

## SYNTHESIS, CHARACTERIZATION AND ANTIOXIDANT ACTIVITY OF LANTHANIDE(III) COMPLEXES WITH TRIDENTATE SCHIFF BASE LIGAND. X-RAY CRYSTAL STRUCTURE OF THE Ce(III) COMPLEX

Mbossé NDIAYE GUEYE<sup>a</sup>, Moussa DIENG<sup>a\*</sup>, Ibrahima Elhadji THIAM<sup>a</sup>, Mouhamadou Moustapha SOW<sup>a</sup>, Rokhaya GUEYE SYLLA<sup>a</sup>, Aliou Hamady BARRY<sup>b2</sup>, Mohamed GAYE<sup>a</sup> and Pascal RETAILLEAU<sup>c</sup>

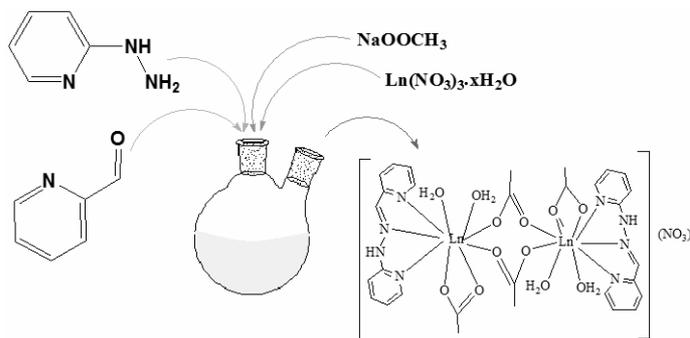
<sup>a</sup> Department of Chemistry, University Cheikh Anta Diop, Dakar, Sénégal

<sup>b</sup> Department of Chemistry, University of Nouakchott, Mauritania

<sup>c</sup> Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS-UPR2301, 1 Avenue la Terrasse, 91198 Gif sur Yvette, France

Received July 25, 2016

The tridentate N<sub>4</sub>-type Schiff base was synthesized in situ from the condensation reaction of 2-hydrazinopyridine and pyridine-2-carbaldehyde. Novel lanthanide(III) complexes were isolated when lanthanide(III) nitrate salt were added to the solution of the ligand. The complexes were characterized by IR spectra, room temperature magnetic measurement, elemental analyses and the structure of the Ce(III) complex was determined by X-ray single crystal diffraction. The complex crystallizes in the monoclinic system with space group *P21/c*. The geometry around the metal center shows distorted tricapped trigonal prism. It is noteworthy that the tridentate Schiff base acts as tridentate ligand leading nine-coordinate complex.



### INTRODUCTION

Owing to their low toxicity, the chemistry of the lanthanide ions has been widely studied in the past two decades. Their potential uses as diagnostic tools in biology and their paramagnetic and luminescent properties<sup>1-5</sup> reinforce the interest of chemist in these kind of compounds. A few years ago we initiated a project concerning rare earth metal chemistry<sup>6</sup> in a search for unusual molecular materials.<sup>7</sup> By use of an acyclic Schiff's base it is possible to introduce two identical or different lanthanide ions and to study their physicochemical properties.<sup>8,9</sup> Attention has been devoted to the

study of spectroscopic properties and crystal structures. The formation of acyclic complexes depends on the dimension of the cavities, on the flexibility of the arms, on the nature of the donor atoms and on the complexing properties of the anions acting as counter ions.<sup>10</sup> This paper is devoted to the homobinuclear lanthanides species derived from 1-(pyridin-2yl)-2-(pyridine-2-ylmethylene)hydrazine (HL). HL is an acyclic ligand bearing nitrogen donors containing one coordination cavity which can encapsulate large ions such as lanthanides.<sup>11</sup> In order to understand the coordination chemistry we synthesized a series of binuclear complexes and investigated the

\* Corresponding author: mohamedl.gaye@ucad.edu.sn

spectroscopic properties. The results of spectroscopic studies and crystal structure show that the ligand acts as tridentate leading isotype lanthanide complexes of cerium, praseodymium, and gadolinium. The structure of  $[\{\text{Ce}(\text{HL})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2\}_2(\mu\text{-CH}_3\text{COO})_2](\text{NO}_3)_2$  has been elucidated by X-ray diffraction.

## RESULTS AND DISCUSSION

The acyclic polydentate ligand, 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene)hydrazine, abbreviated as HL, was prepared *in situ* by the 1:1 condensation reaction of 2-hydrazinopyridine and 2-pyridine carbaldehyde in ethanol. The reaction of the *in situ* prepared ligand solution,  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , and  $\text{NaOOCCH}_3$  with a 1:1:3 molar ratio in ethanol gave yellow powder. The formula of these powders are confirmed as  $[\{\text{Ln}(\text{HL})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2\}_2(\mu\text{-CH}_3\text{COO})_2](\text{NO}_3)_2$ , with Ln= Ce, Pr, Gd and Er.

All IR spectra of the complexes show in the range of 1560–1550 and 1448–1435  $\text{cm}^{-1}$  bands which are assigned respectively to asymmetric  $\nu_{\text{as}}(\text{COO})$  and symmetric  $\nu_{\text{s}}(\text{COO})$  stretching vibrations of acetate group.<sup>12</sup> The position of these asymmetric and symmetric bands are very close proximity in all spectra of the complexes indicating that the coordination modes of the different acetate groups are similar in all these compounds. The values of  $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$  are in the range admitted for multiple coordination modes of acetate groups.<sup>13</sup> This coordination behaviors of the acetate groups were further confirmed by X-ray studies of the cerium complex. In the X-ray structure of this binuclear complex, each Ce(III) ions have one acetate behaving as bidentate chelating and two others acting as bridge between the two cerium ions. In both spectra medium bands around 1590  $\text{cm}^{-1}$  are observed and assigned to the  $\nu(\text{C}=\text{N})$  vibration. On comparison, the C=N absorption band of the free ligand was expected around 1630  $\text{cm}^{-1}$  as observed in the literature.<sup>14</sup> This fact is indicative of a decrease in the stretching force constant of the C=N bond as a consequence of the coordination of the imino nitrogen atom to the lanthanide ion. The broad band of medium intensity that appears at *ca.* 3220 and 820  $\text{cm}^{-1}$  are due to the coordinated water molecule.<sup>15</sup> The absorption band at  $\sim 1580 \text{ cm}^{-1}$  is attributed to stretching vibration of the pyridine

ring. The strong and sharp band observed in all the spectra at around 1365  $\text{cm}^{-1}$  is characteristic of uncoordinated nitrate ion.<sup>16</sup> 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 all the complexes. The conductance values lie in the range observed for 1:2 electrolyte (65–90  $\text{cm}^2 \times \text{mol}^{-1}$ ) in DMF.<sup>17</sup> The  $\mu_{\text{eff}}$  values of the lanthanide complexes show that these are paramagnetic. This paramagnetic behavior is consistent with the presence of unpaired 4f electrons. The observed  $\mu_{\text{eff}}$  values are in close proximity to the values for the free metal ions reported by Van Vleck and Frank.<sup>18</sup> This shows that the magnetic moments of the  $\text{Ln}^{3+}$  ions are not affected by the ligand field. The 4f-electrons are not involved in the coordination. These facts observed from the spectroscopy study are in accordance with the measured molar conductivities.

Owing to these observations and the results of the elemental analysis, the reported four binuclear Lanthanide(III) compounds are isotype and can be formulated as binuclear complexes  $[\{\text{Ln}(\text{HL})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2\}_2(\mu\text{-CH}_3\text{COO})_2](\text{NO}_3)_2$ . These considerations on the geometrical features for these complexes are in complete agreement as that elucidated by X-ray crystallography of the Ce(III) complex.

Partially labeled plot of the half of the centrosymmetric binuclear cerium(III) complex and one nitrate anion is shown in Fig. 1a and the crystal structure of asymmetric unit is presented in Fig. 2. The coordination polyhedra of the Ce(III) ion is shown in Fig. 1b. Selected interatomic distances and angles are listed in Table 1. The structure of the complex is consistent with  $[\{\text{Ce}(\text{HL})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2\}_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$ . Two non-coordinated nitrate anions per two Ce-containing unit, intervene as counter anions. Both lanthanide cations in this structure are nine coordinated. The coordination sphere around each ion is composed by two nitrogen pyridine atoms, one imino nitrogen atom, two oxygen atoms from one acetate group acting as bidentate-chelating, two oxygen atoms from two acetate groups acting in bridging fashion between two lanthanide cations and two oxygen atoms from two coordinated water molecules. The complex crystallizes in the monoclinic space group  $P2_1/c$ . The coordination of the organic ligand to Ce results in the formation of

two five membered (LnNCCN and LnNNCN) chelating rings. In the complex the Ce–N bonds involving the pyridine and the azomethine nitrogen atoms show the largest metal–ligand distances (Ce1–N1 = 2.676(2) Å, Ce1–N2 = 2.680(2) Å and Ce1–N3 = 2.707(3) Å). The Ce–O bonds involving the acetate oxygen atoms acting as bidentate-chelating are in the range 2.556(2)–2.582(2) Å while the Ce–O bonds of acetate acting as bridges have the shortest lengths in the range 2.428(2)–2.454(2) Å. All these values are comparable to those found in acetate complexes.<sup>19</sup> The water oxygen atoms acting as monodentate ligand have bonds distances in the range 2.536(2)–2.545(2) Å and are comparable to the values in the complex [Sm<sub>2</sub>(TPTZ)<sub>2</sub>(o-BrBA)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>] (where TPTZ is 2,4,6-tri(2-pyridyl)-s-triazine and o-BrBA is o-bromobenzoate).<sup>20</sup> The Ce–Ce distance is 4.8568(5) Å. The C1–N2 distance and its related symmetry are consistent with double bond character. The bond angles of the ligands, which involve the Ce(III) ion, are respectively N1–Ce1–N2 (59.99(8)°), N2–Ce1–N3 (60.12(9)°) and are slightly largest than the bidentate oxygen atoms O4–Ce1–O3 (50.29(7)°). The bond angle of the bridged oxygen atoms of the acetate groups, O5–Ce1–O6<sup>i</sup>, is 105.66(8)°. The three sets of donor atoms [(N3, O3, O6<sup>i</sup>); (N1, O5, O2W) and (N2, O4, O1W)] form three planes. The angle sum subtended by the three sets of donor atoms at Ce1 are respectively 359.98°, 359.85° and 359.15°. Two possible coordination polyhedra with nine vertexes are known. For Ce1, the best representation of environment geometry is a distorted tricapped trigonal prism, the three cap positions being occupied by O4, N2 and OW1 (Fig. 1b).

Intramolecular hydrogen-bond contacts involve the OH groups of the coordinated water molecules and the O–NO<sub>2</sub> of the ionic nitrate counter-ions.

Intermolecular hydrogen-bond contacts involve NH groups of the organic ligand as well as the hydroxyl groups of coordinated water molecule and the coordinated O atoms of the bidentate-chelating acetate (Table 2). Intermolecular hydrogen-bond contacts involving the OH groups of the coordinated water molecules and O atoms of uncoordinated nitrate groups are also observed. (Table 2). The hydrogen bonds connect the chains into a three-dimensional network (Fig. 2.)

To evaluate the antioxidant activity of organic or inorganic compounds, the method of scavenging DPPH is largely used in literature.<sup>21–23</sup> The antioxidant activity of the ligand HL and its Ln(III) complexes (**1** – **3**) have been substantially investigated. Fig. 3 shows the plots of DPPH• free radical scavenging activity (%) for ascorbic acid, the ligand HL and its four Ln(III) complexes. The effect of antioxidants on DPPH• radical scavenging is due to their hydrogen donating ability. DPPH• is a stable free radical and accepts an electron or hydrogen radical to become a stable molecule. It is observed that the scavenging activity increases with increasing lanthanide complex concentration in the range tested. The free ligand HL has scavenging activity between 5% and 60% within the investigated concentration range due to the NH groups which can react with DPPH• radical by the typical H-abstraction<sup>24</sup> reaction to form a stable radical. As shown in Fig. 3, Ln(III) complexes are significantly more efficient in quenching DPPH• radical than the free ligand HL. In fact, when the ligand HL is coordinated to the Ln<sup>3+</sup> the electron density is drawn from the nitrogen atom resulting in N–H bond more polarized. The hydrogen atom has a greater tendency to ionize than those in the free ligand HL in methanol. The H-abstraction reaction possibility is drastically increased.

Table 1

Selected bond lengths (Å) and bond angles (°) for complex Ce

Ce1–O5	2.428 (2)	Ce1–O3	2.582 (2)	O5–Ce1–O6 <sup>i</sup>	105.66 (8)	O4–Ce1–N2	110.51 (7)
Ce1–O6 <sup>i</sup>	2.454 (2)	Ce1–N1	2.676 (2)	O6 <sup>i</sup> –Ce1–O3	128.24 (8)	O5–Ce1–N2	127.16 (8)
Ce1–O1W	2.536 (2)	Ce1–N2	2.680 (2)	O4–Ce1–O3	50.29 (7)	O6 <sup>i</sup> –Ce1–N3	147.41 (8)
Ce1–O2W	2.545 (2)	Ce1–N3	2.707 (3)	O6 <sup>i</sup> –Ce1–N2	127.14 (7)	O4–Ce1–N3	129.19 (7)
Ce1–O4	2.556 (2)	N2–C1	1.299 (4)	O3–Ce1–N1	72.18 (8)	N1–Ce1–N3	120.05 (9)

Symmetry code: (i) –x+1, –y+1, –z+1

Table 2

Hydrogen bond in the Ce complex

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...O7	0.825 (17)	1.94 (2)	2.751 (4)	166 (3)
O1W—H1WB...O4 <sup>i</sup>	0.822 (18)	1.911 (19)	2.726 (3)	171 (4)
O2W—H2WA...O8 <sup>ii</sup>	0.825 (17)	2.19 (2)	2.985 (4)	162 (3)
O2W—H2WA...O7 <sup>ii</sup>	0.825 (17)	2.63 (3)	3.347 (4)	147 (3)
O2W—H2WB...O9	0.834 (17)	1.966 (19)	2.786 (3)	168 (4)
N4—H4N...O3 <sup>iii</sup>	0.922 (19)	2.52 (3)	3.222 (4)	133 (3)

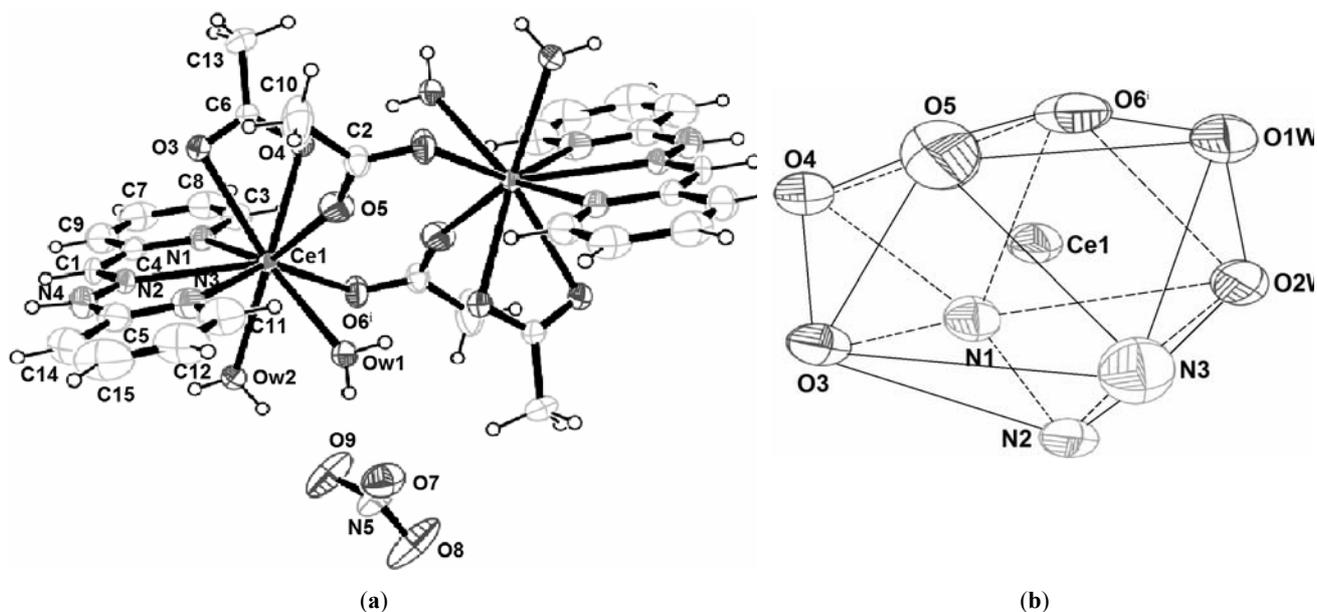
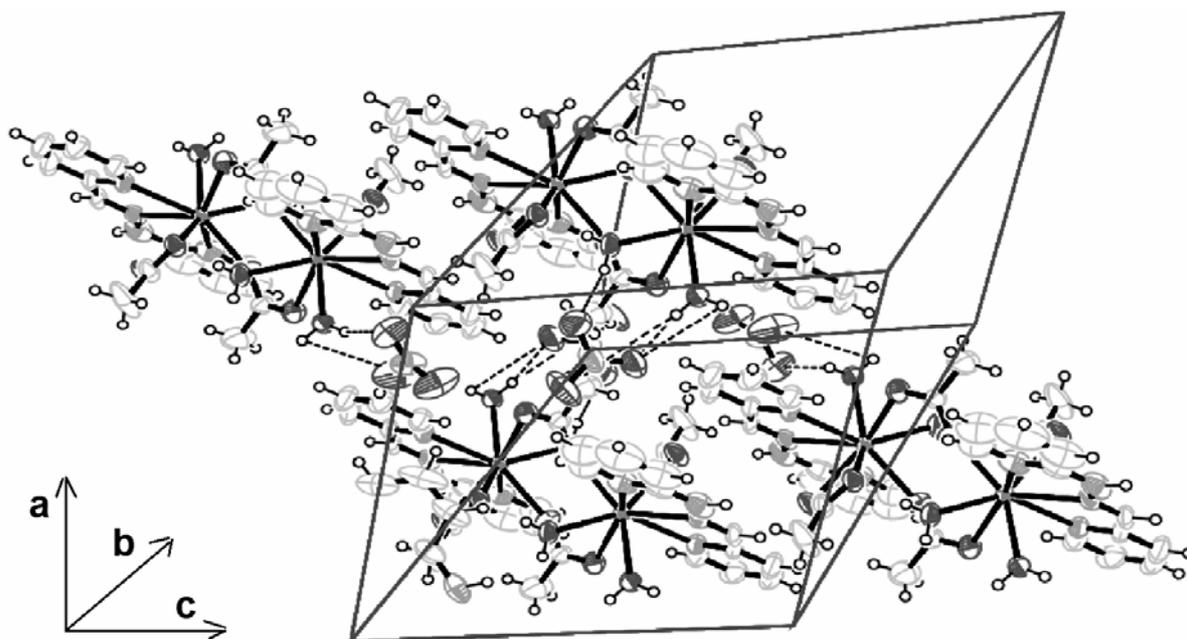
Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, -y+3/2, z-1/2$ ; (iii)  $-x+1, -y+1, -z$ .Fig. 1 – (a) Crystal structure of the centrosymmetric binuclear Ce (III) complex (the asymmetric unit is represented by half of the binuclear complex and one nitrate anion). (b) Plot showing the coordination sphere of Ce (III). Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, -y+3/2, z-1/2$ ; (iii)  $-x+1, -y+1, -z$ .

Fig. 2 – Perspective view of the three dimensional supramolecular network constructed by hydrogen bond interactions between Ce (III) complexes.

Table 3

## X-Ray single-crystal data

Color/shape	Yellow/plate
Chemical Formula	$C_{30}H_{40}Ce_2N_8O_{12} \cdot 2(NO_3)$
Molecular weight	1108.96
Crystal System, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
Crystal size	$0.10 \times 0.08 \times 0.07$
a, b, c (Å)	11.1127 (9), 17.9877 (15), 11.9542 (10)
$\beta$ (°)	114.740 (8)
$V$ (Å <sup>3</sup> )	2170.2 (3)
Z	2
$D_{calc}$ (g cm <sup>-3</sup> )	1.697
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	2.15
$\lambda$ (Å)	0.71073
$F$ (000)	1100
No. of restraints	7
No. of measured reflections	19702
No. of independent reflections	4936
No. of observed reflections [ $I > 2\sigma(I)$ ]	4583
Parameters refined	288
Final R indices	R1 = 0.0237, wR2 = 0.0601
R indices for all data	R1 = 0.0264, wR2 = 0.0590
Goodness-of-fit	1.10
$\Delta\rho$ (e Å <sup>-3</sup> )	0.72, -0.36

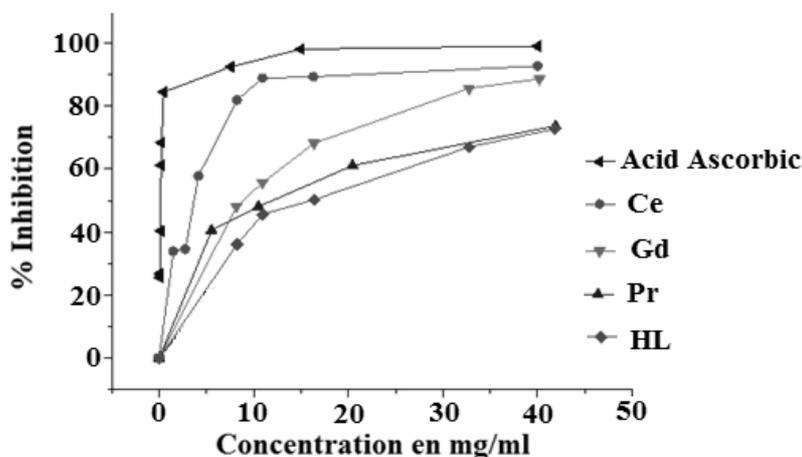


Fig. 3 – Antioxidant activity of the ligand and the lanthanide complexes.

The values of IC<sub>50</sub> of the ligand **HL** and complexes **1** – **3** at 40 mg/L on the DPPH<sup>•</sup> radical scavenging effects are respectively  $16.32 \pm 0.03$ ,  $3.72 \pm 0.02$ ,  $12.05 \pm 0.04$  and  $8.95 \pm 0.01$  M, respectively. The values of IC<sub>50</sub> present the order **1** < **3** < **2** < **HL**. These observations are indicative that the DPPH<sup>•</sup> radical scavenging effects of Ln(III) complexes are much higher than that of the free ligand. We compare these values with the ability of ascorbic acid which is a well-known

natural antioxidant compound. The 50% inhibitory concentration (IC<sub>50</sub>) value of the ascorbic acid is  $0.175 \pm 0.001$  M. These results imply that the ascorbic acid has a preferable ability to scavenge the DPPH<sup>•</sup> than the four Ln(III) complexes which have better IC<sub>50</sub> than the free ligand. It can be concluded that the less scavenging activity exhibited by the ligand can be explained by the chelation of ligand with the central metal atom.<sup>25</sup>

## EXPERIMENTAL

### Materials and procedures

2-hydrazinopyridine, 2-pyridinecarbaldehyde and the lanthanide nitrate salts were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. The analyses for carbon, hydrogen and nitrogen were carried out using a LECO CHNS-932 instrument. The IR spectra were recorded as KBr discs on a Bruker IFS-66 V spectrophotometer (4000–400  $\text{cm}^{-1}$ ). The molar conductance of  $10^{-3}$  M solutions of the metal complexes in methanol were measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples {calibrant  $\text{Hg}[\text{Co}(\text{SCN})_4]$ } were measured using a Johnson Matthey scientific magnetic susceptibility balance.

### Preparation of the complexes

A mixture of 2-hydrazinopyridine (1 mmol) and 2-pyridinecarbaldehyde (1 mmol) in ethanol (15 mL) was stirred under reflux during 30 min. A mixture of sodium acetate (3 mmol) and  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln}=\text{Ce}$ , Pr or Gd) (1 mmol) in ethanol (10 mL) was added to a solution. The mixture was stirred for 30 min and the resulting yellow solution was filtered-off and the filtrate was kept at 298 K. Yellow powder began to appear after one day and were collected by filtration.

$[\text{C}_{30}\text{H}_{40}\text{Ce}_2\text{N}_8\text{O}_{12} \cdot 2(\text{NO}_3)]$  (1). Yield 55 %. Anal. calc. C, 32.49; H, 3.64; N, 12.63. Found: C, 32.41; H, 3.69; N, 12.86%.  $\mu_{\text{eff}}(\mu_{\text{B}})$ : 2.51.  $\Lambda_{\text{M}}(\text{S cm}^2 \text{mol}^{-1})$ : 90. IR ( $\text{cm}^{-1}$ ): 3225, 1588, 1575, 1558, 1445, 1365, 820.

$[\text{C}_{30}\text{H}_{40}\text{Pr}_2\text{N}_8\text{O}_{12} \cdot 2(\text{NO}_3)]$  (2). Yield 65 %. Anal. calc.: C, 32.45; H, 3.63; N, 12.61. Found: C, 32.48; H, 3.69; N, 12.37%.  $\mu_{\text{eff}}(\mu_{\text{B}})$ : 3.15.  $\Lambda_{\text{M}}(\text{S cm}^2 \text{mol}^{-1})$ : 70. IR ( $\text{cm}^{-1}$ ): 3220, 1593, 1580, 1558, 1443, 1368, 821.  $[\text{C}_{30}\text{H}_{40}\text{Gd}_2\text{N}_8\text{O}_{12} \cdot 2(\text{NO}_3)]$

(3). Yield 71%. Anal. calc.: C, 31.52; H, 3.53; N, 12.25. Found: C, 31.45; H, 3.56; N, 12.32 %.  $\mu_{\text{eff}}(\mu_{\text{B}})$ : 7.75.  $\Lambda_{\text{M}}(\text{S cm}^2 \text{mol}^{-1})$ : 89. IR ( $\text{cm}^{-1}$ ): 3228, 1585, 1577, 1555, 1448, 1370, 825.

### Antioxidant activities

The methanol solution of 3.9 mL DPPH $\cdot$  (40mg/L) was added to test compounds (100  $\mu\text{L}$ ) at different concentrations. The mixture was shaken vigorously and incubated in dark for 30 min at room temperature. After the incubation time, the absorbance of the solution was measured at 517 nm by using UV-vis spectrophotometer mini-1240 SHIMADZU. The DPPH $\cdot$  radical scavenger effect was calculated using the following equation: Scavenging activity (% control) =  $[(A_{\text{control}} - A_{\text{sample}})/A_{\text{control}}] \times 100$  where  $A_{\text{control}}$  is the absorbance of the control reaction and  $A_{\text{sample}}$  is the absorbance of the test compound. Tests were carried out in triplicate. Ascorbic acid was used as positive control.

### X-ray crystal structure determination

Slow evaporation of an ethanol solution gave X-ray quality crystals of the cerium complex  $[\text{C}_{30}\text{H}_{40}\text{Ce}_2\text{N}_8\text{O}_{12} \cdot 2(\text{NO}_3)]$ . Details of the X-ray crystal structure solution and refinement are given in Table 3. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized

Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. Complex scattering factors were taken from the program package SHELXL. 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. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using ORTEP-3.

A solution of the cerium(III) complex was dissolved in ethanol solution at room temperature. The solution was left for slow evaporation. Crystals suitable for X-ray diffraction were obtained after three days and were characterized by X-ray crystallography. CCDC Code: 1494539 contains the supplementary crystallographic data. These data can be obtained from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## CONCLUSIONS

In conclusion, tridentate ligand was synthesized and reacted in situ with lanthanide nitrate and sodium acetate to yield binuclear lanthanide compounds of Ce, Pr, Gd and Er. These complexes were characterized by spectroscopic studies, elemental analyses, molar conductivity and room temperature magnetic moment measurements. Suitable X-ray crystal diffraction were obtained for the Ce complex. The X-ray structure determination reveal that the Ce ion is nine coordinated with two pyridine nitrogen atoms, one imine nitrogen atom, four oxygen atoms from acetate groups and two water oxygen atoms resulting in a distorted tricapped trigonal prism geometry. The antioxidant activities of the complexes were investigated. For DPPH, these lanthanide complexes show activity concentration dependence.

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