



## 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

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### Abstract

The use of N'-(1-(pyridin-2-yl)ethylidene)nicotinohydrazide (HL) in lanthanide(III) chemistry has yielded one mononuclear and one dinuclear complexes. The 1:1 Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O or Pr(CH<sub>3</sub>COO)<sub>3</sub>·6H<sub>2</sub>O/HL in methanol afforded the complexes [Nd(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·(NO<sub>3</sub>)] (**1**) and {[Pr(L)(η<sup>2</sup>-OOCCH<sub>3</sub>)(H<sub>2</sub>O)](η<sup>1</sup>:η<sup>2</sup>:μ-OOCCH<sub>3</sub>)<sub>2</sub>[Pr(L)(η<sup>2</sup>-OOCCH<sub>3</sub>)(H<sub>2</sub>O)]} (**2**). The structures of the complexes were solved by single crystal X-ray crystallography. In the mononuclear complex, the Nd<sup>3+</sup> atom is coordinated by two neutral molecules of ligand acting in tridentate fashion, two nitrate anions acting in bidentate manner and two coordinated water molecules yielding a twelve-coordinated Nd atom. In the complex (**2**) the Pr<sup>3+</sup> atoms are doubly bridged by two acetates anions and each metal ion is coordinated by one tridentate monodeprotonated molecule ligand, one bidentate acetate group and one coordinated water molecule. Each Pr<sup>3+</sup> atom is nine-coordinated with an environment best described as a tricapped prismatic geometry. Complex **1** crystallizes in the monoclinic space group C2/c with the following parameters:

Received: June 4, 2021; Accepted: July 2, 2021

Keywords and phrases: Schiff base, complex, lanthanide, tricapped prism.

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$a = 22.7657(8) \text{ \AA}$ ,  $b = 8.4276(3) \text{ \AA}$ ,  $c = 18.0831(7) \text{ \AA}$ ,  $\beta = 114.851(2)^\circ$ ,  $V = 3148.2(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $R_1 = 0.032$ ,  $wR_2 = 0.098$ . Complex **2** crystallizes in the monoclinic space group  $P2_1/n$  with the following parameters:  $a = 11.5388(6) \text{ \AA}$ ,  $b = 14.1087(8) \text{ \AA}$ ,  $c = 12.2833(6) \text{ \AA}$ ,  $\beta = 102.211(2)^\circ$ ,  $V = 1954.45(18) \text{ \AA}^3$ ,  $Z = 2$ ,  $R_1 = 0.029$ ,  $wR_2 = 0.066$ . The supramolecular structures are consolidated by multiple hydrogen bonds.

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## 1. Introduction

The polyfunctional acyclic and asymmetric ligands and their complexes represent an essential component of coordination chemistry [1–9]. These ligands are largely used for the synthesis of complexes with biochemical and physical properties [10–13]. The formation of acyclic ligand complexes depends on the flexibility of the coordinating groups [14–16], the nature of the donor atoms [17–19] and the complexing properties of the ions acting as counter-anions [20–22]. The use of Schiff bases in coordination chemistry has made it possible to develop molecular materials with specific properties [23–25]. This article describes the tridentate Schiff base obtained by the reaction between nicotinohydrazide and acetylpyridine. The flexibility and the numerous coordination sites of the resulting acyclic ligand provide several possible structures with lanthanide ions [26–28]. Using the ligand  $N^-(1-(\text{pyridin-2-yl})\text{ethylidene})\text{nicotine hydrazide}$  (HL) in presence of neodymium nitrate or praseodymium acetate salts yield complexes of  $\text{Nd}^{3+}$  or  $\text{Pr}^{3+}$  with different behavior of the anions. The complexes are characterized by IR spectra, room temperature magnetic measurement and elemental analyses. The structures of the Nd(III) and Pr(III) complexes was determined by X-ray single crystal diffraction.

## 2. Materials and Methods

### 2.1. Starting materials and instrumentations

2-acetylpyridine and nicotinohydrazide 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  $4000\text{--}400 \text{ cm}^{-1}$  region. The  $^1\text{H}$  NMR spectra were recorded at 300 MHz and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra at 75 MHz on a Bruker AC-300 instrument.

## 2.2. Synthesis of *N'*-(1-(pyridin-2-yl)ethylidene)nicotinothiazide (HL)

In a 100 mL flask, 0.7566 g (5.5 mmol) of nicotinothiazide and 20 mL of methanol were mixed. A methanolic solution (20 mL) of acetylpyridine 0.6627g (5.5 mmol) was added dropwise. The resulting yellow mixture was heated under stirring at reflux for 3 hours. On cooling, the yellowish solution was left on slow evaporation for a few days. The white solid which appears was recovered by filtration, washed with ether (2 x 10 mL), and dried in the air.

Yield : 55%. Anal. Calc for  $C_{13}H_{12}N_4O$  : C, 64.99; H, 5.03; N, 23.32. Found: C, 65.02; H, 5.05; N, 23.29. (300 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 11.13 (s, NH, 1H); 9.05–7.43 (m, H-Ar, 8 H); 2.53 (s, -CH<sub>3</sub>-, 3 H). NMR <sup>13</sup>C [DMSO, 300 MHz, ( $\delta$ , ppm)] : 13.32 (CH<sub>3</sub>-); 120.92 (C<sub>Ar</sub>); 120.96 (C<sub>Ar</sub>); 123.89 (C<sub>Ar</sub>); 123.92 (C<sub>Ar</sub>); 130.21 (C<sub>Ar</sub>); 136.37 (C<sub>Ar</sub>); 137.18 (C<sub>Ar</sub>); 149.18 (C<sub>Ar</sub>); 152.84 (C<sub>Ar</sub>); 155.48 (C<sub>Ar</sub>); 155.78 (C=N); 163.37 (C=O). IR (cm<sup>-1</sup>): 3500, 1642, 1596, 1539, 1494, 1480, 1030, 794, 734, 700.

## 2.3. Synthesis of the complex [Nd(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>) (1)

In a 100 mL flask containing methanol (10 mL) was added (0.1 g, 0.42 mmol) of the HL ligand. The mixture was stirred until complete dissolution of the organic compound. A 10 mL methanolic solution containing Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.1841 g, 0.42 mmol) was added. The resulting solution was stirred and heated at reflux for 3 hours. On cooling the precipitate which appears was collected by filtration and washed with ether (2 x 10 mL) and air dried. The filtrates were left under slow evaporation. Few days after, colorless crystal of the Nd(III) complex, suitable for X-ray diffraction, were collected.

Yield 61 %. Anal. Calc for  $C_{26}H_{28}N_{11}O_{13}Nd$ : C, 36.88; H, 3.33; N, 18.19. Found: C, 36.85; H, 3.35; N, 18.17. IR (cm<sup>-1</sup>): 1639, 1585, 1545, 1471, 1380, 1304, 1197, 1077, 1030, 925, 858, 776.  $\mu_{\text{eff}} = 3.15 \mu_B/Nd^{3+}$ . Conductance  $\Lambda$  (S.cm<sup>2</sup>.mol<sup>-1</sup>) : 83.

## 2.4. Synthesis of the complex {[Pr(L)( $\eta^2$ -OOCCH<sub>3</sub>)(H<sub>2</sub>O)]( $\eta^1$ : $\eta^2$ : $\mu$ -OOCCH<sub>3</sub>)<sub>2</sub>[Pr(L)( $\eta^2$ -OOCCH<sub>3</sub>)(H<sub>2</sub>O)]} (2)

In a 100 mL flask containing methanol (10 mL) was added (0.1 g, 0.42 mmol) of the HL ligand. The mixture was stirred until complete dissolution of the organic compound. A 10 mL methanolic solution containing Pr(OAc)<sub>3</sub>·6H<sub>2</sub>O (0.1336 g, 0.42 mmol) was added. The resulting solution was stirred and heated at reflux for 3 hours. On cooling the precipitate which appears was collected by filtration, washed with ether (2 x 10 mL) and

air dried. The filtrates were left under slow evaporation. Few days after, colorless crystal of the Pr(III) complex, suitable for X-ray diffraction, were collected.

Yield 61 %. Anal. Calc for  $C_{34}H_{34}N_8O_{12}Pr_2$ : C, 39.70; H, 3.33; N, 10.89. Found: C, 39.68; H, 3.31; N, 10.87. IR ( $cm^{-1}$ ): 1639, 1556, 1434, 1305, 1197, 1030, 1077, 925, 858, 776.  $\mu_{eff} = 3.18 \mu_B/Pr^{3+}$ . Conductance  $\Lambda$  ( $S.cm^2.mol^{-1}$ ): 6.

## 2.5. X-ray crystallography

Crystals suitable for single-crystal X-ray diffraction, of the reported compound, was grown by slow evaporation of DMF solution of the compound. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Bruker APEX-II CCD diffractometer with graphite monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data were corrected for Lorentz and polarization effects. The structure was solved and refined using the Bruker SHELXTL Software Package [29]. All the structures were refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [30]. H atoms of the NH groups was located in the Fourier difference maps and refined without restraints. Other H atoms were geometrically optimized and refined as riding on their carriers with  $U_{iso}(H) = 1.2U_{eq}(C)$  (1.5 for CH<sub>3</sub> group). Molecular graphics were generated using ORTEP-3 [31].

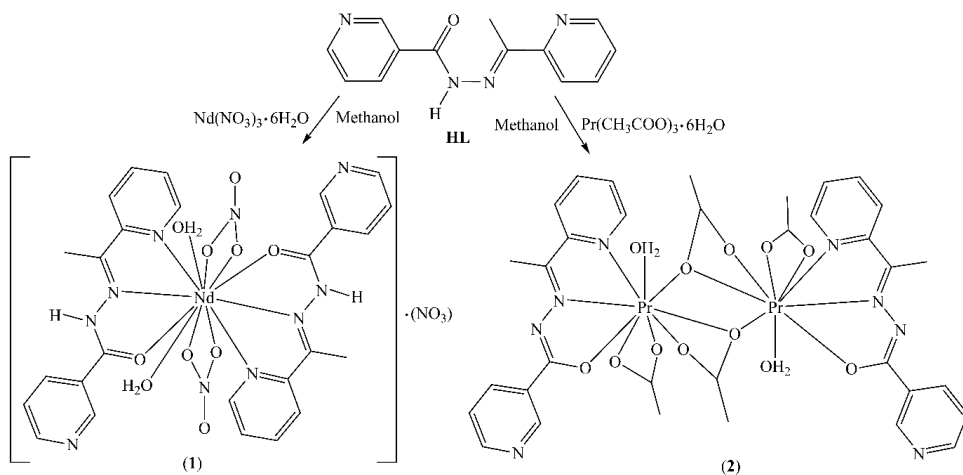
## 3. Results and Discussion

### 3.1. General study

HL react with  $LnX_3 \cdot 6H_2O$  ( $Ln = Nd, X = NO_3^-$ ;  $Ln = Pr, X = CH_3COO^-$ ) to afford mononuclear complex for Nd(III) and a dinuclear complex for Pr(III) as shown in scheme 1. The infrared spectrum of the HL ligand shows two bands pointed at  $1656 \text{ cm}^{-1}$  attributed to the vibration of the C=O and at  $1583 \text{ cm}^{-1}$  attributed to C=N. The vibration band of the N-H bond appears at  $3500 \text{ cm}^{-1}$ , while the band of the N-N moiety is pointed at  $1030 \text{ cm}^{-1}$ . Additional bands, characteristic of the aromatic ring, are pointed in the range  $1596\text{--}1471 \text{ cm}^{-1}$ .

The  $^1H$  NMR spectrum reveals a complex signal between 7.43 ppm and 9.05 ppm attributed to the protons of the aromatic rings. The signal which appears as a doublet at 2.53 ppm is attributed to the proton of the methyl group. The signal at 11.13 ppm is assigned to the HN of the hydrazine moiety. The assignments of these signal are

correlated to the signals of the  $^{13}\text{C}$  NMR spectrum which reveals a signal at 13.32 ppm indicative of the presence of  $-\text{CH}_3$  group and a signal at 155.48 ppm attributed to imine carbon atoms. The signal at 163.37 ppm is attributed to the  $\text{C}=\text{O}$ . Additional signals in the range 120 ppm–137 ppm are attributed to the carbon atoms of the pyridine rings.



**Scheme 1.** Synthesis procedure of the complex (1) and the complex (2).

Upon coordination the band due to  $\text{C}=\text{N}$  shift to low frequencies for both complexes. For compounds **1** and **2** the bands of the  $\text{C}=\text{N}$  are pointed at  $1539\text{ cm}^{-1}$  and  $1535\text{ cm}^{-1}$  respectively. This fact is indicative of the involvement of the azomethine nitrogen atom in the coordination to the lanthanide ions. For complex **1**, bands pointed at  $1471$ ,  $1380$ ,  $1304$  and  $1030\text{ cm}^{-1}$  are indicative of the presence of nitrate moiety. Information regarding the possible bonding modes of the nitrate group can be obtained from the positions of the bands. The band at  $1471\text{ cm}^{-1} \nu(\text{N}=\text{O})$  ( $\nu_1$ ), band at  $1304\text{ cm}^{-1} \nu_{\text{as}}(\text{NO}_2)$  ( $\nu_5$ ) and band at  $1030\text{ cm}^{-1} \nu_s(\text{NO}_2)$  ( $\nu_2$ ) are indicative of a coordinated nitrate. The separation  $\Delta\nu = \nu_1 - \nu_5$  was used as criterion of differentiation between mono and bidentate chelating nitrates, with  $\Delta\nu$  increasing as the coordination changes from mono to bidentate and/or bridging modes [32]. The magnitude of this separation for the complex  $\Delta\nu = 167\text{ cm}^{-1}$  is indicative of a bidentate chelating nitrate. The additional sharp and intense band at  $1380\text{ cm}^{-1}$  is characteristic of a non-coordinated nitrate group [33].

Asymmetric and symmetric bands of  $\text{COO}$  group in acetic acid are respectively  $1585\text{ cm}^{-1}$  ( $\nu_{\text{as}}$ ) and  $1397\text{ cm}^{-1}$  ( $\nu_s$ ) [34]. Upon coordination to praseodymium ion the IR bands of the acetate groups were shifted. In the IR spectrum of **2**, the  $\nu_{\text{as}}(\text{COO})$  shifted to  $1556$

$\text{cm}^{-1}$ , while the  $\nu_s(\text{COO})$  appears at  $1434 \text{ cm}^{-1}$ . The  $\Delta\nu(\nu_{\text{as}} - \nu_s)$  of the carboxylate group is a criterion used to determine the coordination mode of the carboxylate moiety to the metal ion [35,36]. When  $\Delta\nu$  varies between  $160$  and  $175 \text{ cm}^{-1}$ , the acetate group acts as counter ion. When the value of  $\Delta\nu$  is larger than  $175 \text{ cm}^{-1}$ , the acetate group acts in monodentate fashion. Lower value of  $\Delta\nu$  ( $< 160 \text{ cm}^{-1}$ ) is indicative of an acetate group acting in bidentate manner. Considering the  $\Delta\nu$  value of  $122 \text{ cm}^{-1}$  for the complex (**2**), we can say that the acetate group acts in bidentate chelating fashion to the praseodymium(III) ion.

The magnetic moments values of the neodymium(III) and praseodymium(III) complexes are respectively  $3.15 \mu_B$  and  $3.18 \mu_B$  per atom, respectively. The values are consistent with the presence of unpaired  $4f$  electrons and are close to the values for the free metal ions reported in the literature [37]. In these complexes, the magnetic moment are not affected by the ligand field, suggesting that the  $4f$  electrons do not take part in bond formation. Molar conductivities were measured for freshly prepared solutions in DMF and after standing for two weeks. The conductivities increased very slightly with time in dmf for both complexes. The coordination moieties present cannot be replaced by the solvent molecules. Molar conductance value of  $83 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in dmf is indicative of 1:1 electrolyte for complex **1**. Complex **2** is neutral electrolyte as shown by the molar conductance value of  $6 \text{ Scm}^2\text{mol}^{-1}$  in dmf [38].

The results of the elemental analysis, the IR spectra data, magneticmoment measurements and conductivities measurements allow to formulate the neodymium(III) and praseodymium(III) complexes as mononuclear structure  $[\text{Nd}(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)$  and dinuclear structure  $\{[\text{Pr}(\text{L})(\eta^2\text{-OOCCH}_3)(\text{H}_2\text{O})](\eta^1:\eta^2:\mu\text{-OOCCH}_3)_2[\text{Pr}(\text{L})(\eta^2\text{-OOCCH}_3)(\text{H}_2\text{O})]\}$ . These spectroscopic observations on the geometrical features are in accordance with those obtained for X-ray crystallography analyses of the Nd(III) and Pr(III) complexes.

**Table 1.** Crystal data and details of the structure determination for (**1**) and (**2**).

Empirical formula	$\text{C}_{26}\text{H}_{28}\text{N}_{11}\text{NdO}_{13}$	$\text{C}_{34}\text{H}_{38}\text{N}_8\text{O}_{12}\text{Pr}_2$
Formula weight (g/mol)	846.83	1032.54
Crystal system	Monoclinic	Monoclinic
Space group	$\text{C2/c}$	$\text{P2}_1/\text{n}$

Crystal size (mm)	0.10 × 0.09 × 0.09	0.14 × 0.12 × 0.12
Mo K $\alpha$ (Å)	0.71073	0.71073
Temperature (K)	173	173
<i>a</i> (Å)	22.7657(8)	11.5388(6)
<i>b</i> (Å)	8.4276(3)	14.1087(8)
<i>c</i> (Å)	18.0831(7)	12.2833(6)
$\beta$ (°)	114.851(2)	102.211(2)
<i>V</i> (Å <sup>3</sup> )	3148.2(2)	1954.45(18)
<i>Z</i>	4	2
<i>D</i> <sub>cal</sub> (g cm <sup>-3</sup> )	1.787	1.755
F(000)	1700	1024
$\mu$ (mm <sup>-1</sup> )	1.74	2.53
$\theta_{\max}$ (°)	30.098	30.085
<i>h, k, l</i> ranges	-32 ≤ <i>h</i> ≤ 32, -11 ≤ <i>k</i> ≤ 11, -25 ≤ <i>l</i> ≤ 25	-14 ≤ <i>h</i> ≤ 16, -19 ≤ <i>k</i> ≤ 19, -17 ≤ <i>l</i> ≤ 12
Measured reflections	151435	21217
Independent reflections	4584	5531
Reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4194	4665
<i>R</i> <sub>int</sub>	0.042	0.052
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.028	0.029
<i>wR</i> <sub>2</sub>	0.089	0.066
Data/parameters/restraints	4584/259/9	5531/261/3
Goodness-of-Fit	0.95	1.05
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.05, -3.49	0.64, -0.66

### 3.2. Molecular structure of complex (1)

The complex crystallizes in the monoclinic system with the space group C2/c. Partially labelled plot of the mononuclear structure of Nd(III) complex is shown in Figure 1. Selected interatomic distances are listed in Table 2. The structure of the

complex is consistent with the  $[\text{Nd}(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\cdot(\text{NO}_3)$  formulation. The asymmetric unit contains one  $\text{Nd}^{3+}$ , two neutral organic ligand, three nitrate ions and two water molecules. These species are associated as a cation  $[\text{Nd}(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]^+$  while one nitrate anion  $\text{NO}_3^-$  remains free. The crystallographic study shows that the cation is formed with 1:2  $[\text{Nd}:\text{HL}]$  and 1:2  $[\text{Nd}:\text{NO}_3^-]$ . In the complex each Schiff bases molecules acts in tridentate fashion through one azomethine nitrogen atom, one pyridine nitrogen atom and one carbonyl oxygen atom resulting in two membered chelating rings  $\text{NdOCCN}$  and  $\text{NdNCCN}$ . The Nd center is twelve-coordinated and the geometry around the lanthanide ion can be described as an icosahedron. The  $\text{Nd}-\text{O}_{\text{hydrazino}}$  distances and  $\text{Nd}-\text{O}_{\text{water}}$  distances are respectively 2.4772(19) Å and 2.4665(19) Å. The  $\text{Nd}-\text{O}$  distances, when O is from the bidentate nitrate groups are in the range 2.581(5)–2.637(4) Å and are the longest  $\text{Nd}-\text{O}$  distances. These observations are in consistency with those reported in the literature [39]. The  $\text{Nd}-\text{N}(\text{pyridine})$  and  $\text{Nd}-\text{N}(\text{imine})$  distances are 2.644(3) Å and 2.685(2) Å respectively, with the longer distance belonging to the imino nitrogen atom. The relation observed between the  $\text{Nd}-\text{N}$  distances in the complex is in contrast with those observed for the complex  $[\text{Nd}(\text{NCS})(\text{NO}_3)(\text{C}_{13}\text{H}_{11}\text{N}_3\text{O})_2(\text{H}_2\text{O})\text{NO}_3\cdot 2.33\text{H}_2\text{O}$  [39]. In the chain  $-\text{C}6-\text{N}2-\text{N}3\text{H}-\text{C}8(\text{O}1)-$ ,  $\text{C}6-\text{N}2$  and  $\text{C}8-\text{O}1$  bond lengths values of 1.278(4) Å and 1.243(3) Å are consistent with double bond character while  $\text{C}8-\text{N}3$  distance of 1.332(4) Å and  $\text{N}2-\text{N}3$  distance of 1.383(3) Å are indicative of a simple bond character. All these observations show clearly that iminolisation does not undergo for the hydrazino moiety upon coordination. Numerous intra and inter molecular hydrogen bonds (Table 3, Figure 2) consolidate the structure in a three-dimensional network (Figure 3).

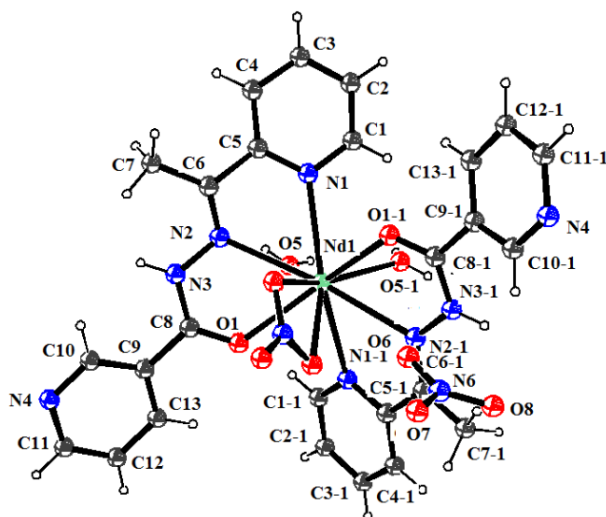
**Table 2.** Selected bond lengths (Å) for complexes **1** and **2**.

$\text{Nd}1-\text{O}5$	2.4665(19)	$\text{Nd}1-\text{O}2$	2.637(4)
$\text{Nd}1-\text{O}5^i$	2.4665(19)	$\text{Nd}1-\text{O}2^i$	2.637(4)
$\text{Nd}1-\text{O}1^i$	2.4772(19)	$\text{Nd}1-\text{N}1^i$	2.644(3)
$\text{Nd}1-\text{O}1$	2.4773(19)	$\text{Nd}1-\text{N}1$	2.644(3)
$\text{Nd}1-\text{O}4^i$	2.581(5)	$\text{Nd}1-\text{N}2$	2.685(2)
$\text{Nd}1-\text{O}4$	2.581(5)	$\text{Nd}1-\text{N}2^i$	2.685(2)

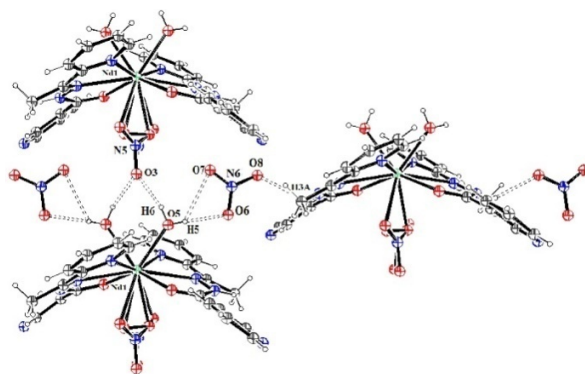


Pr1—O1	2.4200(19)	Pr1—O6 <sup>ii</sup>	2.555(2)
Pr1—O5	2.4550(19)	Pr1—N2	2.594(2)
Pr1—O3	2.484(2)	Pr1—N3	2.612(2)
Pr1—O8	2.4965(19)	Pr1—O5 <sup>ii</sup>	2.6712(18)
Pr1—O2	2.537(2)		

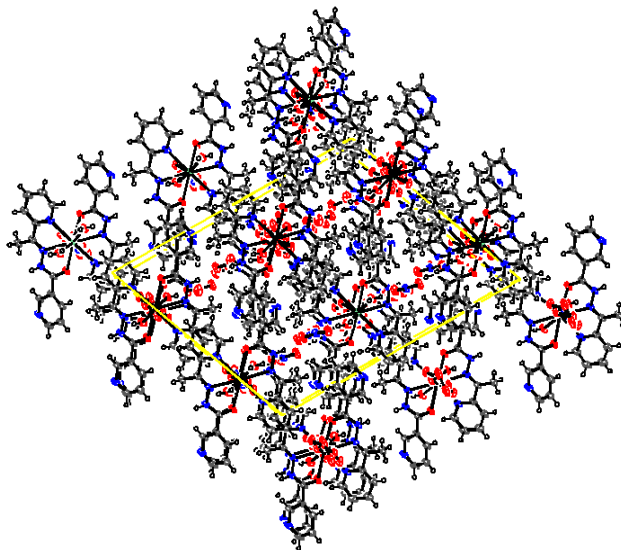
Symmetry code: (i)  $-x+1, y, -z+1/2$ ; (ii)  $-x+1, -y+1, -z+1$ .



**Figure 1.** ORTEP plot (30% probability ellipsoids) showing the structure of (1). One coordinated nitrate group was omitted for clarity.



**Figure 2.** Plot showing the inter and intramolecular hydrogens bonds in the crystal.



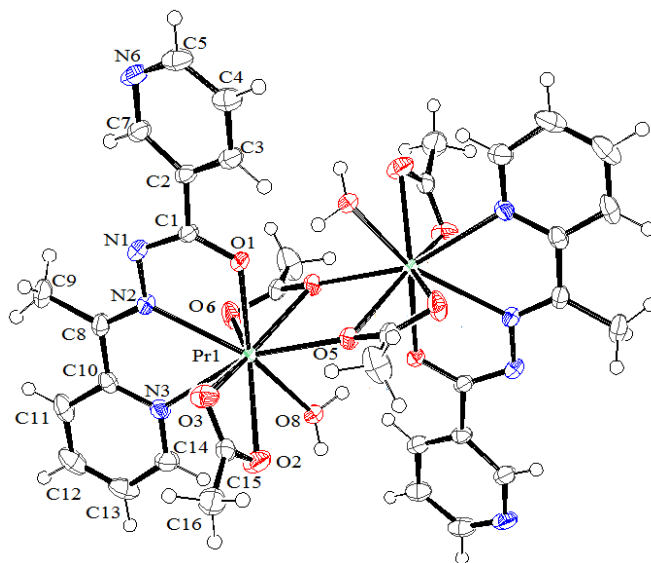
**Figure 3.** The packing of the complex(1) in the crystal structure.

### 3.3. Molecular Structure of Complex (2)

The complex crystallizes in the monoclinic system with the space group  $P2_1/n$ . Partially labelled plot of the dinuclear structure of Pr(III) complex is shown in Figure 4 and the coordination polyhedral is illustrated in Figure 5. Selected interatomic distances are listed in Table 2. The structure of the complex is consistent with the  $\{[\text{Pr}(\text{L})(\eta^2\text{-OOCCH}_3)(\text{H}_2\text{O})](\eta^1:\eta^2:\mu\text{-OOCCH}_3)_2[\text{Pr}(\text{L})(\eta^2\text{-OOCCH}_3)(\text{H}_2\text{O})]\}$  formulation. The asymmetric unit contains two  $\text{Pr}^{3+}$ , two monodeprotonated organic ligand, four acetate ions and two water molecules. The crystal structure is formed by two analogous entities of  $[\text{Pr}(\text{L})(\eta^2\text{-OOCCH}_3)(\text{H}_2\text{O})]$  which are bridged by two acetate groups acting in  $\eta^1:\eta^2:\mu\text{-OOCCH}_3$  mode. Each  $\text{Pr}^{3+}$  is coordinated by one ligand molecule through one azomethine nitrogen atom, one pyridine nitrogen atom and one carbonyl oxygen atom resulting in two membered chelating rings  $\text{PrOCCN}$  and  $\text{PrNCCN}$ . The  $\text{Pr}^{3+}$  ion is coordinated by one acetate group in chelating–bidentate mode and one water molecule. The  $\text{Pr}^{3+}$  ion is nine–coordinated.

The Pr–O distances are in the range 2.4200(19)–2.6712(18) Å and are typical of a chelating–bidentate acetate group [40]. The two metal centers are finally bridged by a pair of chelating–bridging acetate ligands which are acting in  $\eta^1:\eta^2:\mu_2\text{-OOCCH}_3$  mode. Two different bond values are noted: two typical bond values of 2.455(19) Å and

2.6712(18) Å (Pr1–O5 and Pr1–O5<sup>i</sup>) and 2.555(2) Å (Pr1–O6<sup>i</sup>). These values are comparable to values noted from literature [41]. The largest Pr–O (Pr1–O5<sup>i</sup> = 2.6712(18) Å) distance is observed in the chelating–bridging coordination mode  $\eta^1:\eta^2:\mu_2$ -OOCH<sub>3</sub>, while the shortest Pr–O (Pr1–O3 = 2.484(2) Å) bond length is observed in the chelating coordination mode  $\eta^2$ -OOCH<sub>3</sub>. The Pr–N distances are 2.594(2) Å and 2.612(2) Å. The longest Pr–N distance is due to the nitrogen atom belonging to pyridine ring, as observed for similar complexes [42]. The C–O bond in the coordinated acetate groups has an intermediate character between single C–O bond and double C=O bond. In fact, the bond lengths values observed in both coordinated acetate groups for C–O [1.249(3) Å–1.273(3) Å] are shorter than those of a single C–O bond (1.430 Å) and longer than those of a double bond (1.220 Å). The N2–C8 bond length value of 1.290(4) Å is consistent with double bond character. The Pr...Pr distance bridged by two acetate anions is 4.2777(6) Å. All the bond lengths are normal and fall within similar ranges to those reported for dinuclear lanthanide complexes with the same hydrazone ligand [42,43]. The chelation of the hydrazino ligand to the Pr<sup>3+</sup> cation results in two five-membered rings (PrNCNN and PrNCCN) with bite angles of 61.46 (8)° (N2–Pr1–N3). The bond angles of the ligands, which involve the Pr(III) ion, are slightly largest than the angle subtended by the oxygen atoms of the bidentate chelating acetate groups : O2–Pr1–O3 = 51.71(7)° and O5<sup>i</sup>–Pr1–O6<sup>i</sup> = 49.43(6)°. These angle values are comparable to the values reported for the complex [Pr(C<sub>9</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)(H<sub>2</sub>O)]<sub>2</sub> [40]. The bond angle value of 68.23(7)° of the bridged oxygen atoms of the  $\eta^1:\eta^2:\mu_2$ -acetate groups [O5–Pr–O5<sup>i</sup>] is comparable with the angle value observed in homologous complex of [Tb<sub>2</sub>(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>·4H<sub>2</sub>O] [44]. The value of the bridging angle Pr1–O5–Pr1<sup>i</sup> [111.77(7)°] is in the range expected for  $\eta^1:\eta^2:\mu_2$ -acetate groups [34]. The dihedral angle formed by the planes of the two terminal pyridine rings is 15.61°. The three sets of donor atoms [(O1, N3, O5)], [(O2, O6, N2)] and [(O3, O5<sup>i</sup>, O8)] form three plane with the sums of the angles at Pr1 being 358.19°, 359.21° and 349.03° respectively. Two coordination polyhedral with nine vertices are known. The coordination sphere around the nine-coordinated praseodymium atom is best described as a distorted tricapped trigonal prism in which N2, O2 and O5 are the caps as shown in Figure 5. Numerous intra and inter molecular hydrogen bonds (Table 3, Figure 6) consolidate the structure in a three-dimensional network.



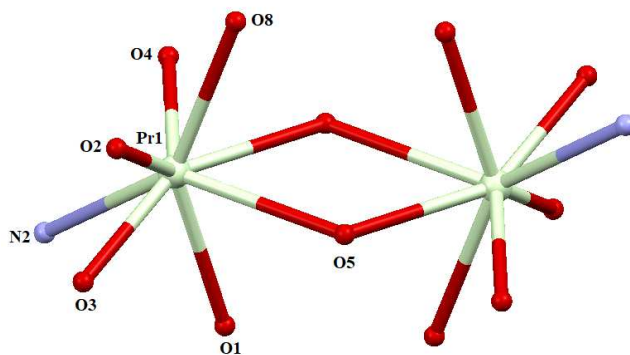
**Figure 4.** ORTEP plot (30% probability ellipsoids) showing the structure of (2).

**Table 3.** Intra and inter molecular hydrogen bonds.

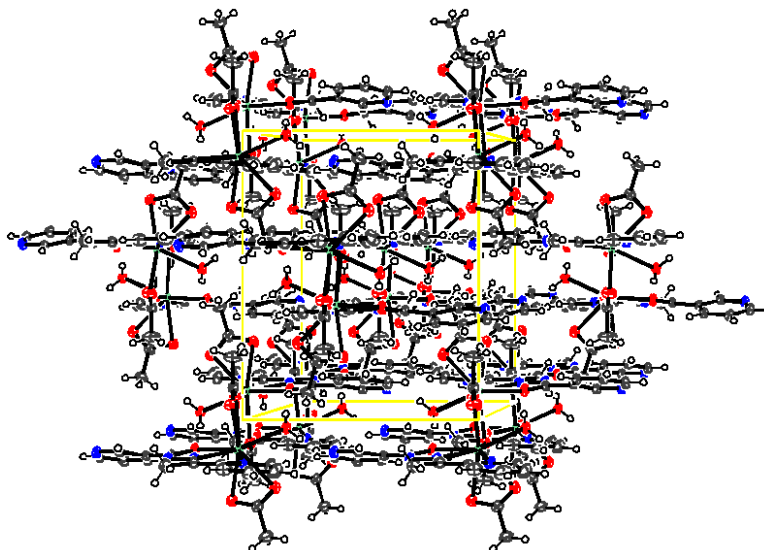
<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
Complex 1				
C7—H7A...N4 <sup>i</sup>	0.980	2.476	3.374	152.12
N3—H3A...O8 <sup>ii</sup>	0.880	2.115	2.830	137.87
C12—H12...O6 <sup>iii</sup>	0.950	2.565	3.474	160.36
O5—H5...N6 <sup>iv</sup>	0.777	2.573	3.284	152.93
O5—H5...O7 <sup>iv</sup>	0.777	2.494	3.008	125.01
O5—H5...O6 <sup>iv</sup>	0.777	1.964	2.740	177.09
O5—H6...O3 <sup>iv</sup>	0.813	2.141	2.855	146.55
O5—H6...O3 <sup>v</sup>	0.813	1.832	2.619	162.32
Complex 2				
O8—H8A...O1	0.86(2)	1.92(2)	2.764(3)	165(2)
O8—H8B...N6	0.85(2)	1.98(2)	2.760(3)	153(2)

C4–H4...O3	0.95	2.48	3.332(4)	149
C11–H11...O6	0.95	2.36	3.212(4)	149
C13–H13...O3	0.95	2.31	3.119(4)	142

Symmetry codes : (i)  $-x+1/2, y+1/2, -z+1/2$ ; (ii)  $x-1/2, y+1/2, z$ ; (iii)  $x-1/2, -y+1/2, z-1/2$ ; (iv)  $x, y+1, z$ ; (v)  $-x+1, y+1, -z+1/2$ .



**Figure 5.** Plot showing the coordination sphere of the two  $\text{Pr}^{3+}$  ions in the crystal.



**Figure 6.** The packing of the complex(2) in the crystal structure.

#### 4. Conclusion

The reported work is concerned the synthesis of a Schiff base and its use to prepare a new mononuclear Nd(III) complex and a new dinuclear Pr(III) complex. The reaction of the Schiff base and  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Pr}(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}$  salts afford mononuclear compound  $[\text{Nd}(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_3$  and dinuclear  $\{[\text{Pr}(\text{L})(\eta^2\text{-OOCCH}_3)(\text{H}_2\text{O})](\eta^1:\eta^2:\mu\text{-OOCCH}_3)_2[\text{Pr}(\text{L})(\eta^2\text{-OOCCH}_3)(\text{H}_2\text{O})]\}$  complex. In the yielded crystals, the Nd(III) ion is twelve coordinated, while the Pr(III) ion is nine coordinated. In the crystal (1) the coordination polyhedron around the metal center is best described as an icosahedron. In the dinuclear complex the two Pr(III) ions are bridged by two acetate groups acting in  $\eta^1:\eta^2:\mu\text{-OOCCH}_3$  mode. The geometries around the two Pr(III) ions in complex (2) are best described as a distorted tricapped trigonal prism.

#### 5. Supporting Information

CCDC-2087203 and 2087202 contain the supplementary crystallographic data for complex (1) and complex (2) respectively. 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](mailto: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.

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