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Preparation, Characterization of Some Lanthanide(III) Complexes of *N′*-(phenyl(pyridin-2-yl)methylene)nicotinohydrazide

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Abstract

The present investigation describes the synthesis and structural study of the ligand *N′*-(phenyl(pyridin-2-yl)methylene)nicotinohydrazide (H*L*), which was used to generate two type complexes formulated as $[Ln(HL)_2(NO_3)_2(H_2O)]\cdot(NO_3)$ (Ln = La (**1**) and Pr (**2**)) and $[Ln(HL)_2(NO_3)(H_2O)_2]\cdot(NO_3)_2$ (Ln = Nd (**3**), Sm (**4**), Gd (**5**) and Tb (**6**)). The ligand and the complexes are characterized by NMR, UV-Visible and FTIR spectroscopies, conductivity measurements and room temperature magnetic moment measurements. The $[La(HL)_2(NO_3)_2(H_2O)]\cdot(NO_3)$ compound crystallizes in the orthorhombic space group *Pbcn* with the following unit cell parameters: a = 16.8634(8) Å, b = 8.0615(4) Å, c = 30.2833(15) Å, V = 4116.8(3) Å^3, Z = 8, R_1 = 0.049 and wR_2 = 0.120. The structure reveals that two neutral ligand molecules in η^3-mode, two bidentate nitrate groups in η^2-mode and one water molecule coordinate the central La^{3+}. Each organic molecules acts through one carbonyl oxygen atom, one azomethine nitrogen atom and one nitrogen atom from a pyridine ring. The lanthanide ion has a coordination number of 11 and the coordination environment can be described as distorted pentacapped trigonal prism. Numerous hydrogen bonds link the molecules into three-dimensional network.

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1. Introduction

The Schiff bases resulting from the condensation reaction of nicotinic hydrazide and a ketoprecursor such as aldehydes and ketones are widely used in the synthesis of organic ligands in order to prepare coordination compounds with lanthanide ions and transition metals ions [1–5]. These complexes are particularly interesting in various fields such as magnetism [6], catalysis [7], in medicine [8], and luminescence [9, 10]. The presence of phenolic moiety suggests that these complexes can be antioxidants as reported in the literature [11] but also as antibacterial agents [12, 13]. In recent studies, nicotinic hydrazide complexes were prepared and showed enzyme-like activities [14, 15]. It is in this context that we have undertaken to synthesize complexes at room temperature using nicotinic hydrazide and 2-benzoylpyridine in the presence of lanthanide salts. Several complexes have been isolated in powder form and are characterized by different techniques.

2. Experimental

2.1. Materials and procedures

Nicotinic acid hydrazide, 2-hydroxy-3-methoxybenzaldehyde as well as $Ln(NO_3)_3 \cdot nH_2O$ (Ln = La(III), Pr(III), Nd(III), Sm(III), Gd(III) or Tb (III)) were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. Elemental analyzes were performed in a Carlo-Erba EA microanalyzer. Infrared spectra were recorded as KBr discs on a Bruker IFS-66V spectrophotometer. LSI-MS were recorded using a MicromassAutospec spectrometer with 3-nitrobenzyl alcohol as the matrix. The ^{1}H and ^{13}C NMR spectra were recorded in dmso-d_6 on a Bruker 500 MHz spectrometer at room temperature using TMS as an internal reference. The UV-Vis spectra were run on a Shimadzu UV-2501 PC Recording spectrophotometer (1000-200 nm). The molar conductance of 10^{-3} M in DMF 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 Mattey scientific magnetic susceptibility balance {calibrant $Hg[Co(SCN)_4]$}. Melting points were recorded on a Büchi apparatus and are incorrect.

2.2. Synthesis of *N′*-(phenyl(pyridin-2-yl)methylene)nicotinohydrazide (HL)

In a 250 mL round bottomed flask, introduce the benzoylpyridine (2.67 g; 14.58

mmol) in 20 mL of absolute ethanol. After dissolution, add nicotinic hydrazide (2.00g; 14.58 mmol) previously dissolved in 20 mL of ethanol. The mixture is refluxed for four hours. After filtration, a limpid brown solution is obtained. Left for slow evaporation, the solution gives crystals suitable for X-ray diffraction. IR ν(cm^{-1}): 3062 (NH); 2924 $(C\text{-}H)_{Ar}$; 1684 (C=O); 1583 (C=N); [1541-1422] $(C=C)_{Ar}$; 1282 (C-N); 1142 (N-N); 804; 749; 699; 650; 614 $(C\text{-}H)_{Ar}$. ^1H NMR (δ, ppm): 8.73 (s, 1H, HC=N); [7.39-8.20] (m, 13H, H_{Ar}); 9.01 (s, 1H, NH). ^{13}C NMR (δ, ppm): 161.46 (C=O); 152.30 (C=N); 151.68; 148.72; 138.11; 137.71; 136.78; 135.39; 135.22; 130.61; 129, 23; 128.34; 124, 91; 124.08; 123.76 (C_{Ar}).

2.3. General procedure for the synthesis of lanthanide complexes with the ligand HL

In a 100 mL round bottomed flask containing 10 mL of methanol, dissolve the ligand (H*L*) (0.100 g; 0.30 mmol). A brown solution is obtained. To this solution, add 0.24 mmol of $Ln(NO_3)_3{\cdot}xH_2O$ already dissolved in 10 mL of ethanol. The resulting solution was stirred at room temperature for one hour, then filtered and left for slow evaporation. After one week, the precipitate recovered was washed with 2 x 5 mL methanol followed by 2 x 5 mL ether before dried in the open air. The solids obtained are then recrystallized from the solvent mixture DMF/EtOH (50/50). After three weeks, yellow crystals which can be analyzed by X-ray diffraction are recovered for the La(III) complex.

$[La(HL)_2(NO_3)_2(H_2O)]{\cdot}(NO_3)$ (**1**). Green, yield 37%, M.P. (°C) > 260. Anal. calc. for $[C_{36}H_{30}N_{11}O_{12}La]$: C, 45.63; H, 3.19; N, 16.26. Found: C, 45.60; H, 3.17; N, 16.24 %. IR (ν, cm^{-1}): 3415 (OH_{water}), 1625 (C=O), 1588 (C=N), 1538 (C=Npyridine), [1465 $\nu_1(NO_3)$, 1294 $\nu_5(NO_3)$, 1090 $\nu_2(NO_3)$] for bidentate chelating nitrate and 1368 $\nu_3(NO_3)$ for ionic nitrate. Molar conductivity Λ ($\Omega^{-1}cm^2mol^{-1}$) : 95 (fresh solution), and 172 (two weeks later). UV-visible (λ, nm) 257, 275, 318, 360, 388, 473, 510. Magnetic moment $\mu_{eff}(\mu_B)$ = 00.0.

$[Pr(HL)_2(NO_3)_2(H_2O)_2]{\cdot}(NO_3)$ (**2**). Green, yield 33%, MP(°C) > 260. Anal. calc. for $[C_{36}H_{30}N_{11}O_{12}Pr]$: C, 45.53; H, 3.18; N, 16.23. Found: C, 45.51; H, 3.17; N, 16.20 %. IR (ν, cm^{-1}) 3399 (OH_{water}), 1625 (C=O), 1597 (C=N), 1536 ($C=N_{pyridine}$), [1479 $\nu_1(NO_3)$, 1305 $\nu_5(NO_3)$, 1086 $\nu_2(NO_3)$] for chelating nitrate bidentate and 1366 $\nu_3(NO_3)$ for ionic nitrate. Molar conductivity Λ ($\Omega^{-1}cm^2mol^{-1}$) : 93 (fresh solution), and 198 (two weeks later). UV-visible (λ, nm) 257, 284, 316, 361, 389, 484, 510. Magnetic moment $\mu_{eff}(\mu_B)$ = 3.50.

$[Nd(HL)_2(NO_3)(H_2O)_2]\cdot(NO_3)_2$ (**3**). Greenish, yield 31%, MP(°C) > 260. Anal. calc. for $[C_{36}H_{30}N_{11}O_{12}Nd]$: C, 45.37; H, 3.17; N, 16.17. Found: C, 45.35; H, 3.15; N, 16.15 %. IR (ν, cm^{-1}) 3390 (OH_{water}), 1629 (C= O), 1594 (C=N), 1533 ($C{=}N_{pyridine}$), [1458 $\nu_1(NO_3)$, 1282 $\nu_5(NO_3)$, 1056 $\nu_2(NO_3)$] for nitrate bidentate chelator and 1375 $\nu_3(NO_3)$ for ionic nitrate. Molar conductivity Λ ($\Omega^{-1}cm^2mol^{-1}$) : 138 (fresh solution), and 213 (two weeks later). UV- visible (λ, nm) 257, 282, 318, 363, 389, 405, 513. Magnetic moment $\mu_{eff}(\mu_B)$ = 2.89.

$[Sm(HL)_2(NO_3)H_2O]\cdot(NO_3)_2$ (**4**). Yellow, yield 31%, MP(°C) > 260. Anal. calc. for $[C_{36}H_{30}N_{11}O_{12}Sm]$: C, 45.08; H, 3.15; N, 16.07. Found: C, 45.05; H, 3.13; N, 16.05 %. IR (ν, cm^{-1}) 3408 (OH_{water}), 1627 (C= O), 1595 (C=N), 1534 ($C{=}N_{pyridine}$), [1459 $\nu_1(NO_3)$, 1283 $\nu_5(NO_3)$, 1057 $\nu_2(NO_3)$] for nitrate bidentate chelator and 1376 $\nu_3(NO_3)$ for ionic nitrate. Molar conductivity Λ ($\Omega^{-1}cm^2mol^{-1}$) : 120 (fresh solution), and 150 (two weeks later). UV-visible λ(nm) 257, 284, 316, 361, 389, 402, 516. Magnetic moment $\mu_{eff}(\mu_B)$ = 2.23.

$[Gd(HL)_2(NO_3)H_2O](NO_3)_2$ (**5**). Yellow, yield 31%, MP(°C) >260. Anal. calc. for $[C_{36}H_{30}N_{11}O_{12}Gd]$: C, 44.76; H, 3.13; N, 15.95. Found: C, 44.74; H, 3.11; N, 15.92 %. IR (ν, cm^{-1}) 3210 (OH_{water}), 1620 (C=O), 1598 (C=N), 1547 ($C{=}N_{pyridine}$), [1477 ν_1(NO3), 1303 $\nu_5(NO_3)$, 1097 $\nu_2(NO_3)$] for chelating nitrate bidentate and 1374 $\nu_3(NO_3)$ for ionic nitrate. Molar conductivity Λ ($\Omega^{-1}cm^2mol^{-1}$) : 130 (fresh solution), and 235 (two weeks later). UV-visible λ(nm) 257, 281, 318, 363, 389, 407, 505. Susceptibility Magnetic $\mu_{eff}(\mu_B)$ = 7.14.

$[Tb(HL)_2(NO_3)(H_2O)](NO_3)_2$ (**6**). Green, yield 44%, MP(°C) >260. Anal. calc. for $[C_{36}H_{30}N_{11}O_{12}Tb]$: C, 44.69; H, 3.13; N, 15.92. Found: C, 44.67; H, 3.10; N, 15.90 %. IR (ν, cm^{-1}) 3223 (OH_{water}), 1620 (C=O), 1595 (C=N), 1532 ($C{=}N_{pyridine}$), [1475 $\nu_1(NO_3)$, 1303 $\nu_5(NO_3)$, 1099 $\nu_2(NO_3)$] for chelating nitrate bidentate and 1378 $\nu_3(NO_3)$ for ionic nitrate. Molar conductivity Λ ($\Omega^{-1}cm^2mol^{-1}$) : 130 (fresh solution), and 216 (two weeks later). UV- visible λ(nm) 257, 281, 313, 359, 375, 402, 510. Magnetic moment $\mu_{eff}(\mu_B)$ = 10.06.

2.4. Crystal structure determination

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of MeOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a

Rigaku XtaLAB PRO diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Using Olex2 [16] the structures were solved by intrinsic phasing methods with SHELXT [17] and SHELXL [18] was used for full matrix least squares refinement. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [19].

Table 1. Crystal and structure refinement data for complex $[La(HL)_2(NO_3)_2H_2O]\cdot(NO_3)$ (**1**).

Chemical Formula	$C_{36}H_{30}N_{11}O_{12}La$
Formula weight	947.61
Temperature (K)	293
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	16.86342 (8)
b (Å)	8.0615 (4)
c (Å)	30.2833 (15)
V (Å^3)	4116.8 (3)
Z	8
Radiation type	MoKα
D_{calc} g/cm^3	1.503
μ (mm^{-1})	1.11
F(000)	1872
θ (°)	2.8-29.4
h, k, l	$-22 \le h \le 23$; $-10 \le k \le 11$; $-41 \le l \le 41$
No. of measured reflections	17613
No. of independent reflections	5710
No. of observed reflections	3865
R_{int}	0.034
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	$R_1 = 0.058$, $wR_2 = 0.152$
Indices R (all data)	$R_1 = 0.0754$, $wR_2 = 0.1444$
GOF	1.33
Parameters / restreints	286/0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^3)	2.53, -1.06

3. Result and Discussions

3.1. General study

The infrared spectrum of the ligand presents towards the high frequencies two bands pointed at 3062 and 2924 cm^{-1} attributed respectively to the vibration of valence ν(N-H) and that of ν(C-H) of the aromatic rings. The vibration of the carbonyl group C=O is identified at 1684 cm^{-1} and that of the imine function C=N at 1630 cm^{-1} [20]. Between 1541 and 1422 cm^{-1} the ν(C=C) vibrations of the aromatic rings show up, while the ν(C=N) band of the pyridine ring is located at 1583 cm^{-1}. The band pointed at 1282 cm^{-1} is attributed to the valence vibration ν(C-N). The vibration of the N-N bonds is located at 1142 cm^{-1}. The deformation vibrations of the aromatic C-H bonds are located between 804 and 614 cm^{-1}. Spectral analyzes of Nuclear Magnetic Resonance of the proton ^{1}H, of carbon ^{13}C are carried out using dmso-d$_6$ solutions. The ^{1}H NMR spectrum indicates a set of signals in the form of multiplets between 7.39 and 8.20 ppm and integrating eight protons attributed to those of the aromatic nuclei of this ligand. In addition to these signals, two singlets are identified at 8.73 and 9.01 ppm and each integrating a proton attributed respectively to the proton H15 and that of NH [21]. The ^{13}C NMR spectrum indicates the signal of the carbon of the carbonyl function (**C**=O) at 160.10 ppm and that of the carbon of the imine function (**C**=N) at 148.91 ppm [9, 11]. The signal in the range 123.10—148.34 are assigned to the aromatic carbon atoms. The mass spectrum confirms the formation of the H*L* ligand with the presence of the peak at m/z=303.12 corresponding to the mass of the protonated molecular fragment [H*L*+H$^+$] (M+1). It should be recalled that we have determined the X-ray structure of this organic ligand examined its antioxidant activities [22]. The infrared spectrum of the HL ligand shows bands at 1684, 1635 and 1583 cm^{-1} attributed, respectively, to the vibrations ν(C=O) of the carbonyl, ν(C=N) of the azomethine function and ν(C=N) of the pyridine ring. On the spectra of the complexes, these bands are observed with a shift towards low frequencies, respectively, in the regions (1633-1620 cm^{-1}), (1597-1588 cm^{-1}) and (1547-1532 cm^{-1}). This fact indicates the coordination to the metal of the oxygen atom of the carbonyl, the nitrogen atom of the azomethine function and the nitrogen atom of the pyridine [23]. In the high-frequencies region of the spectra of all the complexes, the broad bands pointed between 3210 and 3415 cm^{-1} are attributed to the ν(OH) vibration of the coordinated water molecule [24]. On all the spectra, the three bands observed in the regions (1479-1459 cm^{-1}), (1305-1282 cm^{-1}) and (1099-1056 cm^{-1}) are respectively due to the $\nu_{as}(NO_2)$ (ν_1), $\nu_s(NO_2)$ (ν_5) and ν(N=O) (ν_2) vibrations of the coordinated nitrate group (NO_3^-). The magnitude value ($\Delta\nu = \nu_1$-ν_5) between 171 and 176 cm^{-1} shows that the nitrate group acts as a bidentate chelating ligand [25]. The ν_3 vibration band of free nitrate (NO_3^-) of the lanthanum complex **1** is observed on the FTIR spectrum as a sharp band at *ca.*1379 cm^{-1}. The infrared spectroscopic data of the complexes are collected in Table 2. The conductometric measurements are taken in a millimolar solution of DMF. In fresh solution, the values obtained for the lanthanum complex (**1**) (93 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) and praseodymium complex) (95 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) (**2**) are indicative of a 1:1 electrolyte [26], while the other DMF solution of complexes of neodymium (**3**), samarium (**4**), gadolinium (**5**) and terbium (**6**) display Λvalues in the range 120 and 138 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. These conductivity values are consistent with 2:1 electrolyte. After two weeks of storage, the values increase significantly for all complexes except for complex **4**. Complex **1** becomes 2:1 electrolyte, complexes **2**, **3**, **5** and **6** become 3:1, while complex **4** remains 2:1 electrolyte. According to these conductometric data, only the complex **4** is stable in DMF solution. The conductivity measurement data of the complexes are grouped together in Table 3.

Based on spectroscopic, magnetic and conductimetric analyzes we concluded that the complexes are mononuclear. This indication is confirmed by both infrared spectroscopy and conductometric data. In the structure of these complexes, the ligand is tridentate and is coordinated to the lanthanide cations through the oxygen atom of the carbonyl function, the nitrogen atom of the azomethine function and the nitrogen atom of the pyridine ring. It is also noted that in the solid state, the complexes are in salt form.

The UV-visible spectra of the complexes recorded in DMF are similar and the absorption bands observed in (257-284) and (313-389) nm regions, which are also present in the spectrum of the free ligand are attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The additional absorption bands observed between 402 and 483 nm are assigned to the charge transfers of the C=N chromophore of the coordinated ligand. On all the spectra of the complexes, we observe the presence of bands of low intensity in the region (505-516 nm), which can be attributed to the 4f →4f transitions of Ln^{3+} ions. These forbidden electronic transitions can become allowed after elimination of the degeneracy of the 4f orbitals by an external crystal field. For this purpose, we observe weak bands of f-f transitions which are often obscured by the intense bands of charge transfers [27, 28] .

Apart from the diamagnetic lanthanum complex (**1**), magnetic measurements at room temperature show that the complexes are paramagnetic. The values of magnetic moments found are very close to those of free ions [29]. This result shows that the complexes are mononuclear. The UV-visible spectrophotometric data and magnetic measurements of the complexes are recorded in Table 4. Structures are proposed in Figure 1.

Table 2. Infrared data of the ligand HL and the complexes.

Compounds	$\nu_{OH}(H_2O)$	$\nu_{C=O}$	$\nu_{C=N}$(imine)	$\nu_{C=N}$(pyridine)	NO_3^-				
					ν_1	ν_5	ν_2	ν_3	$\Delta = \nu_1$-
HL	-	1684	1635	1583	-	-	-	-	-
1	3415	1625	1588	1538	1465	1294	1090	1368	171
2	3399	1625	1597	1536	1479	1305	1086	1366	174
3	3390	1629	1594	1533	1458	1282	1056	1375	176
4	3408	1627	1595	1534	1459	1283	1057	1376	176
5	3210	1620	1598	1547	1477	1303	1097	1374	174
6	3223	1620	1595	1532	1475	1303	1099	1378	172

Table 3. Conductimetric data of complexes in DMF.

Compounds	Fresh DMF solution		15days (after)	
	Λ ($\Omega^{-1}cm^2mol^{-1}$)	Electrolyte	Λ ($\Omega^{-1}cm^2mol^{-1}$)	Electrolyte
1	95	1 : 1	172	2 : 1
2	93	1 : 1	198	3 : 1
3	138	2 : 1	213	3 : 1
4	120	2 : 1	150	2 : 1
5	130	2 : 1	235	3 : 1
6	130	2 : 1	216	3 : 1

Table 4. UV-Visible and Magnetic moments of the complexes.

Compounds	UV-visible λ(nm)	μ_{eff} (μB)
HL	257, 275, 315, 361	
1	257, 275, 318, 360, 388, 473, 510	Diam.
2	257, 284, 316, 361, 389, 484, 510	3.50
3	257, 282, 318, 363, 389, 405, 513	2.89
4	257, 284, 316, 361, 389, 402, 516	2.23
5	257, 281, 318, 363, 389, 407, 505	7.14
6	257, 281, 313, 359, 375, 402, 510	10.06

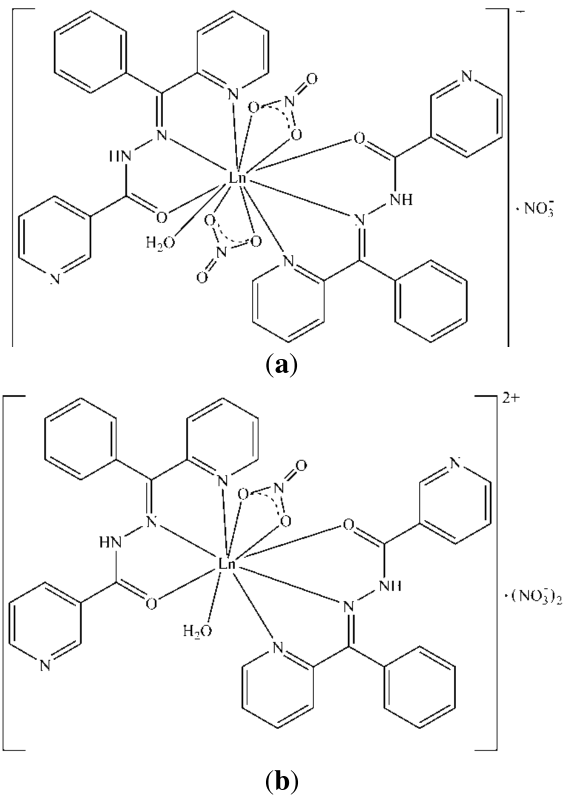

Figure 1. Proposed structures: (a) complex **1** and **2**, (b) complexes **3**, **4**, **5** and **6**.

3.2. Structure description of the complex [La(η^3-HL)$_2$(η^2-NO$_3$)$_2$(η-H$_2$O)]·(NO$_3$) (1)

Once isolated, complex **1** was found to be air-stable and soluble in common organic solvents such as methanol, DMF and DMSO. The mononuclear complex [La(η^3-HL)$_2$(η^2-NO$_3$)$_2$(η-H$_2$O)]·(NO$_3$) (**1**) crystallizes in the orthorhombic system *Pbcn*. Crystal and structure refinement data are consigned in Table 1. The selected bond lengths and angles are summarized in Table 5. The ORTEP plots is shown in Figure 2. The asymmetric unit contains one lanthanum ion, two neutral ligand molecules, one coordinated water molecule, two coordinated nitrate anions and one uncoordinated nitrate anion. Each of the two ligand molecules is coordinated to the La^{3+} in η^3-mode, through one carbonyl nitrogen atom, one azomethine nitrogen atom and one nitrogen pyridine atom. Each of the two coordinated nitrate anions acts in bidentate chelating η^2-mode. Thus, the central metal atom is eleven coordinated (Figure 3). The environment around the La(III) is best described as a distorted pentacapped trigonal prism. The interatomic distance La—O1(carbonyl) which is equal to 2.506(4) Å, is shorter than those of La—ONO_2 of bidentate nitrate anions, which are respectively 2.733(5) Å [La—O3] and 2.741 (6) Å [La—O4]. These values are in the range expected for La—ONO_2 [30–32]. The La—O bond involving coordinated water molecule has a distance of 2.560 (7) Å [La—O5] which is shorter than the bond length La—OH_2(2.659(3) Å) reported for a similar complex [33]. The La—N involving the azomethine nitrogen atom and the pyridine nitrogen atom are the longest distance with respective values of 2.780(5)Å [La—N2] and 2.760(5) Å [La—N1] (Table 5). The bond lengths of the La—$O_{carbonyl}$ and La—$N_{azomethine}$ are similar to those reported by Tamboura *et al.* [34] for the complex $[La_2(H_2L)_3(C_2H_5OH)_2](Cl)(NO_3)_2((CH_3)_2CO)_2(H_2O)_2$ (H_2L = 2,6-diformyl-4-chlorophenol-benzoyl-hdrazone). The NO_3 groups are virtually planar, and the La atom bonded to them are near their mean planes (rms 0.1178) with a maximum deviation of 0.1120 (2) Å for La1. Each of the ligand forms two five membered rings LaOCNN and LaNCCN with bites angles 57.58(10)° of and 58.79(10)°. For the ligand, the benzene ring [C7—C12] is twisted toward the two pyridine rings with dihedral angles of 62.190(2)° [C1—C5/N1] and 61.053(2)°[C14—C18/N4]. The two pyridine rings are quite coplanar with dihedral angle of 2.290(3)°.

The hydrogen atom from each NH group is involved in an intramolecular N—H···ONO_2 hydrogen bond with an oxygen atom of uncoordinated nitrate group. An oxygen of a coordinated nitrated groups acts as donor in a C—H···O hydrogen bond thus forming a *S*(5) ring. Intramolecular hydrogen bonding in which the coordinated water molecule acts as donor and the nitrogen atom and the oxygen atom of the same nitrate group act as acceptor [O5—H5···$N5^{ii}$; O5—H5···$O3^{ii}$ ii = −x+1, y+1, −z+1/2] (Table 6) interconnect the molecules (Figure 4).

Table 5. Selected geometric parameters (Å, °).

Bond	Distance	Bond	Angle
La1—O1	2.505 (3)	$O1^i$—La1—$N2^i$	58.79 (10)
La1—$O1^i$	2.505 (3)	O1—La1—$N2^i$	105.05 (11)
La1—$O2^i$	2.730 (4)	$O1^i$—La1—N2	105.06 (11)
La1—O2	2.730 (4)	O1—La1—N2	58.79 (10)

La1—O4	2.741 (4)	O2^{i}—La1—N1	68.45 (11)
La1—O4^{i}	2.741 (4)	N1i—La1—N1	175.82 (15)
La1—O5	2.559 (5)	N2^{i}—La1—N1$_{i}$	57.28 (10)
La1—N1	2.778 (3)	N2—La1—N1	57.28 (10)
La1—N1^{i}	2.778 (3)	N2^{i}—La1—N1	124.49 (10)
La1—N2^{i}	2.762 (3)	O5—La1—O4^{i}	129.17 (8)
La1—N2	2.762 (3)	N2—La1—N2^{i}	138.80 (15)

Symmetry code: (i) −x+1, y, −z+1/2.

Table 6. Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O7	0.86	2.27	2.907(10)	131.0
C1—H1···O2^{i}	0.93	2.48	3.053(6)	120.1
O5—H5···O3^{ii}	0.88(2)	1.97(2)	2.842(5)	175(7)
O5—H5···N5^{ii}	0.88(2)	2.55(3)	3.369(6)	156(6)

Symmetry codes: (i) −x+1, y, −z+1/2; (ii) −x+1, y+1, −z+1/2.

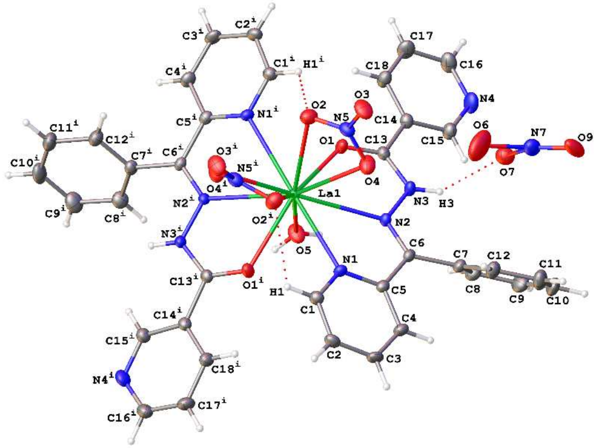

Figure 2. Crystal structure of the dinuclear complex $[La(HL)_2(NO_3)_2(H_2O)]\cdot(NO_3)$ **(1).**

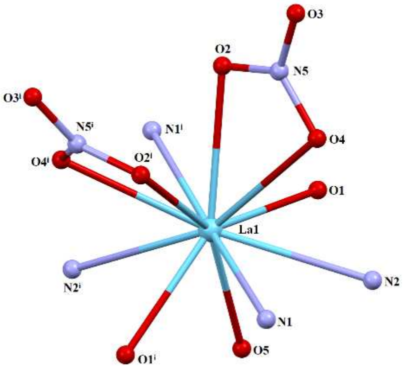

Figure 3. Coordination scheme of complex **1**.

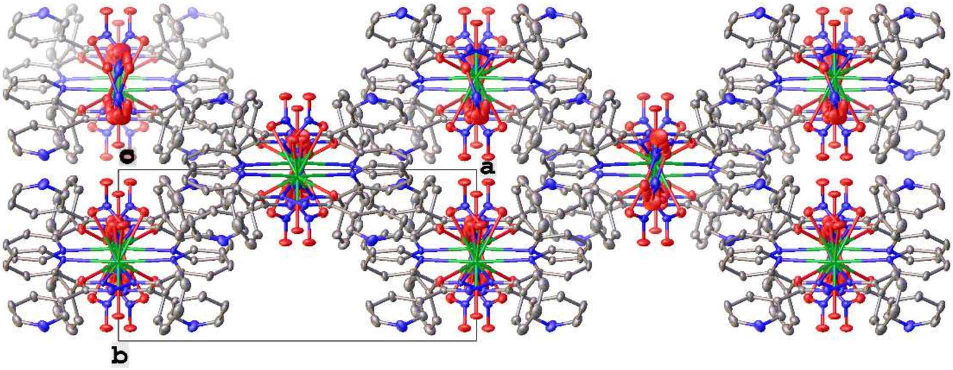

Figure 4. Crystal packing of **1** as seen along c axis.

4. Conclusion

This present work describes the results of the preparation of coordination complexes of lanthanide (III) ions with the ligand *N'*-(phenyl(pyridin-2-yl)methylene)nicotine-hydrazide (H*L*). The ligand and the complexes are characterized by different spectrometric methods to confirm their structures in solid state and in solution. FTIR spectroscopy shows that the ligand remains in its neutral form upon complexation. The coordinate nitrate cations act as bidentate chelating while the others nitrate cations remain free. UV-Vis spectrophotometry indicates internal transition in the ligand and metal ligand charge transfer. Conductimetric studies shows that complex **1** and **2** are 1:1 electrolyte while complexes **3**-**6** are 2:1 electrolyte in fresh DMF solutions. The structure of the complex **1** was elucidated by X-ray diffraction study and formulated as $[La(HL)_2(NO_3)_2(H_2O)]\cdot(NO_3)$.

5. Supplementary data

CCDC: 2256400 contains the supplementary crystallographic data for the complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk.

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