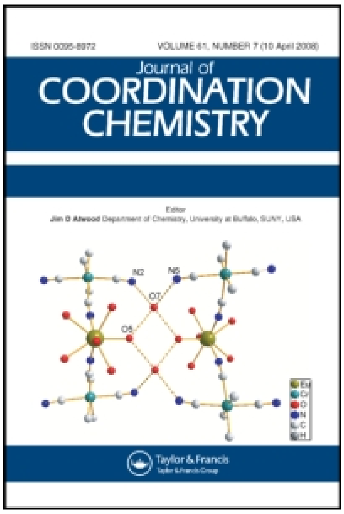

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Interactions of trivalent lanthanide cations with a hexadentate Schiff base derived from the condensation of ethylenediamine with 8-hydroxyquinoline-2-carboxaldehyde

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Interactions of trivalent lanthanide cations with a hexadentate Schiff base derived from the condensation of ethylenediamine with 8-hydroxyquinoline-2-carboxaldehyde

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Lanthanide(III) complexes [Ln$(NO_3)_2$(HL)] where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Lu and LH_2 = *N*,*N*′-*bis*(quinolin-8-ol-2-ylmethylidene)ethane-1,2-diamine, have been obtained by direct reaction of the di-Schiff base ligand and the corresponding hydrated lanthanide(III) nitrates in methanol/DMF solvent systems. All complexes were characterized with microanalyses, spectroscopically (IR and electronic spectra) and thermogravimetrically. Theoretical studies have also been undertaken to estimate possible structures. All the data are discussed in terms of the nature of the bonding and the possible structural types. All complexes appear to be monomeric with the organic ligand being singly deprotonated and behaving as a hexadentate chelating ligand.

Keywords: Lanthanide(III) complexes; Hexadentate Schiff base; Spectroscopic characterization; Theoretical studies

1. Introduction

Schiff-base metal complexes have been known since the nineteenth century, playing a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [1].

The ability of lanthanide cations to promote Schiff base condensation of the appropriate diamine and dicarbonyl precursors, giving access to complexes of otherwise inaccessible ligands in combination with the applications of lanthanide macrocyclic complexes emerging from biology and medicine have boosted research on these areas [2]. These applications, NMR contrast agents, biological markers, photodynamic therapy and phosphoryl transfer catalysts, etc., demand high thermodynamic and kinetic stability of the complexes [3]. Numerous articles have been published on lanthanide complexes with the hexadentate Schiff base derived by

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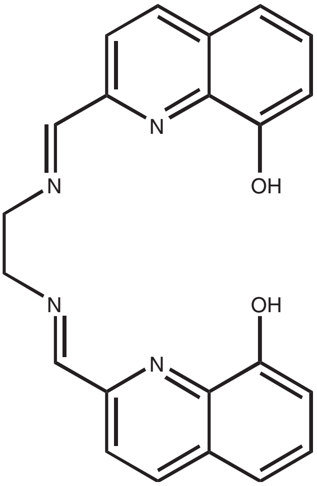


Scheme 1. The ligand *N*,*N*′-*bis*(quinolin-8-ol-2-ylmethylidene)ethane-1,2-diamine (LH_2) is shown.

condensation of 2,6-diacetylpyridine and ethylenediamine [4–14]. These complexes are stable enough under physiological conditions. However, the literature is quite scarce in dealing with the various aspects involving different physicochemical properties and complexation behaviour of tetradentate Schiff bases [2].

Previously, we have reported the synthesis and the structural and spectroscopic characterization of lanthanide complexes with *bis*[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine [15], *bis*(pyridin-2-ylmethylene)benzene-1,2-diamine [16] and *bis*(pyridin-2-ylmethylene)cyclohexane-1,2-diamine [17]. Apart from the special structural interest of the products, we found that they are not stable in aqueous media leading to solutions with $[Gd(H_2O)_9]^{3+}$. Bearing in mind the instability of the tetradentate di-Schiff base complexes, we decided to design open chain Schiff bases with higher dendicity (i.e., 6) and study their complexes. Our first approach is the title ligand (scheme 1), which, in addition to four nitrogen donors contains two other groups available for coordination. These hydroxyl groups can be relatively easily deprotonated and lead to lanthanide complexes with 2+ or 1+ charge. The 8-hydroxyquinoline moiety is well known in coordination chemistry and we have studied extensively the coordination properties of the four-nitrogen part of the ligand.

Herein we report the synthesis and the spectroscopic characterization of the new ligand, the synthesis and physicochemical and spectroscopic characterization of several new lanthanide(III) complexes, as well as theoretical studies on the organic molecule and the coordination compounds.

2. Experimental

2.1. *Materials*

All manipulations were performed under aerobic conditions. Hydrated lanthanide salts and organic reagents were purchased from Aldrich. Solvents were of analytical grade and used without further purification.

2.2. *Instrumentation*

C, H and N analyses were conducted by the University of Ioannina, Greece, Microanalytical Service. IR spectra (4000–370 cm^{-1}) were recorded on a Perkin Elmer Spectrum GX FT-IR System with samples prepared as KBr pellets. Room temperature magnetochemical measurements were performed on a Johnson Matthey Magnetic Susceptibility Balance with the Evans method. The visible spectra were recorded on a Jasco 530 spectrophotometer, in 0.002 M solutions in DMF. UV/Vis diffuse reflectance spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer with a Shimadzu integration sphere. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 and Bruker AMX 400 MHz spectrometers at 300 K. DMSO-d^6 was used as a solvent. Thermal studies were carried out on a Shimadzu DTG-60 simultaneous DTA-TG apparatus, under N_2 or forced air flow (50 cm^3 min^{-1}) with a heating rate of 5°C min^{-1}. Sample sizes were about 5 mg. X-ray powder diffraction patterns were recorded on a Siemens (now Bruker) D8 ADVANCE diffractometer. Conductivity measurements were carried out with a Methrohm – Herisau E-527 instrument using 0.001 M solutions of the complexes in DMF or DMSO at 25°C.

The geometry optimization of the lanthanum complex was computed using the Augmented MM3 method which is implemented in the CacheWorksystem Pro and DFT method which is implemented in Gaussian 98. The augmented MM3 optimization result was used for the DFT calculation. DFT calculation was performed with Becke's three parameter hybrid functional with Lee, Yang and Parr correlation functional (B3LYP) with the Los Alamos LANL2DZ split valence basis set. After geometry optimization the vibrational spectrum was evaluated to check that no imaginary frequency is present.

Preparation of the ligand (LH_2) (2,2′-(1*E*,1′*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))-*bis*(methan-1-yl-1-ylidene)diquinolin-8-ol). To a stirred solution of 8-hydroxyquinoline-2-carboxaldehyde (1 g, 5.77 mmol) in ethanol 0.18 mL ethylendiamine (0.16 g, 2.66 mmol) was added and the resulting solution was refluxed for 5 h in 75°C. The colour of the solution gradually changed from yellowish to brownish orange and a yellow solid formed gradually. The solid was filtered and washed with cold diethylether and dried in vacuum. Yield 50% (0.5 g). Anal. Calcd For $C_{22}H_{18}N_4O_2$, (%): C, 71.3; H, 4.91; N, 15.12. Found: C, 72.54; H, 4.97; N, 15.22. Selected IR data (cm^{-1}): 3436 (ν(O–H)); 3052 (ν(C–H) ar); 2922, 2877 (ν (C–H) al); 1645 (ν (C=N); 1468 (s (C=C)); 1284 (s (CH_2)); 1200 (s (C–O)); 854 (s (C–C)); 762 (s (C–N): m.p. 171°C. UV–Vis (in DMF) 272, 456 nm. ^{1}H-NMR (DMSO, ppm, 400 MHz, Ar = Aromatic ring) δ: 4.09 (s, 4H, CH_2-CH_2), 7.11 (d, 2H, Ar), 7.38 (t, 2H, Ar), 7.47 (t, 2H, Ar), 8.04 (d, 2H, Ar), 8.22 (d, 2H, Ar H), 8.58 (s, 2, CH=N), 9.73 (sb, 2H, C–OH); ^{13}C-NMR (DMSO, ppm, 40 MHz) δ: 69.1 (CH_2), 113.4, 121.0, 123.1, 127.2, 132.1, 135.7, 138.1, 142.7 (Ar), 154.1 (Ar, C–OH), 155.7 (CH=N). ESI MS (negative in MeOH): *m*/*z* 369 (LH^-, $[C_{22}H_{17}N_4O_2]^-$.

Preparation of the complexes. All complexes were prepared from 1 : 1 reactions of the ligand and the lanthanide nitrates in ethanol. The yields were about 50%.

A representative synthetic procedure is presented below.

$La(LH_2)(NO_3)_2$ (1). To a stirred solution of LH_2 (0.02 g, 0.57 mmol) in ethanol (30 mL) was added a solution of $La(NO_3)_3 \cdot 6H_2O$ (0.024 g, 0.57 mmol) in 2 mL methanol. A small amount of a yellow–orange solid was formed during addition. The resulting mixture was stirred for 1 h and the amount of solid increased. The solid was filtered, washed with cold EtOH (3 × 5 mL) and diethylether (2 × 5 mL) and dried in vacuum over silica gel. Overall yield (0.02 g, 50% based on La^{3+}).

3. Results and discussion

3.1. *Synthesis and characterization of the ligand*

The potentially hexadentate ligand LH_2 is produced by reaction between ethylenediamine and 8-hydroxyquinoline-2-carboxaldehyde, which proceeds smoothly in refluxing ethanol, and the amount of the reaction product increases gradually leading to a reasonable yield of about 50%. Complete condensation of all primary amino groups is confirmed by the lack of N–H stretching bands in the IR 3150–3450 cm^{-1} region and the presence of strong C=N stretching bands for the organic molecule. This conclusion is also supported by the ^{1}H-NMR data which show not only the absence of N–H hydrogen resonances but also the presence of CH=N hydrogen resonances at about 8.5 ppm. ^{1}H- and ^{13}C-NMR spectra, mass spectral and infrared data for the ligand are completely consistent with the formulation indicated in scheme 1.

3.2. *Synthesis and physical properties of the complexes*

The formulae of the compounds, preparation yields, analytical data, effective magnetic moments and molar conductivity values are given in table 1. Generally all complexes

Table 1. Analytical data and physical properties of the prepared compounds.

				Elemental analysis				
A/A	Formula	Yield (%)	M.p. (°C)	% C	% H	% N	μ_{eff} (BM)	Λ_M ($Ohm^{-1} cm^2 mol^{-1}$, 10^{-3} M at 25°C)
	LH_2	65	171	71.16	4.78	15.07		
1	$[La(LH)(NO_3)_2] \cdot MeOH$	55		41.82	2.73	13.39	dia	7
2	$[Pr(LH)(NO_3)_2]$	61		42.00	2.34	13.51	2.57	13
3	$[Nd(LH)(NO_3)_2]$	57		41.44	2.42	13.17	3.61	21
4	$[Sm(LH)(NO_3)_2]$	59		40.97	2.67	12.78	1.58	17
5	$[Eu(LH)(NO_3)_2]$	63		40.91	2.51	12.96	3.47	15
6	$[Gd(LH)(NO_3)_2]$	58		40.61	3.01	12.81	7.98	9
7	$[Tb(LH)(NO_3)_2]$	69		40.12	2.31	12.77	9.81	14
8	$[Dy(LH)(NO_3)_2]$	67		40.61	2.61	12.71	10.41	11
9	$[Ho(LH)(NO_3)_2]$	72		40.37	2.54	12.71	10.57	18
10	$[Er(LH)(NO_3)_2]$	71		40.10	2.44	12.70	9.48	13
11	$[Yb(LH)(NO_3)_2]$	74		39.87	2.40	12.73	4.46	16
12	$[Lu(LH)(NO_3)_2]$	69		39.61	2.51	12.47	dia	10

are insoluble in most common organic solvents, being soluble only in DMSO and slightly soluble in DMF. Because of the insolubility of the complexes in suitable solvents, we could not grow crystals for single-crystal X-ray structural studies.

The Λ_M values of all the complexes in DMSO are in accord with this group of complexes being formulated as non-electrolytes [18]. The conductivity measurements were made immediately after the solid compounds were dissolved. When the solutions warmed up, at ca 60°C and were left undisturbed for a few hours, the second conductivity measurements suggested 1 : 2 electrolytes and replacement of the nitrato ligands by DMSO molecules. The X-ray powder diffraction patterns indicate that the products are not contaminated with the starting materials and that they can be separated into three groups of isostructural compounds. The first group includes complexes **2–6**, the second complexes **7–11**, and the third complexes **12** and **13**. The room temperature effective magnetic moments of the complexes show little deviation from the Van Vleck theoretical values (see table 1).

All complexes behave similarly when heated under nitrogen. Complex **1** loses its methanol molecule at about 80°C, suggesting coordination of the solvent on La(III), while the rest of the solids show no curve inflections about that temperature. The intermediate of **1** and all other complexes are reasonably stable (up to ca 300°C) and decompose violently due to the nitrates. The final residues, which are obtained above 600°C, correspond to the sesqui-oxides except for **2**, which corresponds to Pr_6O_{11}.

3.3. *IR spectra*

Tables 2 and 3 give diagnostic IR bands. In the ν(O–H) region, the spectra of **2–13** show one medium, relatively sharp band at 3370–3320 cm^{-1} attributed to the hydrogen bonded phenoxide group. The corresponding band for the ligand appears at slightly higher frequency, suggesting weaker O–H bonds in the complexes, and possible coordination of the oxygen atom to the metal atoms. The suggested intramolecular hydrogen bonds are another reason for this weakening of the O–H bond in the complexes.

IR spectra of complexes containing ligands with two pyridines may be reliably used as a guide to pyridine coordination and the criteria employed have been adequately discussed [19–25]. Careful study of multiplicity and shifts of mid- and far-IR bands associated with internal modes of vibration of the pyridine rings, can lead to fairly clear structural conclusions. The bands most affected by coordination, are the four ν(C=N) and ν(C=C) bands observed between 1610 and 1410 cm^{-1}, the ring breathing mode near 1000 cm^{-1}, an out-of-plane CH deformation near 800 cm^{-1} and the two in-plane and out-of-plane ring deformation bands at ca 600 and 400 cm^{-1}, respectively. These characteristic bands of the pyridine ring are single in both the spectrum of LH_2, and its lanthanide complexes suggesting the presence of equivalent aromatic 'arms' of the ligand.

The vibrational spectra of the complexes suggest that the ligand utilizes all available donors for coordination. In addition the systematic appearance of weak broad bands that can be attributed to O–H stretches of hydrogen bonded groups supports the suggested structures.

Table 2. Diagnostic IR bands (cm^{-1}) of LH_2 and its lanthanide(III) complexes.

Assignment	LH_2	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
ν(O–H)	3430s, 2361m	3395mb, 2485w	3421m, 2491w	3405m, 2508w	3398m, 2498w	3429mb, 2516w	3417m, 2502w	3419m, 2483w	3400m, 2487w	3398m, 2473w	3422m, 2501w	3429m, 2492w	3399m, 2499w	3399m, 2509w
ν(C–H)	3054w, 2922w, 2877w	3062w, 2931w	3068w, 2915w	3069w, 2937w	3057w, 2925w	3070w, 2928w	3069w, 2930w	3058w, 2933w	3061w, 2918w	3055w, 2920w	3063w, 2925w	3070w, 2917w	3068w, 2908w	3058w, 2921w
ν(C=N)	1643s	1650s, 1612m	1647s, 1608m	1651s, 1609m	1649s, 1611m	1651s, 1605m	1647s, 1611m	1650s, 1609m	1647s, 1613m	1652s, 1604m	1649m, 1607m	1646s, 1610m	1650s, 1610m	1646s, 1609m
ν(CN) and ν(CC) ring	1564m, 1508s, 1468vs, 1436w	1558m, 1459s	1531w, 1460s	1547m, 1463s	1557w, 1461s	1563w, 1464s	1560w, 1465s	1537w, 1466s	1540w, 1461s	1555w, 1462s	1557m, 1460m	1560w, 1458s	1548w, 1460s	1551w, 1461s
$\delta(CH_2)$	1373w, 1328mw	1380m, 1340m	1381m, 1342m	1379m, 1337m	1382m, 1338m	1382m, 1342m	1378m, 1339m	1379m, 1340m	1380m, 1339m	1375m, 1337m	1376m, 1340m	1378m, 1341m	1380m, 1344m	1378m, 1339m
ν(C–O)	1255m, 1233m, 1198ms	1233w, 1215w	1231w, 1214w	1234w, 1215w	1232w, 1213w	1231w, 1211w	1234w, 1215w	1235w, 1214w	1235w, 1216w	1236w, 1216w	1235w, 1214w	1237w, 1216w	1237w, 1217w	1239w, 1218w
ν(C–C)	1168m, 1086ms	1170m, 1088ms	1172w, 1089m	1171w, 1090m	1173w, 1098m	1175w, 1100m	1174w, 1097m	1175w, 1099m	1173w, 1094m	1174w, 1099m	1172w, 1100m	1174w, 1091m	1177w, 1097m	1173w, 1101m
Ring breathing	1026m, 970mw	1031m, 981mw	1037m, 979mw	1035m, 987mw	1037m, 990m	1040m, 994m	1038m, 989m	1039m, 984m	1033m, 991m	1036m, 992m	1038m, 993m	1039m, 989m	1040m, 991m	1040m, 994mw
Out of plane C–H def.	853ms	819mw	817w	815w	817w	815w	814m	816m	818m	818m	815w	817m	819m	815mw
ν(C–N)	763m	761m	760m	764m	762m	762m	763m	760m	759m	761m	762m	763m	761m	760m
δ(ring) in plane	556ms	608w, 591w	611w, 588mw	611w, 589mw	612w, 590mw	614w, 586mw	615w, 587w	610w, 592mw	613w, 589w	612w, 590mw	613w, 591w	611w, 592w	613w, 593w	615w, 590w
δ(ring) out of plane	487mw, 441w	491mw, 451w	496mw	494mw	495mw	497mw	493w	498mw	492mw	496mw	493mw	494mw	497mw	493mw

Table 3. Characteristic nitrate IR bands (cm^{-1}) for the lanthanide(III) complexes of LH_2.

Assignment	ν_1 (A_1)	ν_4 (B_2)	ν_2 (A_1)	ν_6 (B_1)	ν_5 (B_2)
1	1462sb	1281s	1017m	829m	722w
2	1464s	1285s	1020m	831m	709mw
3	1463s	1283s	1023s	328m	718mw
4	1465sb	1282s	1019m	835m	722m
5	1466sb	1284s	1029m	838m	726m
6	1467s	1284s	1023s	837m	724mw
7	1465sb, 1430m	1284s, 1307m	1027s	838m	727m
8	1469sb, 1432m	1281s, 1306m	1022s	840m	722m
9	1467sb, 1429m	1283s, 1309m	1025m	839m	724m
10	1470s, 1431m	1291s, 1311m	1029s	838m	723mw
11	1468sb, 1440m	1288s, 1310m	1031s	841m	720w
12	1455s	1317sb	1030m	839m	704w
13	1459sb	1327s	1028s	838m	706mw

Table 4. Bonding parameters, calculated from the solid state f–f spectra for the prepared complexes.

A/A	Complex	$\bar{\beta}$	δ (%)	$b^{1/2}$
3	$[Pr(LH)(NO_3)_2]$	1.004	−0.31	–
4	$[Nd(LH)(NO_3)_2]$	1.001	−0.11	–
5	$[Sm(LH)(NO_3)_2]$	0.999	+0.11	0.023
10	$[Ho(LH)(NO_3)_2]$	0.997	+0.39	0.046
11	$[Er(LH)(NO_3)_2]$	0.996	+0.30	0.039

In the spectra of **1**–**13** the frequencies of the bands assigned as vibrational modes of the nitrate groups (table 3) suggest the absence of ionic nitrates. Though there is a band at about 1380 cm^{-1} in the IR spectra of the complexes it cannot be assigned to the $\nu_3(E')$ of the ionic D_{3h} nitrate due to its shape and intensity. The other vibrational nitrate fundamentals suggest chelating bidentate nitrato groups, for complexes **1**–**6**, as the separation of the two highest frequency bands is large (ca 210 cm^{-1}); the possibility of bridging nitrato groups is ruled out, because the highest frequency nitrato mode appears below 1550 cm^{-1}. For complexes **7**–**11** there are two pairs of bands at high frequency suggesting two different kinds of coordinated nitrato ligands, i.e. bidentate chelating and monodentate. Complexes **12** and **13** show nitrate bands attributable to only monodentate nitrates since the separation of the high energy bands is well below 210 cm^{-1} (ca 130 cm^{-1}). This grouping of the complexes is in agreement with the XRPD data that exclude only lanthanum complex **1** that contains coordinated methanol.

3.4. *Electronic spectra*

The electronic diffuse reflectance spectra of the complexes involve mainly intraligand and f–f transitions. The values of the bonding parameters β (nephelauxetic ratio), δ (Sinha's parameter) and $b^{1/2}$ (covalent factor) of the Pr^{III}, Nd^{III}, Sm^{III}, Ho^{III} and Er^{III} complexes (table 4), calculated from the solid state f–f spectra by standard equations [26–28] indicate that the interaction between the trivalent lanthanides and the ligands is essentially electrostatic and that there is very small participation of the 4f orbitals in bonding [26–28].

The shape and fine structure of the same hypersensitive f–f bands for Nd^{III}, Ho^{III} and Er^{III} have been related to coordination number [29]. For Nd^{III} four transitions are sensitive to coordination environment but one, the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4G_{7/2}$ at about 590 nm, is particularly so. By comparing the spectra of standard Nd^{III} compounds with those of our complexes in the region of the above-mentioned transition, it is concluded that **4** is nine or ten coordinate [29, 30]. Analogous studies [19, 29] for the Ho^{III} (in the region of the *hypersensitive* $^5I_8 \rightarrow {}^5G_6$, $^5F_1$ transition at about 450 nm) and Er^{III} (in the region of the *hypersensitive* $^4I_{15/2} \rightarrow {}^2H_{11/2}$, transition at about 530 nm) complexes demonstrate that **10** and **11** are eight coordinate.

3.5. *Theoretical calculations*

DFT calculations were used in the case of $[La(LH)(NO_3)_2]$ complex without and with methanol (**1A** and **1B**, respectively, scheme 2) and the results were compared with the experimental ones.

Tables 5 and 6 include Dipole Moments and Mulliken charges, respectively for both **1A** and **1B** complexes

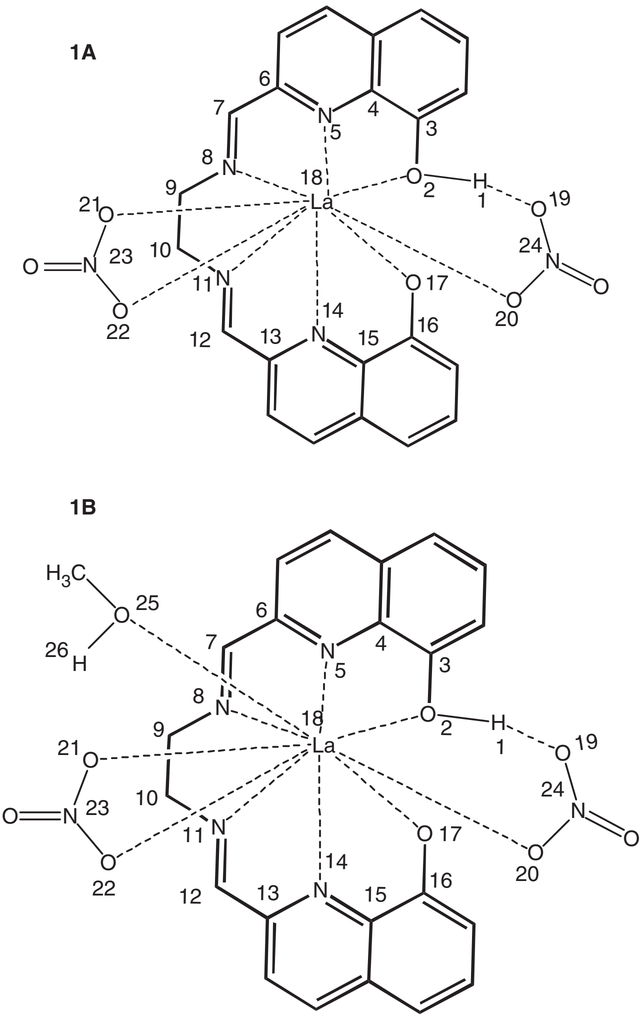
The DFT calculated lengths of chemical bonds of La(18)–N(14) and La(18)–N(5) in **1A** and **1B** complexes were found as 2.75, 2.80 and 2.72, 2.79 Å respectively (table 7). In the literature La–N bond lengths were reported within the range of 2.73–2.76 Å [7, 31, 32]. These very small differences between the theoretically calculated and experimentally measured results obviously originates from the difference in the structures of the two molecules studied. The presence of the short chemical bond between the metal atom and the deprotonated oxygen atom of the ligand studied might be due to other reasons.

The theoretically calculated La(18)–N(11) and La(18)–N(8) bond lengths were found as 2.78, 2.84 and 2.76, 2.88 Å in **1A** and **2B** complexes respectively (table 7). The experimental values reported in the literature are within the range of 2.704–2.810 Å [7, 31, 32].

When we examine the bonds of the NO_3^- groups with the metal, namely La(18)–O(20), La(18)–O(21), La(18)–O(22) the results found are 2.48, 2.64 and 2.69 Å in complex **1A** and 2.55, 2.73 and 2.68 Å in complex **1B** respectively (table 7). The reported literature values lie in the range of 2.689–2.679 Å [7, 31, 32]. The difference of 0.13–0.20 Å between literature and calculated values may rise from the presence of two NO_3^- groups, with the one of them forming a H-bonding interaction between the hydrogen atom of the OH group which in turn leads lanthanum to approach the other O atom not participating in H-bonding.

The N(8)–L(18)–N(5) angles in **1A** and **1B** were calculated to be 59.003 and 59.073°, respectively (table 7). This angle was measured to be 59.0° in similar complexes [7]. The N(5)–La(18)–N(11) angles in **1A** and **1B** were calculated as 115.85 and 117.279°, respectively (table 7); this angle was reported to be 116.2° in the literature [7]. The N(5)–La(18)–(N14) angle in **1A** and **1B** were calculated as 171.47 and 164.60°, respectively (164.3° in the literature) [7]. N(11)–La(18)–(N14) angles in **1A** and **1B** were calculated at 60.33 and 59.68°, respectively. The literature value was 59.2° [7].

The O(22)–La(18)–O(21) in **1A** and **1B** were calculated at 50.07 and 50.79° respectively. In the literature the reported values are in the range of 44.67–46.86 [7, 33].



Scheme 2. Complexes of La(III) with the ligand LH_2, not containing methanol **1A** and containing a methanol molecule **1B** are shown.

Table 5. DFT calculated *E*, ZPE *vs*. dipole moment values of **1A** and **1B**.

	E (Hartree)	ZPE (Hartree)	*E* + ZPE	Dipole moment (Debye)
1A	−1809.92495294	0.381124	−1809.54379894	8.6331
1B	−1925.66649020	0.434841	−1925.23164920	6.1915

Table 6. DFT calculated Mulliken charges of some atoms in **1A** and **1B**.

	O2	N5	N8	N11	N14	O17	O19	O20	O21	O22	O23
1A	−0.602	−0.199	−0.120	−0.174	−0.230	−0.549	−0.317	−0.399	−0.327	−0.345	–
1B	−0.606	−0.191	−0.098	−0.160	−0.218	−0.604	−0.320	−0.378	−0.301	−0.348	−0.584

Table 7. DFT calculated bond lengths (Å), angles and dihedral angles (°) for $La(LH_2)(NO_3)_2$ **(1A)** and $La(LH_2)(MeOH)(NO_3)_2$ **(1B)**.

	1A	**1B**		**1A**	**1B**		**1A**	**1B**
La(18)–O(2)	2.64	2.67	La(18)–O(22)	2.69	2.68	La(18)–N(11)–C(12)–C(13)	0	3.360
La(18)–N(5)	2.80	2.79	La(18)–O(25)	–	2.60	La(18)–N(14)–C(13)–C(12)	−0.360	−7.320
La(18)–N(8)	2.84	2.88	La(18)–O(2)–C(3)–C(4)	−8.560	−20.660	La(18)–N(11)–C(15)–C(16)	0.310	5.940
La(18)–N(11)	2.78	2.76	La(18)–N(5)–C(4)–C(3)	12.460	22.820	La(18)–O(17)–C(16)–C(15)	−1.380	−6.350
La(18)–N(14)	2.75	2.72	La(18)–N(5)–C(6)–C(7)	−13.20	−24.800	La(18)–O(20)–N(24)–O(19)	−25.420	−12.560
La(18)–O(17)	2.44	2.51	La(18)–N(8)–C(7)–C(6)	16.620	22.720	La(18)–O(2)–H(1)–O(19)	63.380	33.690
La(18)–O(20)	2.48	2.55	La(18)–N(8)–C(9)–C(10)	37.900	30.970	O(2)–H(1)–O(19)–N(24)	−41.850	−11.590
La(18)–O(21)	2.64	2.73	La(18)–N(11)–C(10)–C(9)	48.880	48.880	La(18)–O(22)–N(23)–O(21)	−3.570	0.570
O(17)–H(26)	–	1.79	O(17)–La(18)–O(25)–H(26)	–	5.910			

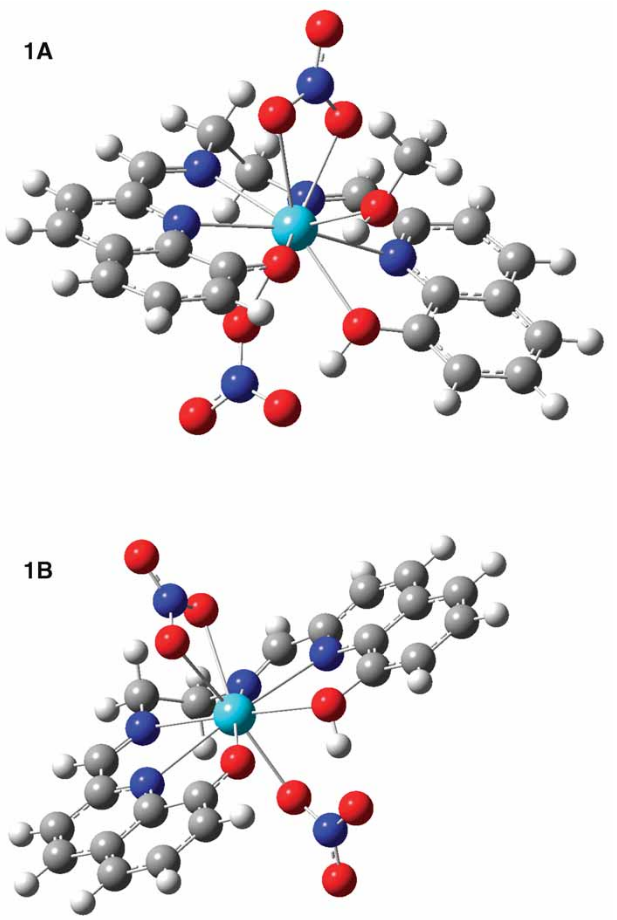


Figure 1. DFT geometry of La(LH_2)(NO_3)$_2$ **(1A)** and La(LH_2)(NO_3)$_2$(MeOH) **(1B)**.

The small differences between the theoretically calculated and experimentally measured results, obviously originates from NO_3^- coordination in the molecules.

DFT calculated results allow us to predict a correct structure for the metal-ligand complexes (figure 1). The comparison with the literature reported X-ray structures of similar complexes supports the predicted structure. Furthermore, comparing the results obtained for **1A** and **1B** the complex becomes more stable when it traps a solvent molecule (table 7).

The structure of **1A** can be a reference for other series of lanthanide complexes. It can also be a model for X-ray powder determined in other similar isostructural molecules, as well.

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