} shift to a higher wavelength at 288 nm. This fact is diagnostic of the presence of a phenol group in the ligand molecule [18]. An intense band appears at 337 nm and is assigned to a $\pi \rightarrow \pi^*$ transition of the C=N chromophore. A $n \rightarrow \pi^*$ transition attributed to the C=O chromophore is observed in the spectrum of the ligand at 372 nm. Upon coordination to lanthanide(III) ions, the spectra of the complexes show a new band around 284 nm indicating of the deprotonation of the phenol group yielding a phenolate oxygen atom which can coordinate easily to the metal center [18]. The bands due to the C=N and C=O chromophores are shifted to lower wavelengths, supporting the coordination of ligand through the imino nitrogen atom and the carbonyl oxygen atoms to the metal center. The band near 402 nm appearing in whole spectra of the complexes is attributed to intense charge-transfer transitions which can obscure the f-f bands [30].

3.2. Description of the structures

Suitable single-crystals for X-ray diffraction of the Gd (III) (**1**), Tb (III) (**2**) and Eu (III) (**3**) complexes were obtained by slow solvent evaporation at room temperature. Crystal data, collection and refinement parameters are listed in **Table 2**. Selected bond lengths and angles are summarized in **Table 3**. Partially labelled plots of the dinuclear structures of complexes **1-3** and their coordination polyhedra are shown in **Figure 1**, **Figure 2** and **Figure 3**, respectively.

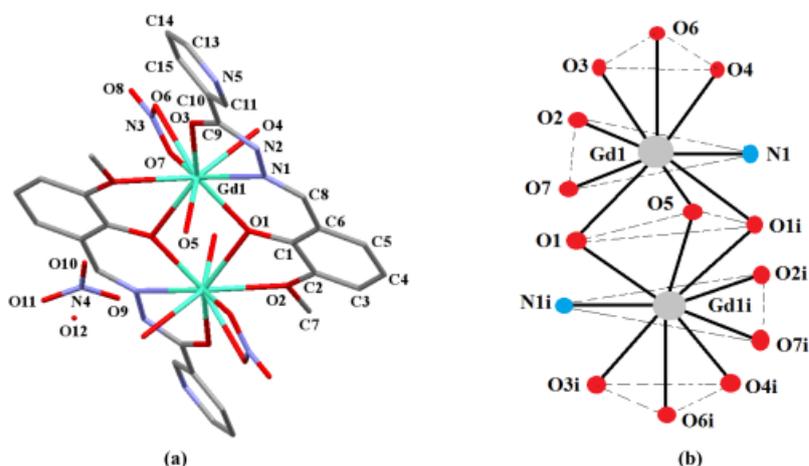
3.2.1. Complex 1 and 2.

The complexes $\{[\text{Gd}(\text{HL})(\text{H}_2\text{O})_2(\text{NO}_3)]_2 \cdot (\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2\}$ (**1**) and $\{[\text{Tb}(\text{HL})(\text{H}_2\text{O})_2(\text{NO}_3)]_2 \cdot (\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2\}$ (**2**) are isomorphous. Both complexes crystallize in the triclinic system with the space group P-1. The *ORTEP* view of the structures are shown in **Figures 1-2**. The asymmetric unit contains one dinuclear molecule composed by two lanthanide (Ln = Gd, Tb) atoms, two monodeprotonated organic molecule ligand, four coordinated water molecules, two bidentate nitrate groups, two uncoordinated water molecules and two uncoordinated nitrate groups. Each ligand molecule is coordinated to one Ln (III) ion through one carbonyl oxygen atom and one azomethine nitrogen atom; the methoxy oxygen atom is coordinated to the other Ln (III) ion and the phenolate oxygen acting as bridge between the two Ln (III) ions. Each Ln (III) is coordinated to two water molecule and one bidentate nitrate group. Both Ln (III) ions are nine coordinated. The coordination of the ligand to the metal center results in the formation of a six and a five membered chelating rings (LnNCCCO, LnNNCO and LnOCCO). The largest distance around the Ln atom is found with the bidentate chelating nitrate group Gd—O7 = 2.567 (2) Å and Tb—O7 = 2.567 (2) Å as found in the literature [3]. For the distances involving the coordinated atoms of the ligand to the lanthanide ion, those with the hydrazonic nitrogen atom and the methoxy oxygen atom are the largest (Gd1—N1 = 2.546 (2) Å, Gd1—O2 = 2.5135 (19) Å and Tb1—N3 = 2.524 (2) Å, Tb1—O3 = 2.5106 (19) Å). Those distances are comparable to those found for similar complexes [31]. The distances involving the phenolate oxygen atom which acts as bridge are Gd—O1 = 2.2953 (17) Å, Gd—O1_i = 2.4241 (18) Å and Tb—O2 = 2.2824 (17) Å, Tb—O2_{ii} = 2.410 (2) and are comparable with those reported for similar complexes [32]. The distances involving the oxygen water molecules are in the range [2.3685 (19)—2.409 (2) Å] are in accordance with the reported values in the literature [33]. The bond distances O3—C9 = 1.254 (4) Å and N1—C8 = 1.270 (3) Å for complex **1** and O1—C6 = 1.247 (5) Å and N3—C7 = 1.281 (3) Å for complex **2** and their related symmetry are double bond character while the distances of 1.328 (3) Å related to N2—C9 in complex **1** and 1.341 (3) Å related to N2—C6 in complex **2** and their symmetry are consistency with single bond character. For the bond angles involving the coordinated atoms of the ligand to the lanthanide (III) ion are 64.14 (7)° for O3—Gd—N1, 73.82 (6)° for O1—Gd—N1, 64.44 (7)° for O1—Tb1—N3 and 74.18 (7)° for O2—Tb1—N3. Three planes which lies upon, medium and under the sheets of Gd(III) are constituted by [(O3, O4, O6); (N1, O2, O7) and (O1, O5, O1_i)] for Gd1 and [(O1, O5, O1_i); (O3_i, O4_i, O6_i) and (N1_i, O2_i, O7_i)] for Gd1_i. The Gd1 and the Gd1_i atoms lies respectively in the planes defined by (N1, O2, O7) and (N1_i, O2_i, O7_i) with the sums

of the angles subtended by these donor atoms are both equal to 357.20° . In the complex **2** three plane defined as [(O1, O6, O4); (N3, O3, O7) and (O2, O5, O2i)] for Tb1 and [(O2, O5, O2i); (O1i, O6i, O4i) and (N3i, O3i, O7i)] for Tb1i. The Tb1 and the Tb1i atoms lies respectively in the planes defined by (N3, O3, O7) and (N3i, O3i, O7i) with the sums of the angles subtended by these donor atoms are both equal to 357.26° .

3.2.2. Complex 3

The complex $\{[\text{Eu}_2(\text{HL})_2(\text{H}_2\text{O})_2(\text{NO}_3)_3] \cdot (\text{NO}_3) \cdot (\text{H}_2\text{O})_2\}$ (**3**) crystallizes in the triclinic system with the space group P-1. The ORTEP diagram is depicted in **Figure 3**. The asymmetric unit of the compound contains a discrete $[\text{Eu}_2(\text{HL})_2(\text{H}_2\text{O})_2(\text{NO}_3)_3]^+$ cation, one free nitrate anion and two uncoordinated water molecules. In the discrete anion two Eu (III) ions, two monodeprotonated organic ligand molecules, two chelating bidentate nitrate groups, one chelating bidentate and bridged nitrate anion and two coordinated water molecules are present. The two Eu (III) centers have different environment. The two metal centers are bridged by two phenolate oxygen atoms and one oxygen atom from a nitrate group. Each Eu (III) center is coordinated by one carbonyl oxygen atom and one azomethine nitrogen atom of one ligand molecule and a methoxy oxygen atom of another ligand molecule. Each Ln (III) is also coordinated to two water molecule and one bidentate nitrate group. In addition Eu1 is coordinated with another chelating bidentate nitrate of which one of the oxygen atoms acts as bridge with Eu2. These facts result in different coordination number for the two metal centers: Eu1 is ten-coordinated while Eu2 is nine-coordinated. The coordination of the ligand molecules to Eu results in the formation of five EuOCNN and six EuNCCCO membered chelating rings, which share one Eu–N bond and a five membered ring EuOCCO from the second ligand molecule. In the two first rings, the Eu–N bonds have the largest metal–ligand distances [Eu1–N2 = 2.511(8) Å, Eu2–N4 = 2.537(8) Å]. The Eu–O bonds involving the hydrazone oxygen have metal–ligand distances comparable in the two ligand molecules [Eu1–O1 = 2.490(7) Å and Eu2–O4 = 2.340(7) Å]. The phenolic oxygen atoms, acting as bridges between the two Eu atoms, have metal–ligand distances in the range 2.256(3)–2.374(3) Å. Those values are shorter than the distances Eu–O13 in which the oxygen atom from the nitrate group acts as bridge [Eu1–O13 = 2.661(7) Å and Eu2–O13 = 2.513(8) Å]. The Eu1...Eu2 distance is 3.681 Å. Eu1 is positioned on a plane formed by (O10, O12, O7w) with the sum of the angles subtended by the three set donor atoms of 359.25° . Two other planes defined respectively by (O2, O5, O13) and (O6, O9, N2) lie upon and under the sheet of Eu1. The O1 atom is under the plane (O6, O9, N2). The coordination geometry around the Eu1 center can be regarded as a 1333 stacking pattern as reported by Bu [34]. The coordination geometry around the nine-coordinated Eu2 center is best described as a monocapped square antiprism [35].



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