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Syntheses, Characterization, and X-ray Crystal Structure of Binuclear Lanthanide Complexes Assembled with Schiff Base and Acetate

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Abstract

Herein we reported the binuclear complexes of the 1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine ligand (HL) $[Ln_2(HL)_2(CH_3COO)_6]\cdot n(H_2O)$ (Ln = Y, Pr, Gd and Er). The binuclear complexes are characterized by IR and physical measurement. Spectroscopic evidence indicated that the Schiff base HL behave an N_3 coordination tridentate ligand. The complexes are formulated as [{Ln(1-(pyridin-2-ylmethylidene-κN)-2-(pyridin-2-yl-κN) hydrazine-κN^1) (η^2-$OOCH_3)_2$} {η^1:η^2:μ_2-$OOCH_3$}$_2$ {Ln(1-(pyridin-2-ylmethylidene-κN)-2-(pyridin-2-yl-κN) hydrazine-κN^1)) (η^2-$OOCH_3)_2$}]$\cdot n(H_2O)$. The structure of the praseodymium complex was elucidated by X-ray diffraction analysis. Suitable crystals were grown by slow evaporation of methanol solution. The asymmetric unit of the compound contains two neutral ligand molecules, two Pr^{3+} ions, four acetate anions acting in η^2-$OOCH_3$ mode, two acetate anions acting in η^1:η^2:μ_2-$OOCH_3$ mode, and three uncoordinated water molecules. The praseodymium atom is ten coordinated and the coordination sphere is best described as a distorted bicapped square antiprism. The $Pr^{III}\cdots Pr^{III}$ distance is 4.2777(6) Å and the bridging angle Pr—O—Pr and O—Pr—O are respectively 115.8(3)° and 64.2(3)°. The structure is consolidated by intra and intermolecular hydrogen bond.

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Keywords and phrases: lanthanide; 2-hydrazinopyridine; 2-pyridinecarbaldehyde; X-ray structure.

1. Introduction

The coordination chemistry of lanthanide is largely investigated by chemist in the two last decades [1-5]. Indeed, a wide variety of compounds with intriguing structures and atypical properties are reported in recent years [6-8]. The potential use in fields such as medical diagnostics [9], catalysis [10,11], luminescence [12,13], or magnetism [14,15] is increasing the interest of researchers. Polydentate ligands containing different donor sites are developed to generate special topological structures with lanthanide ions [16]. Combined with co-ligands such as the acetate moiety, these ligands allow the preparation of polyvalent coordination compounds by meticulously controlling the process [2,17]. Indeed, the mode of coordination depends on the reaction conditions. Interest is given to ligands having both soft and hard donor sites such as sulfur, nitrogen, and oxygen. The complexation of these types of ligands with metal ions often improves the biological properties of the complexes relative to the free ligand [18,19]. Compounds obtained from hydrazone ligand have shown antioxidant, antitumor, antiviral, and anti-inflammatory activity. Several authors [20,21] have used ligand analogous to 1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine (HL) in the presence of acetate ions to prepare coordination compounds. Our group has already used this ligand in the presence of sodium acetate and hydrated lanthanide nitrate to prepare several complexes [22-25]. In all these complexes the acetate group is either bidentate chelating η^2-$OOCH_3$ or bidentate bridging η^2:μ_2-$OOCH_3$. In the present study, a mixture of the HL ligand and hydrated lanthanide acetate gives a homo dinuclear complexes of lanthanide (Y^{3+}, Pr^{3+}, Gd^{3+}, Er^{3+}) in which two modes of coordination of the acetate group are observed: η^2-$OOCH_3$ and η^1:η^2:μ_2-$OOCH_3$. The structure of [{Pr(1-(pyridin-2-ylmethylidene-κ*N*)-2-(pyridin-2-yl)-κ*N*) hydrazine-κN^1)(η^2-$OOCH_3$)$_2$}{η^1:η^2:μ_2-$OOCH_3$}$_2${[{Pr(1-(pyridin-2-ylmethylidene-κ*N*)-2-(pyridin-2-yl)-κ*N*) hydrazine-κN^1)(η^2:$OOCH_3$)$_2$}}]·3(H_2O) has been elucidated by X-ray diffraction.

2. Materials and Methods

2.1. Starting materials and instrumentations

2-Hydrazinopyridine,2-pyridinecarboxaldehyde, and lanthanide acetate were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. The ligand (HL) was synthesized *in situ*. 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 molar conductance of 1×10^{-3} M in DMSO solutions of the metal complexes was measured at 25°C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Mattey scientific magnetic susceptibility balance (Calibrant: $Hg[Co(SCN)_4]$).

2.2. Synthesis and characterization of 1, 2, 3 and 4

A mixture of 2-hydrazinopyridine (1 mmol) and 2-pyridinecarbaldehyde (1 mmol) in ethanol (15 mL) was stirred under reflux during 30 min. An ethanol solution of $Ln(CH_3OO)_3{\cdot}nH_2O$ (1 mmol)(Ln = Y, Er; Gd, Pr) in ethanol (10 mL) was added to the solution. The mixture was stirred for 30 min and the resulting yellow solution was filtered and the filtrate was kept at 298 K. A yellow powder appeared after one day and was collected by filtration. Recrystallisation in methanol solution afforded suitable X-ray diffraction crystal of the complex or praseodymium.

$[Y_2(HL)_2(OOCH_3)_6]{\cdot}2(H_2O)$ (**1**). Yield : 59%. $C_{34}H_{48}N_8O_{14}Y_2$. Elemental Anal. Found (Calcd.) (%):C, 42.07 (42.05); H, 4.98 (4.95); N, 11.54 (11.51).IR (cm^{-1}) :3425, 3290, 1600, 1582, 1560, 1448, 1379, 1134, 1013, 827.μ_{eff} (μ_B): diamagnetic. Λ_M(S cm^2 mol^{-1}) :9.

$[Pr_2(HL)_2(OOCH_3)_6]{\cdot}3(H_2O)$ (**2**). Yield :69%. $C_{34}H_{50}N_8O_{15}Pr_2$. Elemental Anal. Found (Calcd.) (%):C, 37.37 (37.35); H, 4.61 (4.58); N, 10.26 (10.23).IR (cm^{-1}) :3420, 3292, 1595, 1580, 1555, 1445, 1380, 1143, 1015, 825.μ_{eff} (μ_B): 5.22. Λ_M(S cm^2 mol^{-1}): 25.

$[Gd_2(HL)_2(OOCH_3)_6]{\cdot}4(H_2O)$ (**3**). Yield :48%. $C_{34}H_{52}N_8O_{16}Gd_2$. Elemental Anal. Found (Calcd.) (%):C, 35.72 (35.69); H, 4.58 (4.55); N, 9.80 (9.76).IR (cm^{-1}) :3429, 3288, 1592, 1580, 1552, 1440, 1378, 1143, 1012, 823.μ_{eff} (μ_B): 13.25.Λ_M(S cm^2 mol^{-1}) :16.

$[Er_2(HL)_2(OOCH_3)_6]{\cdot}2(H_2O)$ (**4**). Yield :44%. $C_{34}H_{48}N_8O_{14}Er_2$. Elemental Anal. Found (Calcd.) (%):C, 36.22 (36.20); H, 4.29 (4.25); N, 9.94 (9.92).IR (cm^{-1}) :3412, 3285, 1589, 1578, 1550, 1435, 1375, 1143, 1011,820.μ_{eff} (μ_B):16.45.Λ_M(S cm^2 mol^{-1}) :22.

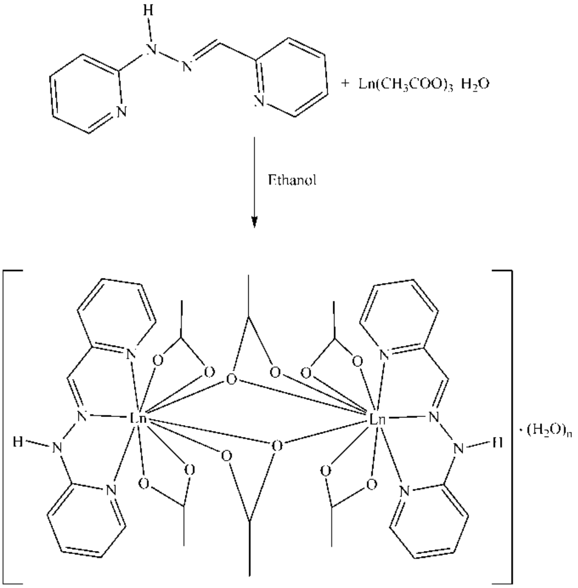
2.3. X-ray crystallography

Crystals suitable for single-crystal X-ray diffraction, of the Pr(III) complex, 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 an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoKα radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [26]. 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 [27]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using *ORTEP-3* [28].

3. Results and Discussion

3.1. General study

The strong band expected at *ca.* 1630 cm^{-1}due to C=N for the free ligand is shifted to low frequencies and appears in the range 1600-1589 cm^{-1} in the spectra of **1**-**4**. This is indicative of the involvement of the azomethine nitrogen atom in the coordination to the lanthanide ion. The bands located in the range 3285-3292 cm^{-1} in the spectra of the complexes **1**-**4** is attributed to the N—H stretching vibrations. This band which is located at 3290 cm^{-1}in the spectrum of the free ligand remained unaffected upon coordination, precluding the non-involvement of this nitrogen atom in the coordination. The IR bands of the acetate groups in the spectra of the complexes are compared with those of the free acetic acid. The spectrum of the free acetic acid presents two mains bands at 1585 cm^{-1} and 1397 cm^{-1}, which are attributed respectively to the ν_{as}(COO) and ν_s(COO) stretching vibrations [2]. Upon coordination to lanthanide ion these bands were shifted. The ν_{as}(COO) shifted to high frequencies and are in the range 1578-1582 cm^{-1} for complexes **1**-**4**. The symmetrical resonance split into two components. One band appears in higher frequency (1438-1145 cm^{-1}) while the other bands appears at lower frequency (1375-1380 cm^{-1}) comparatively to the ν_s(COO) value of 1397 cm^{-1} in the free acetic acid. These observations are indicative of the presence of two different coordination modes of the acetate groups [29]. The presence of water molecules in whole complexes was proved by the strong and broad bands which appear in the range 3412-3429 cm^{-1}. The N—N band appears at *ca.* 1010 cm^{-1}. The magnetic moment values of 5.22 μ_B, 13.25 μ_B and 16.45 μ_B for complexes **2**, **3** and **4** respectively, 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. The molar conductivities of the complexes were measured in dimethylsulfoxide (dmso) for freshly prepared solutions and after standing for two weeks. No variation of the conductivities values is observed with time in dmso for all the complexes. This is indicative of high stability of these acetate complexes in dmso solutions. The values of these conductance are in the range 9-25 $Ohm^{-1}cm^2mol^{-1}$ in dmso and are in accordance with non-electrolytes nature of the complexes in this solvent [30]. These facts are in accordance with the infrared spectra where the compounds were formulated as neutral acetato complexes. The behaviors of the complexes in solid state are not different from the behaviors of the compounds in dmso the solution.



Scheme 1. Chemical diagrams for $[Ln_2(HL)_2(CH_3COO)_6]\cdot n(H_2O)$.

3.2. Molecular structure of complex 2

The complex formulated as [{Pr(1-(pyridin-2-ylmethylidene-κN)-2-(pyridin-2-yl-κN)hydrazine-κN^1) (η^2-$OOCH_3)_2$} {η^1:η^2:μ_2-$OOCH_3$}$_2$ {Pr(1-(pyridin-2-ylmethylidene-κN)-2-(pyridin-2-yl-κN) hydrazine-κN^1) (η^2-$OOCH_3)_2$}]$\cdot$n(H_2O)(**2**) 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 binuclear complex is illustrated in Figure 1. Selected bonds lengths and angles are listed in Table 2.

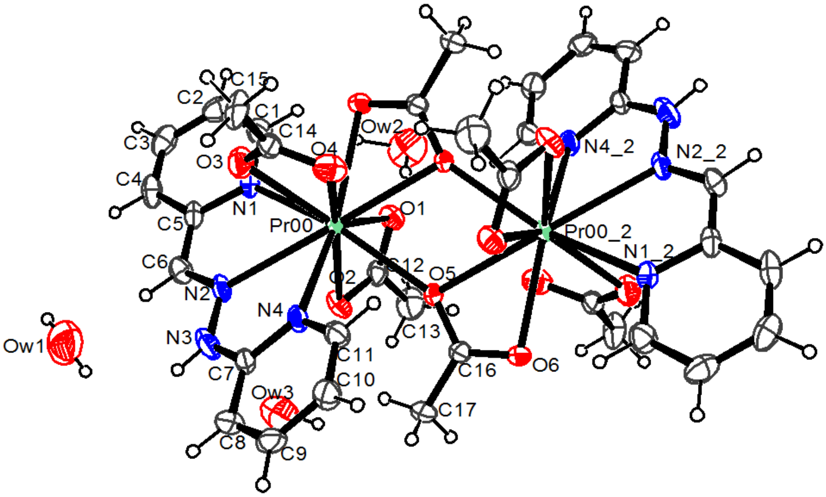


Figure 1. *ORTEP* Plot (30% probability ellipsoids) showing the structure of the binuclear complex **2**.

The acetato-bridged complex **2** displays a structure constructed from two identical entities {Pr(1-(pyridin-2-ylmethylidene-κN)-2-(pyridin-2-yl)-κN) hydrazine-κN^1) (η^2-$OOCH_3$)$_2$} bridged by two acetateanions acting in η^1:η^2:μ_2-$OOCH_3$ modes, yielding a dinuclear neutral complex. Each Pr^{III} ions is coordinated by one HL ligand through two 2-pyridyl nitrogen atoms and one imino nitrogen atom. Additionally, each Pr^{III} ion is coordinated by two chelating-bidentate acetate groups acting in η^2-$OOCH_3$ mode. The Pr—O distances are in the range 2.507 (7)—2.684 (8) Å and are typical of a chelating-bidentate acetate group [31]. The two metal centers are finally bridged by a pair of chelating-bridging acetato ligands which are acting in η^1:η^2:μ_2-$OOCH_3$ (Figure 2a). Two different bonds values are noted: two typical bond values of 2.465 (6) Å (Pr00i —O5) and 2.531 (7) Å (Pr00—O6) which are shorter than the non-typical bond distance of 2.583 (6) Å (Pr00—O5) which is indicative of a weak bond character. These values are comparable to values noted from literature [32]. The largest Pr—O(Pr00—O4 = 2.684 (8)Å) distance is observed in the chelating coordination mode η^2-$OOCH_3$, while the shortest Pr—O (Pr00—O5^i = 2.465 (6)Å) bond length is observed in the chelating-bridging coordination mode η^1:η^2:μ_2-$OOCH_3$. The Pr—N distances are 2.632 (8)Å, 2.661 (8)Å and 2.688 (8)Å. The longest Pr—N distance is due to the nitrogen atom belonging to the ortho-hydrazino substituted pyridine ring, as observed for similar complexes [22]. 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 [1.232 (11) Å-1.286 (12) 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—C6 bond length value of 1.338(13)Å is consistent with double bond character. The Pr···Pr distance 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 [22,23]. The chelation of the hydrazino ligand to the Pr^{III} cation results in two five-membered rings (PrNCNN and PrNCCN) with bite angles of 60.3(3)° (N1—Pr00—N2) and 59.6(3)° (N2—Pr00—N4). 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 :O3—Pr00—O4 = 48.39(3)° and O5—Pr00—O6 =50.2(2)°. These angle values are comparable to the values reported for the complex $[Pr(C_9H_4N_2O_4)(C_2H_3O_2)(H_2O)]_n$ [31]. The bond angle value of 64.2(3)° of the bridged oxygen atoms of the $\eta^1{:}\eta^2{:}\mu_2$-acetate groups [O5—Pr00—$O5^i$] is comparable with the angle value observed in homologous complex of $[Tb_2(CH_3COO)_6(H_2O)_4]\cdot 4H_2O$ [33]. The value of 115.8(3)° of the bridging angle Pr00—O5—Pr00 is in the range expected for $\eta^1{:}\eta^2{:}\mu_2$-acetate groups [2]. The dihedral angle formed by the planes of the two terminal pyridine rings is 15.61°. The coordination sphere around the ten-coordinated praseodymium atom is best described as a distorted bicapped square antiprism in which N2 and O5 are the caps as shown in Figure 2b. Numerous intra and inter molecular hydrogen bonds (Table 3, Figure 3) consolidate the structure in a three-dimensional network (Figure 4).

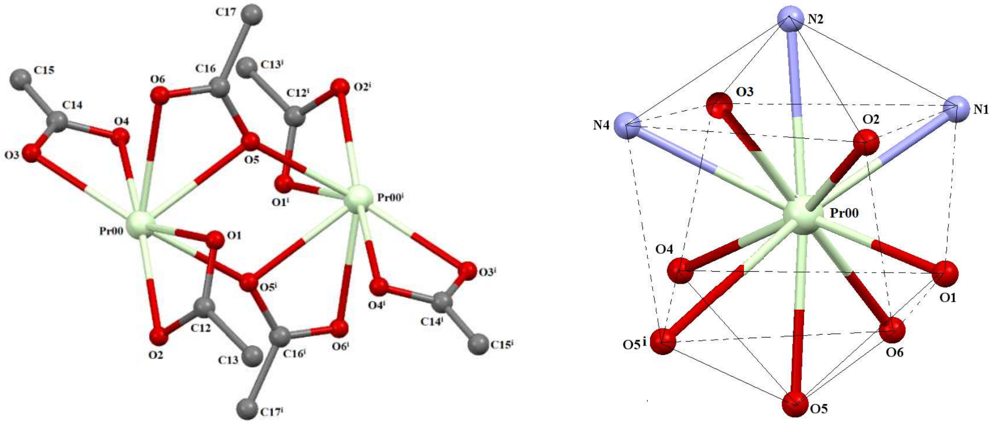


Figure 2. Plot showing the bridging mode of the acetate group (**a**) and the coordination sphere around the Pr^{III} ion in the crystal (**b**).

Table 1. Crystal data, X-ray data collection, data reduction and structure refinement for **2**.

Chemical formula	$C_{34}H_{50}Pr_2N_8O_{15}$
M_r	1092.62
Crystal system, space group	Triclinic,*P-1*
Temperature (K)	293
a,b,c (Å)	9.4073 (6), 10.8511 (5), 11.6136 (4)
α,β, γ(°)	103.521 (4), 98.235 (4), 107.875 (5)
V (Å^3)	1066.99 (10)
Z	5
Calculated density (g.cm^{-3})	1.559
F (000)	514
Radiation type	$\lambda = 0.71073$ Å
μ (mm^{-1})	1.20
Crystal size (mm)	0.15 × 0.10 × 0.08
Data collection	
Diffractometer	XtaLAB AFC12 (RCD3): Kappa single
Absorption correction	Multi-scan
$T_{\min}$. $T_{\max}$	0.893 ; 1.000
Limiting indices	
h	-11→11
k	-13→13
l	-11→13
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7523,3570,2886
R_{int}	0.113
Refinement	
$R[F^2 > 2\sigma(F^2)],wR(F^2),S$	0.067,0.190,1.05
No. of reflections	3570
No. of parameters/restraints	296/0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$. $\Delta\rho_{\min}$ (e Å^{-3})	1.95 & −2.51

Table 2. Selected bond lengths (Å) and angles(°) for the complex 2.

Bond	**bond lengths [Å]**	**Bond**	**bond angles(°)**
Pr00—O5	2.465 (6)	O5—Pr00—O6^{i}	113.9 (2)
Pr00—O2	2.504 (7)	O2—Pr00—O1	51.6 (2)
Pr00—O6^{i}	2.531 (7)	N1—Pr00—N2	60.3 (3)
Pr00—O1	2.539 (7)	O3—Pr00—O4	48.3 (3)
Pr00—O3	2.542 (8)	N2—Pr00—N4	59.6 (3)
Pr00—O5^{i}	2.583 (6)	Pr00—O5—Pr00^{i}	115.8 (3)
Pr00—N1	2.632 (8)	O5— Pr00— O5^{i}	64.2 (3)
Pr00—N2	2.661 (8)	O5—Pr00—O6	50.2 (2)
Pr00—O4	2.684 (8)		
Pr00—N4	2.688 (8)		

Symmetry Codes: (i) −x+1, −y+1, −z+1

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

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
Ow1—Hw1A···Ow3	0.85	2.05	2.77(2)	143
Ow1—Hw1B···Ow2	0.85	1.92	2.75(3)	163
Ow2—Hw2···O1	0.85	2.04	2.879(18)	168
Ow3—Hw3A···Ow1	0.85	2.19	2.77(2)	125
C1—H1···O6	0.93	2.55	3.157(13)	123
C2 —H2···Ow3	0.93	2.37	3.25(2)	158
C6—H6···Ow1	0.93	2.14	3.06(2)	171
C11—H11···O1	0.93	2.52	3.429(13)	165
C15—H15C···Ow1	0.96	2.33	2.87(3)	115
C15—H15C···N3	0.96	2.57	3.269(17)	130

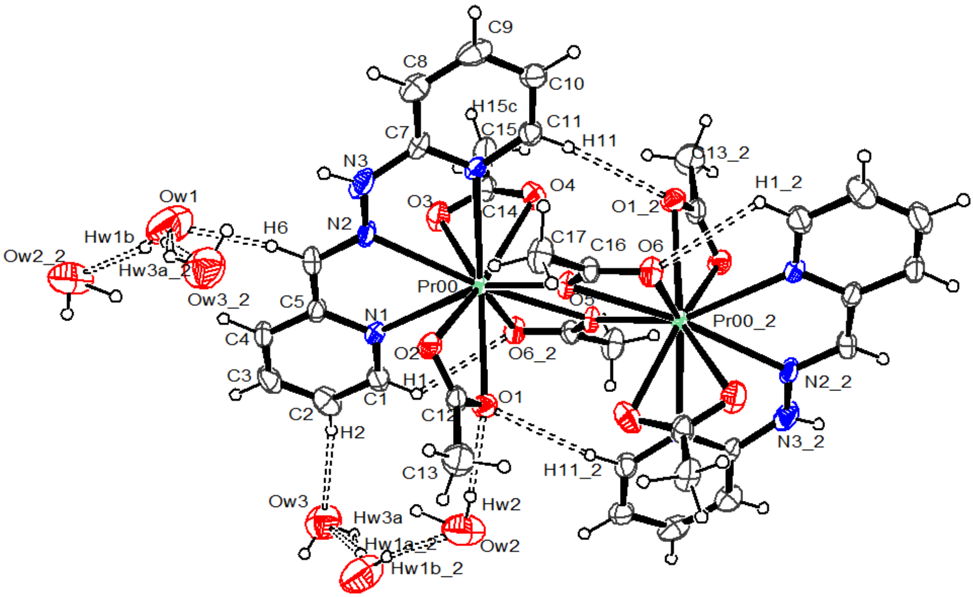


Figure 3. Plot showing the inter and intramolecular hydrogens bonds in the crystal.

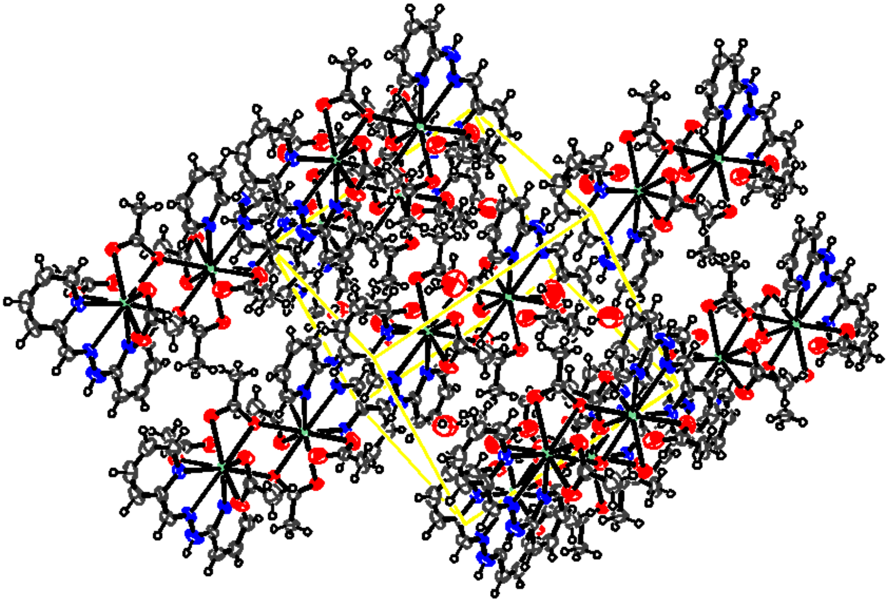


Figure 4. The packing of the complex 2 in the crystal structure.

Conclusion

In summary, we have successfully synthesized and studied the homo binuclear complexes containing Ln (III) ions. A suitable crystal of the complex was obtained by slow evaporation of methanol solution of the Pr^{3+} complex. Infrared spectra of the compounds were discussed in this paper. Crystal data, X-ray data collection, data reduction and structure refinement are studied for the Pr^{3+} complex. The binuclear complex crystallizes in the triclinic system with a space group P-1. The acetate groups act in two different coordination modes :η^2-$OOCH_3$ and η^1:η^2:μ_2-$OOCH_3$. The environments of the ten-coordinated praseodymium (III) ions are best distorted as a distorted bicapped square antiprism. The structure of the complex is consolidated by numerous hydrogen bond.

Supplementary Materials

CCDC-2122385 contains the supplementary crystallographic data for this paper. 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 no conflict of interest.

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