Lanthanide(III) Complexes with Tridentate Schiff Base Ligand, Antioxidant Activity and X-Ray Crystal Structures of the Nd(III) and Sm(III) Complexes

Mbossé Ndiaye Gueye*, Moussa Dieng†, Ibrahima Elhadji Thiam*, Djiby Lo*, Aliou Hamady Barry*, Mohamed Gaye** and Pascal Retailleau†

*Department of Chemistry, University Cheikh Anta Diop, Dakar, Sénégal.
†Department of Chemistry, University of Nouakchott, Mauritania.
‡Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS-UPR2301, 1 Avenue la Terrasse, 91198 Gif sur Yvette, France.

Received 13 September 2016, revised 7 November 2016, accepted 24 November 2016.

ABSTRACT
The tridentate N₄-type Schiff base was synthesized from the condensation reaction of 2-hydrazinopyridine and pyridine-2-carbaldehyde. Neodymium and Samarium complexes were isolated when the corresponding nitrate salt was added to the solution of the ligand. The isolated compounds were characterized by elemental analyses, IR study, room temperature magnetic measurements and single X-ray crystal diffraction of the two crystals. Both complexes crystallize in the monoclinic system with space group $P2_1/c$. The cell parameters of the Nd complex are $a = 11.0927(8)$ Å, $b = 17.9926$ (13) Å, $c = 11.9395(9)$ Å and $\beta = 115.274(5)$ ° while the Sm complex shows parameters cell of $a = 11.0477(8)$ Å, $b = 17.9254$ (13) Å, $c = 11.9149(8)$ Å and $\beta = 115.489(5)$ °. The X-ray study reveals isotopic Nd/Sm binuclear structures were each metal ion is nine-coordinated in the same fashion. Both metal centers have distorted tricapped trigonal prism geometry, with the Schiff base acting as tridentate ligand. The DPPH· radical scavenging effects of the Schiff base ligand and its Ln(III) complexes were screened. The Ln(III) complexes were significantly more efficient in quenching DPPH· than the free Schiff base ligand.

KEYWORDS
Lanthanide complexes, hydrazino, antioxidant activity, X-ray structure.

1. Introduction
In the past decade, the lanthanide coordination chemistry was one of the most focused areas of research.1–3 The intriguing structures4–6 and the potential uses in a wide variety of areas as diagnostic tools in biology7 catalysis,8 luminescence9 and magnetism10 reinforce the interest of chemists in these areas of research. A few years ago our research group initiated a project concerning rare earth metal chemistry11 in a search for unusual molecular materials.12 By use of an acyclic Schiff’s base in presence of acetate groups, it is possible to introduce two identical or different lanthanide ions.15,16 The carboxylate groups can adopt various coordination modes, which may cause the generation of novel structures.17,18 Hydrazones are Schiff base precursors with a triatomic moiety connection of -C = N-NH-. They are widely used in the synthesis of complexes to generate original structures.19,20 Coordination compounds from this type of ligand have a variety of applications. Many results concerning their antibacterial,21 antifungal,22 anticancer23 and antidepressant24 activities have been described in the literature. This report presents the synthesis, characterization, and X-ray structures of neodymium(III) and samarium(III) complexes derived from 1-(pyrydin-2yl)-2-(pyridine-2-ylmethylene)hydrazine (HL). HL is an acyclic hydrazine ligand bearing nitrogen donors containing one coordination cavity which can encapsulate large ions such as lanthanides.

2. 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. $^1$H and $^{13}$C spectra of the compounds were recorded in DMSO-d₆ with TMS as internal reference on a Bruker Advance operating at 250 MHz. The IR spectra were recorded as KBr discs on a Bruker IFS-66 V spectrophotometer (4000–400 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 WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples (calibrated Hg[Co(SCN)₅]) were measured using a Johnson Matthey scientific magnetic susceptibility balance.

2.1. Preparation of the Ligand HL
2-Hydrazinopyridine (1.0913 g, 10 mmol) in 20 mL of ethanol was added to a solution of 2-pyridinecarbaldehyde (1.0711 g, 10 mmol) dissolved in 25 mL of ethanol. The resulting mixture was stirred under reflux during 30 min. After cooling, the volume was completed to 100 mL with ethanol and stored in the refrigerator. 10 mL of this solution was evaporated to dryness and the
NMR spectrum of the resulting liquid was recorded: \( \delta \) (250 MHz, DMSO-d<sub>6</sub>): 11.185(1H, s, H-N-N); 8.542(1H, d, J = 7.5 Hz, H-Py); 8.159(1H, d, J = 1.75 Hz, H-Py); 7.814(1H, s, H-C=N); 7.972(1H, d, J = 7.75 Hz, H-Py); 7.823(1H, dd, J = 1.75 and 7.5 Hz, H-Py); 7.766(1H, mult, H-Py); 7.313(2H, d, J = 7.75 Hz, H-Py); 6.820(1H, dd, J = 7.25 and 7.75 Hz, H-Py). \( \delta \) (250 MHz, DMSO-d<sub>6</sub>): 106.500 (C-8), 115.528 (C-10), 118.810 (C-4), 122.878 (C-2), 136.422 (C-3), 137.989 (C-9), 139.164 (C-6), 147.798 (C-11), 149.180 (C-1), 154.257 (C-7), 155.660 (C-5).

2.2. Preparation of the Complexes
To 10 mL of the solution of the above prepared ligand, a mixture of sodium acetate (3 mmol) and Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (L = Nd or Sm) (1 mmol) in ethanol (10 mL) was added. The mixture was stirred for 30 min and the resulting yellow slightly cloudy solution was filtered-off to discard a small quantity of NaNO<sub>3</sub> and the filtrate was kept at 298 K. Yellow powder began to appear after one day and was collected by filtration. Recrystallization by slow evaporation of an ethanol solution gave X-ray quality crystals of the two compounds [Nd<sub>2</sub>C<sub>30</sub>H<sub>40</sub>N<sub>8</sub>O<sub>12</sub>]<·(NO<sub>3</sub>)<sub>2</sub> (1) and [Sm<sub>2</sub>C<sub>30</sub>H<sub>40</sub>N<sub>8</sub>O<sub>12</sub>]<·(NO<sub>3</sub>)<sub>2</sub> (2).

\[
\text{[Nd}_2\text{C}_{30}\text{H}_{40}\text{N}_8\text{O}_{12}\text{]}\cdot(\text{NO}_3)_2 \quad \text{(1)} \quad \text{Yield 59}\%.
\]

2.3. Antioxidant Activities
The methanol solution of 3.9 mL DPPH* (40 mg L<sup>–1</sup>) was added to test compounds (100 µL) 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-visible spectrophotometer mini-1240 SHIMADZU. The DPPH* radical scavenger effect was calculated using the following equation:

\[
\text{Scavenging activity} (\% \text{ control}) = \left[\frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \right] \times 100
\]

\[A_{\text{control}}\] 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.

2.4. X-ray Crystal Structure Determination
Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an R FUNNIUS kappa CCD diffractometer with graphite monochromatized Mo Kα radiation (\( \lambda = 0.71073\) Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F<sup>2</sup> by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH<sub>2</sub> groups) were geometrically optimized and refined as riding.

Table 1  X-Ray single-crystal data.

<table>
<thead>
<tr>
<th>Empirical formula:</th>
<th>Nd&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;30&lt;/sub&gt;H&lt;sub&gt;40&lt;/sub&gt;N&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;</th>
<th>Sm&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;30&lt;/sub&gt;H&lt;sub&gt;40&lt;/sub&gt;N&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color/shape</td>
<td>Yellow/plate</td>
<td>Yellow/plate</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>1117.20</td>
<td>1129.42</td>
</tr>
<tr>
<td>Crystal System, space group</td>
<td>Monoclinic, P2&lt;sub&gt;1&lt;/sub&gt;/c</td>
<td>Monoclinic, P2&lt;sub&gt;1&lt;/sub&gt;/c</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293</td>
<td>293</td>
</tr>
<tr>
<td>Crystal size/mm × mm × mm</td>
<td>0.15 × 0.07 × 0.08</td>
<td>0.12 × 0.09 × 0.08</td>
</tr>
<tr>
<td>a Å</td>
<td>11.0927 (8)</td>
<td>11.0477 (8)</td>
</tr>
<tr>
<td>b Å</td>
<td>19.9792 (13)</td>
<td>17.9254 (13)</td>
</tr>
<tr>
<td>c Å</td>
<td>11.9395 (9)</td>
<td>11.9149 (8)</td>
</tr>
<tr>
<td>( \alpha^\circ )</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>( \beta^\circ )</td>
<td>115.274 (5)</td>
<td>115.489 (5)</td>
</tr>
<tr>
<td>( \gamma^\circ )</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V Å&lt;sup&gt;3&lt;/sup&gt;</td>
<td>2153.4 (3)</td>
<td>2129.9 (3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( D_0 ) g cm&lt;sup&gt;–3&lt;/sup&gt;</td>
<td>1.722</td>
<td>1.761</td>
</tr>
<tr>
<td>( \mu ) mm&lt;sup&gt;–1&lt;/sup&gt;</td>
<td>2.46</td>
<td>2.81</td>
</tr>
<tr>
<td>F (000)</td>
<td>1108</td>
<td>1116</td>
</tr>
<tr>
<td>( \theta ) range for data collection/°</td>
<td>3.50–27.57</td>
<td>4.68–27.52</td>
</tr>
<tr>
<td>No. reflections/observed</td>
<td>4934/4492</td>
<td>4835/4315</td>
</tr>
<tr>
<td>Data/restraints/parameter</td>
<td>4934/7/286</td>
<td>4835/7/288</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least squares of F&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Full-matrix least squares of F&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Final R indices ([I&gt;2\sigma(I)])</td>
<td>R₁ = 0.0241, wR₂ = 0.0522</td>
<td>R₁ = 0.0239, wR₂ = 0.0585</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0285, wR₂ = 0.0541</td>
<td>R₁ = 0.0280, wR₂ = 0.0597</td>
</tr>
<tr>
<td>( \Delta \rho ) e Å&lt;sup&gt;–3&lt;/sup&gt;</td>
<td>0.50, -0.35</td>
<td>0.63, -0.88</td>
</tr>
</tbody>
</table>
model by AFIX instructions. Molecular graphics were generated using ORTEP-3. The chain bridging the two pyridine rings was found to be disordered such that the mean bond lengths in the chain are far from the mean values observed. This disorder may be explained by the fact that the sequence of atoms C(Py)-CH=N-NH-C(py) overlaps with the sequence C(py)-NH-N=CH-C(py), meaning two orientations of the ligand. In such a case for the refinement, one assumes that atom C (of CH group) from one chain and atom N (of NH group) from the second chain occupy the same position. The same relates inversely. The instructions EXYZ and EADP of SHELXL were used to have the same atomic coordinates and displacement parameters of the disordered atoms. The occupancy factor refines close to 0.5 in the Nd complex and 60:40% occupancy in the Sm complex.

3. Results and Discussion

3.1. General Studies

The acyclic tridentate ligand, 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene)hydrazine, abbreviated as HL, was prepared by the 1:1 condensation reaction of 2-hydrazinopyridine and 2-pyridine carbaldehyde in ethanol. The reaction of Ln(NO₃)₃·xH₂O and NaOOCCH₃ with the prepared ligand solution, with a 1:3:1 molar ratio in ethanol gave yellow powder. The formulae of these powders are further confirmed as [{Ln(HL)(H₂O)₂}₂[µ-CH₃COO]₂] with Ln = Nd and Sm (Scheme 1) by spectroscopic and X-ray analysis.

The ¹H and ¹³C NMR spectra of the hydrazino pyridine derivative ligand and its diamagnetic Nd(III) and Sm(III) complexes are recorded in DMSO-d₆ as shown in experimental section. In the spectrum of the ligand a singlet appearing at 11.185 ppm is attributed to the H-N proton. No shift of this signal was observed in the spectrum of both complexes indicating no deprotonation of the ligand and that the nitrogen atom supporting this proton is not involved in the coordination. The signal attributed to the H-C=N proton is slightly shifted to higher field from 8.144 ppm in the free ligand to 8.096 and 8.135 ppm respectively in the spectra of the Nd and Sm complexes. This fact is indicative of an involvement of the azomethine in the complexation. The pyridine ring protons show also little difference shifts in the spectra of the complexes. Upon complexation the signals of the ¹³C NMR spectra of the complexes show little difference with those of the spectrum of the free ligand. The signal of C=N carbon atom appearing at 139.164 ppm for the free ligand is slightly shifted to 139.171 ppm for Nd(III) complex and 139.153 ppm for Sm(III) complex. The spectrum of Nd(III) complex shows new broad signal at 4.722 ppm due to the protons of the water molecules. The signals of the methyl groups of the acetate moieties are not observed in the NMR spectra of the complexes. They are probably obscured by the intense signal of the DMSO solvent.

Both IR spectra of the two complexes reveal bands which are assigned respectively to asymmetric νₐs(COO) and symmetric νₚs(COO) stretching vibrations of the acetate group in the ranges 1565–1550 and 1450–1440 cm⁻¹. The positions of these asymmetric and symmetric bands are very close proximity in the two spectra of the complexes indicating that the coordination modes of the different acetate groups are similar in all these compounds. The values of Δν = νₚ – νₐ are in the range admitted for multiple coordination modes of acetate groups. This coordination behaviours of the acetate groups were further confirmed by X-ray studies of the complexes. In the X-ray structure of these binuclear complexes, each Ln(III) (Ln=Nd, Sm) ions have one acetate behaving as bidentate chelating and two others acting as bridges between the two lanthanide (III) ions. In both spectra medium bands in the range [1583–1590 cm⁻¹] are observed and assigned to the ν(C=N) stretching vibration which was expected for the free ligand at ~1630 cm⁻¹ as observed in the literature. This observation is a consequence of the decrease of the stretching force constant of the C=N bond, indicating the involvement of the imino nitrogen in the lanthanide ion coordination sphere. The presence of band of medium intensity at ca. 3220 and 820 cm⁻¹ are due to the coordinated water molecules.

The absorption bands at ~1580 cm⁻¹ are attributed to stretching vibration of the pyridine rings. The strong and sharp band observed in all the spectra at around 1370 cm⁻¹ is characteristic of uncoordinated nitrate ion. 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 1:1 electrolytes (70–90 cm$^2$ Ω$^{-1}$ mol$^{-1}$) in DMF. The $\mu_{\text{eff}}$ values of the lanthanide complexes show that they are paramagnetic. This paramagnetic behaviour 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. This shows that the magnetic moments of the 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.

The results of the elemental analysis, IR spectra, magnetic moment measurements and conductivity study lead us to formulate the two binuclear Lanthanide(III) complexes as binuclear isotopic structures $\left[\text{Ln}(\text{HL})(\text{µ-CH$_3$COO})(\text{H}_2\text{O})_2\right] \text{(µ-CH$_3$COO)}\left[\text{Ln}(\text{HL})(\text{µ-CH$_3$COO})(\text{H}_2\text{O})_2\right]$.

3.2. Molecular Structure of Complexes (1) and (2)

Partially labelled plot of the binuclear structures of Nd(III) and Sm(III) complexes are respectively shown in Fig. 1a and Fig. 1b while the coordination polyhedra of the Nd(III) and Sm(III) ions are shown in Fig. 2a and Fig. 2b. Selected interatomic distances and angles are listed in Table 2. The structure of the complexes are consistent with $\left[\text{Ln}(\text{HL})\left(\text{µ-CH$_3$COO}\right)(\text{H}_2\text{O})_2\right] \left(\text{µ-CH$_3$COO}\right)\left[\text{Ln}(\text{HL})\left(\text{µ-CH$_3$COO}\right)(\text{H}_2\text{O})_2\right]$.

The structures of the Nd and Sm complexes of the 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene)hydrazine (HL) ligand were determined by X-ray crystallography. $\left[\text{Nd}(\text{HL})(\text{µ-CH$_3$COO})(\text{H}_2\text{O})_2\right] \left(\text{µ-CH$_3$COO}\right)\left[\text{Nd}(\text{HL})(\text{µ-CH$_3$COO})(\text{H}_2\text{O})_2\right]$ (NO$_3$)$_2$ (1) and $\left[\text{Sm}(\text{HL})(\text{µ-CH$_3$COO})(\text{H}_2\text{O})_2\right] \left(\text{µ-CH$_3$COO}\right)\left[\text{Sm}(\text{HL})(\text{µ-CH$_3$COO})(\text{H}_2\text{O})_2\right]$ (NO$_3$)$_2$ (2) are isostructural and crystallize in the monoclinic space group $\text{P2}_1/c$.

The crystallographic studies show that HL forms complexes with a 1:1 Ln:ligand ratio, in which the Schiff base acts as tridentate ligand. The coordination of the organic ligand to Ln results in the formation of two five membered (LnNCCN and LnNNCN) chelating rings. In these compounds each asymmetric unit comprises a single Ln$^{3+}$ ion coordinated by one tridentate HL ligand, one bidentate chelating acetate ion, one bidentate bridging acetate ion, two coordinated water molecules and one uncoordinated nitrate group. The second half of the molecule is related by crystallography imposed inversion.

Figure 1 Crystal structure of the centrosymmetric binuclear Nd(III) (a) and Sm(III) (b) complexes, showing the atom-numbering scheme in the asymmetric unit (half of the binuclear complex and one nitrate anion).
symmetry (symmetry code: -x, -y, -z). The coordination geometry around each nine-coordinated Ln(III) ion can be described as a distorted tricapped prism formed by the tridentate ligand HL acting through two pyridine nitrogen atoms and one imino nitrogen atom, two oxygen atoms from a bidentate chelating acetate ion, two oxygen atoms from two different bidentate bridging acetate ions and two oxygen atoms from two water molecules. The Nd–N distances are 2.675(3) Å, 2.639(2) Å and 2.637(2) Å while the Sm–N lengths are 2.647(3) Å, 2.609(2) Å and 2.606(2) Å, with the longer distance belonging to the ortho-hydradzino substituted pyridyl nitrogen atom in both complexes. The Ln–O distances, when O is from bidentate cheating acetate, are in the ranges 2.522(2)–2.550(2) Å for Nd complexes and 2.536(2) Å for Sm complexes. These observations are in agreement with those found in literature.28 The Ln–Ow distances are in the range of 2.506(2)–2.513(2) Å for 1 and 2.477(2)–2.479(2) Å for 2 and are comparable to the values in the complex [Ln2(L)6(H2O)2].2H2O (where Ln = Nd or Sm and HL = 4-Hydroxy-6-methylnicotinic acid).39 The bond lengths between carbon and oxygen atoms which are observed in both acetate groups [1.240 (3) Å–1.270 (4) Å] are shorter than that of a simple C–O bond (1.430 Å) and longer than that of a C=O double bond type (1.220 Å). These observations indicate that the bond CO in coordinate acetate moieties has an intermediate character between C–O and C=O.

The average lengths of the Ln–O, when O is from bidentate cheating acetate are 2.536(2) Å for 1 and 2.511(2) Å for 2, Ln–Nare 2.650(2) Å for 1 and 2.621(3) Å for 2 and Ln–O bonds when O is from bidentate bridging acetate (2.509(2) Å for 1 and 2.478(2) Å for 2. All these values are comparable to those found in carbonate complexes.40–42 The Ln–Ln distances are 5.2150 Å for 1 and 4.9550 Å for 2. The C6–N2 (1) and C3–N2 (2) distances and there related symmetry are consistent with double bond character. The bond angles of the ligands, which involve the Nd(III) ion, are respectively N1–Nd1–N2 (61.03(8) °), N2–Nd1–N4 (60.79(9) °) and are slightly largest than those with bidentate oxygen atoms O5–Nd1–O3 (51.08(7) °). The bond angle of the bridged oxygen atoms of the acetate groups, O6–Nd1–O4, is 104.18 (8) °. The three sets of donor atoms [N1, O1W, O6]; (N2, O3, O2W) and (O5, O4, N4)] form three planes in complex 1. The angle sum subtended by the three sets of donor atoms at Nd1 are respectively 359.69 °, 359.26 ° and 359.81 °. In the complex 2 the angle sum subtended by the three sets of donor atoms at Sm1 are respectively 359.67 °, 359.66 ° and 356.79 °. Two possible coordination polyhedra with nine vertexes are known. For Nd1 and Sm1, the best representation of environment geometry is a distorted tricapped trigonal prism, the three cap positions being occupied by O3, N2 and O2W for Nd1 and N1, O6, O1W for Sm1 (Fig. 2). The mean bond lengths in the chain C(Py)-CH=N-NH-C(py) are 1.425, 1.297, 1.309 and 1.416 Å. These bonds values are significantly far from the corresponding mean values for this ligand found on the CSD data (1.450(17) 1.283(15) 1.349(12) 1.376(16) Å). This is indicative of the considerable disorder detected for the C(Py)-CH=N-NH-C(py) chain bridging the two pyridine rings.

Intramolecular hydrogen-bond contacts involve the OH groups of the coordinated water molecules and the O-NO2 of the groups [1.240 (3) Å-1.270 (4) Å] are shorter than that of a simple C–O bond (1.430 Å) and longer than that of a C=O double bond character. These observations indicate that the bond CO in coordinate acetate moieties has an intermediate character between C–O and C=O.

The average lengths of the Ln–O, when O is from bidentate cheating acetate are 2.536(2) Å for 1 and 2.511(2) Å for 2, Ln–Nare 2.650(2) Å for 1 and 2.621(3) Å for 2 and Ln–O bonds when O is from bidentate bridging acetate (2.509(2) Å for 1 and 2.478(2) Å for 2. All these values are comparable to those found in carbonate complexes.40–42 The Ln–Ln distances are 5.2150 Å for 1 and 4.9550 Å for 2. The C6–N2 (1) and C3–N2 (2) distances and there related symmetry are consistent with double bond character. The bond angles of the ligands, which involve the Nd(III) ion, are respectively N1–Nd1–N2 (61.03(8) °), N2–Nd1–N4 (60.79(9) °) and are slightly largest than those with bidentate oxygen atoms O5–Nd1–O3 (51.08(7) °). The bond angle of the bridged oxygen atoms of the acetate groups, O6–Nd1–O4, is 104.18 (8) °. The three sets of donor atoms [N1, O1W, O6]; (N2, O3, O2W) and (O5, O4, N4)] form three planes in complex 1. The angle sum subtended by the three sets of donor atoms at Nd1 are respectively 359.69 °, 359.26 ° and 359.81 °. In the complex 2 the angle sum subtended by the three sets of donor atoms at Sm1 are respectively 359.67 °, 359.66 ° and 356.79 °. Two possible coordination polyhedra with nine vertexes are known. For Nd1 and Sm1, the best representation of environment geometry is a distorted tricapped trigonal prism, the three cap positions being occupied by O3, N2 and O2W for Nd1 and N1, O6, O1W for Sm1 (Fig. 2). The mean bond lengths in the chain C(Py)-CH=N-NH-C(py) are 1.425, 1.297, 1.309 and 1.416 Å. These bonds values are significantly far from the corresponding mean values for this ligand found on the CSD data (1.450(17) 1.283(15) 1.349(12) 1.376(16) Å). This is indicative of the considerable disorder detected for the C(Py)-CH=N-NH-C(py) chain bridging the two pyridine rings.

Intramolecular hydrogen-bond contacts involve the OH groups of the coordinated water molecules and the O-NO2 of the nitrate counter-ions. Furthermore, the intermolecular hydrogen bonds plays an important role in the fabrication of stacking...
structure of the complexes. Intermolecular hydrogen-bond contacts involve NH groups of the organic ligand as well as the hydroxyl groups of coordinated water molecules and the coordinated O atoms of the bidentate-chelating acetate (Table 3). Intermolecular hydrogen-bond contacts involving OH groups of the coordinated water molecules and O atoms of uncoordinated nitrate groups are also observed (Table 3). The hydrogen bonds connect the chains into a three-dimensional network (Fig. 3). The two complexes are isomorphous and have a similar framework.

3.3. Antioxidant Activities Study

To evaluate the antioxidant activity of organic or inorganic compounds, the method of scavenging DPPH$^\cdot$ is largely used in literature. The antioxidant activities of the ligand HL and its Nd(III) (1) and Sm(III) (2) complexes have been substantially investigated. Fig. 4 shows the plots of DPPH$^\cdot$ free radical scavenging activity (%) for ascorbic acid, the ligand HL and its two Ln(III) complexes. The effect of antioxidants on DPPH$^\cdot$ radical scavenging is due to their hydrogen donating ability. DPPH$^\cdot$ 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$^\cdot$ radical by the typical H-abstraction reaction to form a stable radical. As shown in Fig. 4, Ln(III) complexes are significantly more efficient in quenching DPPH$^\cdot$ radical than the free ligand HL. In fact, when the ligand HL is coordinated to Ln$^{3+}$ 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.

The values of IC50 of the ligand HL and complexes (1) and (2) at 40 mg L$^{-1}$ on the DPPH$^\cdot$ radical scavenging effects are 82.38 ± 0.01, 8.01 ± 0.02 and 10.65 ± 0.01 mM, respectively. The values of IC50 present the order 1 < 2 < HL. These observations are indicative that the DPPH$^\cdot$ radical scavenging effects of Ln(III) complexes are higher than that of the free ligand. These values are compared with the ability of ascorbic acid which is a well-known natural antioxidant compound. The 50 % inhibitory concentration (IC50) value of the ascorbic acid is 0.980 ± 0.005 mM. These results imply that the ascorbic acid has a preferable ability to scavenge the DPPH$^\cdot$ than the two Ln(III) complexes which have better IC50 than the free ligand. It can be concluded that the less scavenging activity exhibited by the ligand can be

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Hydrogen bonds for the complexes.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd complex</td>
</tr>
<tr>
<td>D—H···A</td>
<td>D—H·A</td>
</tr>
<tr>
<td>O1W—H1WA···O7</td>
<td>0.824 (17)</td>
</tr>
<tr>
<td>O1W—H1WB···O9 b</td>
<td>0.809 (17)</td>
</tr>
<tr>
<td>O2W—H2WA···O8</td>
<td>0.822 (18)</td>
</tr>
<tr>
<td>O2W—H2WB···O3 4</td>
<td>0.815 (17)</td>
</tr>
<tr>
<td>N3—H3N···O5 4</td>
<td>0.959 (18)</td>
</tr>
</tbody>
</table>

Symmetry codes: (a) -x+1, -y+1, -z+1; (b) x, -y+1/2, z-1/2; (c) -x+1, -y+1, -z, (d) -x+1, -y+1, -z+1; (e) x, -y+1/2, z+1/2; (f) -x+1, -y+1, -z+2.

Figure 3 Chains of hydrogen bonding in the crystal lattice in Nd (a) and Sm (b) complexes.
explained by the chelation of ligand with the central metal atom.\textsuperscript{20}

4. Conclusion

In conclusion, a tridentate ligand (N\textsubscript{3}) was synthesized and reacted with lanthanide nitrate and sodium acetate to yield binuclear lanthanide compounds of Nd and Sm. These complexes were characterized by spectroscopic studies, elemental analyses, molar conductivity and room temperature magnetic moment measurements. Suitable X-ray crystals diffraction were obtained for the Nd and Sm complexes. The X-ray structure determination reveal that the Ln\textsuperscript{3+} 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.

5. Supplementary Data

CCDC 1496016 (1) and 1496018 (2) contain the supplementary crystallographic data for samarium and the neodymium complexes respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk.

References

1 S. Procházková, J. Hraniček, V. Kubíček and P. Hermann, Formation kinetics of europium(III) complexes of DOTA and its bis(phosphonate) bearing analogs. Polyhedron, 2016, 111, 143–149.


26 G.M. Sheldrick, SHELXTL-97, 1997, University of Göttingen, Göttingen, Germany.


Supplementary material to:
M.N. Gueye, M. Dieng, I.E. Thiam, D. Lo, A.H. Barry, M. Gaye and 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,
$^1$H NMR of HL; $HL = \text{structure image}$
$^1$H NMR spectrum of $\{[\text{Nd(HL)}(\eta^3-\text{CH}_3\text{COO})\text{(H}_2\text{O})_2][\mu-\text{CH}_3\text{COO}]\text{[Nd(HL)}(\eta^3-\text{CH}_3\text{COO})\text{(H}_2\text{O})_2]\} \cdot (\text{NO}_3)_2$
$^{13}$C NMR spectrum of \{[Nd(\text{HL})(\eta^2-\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]\}[\mu-\text{CH}_3\text{COO}]_{2}\{[Nd(\text{HL})(\eta^2-\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]\}(\text{NO}_3)_2$
$^{1}H$ NMR spectrum of $\{[[\text{Sm}(\text{HL})(\eta^2\text{-CH}_3\text{COO})(\text{H}_2\text{O})_2][\mu\text{-CH}_3\text{COO}][\text{Sm}(\text{HL})(\eta^2\text{-CH}_3\text{COO})(\text{H}_2\text{O})_2]](\text{NO}_3)_2$
$^1$H NMR spectrum of $\{[\text{Sm}(\text{HL})(\eta^2-\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]\{\mu-\text{CH}_3\text{COO}\}_2[\text{Sm}(\text{HL})(\eta^2-\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]\}_2(\text{NO}_3)_2$