

Synthesis, Spectroscopic, Characterization and X-ray Structures of Lanthanide(III) Complexes Derived from 1,5-bis(phenyl(pyridin-2-yl)methylene)carbonohydrazide

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Abstract: The use of 1,5-bis(phenyl(pyridin-2-yl)methylene)carbonohydrazide (H₂L) in the coordination chemistry of lanthanides (III) yielded complexes in which two ligand molecules are present. The synthesis was carried out using a Ln/H₂L ratio of 1/2 to lead mononuclear complexes of [Ln(H₂L)₂(η²-NO₃)_{3-x}](NO₃)_x (Ln=La (1), Sm (4), Gd (6) and Yb (7)), [Ln(H₂L)₂(NO₃)₃] (Ln=Pr(2), Eu(5)) and a co-crystal {[Nd(H₂L)₂(η²-NO₃)₂(η¹-NO₃)], [Nd(H₂L)₂(η²-NO₃)(η¹-NO₃)(H₂O)]}·(NO₃)₂·2CH₃OH} (3). The structures of the complexes (2) and (3) were solved by X-ray crystallography on a single crystal. In the mononuclear complex of Pr^{III}, two neutral ligand molecules act in tridentate fashion. In the co-crystal complex, one of the Nd^{III} atom is coordinated by two ligand molecules acting tridentately in neutral form and three nitrate anions acting in bidentate fashion while the second Nd^{III} atom is coordinated by two ligand molecules acting tridentately in neutral form, one monodentate nitrate anion, one bidentate nitrate anion and one water molecule. The neutrality of the complex is ensured by one free nitrate anion. Two free methanol molecules are present. Complex (2) crystallizes in the triclinic space group P-1 with the following parameters: a=10.128 (2) Å, b=12.2285 (19) Å, c=20.816 (5) Å, α=85.634 (4)°, β=81.870 (4)°, γ=87.210 (5)°, V=2542.9 (9) Å³, Z=2, R₁=0.0640, wR₂=0.1377. Complex (3) crystallizes in the monoclinic space group P2₁/c with the following parameters: a=10.4554 (12) Å, b=44.089 (6) Å, c=23.212 (3) Å, β=90.851 (2)°, V=10699 (2) Å³, Z=4, R₁=0.0630, wR₂=0.1690. The coordination sphere of the twelve-coordinated Pr^{III} atom is best described as distorted icosahedron. In the co-crystal one of the Nd^{III} atom is eleven-coordinated while the second Nd^{III} atom is ten-coordinated. The environments around the Nd^{III} atoms are respectively best described as distorted pentacapped trigonal prism and a distorted bicapped square antiprism, respectively. Supramolecular structures are consolidated by numerous hydrogen bonds.

Keywords: Schiff Base, Co-crystal, Complex, Lanthanide, Mononuclear

1. Introduction

Carbonohydrazide and its derivatives have been known and widely studied since 1894 [1]. Carbonohydrazide

[(H₂NNH)₂CO] is a symmetrical compound with two identical arms which are very reactive towards carbonyl compounds. These species have been used as precursors for the synthesis of heterocyclic compounds containing nitrogen atoms in the ring and/or in the free arms [2-4]. The

reactivity as well as the biological properties of these derivatives have been studied in recent years for drug development [5, 6] and industrial applications [7, 8]. They are known to have excellent biological activities. They are used as antioxidant [9], analgesic [10], antiplatelet [11], antifungal [2], antimicrobial [12], anticonvulsant [13], antidepressant [14], anti-inflammatory [15], anti-tuberculosis [16], anti-HIV [5], anti-diabetic [10, 17] and anti-cancer [3, 18]. In recent years, much attention has been paid to syntheses of acyclic ligands which can give rise to mononuclear lanthanide complexes. While most of the work reported on the Schiff bases of carbonohydrazide focused on their applicability in classical fields, these systems are today increasingly recognized as multitopic ligands for the controlled construction of original metallo-organic architectures such as grids [19, 20]. A considerable amount of work has been done on complexes with carbonohydrazide due to their ability to coordinate with lanthanide or transition metal ions [21–23]. Lanthanide complexes can be used as electroluminescent devices [24, 25], structural probes [26] and in immunobiological assays [27]. In addition to their physical properties [28–32], the antimicrobial, antitumor or antioxidant properties of lanthanide complexes have been explored in recent decades [33–41]. Our research group explored the chemistry of lanthanide compounds containing carbonohydrazide ligands [42]. Our synthetic approach consists in preparing the symmetrical ligand 1,5-bis(phenyl(pyridin-2-yl)methylene)carbonohydrazide (H_2L) which possesses seven potential coordinating sites. Herein, we report a series of new lanthanide (III) complexes derived from H_2L , which acts in a tridentate manner through two nitrogen azomethine atoms and one carbonyl oxygen atom to give mononuclear or dinuclear lanthanide(III) complexes. The crystal structures of the mononuclear Pr^{III} and the dinuclear co-crystal Nd^{III} complexes have been elucidated by single X-ray diffraction.

2. Experimental Section

2.1. General Information

2-benzoylpyridine and carbonohydrazide were commercial products (Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000–400 cm^{-1} region. The 1H NMR spectra were recorded at 300 MHz and $^{13}C\{^1H\}$ NMR spectra at 75 MHz on a Bruker AC-300 instrument. The molar conductance of 10^{-3} M solution of the metal complexes in DMF was measured at 25°C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibility measurements were made on solid complexes using a Johnson-Matthey balance with $Hg[Co(SCN)_4]$ as the calibrator.

2.2. Synthesis of the Ligand H_2L

To a solution of 2-benzoylpyridine (16.28 g, 88.80 mmol) in 20 mL of ethanol was added the carbonohydrazide (4.00 g, 44.40 mmol). The resulting mixture was refluxed for 4 hours. The resulting solution was cooled to room temperature before filtered. Slow evaporation of the filtrate gave brown crystals. The yield of the reaction is 89% and the melting point is between 185–190°C.

IR $\nu(cm^{-1})$: 3160 (NH); 3057 (C-H)_{arom.}; 1698 (C=O); 1570 (C=N); [1502–1420] (C=C)_{arom.}; 1254 (C-N); 1122 (N-N); 792; 739; 682; 650; 619 (C-H)_{arom.} RMN 1H δ (ppm): 8,82 (s, NH); [8,48–7,02] (m, H_{arom.}). RMN ^{13}C δ (ppm): 193,38(C=O); 150,37(C=N); [148,51; 137,64; 132,96; 130,55; 129,95; 128,64; 128,57; 126,71; 124,12; 123,70] (C_{arom.}).

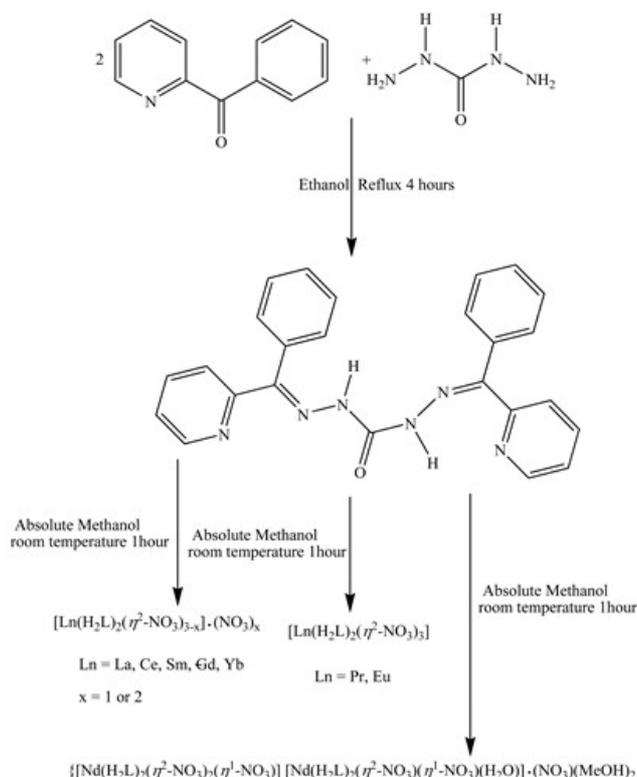


Figure 1. Synthesis scheme of the ligand H_2L and its lanthanide(III) complexes.

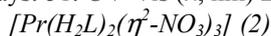
2.3. Synthesis of the Complexes (1-7)

To a solution of H_2L (0.1g, 0.240 mmol) in absolute methanol (10 mL) was added $Ln(NO_3)_3 \cdot nH_2O$ (0.48 mmol) in 10 mL of absolute methanol. A colored solution was obtained. The mixture was stirred for one hour at room temperature and then filtered. The solution was slowly evaporated. After evaporation, a colored solid was obtained.

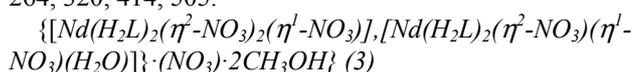


Yield: 71,68%. Color: green. Anal. calc for $LaC_{50}H_{40}N_{15}O_{11}$: C, 51.51; H, 3.46; N, 18.02. Found: C, 51.52; H, 3.47; N, 18.09%. IR (KBr, cm^{-1}): 3329 [$\nu(H_2O)$]; 3077 [$\nu(NH)$]; 1673 [$\nu(C=O)$]; 1515 [$\nu(C=N)$] and (C=C)_{ar}, 1437 [$\nu_1(NO_3)$], 1314 [$\nu_5(NO_3)$], 1039 [$\nu_2(NO_3)$]. μ_{eff} (μ_B) diamagnetic. Λ ($\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$): fresh solution: 88; after 15

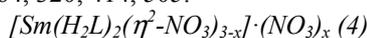
days: 51. UV-Vis (λ , nm) 234, 260, 315, 414, 500.



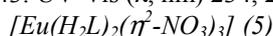
Suitable crystals for X-ray analysis were collected. Yield: 53.57%, Color: green. Anal. calc for $PrC_{50}H_{40}N_{15}O_{11}$: C, 51.42; H, 3.45; N, 17.99. Found: C, 51.39; H, 3.46; N, 17.79%. IR (KBr, cm^{-1}): 3329 [vNH]; 1671 [vC=O]; 1595-1514 [vC=N, v(C=N)py and (C=C)Ar], 1414 [v₁(NO₃)], 1311 [v₅(NO₃)], 1037 [v₂(NO₃)]. $\mu_{eff} (\mu_B) = 2.82$. $\Lambda (\Omega^{-1}\cdot cm^2\cdot mol^{-1})$: fresh solution: 82; after 15 days: 89. UV-Vis (λ , nm) 234, 264, 320, 414, 505.



Suitable crystals for X-ray analysis were collected. Yield: 71.17%, Color: yellow. Anal. calc for $Nd_2C_{102}H_{90}N_{30}O_{25}$: C, 50.53; H, 3.74; N, 17.33. Found: C, 50.51; H, 3.71; N, 17.30%. IR (KBr, cm^{-1}): 3329 [vNH]; 1649 [vC=O]; 1595-1519 [vC=N, v(C=N)py and (C=C)Ar], 1434 [v₁(NO₃)], 1286 [v₅(NO₃)], 1033 [v₂(NO₃)]. $\mu_{eff} (\mu_B) = 5.43$. $\Lambda (\Omega^{-1}\cdot cm^2\cdot mol^{-1})$: fresh solution: 55; after 15 days: 36. UV-Vis (λ , nm) 234, 264, 320, 414, 505.



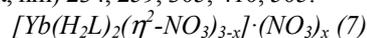
Yield: 20.98%, Color: yellow. Anal. calc for $C_{50}H_{40}N_{15}O_{11}Sm$: C, 51.01; H, 3.42; N, 17.85. Found: C, 51.02; H, 3.45; N, 18.02%. IR (KBr, cm^{-1}): 3329 [vNH]; 1632 [vC=O]; 1595-1513 [vC=N, v(C=N)py and (C=C)Ar], 1465 [v₁(NO₃)], 1303 [v₅(NO₃)], 1026 [v₂(NO₃)]. $\mu_{eff} (\mu_B) = 1.99$. $\Lambda (\Omega^{-1}\cdot cm^2\cdot mol^{-1})$: fresh solution: 199; after 15 days: 143. UV-Vis (λ , nm) 234, 249, 264, 325, 349, 414, 505.



Yield: 43.55%, Color: yellow. Anal. calc for $C_{50}H_{40}N_{15}O_{11}Eu$: C, 50.94; H, 3.42; N, 17.82. Found: C, 51.02; H, 3.43; N, 17.89%. IR (KBr, cm^{-1}): 3344 [vNH]; 1695 [vC=O]; 1571-1513 [vC=N, v(C=N)py and (C=C)Ar], 1423 [v₁(NO₃)], 1314 [v₅(NO₃)], 1024 [v₂(NO₃)]. $\mu_{eff} (\mu_B) = 0.57$. $\Lambda (\Omega^{-1}\cdot cm^2\cdot mol^{-1})$: fresh solution: 28; after 15 days: 22. UV-Vis (λ , nm) 234, 264, 320, 410, 505.



Yield: 31.25%, Color: yellow. Anal. calc for $C_{50}H_{40}N_{15}O_{11}Gd$: C, 50.71; H, 3.40; N, 17.74. Found: C, 50.72; H, 3.42; N, 17.79%. IR (cm^{-1}): 3330 [vNH]; 3043 [vCH_{aromatique}]; 1662 [vC=O]; 1595-1517 [vC=N, v(C=N)py and (C=C)Ar], 1467 [v₁(NO₃)], 1287 [v₅(NO₃)], 1030 [v₂(NO₃)]. $\mu_{eff} (\mu_B) = 7.83$. $\Lambda (\Omega^{-1}\cdot cm^2\cdot mol^{-1})$: fresh solution: 112; after 15 days: 109. UV-Vis (λ , nm) 234, 259, 305, 410, 505.



Yield: 51.37%, Color: green. Anal. calc for $C_{50}H_{40}N_{15}O_{11}Yb$: C, 50.05; H, 3.36; N, 17.51. Found: C, 50.02; H, 3.35; N, 17.49%. IR (KBr, cm^{-1}): 3330 [vNH]; 1657 [vC=O]; 1571-1517 [vC=N, v(C=N)py and (C=C)Ar], 1449 [v₁(NO₃)], 1287 [v₅(NO₃)], 1030 [v₂(NO₃)]. $\mu_{eff} (\mu_B) = 3.17$. $\Lambda (\Omega^{-1}\cdot cm^2\cdot mol^{-1})$: fresh solution: 159; after 15 days: 95. UV-Vis (λ , nm) 234, 249, 259, 289, 410, 515.

2.4. Crystal Structure Determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compounds, were grown by slow evaporation of MeOH solution of the compound. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Rigaku AFC11 007-HF diffractometer with graphite monochromatized CuK α radiation ($\lambda = 1.54184 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. Scattering factors were taken from the program package SHELXTL [43]. The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [44]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH₃ groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [45].

Table 1. Crystallographic data and refinement parameter for the compounds (2) and (3).

Crystal data		
Empirical formula	C ₅₀ H ₄₀ N ₁₅ O ₁₁ Pr (2)	C ₁₀₂ H ₉₀ N ₃₀ O ₂₅ Nd ₂ (3)
Formula weight (g/mol)	1167.88 g/mol	2424.47 g/mol
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 2 ₁ /c
Crystal size (mm)	0.12 x 0.12 x 0.10	0.090 x 0.090 x 0.120
Mo Ka (\AA)	0.71073 \AA	0.71073 \AA
Temperature (K)	173(2) K	173(2) K
a (\AA)	10.128(2)	10.4554(12)
b (\AA)	12.2285(19)	44.089(6)
c (\AA)	20.816(5)	23.212(3)
α ($^\circ$), β ($^\circ$), γ ($^\circ$)	85.634(4); 81.870(4); 87.210(5)	90; 90.851(2); 90
V (\AA^3); Z	2542.9(9); 2	10699(2); 4
D _{cal} (gcm ⁻³)	1.525	1.485
F (000)	1184	4856
μ (mm ⁻¹)	1.034	1.046
θ_{max} ($^\circ$)	27.58	30.01
h, k, l ranges	-13<=h<=13, -11<=k<=15, -27<=l<=27	-11<=h<=11, -62<=k<=62, -32<=l<=32
Measured reflections	39892	140470
Independent reflections	10994	27014
Reflections [I>2 σ (I)]	8222	19323

Crystal data		
R _{int}	0.1084	0.0735
R Indices [I>2σ(I)]	R1=0.0640, wR2=0.1377	R1=0.0630, wR2=0.1526
R Indices (all data)	R1=0.0975, wR2=0.1512	R1=0.0968, wR2=0.1690
Data/parameters/restraints	10994/694/0	27014/1437/11
Goodness-of-Fit	1.071	1.069
Δρ _{max} , Δρ _{min} (eÅ ⁻³)	2.17, -2.09	2.74, -1.11

3. Results and Discussion

3.1. General Study

H₂L (1,5-bis(phenyl(pyridin-2-yl)methylene)carbonohydrazide) was prepared according to Figure 1. The resulting compound is soluble in methanol and ethanol. The ¹H and ¹³C NMR data for the Schiff base, the analytical and spectral data are consistent with the proposed structure.

In the infrared spectrum of the ligand a medium sharp band is observed around 3346 cm⁻¹ which is attributed to the vibration of the N-H bond [42]. The bands at 3160 cm⁻¹ and 3057 cm⁻¹ are attributed to the valence vibrations of C_{Ar}-H bonds [42]. The vibration bands ν_{C=O} and ν_{C=N} were respectively pointed at 1698 cm⁻¹ and 1630 cm⁻¹ [42]. Bands due to ν_{C=N} of the pyridine ring and ν_{C=C} of the phenyl ring are pointed in the range 1570 cm⁻¹—1420 cm⁻¹ [46]. The band pointed at 1254 cm⁻¹ is attributed to the ν_{C-N} bond [47]. The vibration of the N-N bond is identified at 1122 cm⁻¹. Band due to C-H deformation of aromatic ring are observed in the region 792 cm⁻¹—619 cm⁻¹.

The ¹H NMR spectrum shows signals between 7.02 and 8.49 ppm due to the eighteen protons of the two pyridine rings and the two benzene rings of the ligand. In addition, two signals at 8.83 and 9.72 were assigned respectively to the OH and NH protons. The ¹³C NMR spectrum indicates signal at 193.38 ppm attributed to C=O, while the signal of C=N appears at 150.37 ppm. The mass spectrum indicates an ionic mass m/z at 421.17 corresponding to the molecular ion [M-H]⁺. The fragment at m/z=256.11 corresponds to a mono-condensed ionic molecule.

The reaction of 1,5-bis(phenyl(pyridin-2-yl)methylene)carbonohydrazide (H₂L₂) with lanthanide nitrate in methanol afforded complexes formulated as [Ln(H₂L)₂(η²-NO₃)_{3-x}](NO₃)_x (Ln=La (1), Sm (4), Gd (6) and Yb (7)), [Ln(H₂L)₂(NO₃)₃] (Ln=Pr (2), Eu (5) and {[Nd(H₂L)₂(η²-NO₃)₂(η¹-NO₃)]:[Nd(H₂L)₂(η²-NO₃)(η¹-

NO₃)(H₂O)]·(NO₃)·2CH₃OH} (3). The reactions of the ligand with lanthanide salts are depicted in Figure 1. The infrared spectra of the complexes (Table 2) (1-7) show band attributed to the C=N in the range 1600-1570 cm⁻¹. The shift to lower frequencies of this band which was pointed at *ca.* 1630 cm⁻¹ in the infrared spectrum of the free ligand is indicative of the involvement of the azomethine in the coordination. Additionally, the band pointed at 1698 cm⁻¹ due to the carbonyl function is shifted to low frequencies and appears in the range 1673-1632 cm⁻¹ upon coordination to Ln^{III}. The oxygen atom of the carbonyl is involved in the coordination. All the spectra of the compounds (1-7) reveal bands due to a bidentate nitrate group at 1434-1467 cm⁻¹ (ν₁), 1286-1303 cm⁻¹ (ν₂) and 1024-1037 cm⁻¹ (ν₃). For complexes 1, 3, 4, 6 and 7 the sharp and strong band which appears at 1380 cm⁻¹ is indicative of the presence of an ionic nitrate group. Additional bands pointed in the region 3346-3329 cm⁻¹ are observed and are attributed to ν_{N-H} and ν_{O-H} of the coordinated water molecule or uncoordinated methanol molecule. The molar conductivity values of 28 S.cm².mol⁻¹ for complex 5 is indicative of neutral electrolyte in DMF solutions. Complexes 1, 2 and 3 exhibits molar conductivity values in the range 55-88 S.cm².mol⁻¹ in DMF which are in accordance with 1:1 electrolyte nature [48]. Complexes 6 and 7 exhibits molar conductivity values the range 110-155 S.cm².mol⁻¹ in DMF which are indicative of 1:2 electrolyte nature [48]. Complex 4 is a 1:3 electrolyte with a molar conductivity value of 199 S.cm².mol⁻¹ in DMF [48]. Complex 1 is diamagnetic while complexes 2-7 are paramagnetic. The magnetic moment values of 2.82 μ_B (2), 5.43 μ_B (3), 1.99 μ_B (4), 0.57 μ_B (5), 7.83 μ_B (6) and 3.17 μ_B (7), show little deviation from the theoretical values reported for the trivalent lanthanide ions. This observation is indicative that the 4f electrons do not participate in the bond formation of the metal to the ligand [37]. The electronic spectra of the complexes 1-7 show bands in the region 230-320 which are respectively attributed to the intraligand transitions π→π* and n→π*.

Table 2. Magnetic moments, Conductivity values and Main bands of infrared spectra for 1-7.

Ref	N—H	C=O	C=N	NO ₃				Λ (S.cm ² .mol ⁻¹)	μ _{eff} (mB)	λ (nm)
				ν ₁	ν ₂	ν ₅	ν ₃			
H ₂ L	3346	1698	1630	-	-	-	-	-	-	
1	3329	1673	1595	1437	1314	1036	-	88	Diam.	234, 260, 414, 500
2	3329	1671	1595	1414	1311	1037	-	82	2.82	234, 264, 320, 141, 505
3	3329	1649	1595	1434	1286	1033	1380	55	5.43	234, 264, 320, 414, 505
4	3329	1632	1595	1465	1303	1026	-	199	1.99	234, 249, 264, 325, 349, 505
5	3344	1695	1571	1423	1314	1024	-	28	0.57	234, 264, 320, 410, 505
6	3330	1662	1595	1467	1287	1030	-	112	7.83	234, 259, 305, 410, 505
7	3330	1657	1571	1449	1287	1030	-	159	3.17	234, 249, 259, 289, 410, 515

3.2. Description of the Structure of the Complex 2

The complex (2) formulated as $[\text{Pr}(\text{H}_2\text{L})_2(\text{NO}_3)_3]$ crystallizes in the triclinic system with a space group P-1. The crystal data collection and refinement are reported in

Table 1. The ORTEP diagram of the structure of the mononuclear complex is illustrated in Figure 2. Selected bonds lengths and angles are listed in Table 3.

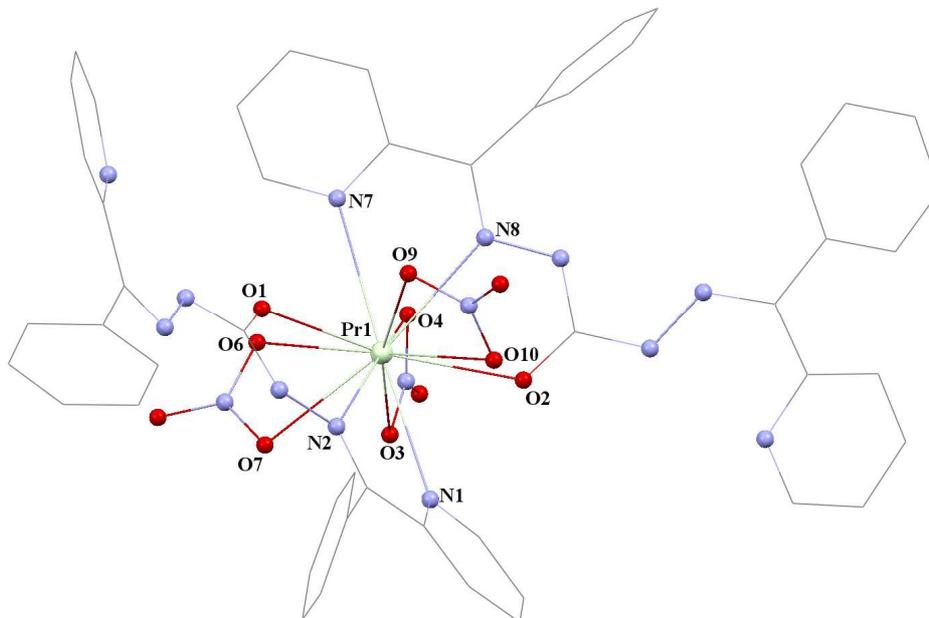


Figure 2. ORTEP Plot (30% probability ellipsoids) showing the structure of the mononuclear complex 2. H atoms are omitted for clarity and only coordinated are labelled.

The complex 2 displays a structure constructed from one Pr^{III} ion, two ligand molecules and three NO_3 anions yielding a mononuclear neutral complex. The Pr^{III} ion is coordinated by two H_2L ligand through one pyridyl nitrogen atom, one imino nitrogen atom and one oxygen atom of the carbonyl function generating two pairs of five membered rings. For each ligand one pyridyl nitrogen atom and one imino nitrogen atom remain uncoordinated.

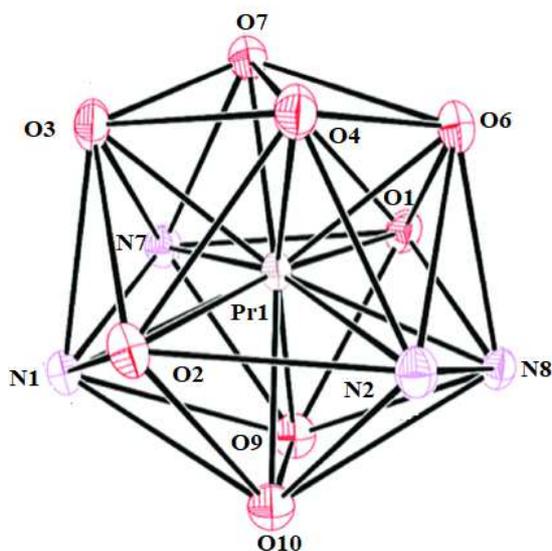


Figure 3. Plot showing the coordination sphere around the Pr^{III} ion in the crystal.

Additionally, each Pr^{III} ion is coordinated by three chelating-bidentate nitrate groups acting in $\eta^2\text{-O}_3\text{N}$ mode, yielding a PrN_4O_8 coordination polyhedron. The $\text{Pr}-\text{O}_{\text{nitrate}}$ distances are in the range 2.570(4)–2.736 (4) Å and are typical of a chelating-bidentate nitrate group [1]. For each nitrate, two different bonds values are noted *ie.* $\text{Pr}-\text{O}_3$ and $\text{Pr}-\text{O}_4$ values are respectively 2.570 (4) Å and 2.607 (4) Å. These observations are indicative that in each nitrate group the bond character of one of the oxygen atoms is stronger than the bond character of the second one. These values are comparable to values noted from literature [49]. The largest $\text{Pr}-\text{O}_{\text{carbonyl}}$ bond length values of 2.567 (7) Å and 2.632 (3) Å are comparable to those of the $\text{Pr}-\text{O}_{\text{nitrate}}$. These values are in the range expected for $\text{Pr}-\text{O}_{\text{carbonyl}}$ bond lengths [50, 51]. The $\text{Pr}-\text{N}_{\text{imino}}$ distances values of 2.752 (4) Å and 2.723 (4) Å are slightly shorter than those of the $\text{Pr}-\text{N}_{\text{pyridyl}}$ bond lengths of 2.767 (4) Å and 2.830 (4) Å as observed for similar complexes [52]. The bite angles values in the five membered rings are in the range [57.0(1)°–59.3(1)°] and are in accordance with the values reported for similar complexes [52]. The bond angles of the ligands [57.0(1) °–59.3(1)°], which involve the $\text{Pr}(\text{III})$ ion, are slightly largest than the angle subtended by the oxygen atoms of the bidentate chelating nitrate groups [47.0(0)°–49.3°]. These angle values are comparable to the values reported for the complex $[\text{Pr}(\text{C}_9\text{H}_4\text{N}_2\text{O}_4)(\text{C}_2\text{H}_3\text{O}_2)(\text{H}_2\text{O})]_n$ [53]. The ligand containing N1 bonds to the metal ion through its N₁, N₂ and O₁ atoms generation two five membered rings. The two rings

$\text{Pr}_1\text{O}_1\text{C}_1\text{N}_1\text{N}_2$ (rms 0.0667 Å) and $\text{Pr}_1\text{N}_2\text{C}_2\text{C}_3\text{N}_3$ (rms 0.1019 Å) are almost planar and form a dihedral angle of 14.008(5)°. Additionally, the pyridine ring $\text{N}_3/\text{C}_3\text{-C}_7$ and the phenyl ring $\text{C}_8\text{-C}_{13}$ form a dihedral angle of 54.479(3)°. These observations are indicative of a twisting to the ligand conformation as shown by the torsion angle $\text{N}_2\text{-C}_2\text{-C}_8\text{-C}_9$ of -57.0(7)°. For the second ligand molecule containing N8, bonds to the metal ion occur through N₈, N₉ and O₂. The two five-membered rings generated by the atoms of the ligand coordinated to the Pr1 ($\text{Pr}_1\text{N}_8\text{N}_7\text{C}_{26}\text{O}_2$ and $\text{Pr}_1\text{N}_8\text{C}_{27}\text{C}_{28}\text{N}_9$) are almost planar with rms deviation of

0.0885 Å and 0.1203 Å respectively. These planes form a dihedral angle of 15.226(1)°. Twisting of the ligand is indicated by the dihedral angle (88.648(2)°) formed by the pyridine ring $\text{N}_9/\text{C}_{28}\text{-C}_{32}$ and the phenyl $\text{C}_{33}\text{-C}_{38}$ group and torsion angle $\text{N}_8\text{-C}_{27}\text{-C}_{33}\text{-C}_{34}$ of -86.1(6)°. This second ligand molecule is slightly more twisted than the first ligand as reflected by the two torsion angle values. The environment around the Pr(III) center is best described as distorted icosahedron (Figure 3). Numerous intra and inter molecular hydrogen bonds (Table 4) consolidate the structure in a three-dimensional network (Figure 4).

Table 3. Selected geometric parameters (Å, °) of compound (2).

Bond	bond lengths [Å]	Bond	bond angles (°)
Pr1—O1	2.567 (3)	O1—Pr1—O2	164.67 (11)
Pr1—O3	2.570 (4)	O1—Pr1—N8	110.78 (12)
Pr1—O7	2.590 (4)	O1—Pr1—N2	59.34 (11)
Pr1—O4	2.607 (4)	O2—Pr1—N2	115.98 (11)
Pr1—O6	2.608 (4)	N8—Pr1—N2	128.01 (13)
Pr1—O9	2.631 (4)	O10—Pr1—N2	66.06 (12)
Pr1—O2	2.632 (3)	O1—Pr1—N3	113.91 (11)
Pr1—N8	2.723 (4)	O2—Pr1—N3	67.87 (11)
Pr1—O10	2.737 (4)	N8—Pr1—N3	120.59 (13)
Pr1—N2	2.752 (4)	N2—Pr1—N3	56.97 (12)
Pr1—N3	2.767 (4)	O1—Pr1—N9	62.37 (11)
Pr1—N9	2.830 (4)	O2—Pr1—N9	113.37 (11)
		N8—Pr1—N9	57.01 (12)
		N3—Pr1—N9	171.03 (12)

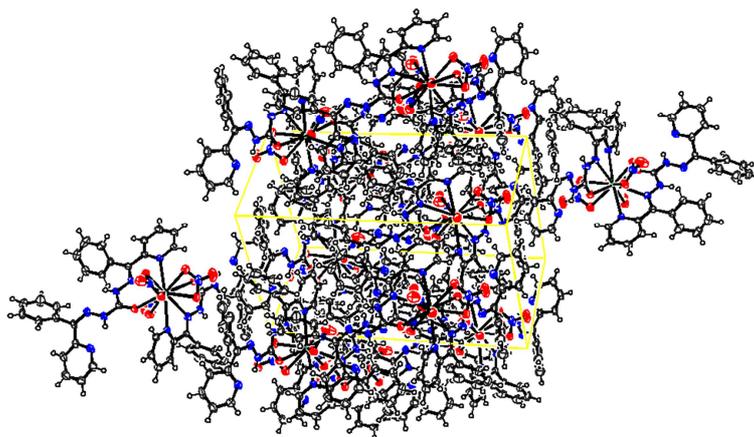


Figure 4. The packing of the complex (2) in the crystal structure.

Table-4. Hydrogen-bond geometry (Å, °) in compound 2.

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...N5	0.88	2.27	2.610 (6)	103
N4—H4A...N6	0.88	1.94	2.601 (6)	131
N7—H7A...N11	0.88	2.21	2.564 (6)	104
N10—H10A...N12	0.88	1.94	2.613 (6)	132
C7—H7...O2	0.95	2.55	2.912 (6)	103
C7—H7...O3	0.95	2.45	3.087 (7)	124
C17—H17...O9 ⁱ	0.95	2.35	3.241 (7)	157
C22—H22...O8 ⁱ	0.95	2.49	3.300 (8)	143
C32—H32...O6	0.95	2.47	3.115 (7)	125
C35—H35...O7 ⁱⁱ	0.95	2.56	3.304 (7)	135
C36—H36...O3 ⁱⁱⁱ	0.95	2.56	3.383 (7)	146
C37—H37...O5 ⁱⁱⁱ	0.95	2.46	3.249 (8)	141
C42—H42...O4 ^{iv}	0.95	2.50	3.439 (7)	168

Symmetry codes: i=-x, -y, 1-z; ii=x, 1+y, z; iii=1-x, 1-y, -z; iv=2-x, 1-y, -z.

3.3. Description of the Structure of the Co-crystal 3

The co-crystal complex $\{[\text{Nd}(\text{H}_2\text{L})_2(\eta^2\text{-NO}_3)_2(\eta^1\text{-NO}_3)] \cdot [\text{Nd}(\text{H}_2\text{L})_2(\eta^2\text{-NO}_3)(\eta^1\text{-NO}_3)(\text{H}_2\text{O})] \cdot (\text{NO}_3) \cdot 2\text{CH}_3\text{OH}\}$ (3) crystallizes in the monoclinic system in the space group $P2_1/c$. The crystal data collection and refinement are reported in Table 1. The ORTEP diagram of the structure of the co-crystal complex is illustrated in Figure 5. Selected bonds lengths and angles are listed in Table 4. Two different mononuclear complexes, one ionic nitrate and two free methanol molecules are present in the asymmetric unit. Each of the two ligand molecules around the Nd1 ion is coordinated to the metal center through one imino nitrogen atom, one pyridyl nitrogen atom and one carbonyl nitrogen atom. Two nitrate groups act in $\eta^2\text{-O}_3\text{N}$ mode, while one nitrate group acts in $\eta^1\text{-O}_3\text{N}$ fashion yielding NdN_4O_7 coordination environment. For the Nd2 ion the two ligand molecules act as for Nd1. One nitrate ion act in bidentate manner, while one nitrate group and one water molecule act in unidentate fashion yielding a ten-coordinated Nd2 ion NdN_4O_6 . The Nd1—O_{nitrate} distances values, involving the bidentate nitrate groups are in the range 2.537(4)—2.575 (4) Å and are shorter than those observed for Nd2—O_{nitrate} which are equal to 2.610 (4) Å. The bond character of the two oxygen atoms are not so different. For the unidentate nitrate, the distances Nd1—O_{nitrate} and Nd2—O_{nitrate} are respectively 2.540(4) Å and 2.435(4) Å. The values are indicative of a stronger Nd—O link comparatively to the bonds issued from the nitrate acting in bidentate fashion. This observation is in accordance with the literature [53]. These values are comparable to values noted from literature [49]. In the two units the Nd—O_{carbonyl} bond is slightly stronger in Nd2 than in Nd1 as shown by the distance values (Nd1—O_{carbonyl}: 2.511 (4) Å and 2.486 (3) Å; Nd2—O_{carbonyl} 2.476 (4) Å and 2.454 (4) Å). These values are in the range expected for Nd—O_{carbonyl} bond lengths [51]. In each unit, the Nd—N_{imino} distances values are comparable to each other, while the eleven-coordinated (Nd1—N5=2.719 (4) Å and Nd1—N8=2.739 (4) Å) unit present longest Nd—N_{imino} distances comparatively to the ten-coordinated unit (Nd2—N17=2.687 (4) Å and Nd2—N23=2.669 (4) Å). Those distances are slightly shorter than the values observed for Nd—N_{pyridyl} bond lengths [2.669 (5) Å - 2.972 (4) Å]. The Nd—N_{pyridyl} bond

lengths in the eleven-coordinated unit are longer (Nd1—N6=2.842 (4) Å and Nd1—N14=2.972 (4) Å) than those in the ten-coordinated unit (Nd2—N18=2.669 (5) Å and Nd2—N24=2.699 (5) Å). All recorded distances are in the range expected for similar complex $\text{Nd}(\text{NCS})(\text{NO}_3)(\text{pbh})_2(\text{H}_2\text{O}) \cdot (\text{NO}_3) \cdot 2,33\text{H}_2\text{O}$ (phb=N'-complex). (pyridin-2ylmethylidene)benzoylhydrazide [51]. Each ligand form a pair of five membered rings with the metal ions. The bite angles values in the five membered rings are in the range [56.8(1) °-62.0(1)°] and are in accordance with the values reported for similar complexes [52]. The ligand containing N5 bonds to the metal ion through its N5, N6 and O1 atoms generation two five membered rings. The two rings Nd1O1C1N4N5 (rms 0.0797 Å) and Nd1N5C14C15N6 (rms 0.0979 Å) are almost planar and form a dihedral angle of 13.421(2)°. Additionally, the pyridine ring N6/C15-C19 and the phenyl ring C20—C25 form a dihedral angle of 73.960(2)°. These observations are indicative of a twisting of the ligand conformation as shown by the torsion angle N5—C14—C20—C25 of -106.2(6)°. For the second ligand molecule containing N8, bonds to the metal ion occur through N8, N9 and O2. The two five-membered rings generated by the atoms of the ligand coordinated to the Nd1 (Nd1N8C27C28N9 and Nd1N8N7C26O2) are almost planar with rms deviation of 0.1018 Å and 0.0647 Å respectively. These planes form a dihedral angle of 9.487(2)°. Twisting of the ligand is indicated by the dihedral angle (65.347(3)°) formed by the pyridine ring N9/C28-C32 and the phenyl C33—C38 group and torsion angle N8—C26—C32—C37 of -113.6(6)°. This second ligand molecule is slightly more twisted than the first ligand as reflected by the two torsion angle values. The same observations are done with the ten-coordinated unit. The twisting of the ligand molecules are indicated by the two torsion angle N17—C52—C58—C59=-117.1(7)° and N23—C77—C83—C84=-77.3(8)° respectively. The environment of the eleven-coordinated Nd(III) center is best described as a distorted pentacapped trigonal prism while the ten-coordinated Nd(III) center is situated in a bicapped square antiprism geometry (Figure 6). Numerous intra and inter molecular hydrogen bonds (Table 5) consolidate the structure in a three-dimensional network (Figure 7).

Table 5. Selected geometric parameters (Å, °) of compound (3).

Bond	bond lengths [Å]	Bond	bond angles (°)
Nd1—O6	2.537 (3)	O2—Nd1—O1	154.57 (12)
Nd1—O9	2.540 (4)	O2—Nd1—O6	135.55 (12)
Nd1—O4	2.565 (3)	O2—Nd1—O3	69.57 (12)
Nd1—O3	2.567 (4)	O6—Nd1—O3	68.74 (12)
Nd1—O7	2.575 (4)	O4—Nd1—O3	50.11 (13)
Nd1—N5	2.719 (4)	O1—Nd1—N5	60.25 (11)
Nd1—N8	2.739 (4)	O1—Nd1—N8	109.82 (12)
Nd1—N6	2.842 (4)	O2—Nd1—O1	154.57 (12)
Nd1—N14	2.972 (4)	O2—Nd1—N5	104.74 (12)
Nd2—O17	2.435 (4)	O1—Nd1—N5	60.25 (11)
Nd2—O13	2.454 (4)	O2—Nd1—N8	59.79 (12)

Bond	bond lengths [Å]	Bond	bond angles (°)
Nd2—O14	2.610 (4)	O1—Nd1—N9	65.23 (11)
Nd2—N18	2.669 (5)	O13—Nd2—O20	138.16 (16)
Nd2—N23	2.669 (4)	O13—Nd2—O12	138.73 (14)
Nd2—N17	2.687 (4)	O13—Nd2—O15	70.05 (14)
Nd2—N24	2.699 (5)	O12—Nd2—O15	71.84 (14)
Nd1—O2	2.487 (3)	O20—Nd2—O14	131.78 (12)
Nd1—O1	2.511 (3)	O17—Nd2—N18	77.51 (14)
Nd1—O6	2.537 (3)	N9—Nd1—N6	172.64 (13)
Nd1—O9	2.540 (4)	O13—Nd2—O12	138.73 (14)
Nd1—O4	2.565 (3)	N18—Nd2—N23	126.77 (14)
Nd1—O3	2.567 (4)	O13—Nd2—N17	114.13 (13)
Nd1—O7	2.575 (4)	O1—Nd1—N8	109.82 (12)
Nd1—N5	2.719 (4)	N5—Nd1—N8	124.81 (12)
Nd1—N8	2.739 (4)	O1—Nd1—N9	65.23 (11)
Nd1—N9	2.768 (4)	N5—Nd1—N9	120.72 (13)
Nd1—N6	2.842 (4)	O2—Nd1—N6	61.25 (11)
Nd2—O17	2.435 (4)	O1—Nd1—N6	114.84 (11)
Nd2—O13	2.454 (4)	N5—Nd1—N6	56.74 (12)
Nd2—O20	2.469 (4)	N18—Nd2—N17	58.68 (14)
Nd2—O12	2.476 (4)	N23—Nd2—N17	165.36 (13)
Nd2—O15	2.610 (4)	O13—Nd2—N24	120.44 (12)
Nd2—O14	2.610 (4)	O12—Nd2—N24	69.67 (13)
Nd2—N18	2.669 (5)	N18—Nd2—N24	153.51 (15)
Nd2—N23	2.669 (4)	N23—Nd2—N24	58.49 (13)
Nd2—N17	2.687 (4)	N17—Nd2—N24	124.02 (14)
Nd2—N24	2.699 (5)	N8—Nd1—N6	117.94 (12)

Table 6. Hydrogen-bond geometry (Å, °) in compound 3.

D—H...A	D—H	H...A	D...A	D—H...A
N4—H4A...N2	0.88	2.22	2.566 (6)	103
N1—H1A...N3	0.88	1.93	2.604 (7)	132
N7—H7A...N11	0.88	2.27	2.602 (6)	102
N10—H10A...N12	0.88	1.93	2.602 (6)	132
N16—H16A...N20	0.88	2.22	2.571 (7)	103
N19—H19A...N21	0.88	1.91	2.586 (10)	132
N22—H22A...N26	0.88	2.25	2.584 (7)	102
N25—H25A...N27	0.88	1.88	2.571 (7)	134
O20—H20A...O24	0.95	2.41	3.061 (10)	125
O20—H20B...O21	0.95	2.01	2.760 (13)	134
O20—H20B...O22	0.95	1.78	2.663 (8)	154
O24—H24B...O20	0.84	2.37	3.061 (10)	140
O25A—H25B...O3	0.84	2.44	2.92 (2)	117
C5—H5...O14	0.95	2.53	3.361 (7)	147
C18—H18...O10	0.95	2.46	3.306 (8)	149
C102—H10A...O25A	0.98	2.00	2.56 (3)	114
C19—H19...O3	0.95	2.39	3.035 (7)	125
C30—H30...O5	0.95	2.52	3.371 (10)	149
C31—H31...O25A	0.95	2.43	3.35 (2)	165
C32—H32...O6	0.95	2.43	3.079 (7)	125
C42—H42...O9	0.95	2.44	3.343 (8)	159
C55—H55...O23	0.95	2.56	3.492 (12)	167
C57—H57...O18	0.95	2.53	3.457 (7)	165
C60—H60...O8	0.95	2.33	3.187 (11)	150
C62—H62...O5	0.95	2.31	3.147 (14)	147
C63—H63...O21	0.95	2.32	3.156 (14)	147
C63—H63...O23	0.95	2.53	3.384 (12)	150
C73—H73...O6	0.95	2.53	3.404 (10)	152
C91—H91...O23	0.95	2.51	3.375 (11)	151
C92—H92...O21	0.95	2.47	3.244 (12)	138
C93—H93...O15	0.95	2.53	3.053 (9)	115
C99—H99...O4	0.95	2.60	3.334 (9)	135

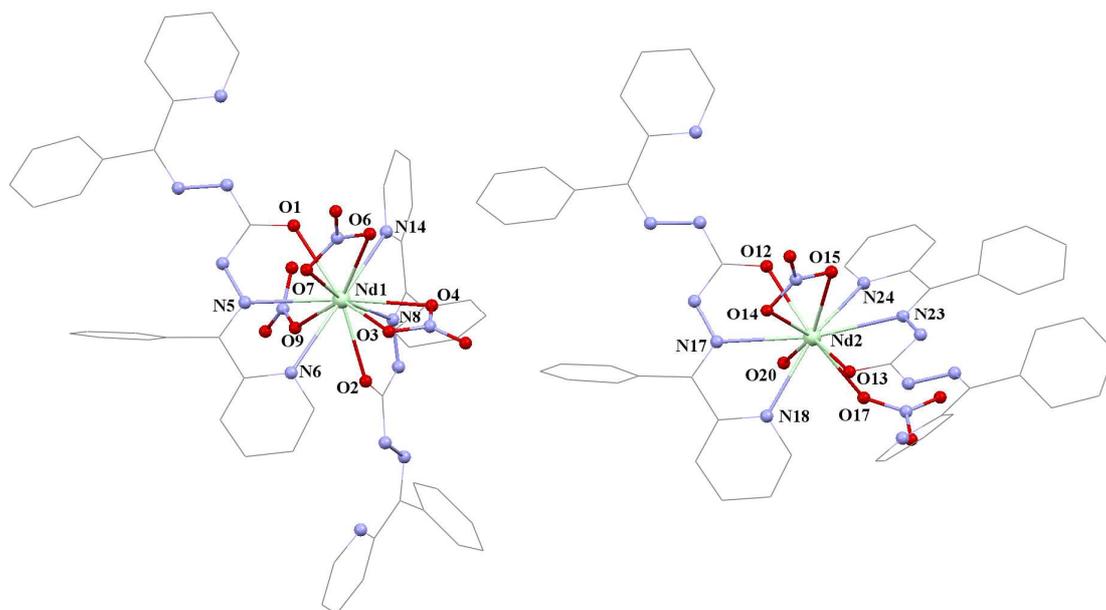


Figure 5. ORTEP Plot (30% probability ellipsoids) showing the structure of the co-crystal complex 3. H atom, free nitrate group and uncoordinated methanol molecules were omitted for clarity. Only coordinated are labelled.

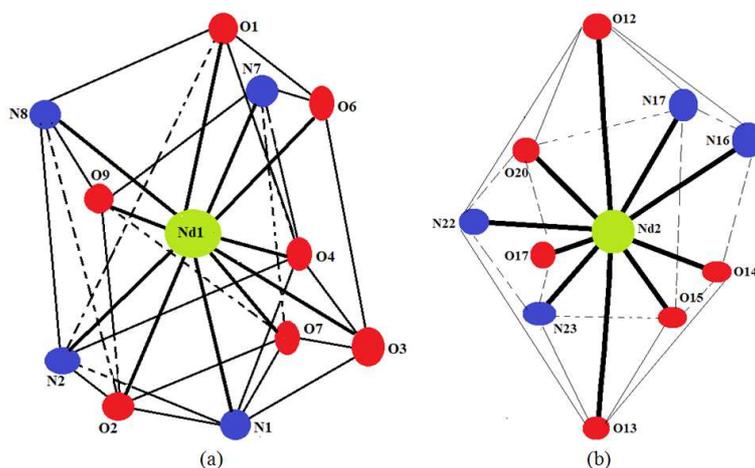


Figure 6. Plot showing the coordination sphere around the Nd^{III} ions in the co-crystal.

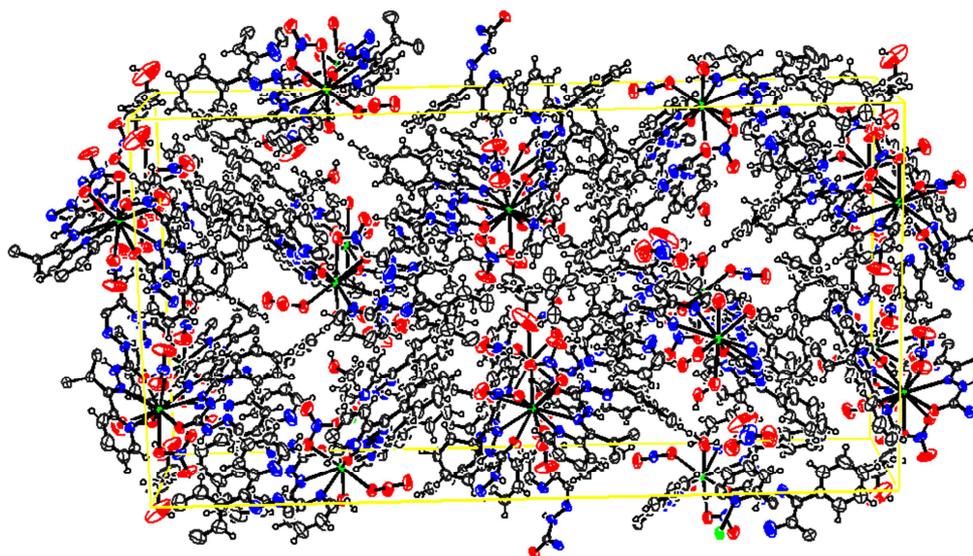


Figure 7. The packing of the complex (3) in the crystal structure.

4. Conclusion

In the present work, we report the synthesis and characterization of a new lanthanide complexes prepared from the symmetrical ligand 1,5-bis(phenyl(pyridin-2-yl)methylene)carbonohydrazide (H_2L_2). All the complexes were characterized by elemental analyse, FT-IR, magnetic measurement, and conductivity measurement. The complexes of La, Sm, Gd and Yb are formulated as mononuclear $[Ln(H_2L)_2(\eta^2-NO_3)_{3-x}](NO_3)_x$. The complexes of Pr and Eu are formulated as neutral mononuclear complexes $[Ln(H_2L)_2(\eta^2-NO_3)_3]$. The complex of Nd appears as a dinuclear formulated as $\{[Nd(H_2L)_2(\eta^2-NO_3)_2(\eta^1-NO_3)], [Nd(H_2L)_2(\eta^2-NO_3)(\eta^1-NO_3)(H_2O)]\} \cdot (NO_3) \cdot 2CH_3OH$. The structures of the complexes of Pr (2) and Nd (3) were determined by X-ray diffraction technics. The complex 2 is a mononuclear complex in which the metal cation is twelve coordinated with a coordination sphere best described as an icosahedron geometry. The Nd(III) complex 3 is a co-crystal in which the two metal cations are respectively eleven-coordinated and ten-coordinated. The coordination sphere are respectively best described as a distorted pentacapped trigonal prism and a bicapped square antiprism geometries.

Supplementary Materials

CCDC- 2130654 and 2130655 contains respectively the supplementary crystallographic data for Pr(III) and Nd(III) complexes. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Conflicts of Interest

The authors declare that they have no competing interest.

References

- [1] T. Curtius, K. Heidenreich, Ueber Hydrazind Azocarbonester, *Berichte der Deutschen Chemischen Gesellschaft* (1894), 27, 773–774.
- [2] Y.-Y. Wu, W.-B. Shao, J.-J. Zhu, Z.-Q. Long, L.-W. Liu, P.-Y. Wang, Z. Li, S. Yang, Novel 1,3,4-Oxadiazole-2-carbohydrazides as Prospective Agricultural Antifungal Agents Potentially Targeting Succinate Dehydrogenase, *Journal of Agricultural Food Chemistry* (2019), 67, 13892–13903.
- [3] Y. Liu, H. Song, Y. Huang, J. Li, S. Zhao, Y. Song, P. Yang, Z. Xiao, Y. Liu, Y. Li, H. Shang, Q. Wang, Design, Synthesis, and Antiviral, Fungicidal, and Insecticidal Activities of Tetrahydro- β -carboline-3-carbohydrazide Derivatives, *Journal of Agricultural Food Chemistry* (2014), 62, 9987–9999.
- [4] Z. Huang, Y. Liu, Y. Li, L. Xiong, Z. Cui, H. Song, H. Liu, Q. Zhao, Q. Wang, Synthesis, Crystal Structures, Insecticidal Activities, and Structure–Activity Relationships of Novel *N'*-tert-Butyl-*N'*-substituted-benzoyl-*N*-[di(octa)hydro]benzofuran{(2,3-dihydro)benzo[1,3]([1,4]dioxine)}carbohydrazide Derivatives, *Journal of Agricultural Food Chemistry* (2011), 59, 635–644.
- [5] R. Ragno, A. Coluccia, G. La Regina, G. De Martino, F. Piscitelli, A. Lavecchia, E. Novellino, A. Bergamini, C. Ciapri, A. Sinistro, G. Maga, E. Crespan, M. Artico, R. Silvestri, Design, Molecular Modeling, Synthesis, and Anti-HIV-1 Activity of New Indolyl Aryl Sulfones. Novel Derivatives of the Indole-2-carboxamide, *Journal of Medicinal Chemistry* (2006), 49, 3172–3184.
- [6] V. Palomo, D. I. Perez, C. Roca, C. Anderson, N. Rodríguez-Muela, C. Perez, J. A. Morales-Garcia, J. A. Reyes, N. E. Campillo, A. M. Perez-Castillo, L. L. Rubin, L. Timchenko, C. Gil, A. Martinez, Subtly Modulating Glycogen Synthase Kinase 3 β : Allosteric Inhibitor Development and Their Potential for the Treatment of Chronic Diseases, *Journal of Medicinal Chemistry* (2017), 60, 4983–5001.
- [7] D. N. Heo, M. A. Alioglu, Y. Wu, V. Ozbolat, B. Ayan, M. Dey, Y. Kang, I. T. Ozbolat, 3D Bioprinting of Carbohydrazide-Modified Gelatin into Microparticle-Suspended Oxidized Alginate for the Fabrication of Complex-Shaped Tissue Constructs, *ACS Applied Materials and Interfaces*. (2020), 12, 20295–20306.
- [8] D. R. Cospers, D. J. Kowalski, Copper-catalyzed autoxidation of carbohydrazide: kinetics and mechanism, *Industrial and Engineering Chemistry Research* (1990), 29, 1130–1136.
- [9] K. Hrušková, E. Potůčková, L. Opálka, T. Hergeslová, P. Hašková, P. Kovaříková, T. Šimůnek, K. Vávrová, Structure–Activity Relationships of Nitro-Substituted Aroylhydrazone Iron Chelators with Antioxidant and Antiproliferative Activities, *Chemical Research in Toxicology* (2018), 31, 435–446.
- [10] M. M. Hanna, New pyrimido[5,4-*e*]pyrrolo[1,2-*c*]pyrimidines: Synthesis, 2D-QSAR, anti-inflammatory, analgesic and ulcerogenicity studies, *European Journal of Medicinal Chemistry* (2012), 55, 12–22.
- [11] S. S. Bharadwaj, B. Poojary, S. K. M. Nandish, J. Kengaiyah, M. P. Kirana, M. K. Shankar, A. J. Das, A. Kulal, D. Sannanigaiah, Efficient Synthesis and in Silico Studies of the Benzimidazole Hybrid Scaffold with the Quinolinyloxadiazole Skeleton with Potential α -Glucosidase Inhibitory, Anticoagulant, and Antiplatelet Activities for Type-II Diabetes Mellitus Management and Treating Thrombotic Disorders, *ACS Omega* (2018), 3, 12562–12574.
- [12] R. M. Zaki, A. M. Kamal El-Dean, S. M. Radwan, A. S. A. Sayed, Synthesis and Antimicrobial Activity of Novel Piperidinyl Tetrahydrothieno[2,3-*c*]isoquinolines and Related Heterocycles, *ACS Omega* (2020), 5, 252–264.
- [13] L. Tripathi, R. Singh, J. P. Stables, Design & synthesis of *N'*-[substituted] pyridine-4-carbohydrazides as potential anticonvulsant agents, *European Journal of Medicinal Chemistry* (2011), 46, 509–518.
- [14] M. Abdel-Aziz, G. E.-D. A. Abu-Rahma, A. A. Hassan, Synthesis of novel pyrazole derivatives and evaluation of their antidepressant and anticonvulsant activities, *European Journal of Medicinal Chemistry* (2009), 44, 3480–3487.

- [15] L. Zhang, L. Shi, S. M. Soars, J. Kamps, H. Yin, Discovery of Novel Small-Molecule Inhibitors of NF- κ B Signaling with Antiinflammatory and Anticancer Properties, *Journal of Medicinal Chemistry* (2018), 61, 5881–5899.
- [16] G. Kumar, V. S. Krishna, D. Sriram, S. M. Jachak, Synthesis of carbohydrazides and carboxamides as anti-tubercular agents, *European Journal of Medicinal Chemistry* (2018), 156, 871–884.
- [17] J. B. Wright, W. E. Dulin, J. H. Markillie, The Antidiabetic Activity of 3,5-Dimethylpyrazoles, *Journal of Medicinal Chemistry* (1964), 7, 102–105.
- [18] D. Das Mukherjee, N. M. Kumar, M. P. Tantak, A. Das, A. Ganguli, S. Datta, D. Kumar, G. Chakrabarti, Development of Novel Bis(indolyl)-hydrazide–Hydrazone Derivatives as Potent Microtubule-Targeting Cytotoxic Agents against A549 Lung Cancer Cells, *Biochemistry* (2016), 55, 3020–3035.
- [19] J. Li, L. Zhang, G.-C. Xu, W.-X. Yu, D.-Z. Jia, A carbohydrazone based tetranuclear Co(II) complex: Self-assembly and magnetic property, *Inorganic Chemistry Communications* (2014), 45, 40–43.
- [20] T. N. Mandal, S. Roy, S. Konar, A. Jana, S. Ray, K. Das, R. Saha, M. S. El Fallah, R. J. Butcher, S. Chatterjee, S. K. Kar, Self assembled tetranuclear Cu₄(II), Ni₄(II) [2 × 2] square grids and a dicopper(II) complex of heterocycle based polytopic ligands - Magnetic studies, *Dalton Transactions* 40 (2011), 40, 11866–11875.
- [21] M. B. Talawar, A. P. Agrawal, J. S. Chhabra, S. N. Asthana, Studies on lead-free initiators: synthesis, characterization and performance evaluation of transition metal complexes of carbohydrazone, *Journal of Hazardous Materials* (2004), 113, 57–65.
- [22] M. M. Sow, O. Diouf, M. Gaye, A. S. Sall, G. Castro, P. Pérez-Lourido, L. Valencia, A. Caneschi, L. Sorace, Sheets of Tetranuclear Ni(II) [2 × 2] Square Grids Structure with Infinite Orthogonal Two-Dimensional Water–Chlorine Chains, *Crystal Growth Design* (2013), 13, 4172–4176.
- [23] F. B. Tamboura, O. Diouf, A. H. Barry, M. Gaye, A. S. Sall, Dinuclear lanthanide(III) complexes with large-bite Schiff bases derived from 2,6-diformyl-4-chlorophenol and hydrazides: Synthesis, structural characterization and spectroscopic studies, *Polyhedron* (2012), 43, 97–103.
- [24] F. B. Tamboura, M. Diop, M. Gaye, A. S. Sall, A. H. Barry, T. Jouini, X-ray structure and spectroscopic properties of some lanthanides(III) complexes derived from 2,6-diacetylpyridine-bis(benzoylhydrazone), *Inorganic Chemistry Communications* (2003), 6, 1004–1010.
- [25] F. B. Tamboura, P. M. Haba, M. Gaye, A. S. Sall, A. H. Barry, T. Jouini, Structural studies of bis-(2,6-diacetylpyridine-bis(phenylhydrazone)) and X-ray structure of its Y(III), Pr(III), Sm(III) and Er(III) complex, *Polyhedron* (2004), 23, 1191–1197.
- [26] W. D. Horrocks, D. R. Sudnick, Lanthanide ion luminescence probes of the structure of biological macromolecules, *Accounts of Chemical Research* (1981), 14, 384–392.
- [27] A. de la Escosura-Muñiz, C. Parolo, A. Merkoçi, Immunosensing using nanoparticles, *Materials Today* 13 (2010), 13, 24–34.
- [28] R. Maouche, S. Belaid, B. Benmerad, S. Bouacida, S. Freslon, C. Daiguebonne, Y. Suffren, G. Calvez, K. Bernot, C. Roiland, L. L. Pollès, O. Guillou, Luminescence properties of lanthanide complexes-based molecular alloys, *Inorganica Chimica Acta* (2020), 501, 119309.
- [29] F. Le Natur, G. Calvez, J.-P. Guégan, L. Le Pollès, X. Trivelli, K. Bernot, C. Daiguebonne, C. Neaime, K. Costuas, F. Grasset, O. Guillou, Characterization and Luminescence Properties of Lanthanide-Based Polynuclear Complexes Nanoaggregates, *Inorganic Chemistry* (2015), 54, 6043–6054.
- [30] X.-W. Zhang, H.-P. Lin, J. Li, L. Zhang, B. Wei, X.-Y. Jiang, Z.-L. Zhang, A very simple method of constructing efficient inverted top-emitting organic light-emitting diode based on Ag/Al bilayer reflective cathode, *Journal of Luminescence* (2012), 132, 1–5.
- [31] Y. Q. Sheng, L. L. Xu, J. Liu, D. Zhai, Z. G. Zhang, Improving monochromaticity of upconversion luminescence by codoping Eu³⁺ ions in Y₂O₃:Ho³⁺, Yb³⁺ nanocrystals, *Journal of Luminescence* (2010), 130, 338–341.
- [32] Y. Hasegawa, Y. Kitagawa, T. Nakanishi, Effective photosensitized, electrosensitized, and mechanosensitized luminescence of lanthanide complexes, *NPG Asia Materials* (2018), 10, 52–70.
- [33] M. A. Fernandez, J. C. Barona, D. Polo-Cerón, M. N. Chaur, Photochemical and electrochemical studies on lanthanide complexes of 6-(hydroxymethyl)pyridine-2-carboxaldehyde[2- methyl-pyrimidine-4,6-diyl] bis-hydrazone, *Revista Colombiana Química* (2014), 43, 5–11.
- [34] M. T. Kaczmarek, M. Zabiszak, M. Nowak, R. Jastrzab, Lanthanides: Schiff base complexes, applications in cancer diagnosis, therapy, and antibacterial activity, *Coordination Chemistry Reviews* (2018), 370, 42–54.
- [35] R. Fouad, Synthesis and characterization of lanthanide complexes as potential therapeutic agents, *Journal of Coordination Chemistry* (2020), 73, 2015–2028.
- [36] J.-D. Londoño-Mosquera, A. Aragón-Muriel, D. Polo Cerón, Synthesis, antibacterial activity and DNA interactions of lanthanide(III) complexes of N(4)-substituted thiosemicarbazones, *Universal Science* (2018), 23, 141–169.
- [37] M. N. Gueye, M. Dieng, I. E. Thiam, D. Lo, A. H. Barry, M. Gaye, P. Retailleau, Lanthanide(III) complexes with tridentate Schiff base ligand, antioxidant activity and X-ray crystal structures of the Nd(III) and Sm(III) complexes, *South African Journal of Chemistry* (2017), 70.
- [38] I. Kostova, M. Traykova, V. Rastogi, New lanthanide complexes with antioxidant activity. *Journal of Medicinal Chemistry* (2008), 4, 371–378.
- [39] T. Sun, Y. Gao, Y. Du, L. Zhou, X. Chen, Recent Advances in Developing Lanthanide Metal–Organic Frameworks for Ratiometric Fluorescent Sensing, *Frontiers in Chemistry* (2021), 8, 624592.
- [40] S. Philip, S. Thomas, K. Mohanan, Synthesis, fluorescent studies, antioxidative and α -amylase inhibitory activity evaluation of some lanthanide(III) complexes, *Journal of Serbian Chemical Society* (2018), 83, 561–574.
- [41] H. E. Yelkenci, N. Öztekin, Separation and Sensitive Detection of Lanthanides by Capillary Electrophoresis and Contactless Conductivity Detection, *Journal of Chromatographic Science* (2017), 55, 465–470.

- [42] T. M. Seck, A. Sy, D. Lo, P. A. Gaye, M. L. Sall, O. Diouf, M. Diaw, M. Gaye, Synthesis, Spectroscopic Studies and X-Ray Diffraction of Heptacoordinated Mn(II) and Co(II) Complexes with Ligands Derived from Carbonohydrazide, *Open Journal of Inorganic Chemistry* (2019), 09, 35–52.
- [43] G. M. Sheldrick, *SHELXT* – Integrated space-group and crystal-structure determination, *Acta Crystallographica Section A Foundations Advances* (2015), 71, 3–8.
- [44] G. M. Sheldrick, Crystal structure refinement with *SHELXL*, *Acta Crystallographica Section C Structural Chemistry* (2015), 71, 3–8.
- [45] L. J. Farrugia, WinGX and ORTEP for Windows: an update. *Journal of Applied Crystallography* (2012), 45, 849–854.
- [46] C.-J. Kuo, R. J. Holmberg, P.-H. Lin, Slight synthetic changes eliciting different topologies: synthesis, structure and magnetic properties of novel dinuclear and nonanuclear dysprosium complexes, *Dalton Transactions* (2015), 44, 19758–19762.
- [47] M. A. E. Shaban, the Chemistry of C-Nucleosides and Their Analogs II: C-Nucleosides of Condensed Heterocyclic Bases, in: A. R. Katritzky (Ed.), Academic Press (1997), 163–337.
- [48] W. J. Geary, The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, *Coordination Chemistry Reviews* (1971), 7, 81–122.
- [49] K. Singh, P. Srivastava, A. K. Patra, Binding interactions with biological targets and DNA photocleavage activity of Pr(III) and Nd(III) complexes of dipyridoquinoxaline, *Inorganica Chimica Acta* (2016), 451, 73–81.
- [50] I. A. Kahwa, F. R. Fronczek, J. Selbin, Partial hydrolysis of homodinuclear macrocyclic complexes of lanthanides with a 2:2 phenolic schiff's base and the crystal and molecular structure of resulting open mononuclear 3:1 Schiff's base complexes of praseodymium(III) and neodymium(III), *Inorganica Chimica Acta* (1988), 148, 273–281.
- [51] D. G. Paschalidis, W. T. A. Harrison, Two mixed-ligand lanthanide-hydrazone complexes: [Pr(NCS)₃(pbh)₂]·H₂O and [Nd(NCS)(NO₃)(pbh)₂(H₂O)]NO₃·2.33H₂O [pbh is N'-(pyridin-2-ylmethylidene)benzohydrazide, C₁₃H₁₁N₃O], *Acta Crystallographica Section E Crystallographic Communications* (2016), 72, 191–195.
- [52] M. Faye, P. A. Gaye, M. M. Sow, M. Dieng, F. B. Tamboura, N. Gruber, M. Gaye, Synthesis, Characterization and Single Crystal X-ray Crystallography of Nd(III) and Pr(III) Complexes with the Tridentate Schiff Base Ligand N'-(1-(pyridin-2-yl)ethylidene)nicotinohydrazide, *Earthline Journal of Chemical Sciences* (2021) 99–117.
- [53] E. A. Mainicheva, A. A. Tripolskaya, O. A. Gerasko, D. Yu. Naumov, V. P. Fedin, Synthesis and crystal structures of Pr^{III} and Nd^{III} complexes with the macrocyclic cavitand cucurbituril, *Russian Chemical Bulletin* (2006), 55, 1566–1573.