European Journal of Chemistry 8 (2) (2017) 137-143

European Journal of Chemistry

Journal webpage: www.eurjchem.com

Synthesis, physical studies and crystal structure determination of Y(III) and Er(III) complexes of 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene)hydrazine

Mbosse Ndiaye Gueye [1], Moussa Dieng [1], Djiby Lo [1], Ibrahima Elhadji Thiam [1],
Aliou Hamady Barry [2], Mohamed Gaye [1,*], Abdou Salam Sall [1] and Pascal Retailleau [3]

[1] *Department of Chemistry, University Cheikh Anta Diop, Dakar, 10700, Senegal*
[2] *Department of Chemistry, University of Nouakchott, Nouakchott, 130301, Mauritania*
[3] *Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS-UPR2301, Gif sur Yvette, 91198, France*

* *Corresponding author at: Department of Chemistry, University Cheikh Anta Diop, Dakar, 10700, Senegal.*
Tel.: +221.77.5555891. Fax: +221.33.8246318. E-mail address: mohamedl.gaye@ucad.edu.sn (M. Gaye).

ARTICLE INFORMATION

DOI: 10.5155/eurjchem.8.2.137-143.1557

Received: 22 February 2017
Received in revised form: 01 April 2017
Accepted: 01 April 2017
Published online: 30 June 2017
Printed: 30 June 2017

KEYWORDS

Complex
Schiff base
Crystal structure
NMR spectroscopy
Antioxidant activity
Magnetic properties

ABSTRACT

Two isotype mononuclear yttrium(III) and erbium(III) complexes, $\{[Y(HL)(OAc)_2(H_2O)_2].(H_2O)\cdot(NO_3)\}$ (1) and $\{[Er(HL)(OAc)_2(H_2O)_2].(H_2O)\cdot(NO_3)\}$ (2), where HL is the neutral Schiff base ligand 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene)hydrazine, and OAc is the acetate anion, have been synthesized and characterized by physicochemical methods and single crystal X-ray determination. Both complexes crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions for complex of Y(III) a = 7.909 (2) Å, b = 11.718 (4) Å, c = 12.497 (3) Å, α = 78.907 (3)°, β = 73.840 (3)°, γ = 72.074 (3)°, V = 1051.26 (6) Å^3, Z = 2, R_1 = 0.051 and wR_2 = 0.112 and for complex of Er(III) a = 7.913 (1) Å, b = 11.719 (2) Å, c = 12.487 (2) Å, α = 78.832 (1)°, α = 73.674 (1)°, γ = 72.012 (1)°, V = 1049.64 (3) Å^3, Z = 2, R_1 = 0.028, and wR_2 = 0.062. In both complexes, the coordination polyhedra around Ln(III) atoms are best described as a distorted tricapped trigonal prism. Antioxidant activities of the ligand and its Y(III) and Er(III) complexes are studied.

Cite this: *Eur. J. Chem.* **2017**, *8(2)*, 137-143

1. Introduction

The use of Schiff bases in coordination chemistry has developed molecular materials with specific properties [1-5]. Catalysis, [6,7] optics [8,9] and molecular magnetism [10,11] has seen spectacular development in recent years through the use of Schiff bases complexes. A thorough review of the literature allowed us to see that a number of metal transition complexes [12-15] from Schiff base derived from 2-hydrazino pyridine were reported while very few rare earth complex [16] was released from this kind of ligand. In fact the ligand 1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)-hydrazine was used to synthesize a unique yttrium [16] complex. The acetate anion is very interesting as co-ligand because of its versality. The acetate anion can have several modes of coordination because of the four coordination sites due to the two electronic pairs per oxygen atom of the carboxylate group. This ability allows the acetate group to coordinate with one, two or three metal centers, allowing the formation of polymer coordination compounds [17,18].

In this paper, the 1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)-hydrazine ligand is used for synthesizing mononuclear lanthanide complexes using acetate anion as co-ligand. Two new complexes $\{[Y(HL)(OAc)_2(H_2O)_2]\cdot(H_2O)\cdot(NO_3)\}$ and $\{[Er(HL)(OAc)_2(H_2O)_2]\cdot(H_2O)\cdot(NO_3)\}$, were prepared and characterized. The antioxidant activities of these compounds have been investigated.

2. Experimental

2.1. Materials and physical methods

Commercially available 2-hydrazinopyridine, 2-pyridine carbaldehyde and 2,2-diphenyl-1-picrylhydrazyl (DPPH•) were purchased from Aldrich and used without further purification. 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 cm^{-1}). The molar conductance of 1×10^{-3} M solutions of the metal complexes in dimethylformamide (DMF) 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 Matthey scientific magnetic susceptibility balance

European Journal of Chemistry
ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online) © 2017 Atlanta Publishing House LLC - All rights reserved - Printed in the USA
http://dx.doi.org/10.5155/eurjchem.8.2.137-143.1557

(Calibrant: Hg[Co(SCN)$_4$]). The ^{1}H and ^{13}C NMR spectra of the Schiff bases were recorded in DMSO-d_6 on a Bruker 250 MHz spectrometer at room temperature using TMS as internal reference. UV-VIS spectra were recorded in methanol solution concentration of 1×10^{-3} M at 25 °C and wavelength was reported in nm using a JENWAY 6505 UV/VIS spectrophotometer.

2.2. Synthesis

2.2.1. Synthesis of HL

The Schiff base ligand 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene)hydrazine (**HL**) was synthesized as follow: 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 solution was completed to 100 mL with ethanol and store in the refrigerator. 10 mL of this solution was evaporated to dryness and the NMR spectrum of the resulting liquid was recorded.

1-(Pyridin-2-yl)-2-(pyridin-2-ylmethylene)-hydrazine (**HL**): Color: Brown liquid. FT-IR (KBr, ν, cm^{-1}): 3204 (NH), 1635 (C=N) (Imine), 1595 (Pyridine ring), 1576 (Pyridine ring), 1147 (N-N). ^{1}H NMR (250 MHz, DMSO-d_6, δ, ppm): 11.185 (s, 1H, HN-N), 8.542 (d, 1H, *J* = 4.75 Hz, H-Py), 8.159 (d, 1H, *J* = 1.75 Hz, H-Py), 8.144 (s, 1H, H-C=N), 7.972 (d, 1H, *J* = 7.75 Hz, H-Py), 7.823 (dd, 1H, *J* = 1.75 and 7.5 Hz, H-Py), 7.766 (m, 1H, H-Py), 7.313 (d, 2H, *J* = 7.75 Hz, H-Py), 6.820 (dd, 1H, *J* = 4.75 and 7.25 Hz, H-Py). ^{13}C NMR (62.5 MHz, DMSO-d_6, δ, ppm): 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=N), 147.798 (C-11), 149.180 (C-1), 154.257 (C-7), 156.660 (C-5). UV/Vis (DMSO, λ_{max}, nm, ε (M^{-1}.cm^{-1})): 310 (1.02), 330 (2.95), 360 (1.09).

2.2.2. Synthesis of the complexes

10 mL of a 100 mM solution of **HL** in ethanol was stirred with sodium acetate (3 mmol) and Ln(NO$_3$)$_3$.6H$_2$O (Ln = Y or Er) (1 mmol) in ethanol (10 mL). The mixture was stirred under reflux for 30 min and the resulting yellow solution was filtered-off and the filtrate was kept at 298 K. Yellowish powder began to appear after one day and was collected by filtration. Upon keeping an ethanol solution of the powder for three days, colored crystals (red for Y and yellow for Er) suitable for X-ray diffraction was afforded.

Complex Y^{3+}: [$C_{15}H_{20}YN_4O_6\cdot(H_2O)\cdot(NO_3)$]. Yield: 59%. Color: Red. FT-IR (KBr, ν, cm^{-1}): 3179 (OH), 1625 (C=N) (Imine), 1607 (Pyridine ring), 1540 (asCOO, carboxylate), 1422 (sCOO, carboxylate), 1363 (NO_3^-), 1143 (N-N), 828 (OH), 775 (Pyridine ring), 746 (Pyridine ring). ^{1}H NMR (250 MHz, DMSO-d_6, δ, ppm): 11.10 (s, 1H, HN), 8.51 (m, 1H, H-Py), 8.11 (m, 2H, H-Py), 7.98 (s, 1H, H-C=N), 7.81 (m, 1H, H-Py), 7.69 (m, 1H, H-Py), 7.28 (m, 1H, H-Py), 7.25 (m, 1H, H-Py), 6.85 (m, 1H, H-Py), 5.00 (b, 6H, H$_2$O), 2.50 (s, 6H, CH$_3$COO). ^{13}C NMR (62.5 MHz, DMSO-d_6, δ, ppm): 107.525 (C-8), 115.512 (C-10), 118.803 (C-4), 122.945 (C-2), 136.421 (C-3), 138.321 (C-9), 139.354 (C=N), 147.942 (C-11), 149.248 (C-1), 154.312 (C-7), 156.748 (C-5). Anal. calcd. for $C_{15}H_{22}N_5O_{10}Y$: C, 34.56; H, 4.25; N, 13.44. Found: C, 34.60; H, 4.18; N, 13.56 %. μ_{eff} (μ_B): Diamagnetic. Λ_M (S.cm^2.mol^{-1}): 89. UV/Vis (DMSO, λ_{max}, nm, ε (M^{-1} cm^{-1})): 315 (0.92), 335 (2.82), 363 (0.89).

Complex Er^{3+}: [$C_{15}H_{20}ErN_4O_6\cdot(H_2O)\cdot(NO_3)$]. Yield: 57%. Color: Yellow. FT-IR (KBr, ν, cm^{-1}): 3180 (OH), 1626 (C=N, Imine), 1608 (Pyridine ring), 1551 (asCOO, carboxylate), 1423 (sCOO, carboxylate), 1365 (NO_3^-), 1143 (N-N), 828 (OH), 768 (Pyridine ring), 746 (Pyridine ring). ^{1}H NMR (250 MHz, DMSO-d_6, δ, ppm): 11.15 (s, 1H, HN), 8.53 (m, 1H, H-Py), 8.14 (m, 2H, H-Py), 7.95 (s, 1H, H-C=N), 7.80 (m, 1H, H-Py), 7.67 (m, 1H, H-Py), 7.31 (m, 1H, H-Py), 7.29 (m, 1H, H-Py), 6.81 (m, 1H, H-Py), 5.00 (b, 6H, H$_2$O), 2.50 (s, 6H, CH$_3$COO). ^{13}C NMR (62.5 MHz, DMSO-d_6, δ, ppm): 106.540 (C-8), 115.570 (C-10), 118.850 (C-4), 122.920 (C-2), 136.470 (C-3), 138.030 (C-9), 139.153 (C=N), 147.840 (C-11), 149.220 (C-1), 154.290 (C-7), 156.700 (C-5). Anal. calcd. for$C_{15}H_{22}N_5O_{10}Er$: C, 30.05; H, 3.70; N, 11.68. Found: C, 30.10; H, 3.76; N, 11.55 %. μ_{eff} (μ_B): 9.52. Λ_M (S cm^2 mol^{-1}): 70. UV-Vis (λ, nm, ε (M^{-1}.cm^{-1})): 317 (0.96), 338 (2.88), 369 (0.93).

2.3. Antioxidant activities

The methanol solution of 3.9 mL DPPH$^\bullet$ (40 mg/L) 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 JENWAY 6505 UV/VIS spectrophotometer. The DPPH$^\bullet$ radical scavenger effect was calculated using the following equation: Scavenging activity (% control) = $[(A_{control} - A_{sample})/A_{control}]\times100$ where $A_{control}$ is the absorbance of the control reaction and A_{sample} is the absorbance of the test compound. Tests were carried out in triplicate. Ascorbic acid (AA) was used as positive control.

2.4. Crystal structure determination

Details of the X-rays 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 [19]. 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 [20]. 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 instructtions. Molecular graphics were generated using ORTEP-3 [21].

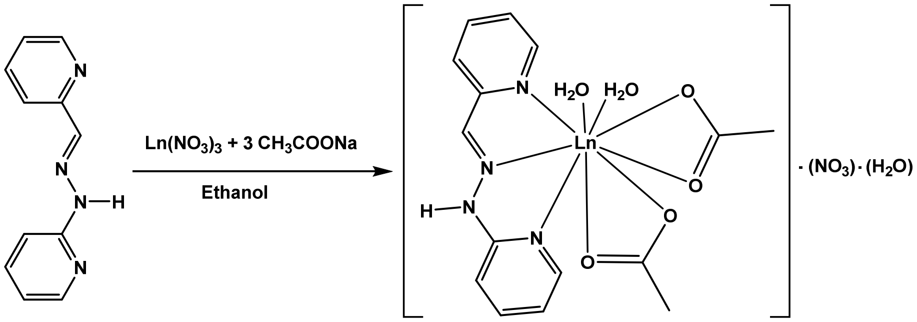
3. Results and discussion

3.1. General studies

The ligand HL was prepared by a facile condensation of 2-hydrazinopyridine and 2-pyridine carboxaldehyde in ethanol (Scheme 1). The lanthanide complexes were synthesized by mixing ligand solution with lanthanide nitrate hexahydrate and sodium acetate in a molar ratio 1:1:3. The afforded compounds are soluble in polar organic solvent such as methanol or DMSO. Elemental analyses gives result in agreement with the chemical formulae obtained from X-ray diffraction study. The complexes behave as 1:1 electrolyte in DMF with Λ_M values (89 Ω^{-1}.cm^2.mol^{-1} for complex Y^{3+} and 70 Ω^{-1}.cm^2.mol^{-1} for complex Er^{3+}) lying in the region reported for 1:1 electrolyte (70-90 Ω^{-1}.cm^2.mol^{-1}) in DMF [22]. Complex Y^{3+} is diamagnetic in nature while complex Er^{3+} shows paramagnetic property with μ_{eff} value of 9.52 μ_B. This value is in close proximity to the value for the free Er^{3+} ion reported by Van Vleck and Frank [23]. The ligand field does not affect the magnetic moment of the Er in the complex indicating no involvement of the 4-f electrons in the coordination. In the infrared spectra of the lanthanide complexes absorption bands pointed in the region 1600-1610 cm^{-1} are assigned to the ν(C=N-NH) vibration which can be comparable to the vibration of the ν(C=N-NH) in the free ligand expected at *ca.* 1630 cm^{-1}.

Table 1. Crystal data and structure refinement for Y^{3+} and Er^{3+} complex.

Parameters	**Complex Y^{3+}**	**Complex Er^{3+}**
Formula	$C_{15}H_{20}YN_4O_6\cdot NO_3\cdot H_2O$	$C_{15}H_{20}ErN_4O_6\cdot NO_3\cdot H_2O$
Empirical formula	$C_{15}H_{22}N_5O_{10}Y$	$C_{15}H_{22}ErN_5O_{10}$
Formula weight	521.28	599.64
Temperature (K)	293(2)	293(2)
Crystal shape/color	Prismatic/red	Prismatic/yellow
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	7.9094(2)	7.91309(14)
b (Å)	11.7180(4)	11.71884(19)
c (Å)	12.4973(3)	12.48666(18)
α (°)	78.907(3)	78.8319(13)
β (°)	73.840(3)	73.6743(14)
γ (°)	72.074(3)	72.0123(15)
Volume (Å^3)	1051.26(6)	1049.64(3)
Z	2	2
ρ_{calc} (g/cm^3)	1.647	1.897
μ (mm^{-1})	2.836	4.060
F(000)	532.0	590.0
Crystal size (mm^3)	0.09 × 0.07 × 0.06	0.08 × 0.07 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection (°)	6.84 to 60.06	6.84 to 60.6
Index ranges	$-10 \le h \le 10$, $-16 \le k \le 16$, $-17 \le l \le 16$	$-11 \le h \le 11$, $-15 \le k \le 16$, $-17 \le l \le 17$
Reflections collected	22716	25647
Independent reflections	5395 [R_{int} = 0.0627]	5545 [R_{int} = 0.0523]
Data/restraints/parameters	5395/7/299	5545/10/303
Goodness-of-fit on F^2	1.070	1.038
Final R indexes [I≥2σ (I)]	R_1 = 0.0511, wR_2 = 0.1082	R_1 = 0.0280, wR_2 = 0.0604
Final R indexes [all data]	R_1 = 0.0692, wR_2 = 0.1123	R_1 = 0.0316, wR_2 = 0.0616
Largest diff. peak/hole (e.Å^{-3})	0.65/-0.58	0.68/-1.00



Scheme 1

The coordination of the ligand via the azomethine nitrogen atom results in the decrease of the stretching force constant of the C=N moiety. Thus the frequency of the vibration of the C=N moiety decreases upon coordination as observed in both spectra of complexes. The presence of broad band of medium intensity at *ca.* 3180 cm^{-1} and a sharp band at *ca.* 828 cm^{-1} are due to the coordinated water molecule [24]. Characteristic strong and sharp band which is attributable to uncoordinated NO_3^- ion is observed at 1363 cm^{-1} for complex Y^{3+} and 1365 cm^{-1} for complex Er^{3+} confirming that both complexes are 1:1 electrolyte. Spectrum of the complex Y^{3+} shows bands at 1540 and 1422 cm^{-1} (Δν = 118 cm^{-1}) while complex Er^{3+} exhibits bands at 1551 and 1423 cm^{-1} (Δν = 128 cm^{-1}). These vibrations are assigned respectively to asymmetric ν_{as}(COO) and symmetric ν_s(COO) stretching vibrations of acetate group [25]. The difference between the frequencies of asymmetric and symmetric vibration ($\Delta\nu = \nu_{as} - \nu_s$) of the carboxylate group is a criterion often used to find the mode of coordination of the carboxylate group [26]. A value of Δν between 160 and 175 cm^{-1} is indicative of an ionic acetate group. A larger Δν value is obtained when the carboxylate group acts as monodentate fashion while a lower value of Δν indicates a bidentate chelating group. Considering the value of Δν in our complexes we can say that we are in the presence of a bidentate chelating acetate group [25].

The electronic spectra of the ligand **HL** and its complexes of Y^{3+} and Er^{3+} were recorded in methanol. Three broad bands were observed on the spectrum of the ligand at absorption maxima of 310, 330 and 360 nm. The band at λ_{max} = 310 nm is attributed to the transitions π-π* of the C=N-NH chromophore and the pyridine rings [27]. The bands at 330 and 360 nm are assigned to the n-π* transitions of the pyridine rings. Both spectra of the complexes are virtually identical. The bands observed in the spectrum of the ligand are slightly shifted to the low energies in the spectra of the complexes, consequence of the coordination of the nitrogen atoms of the pyridine ring and the azomethine atom of the C=N-NH chromophore. No further information is provided by the UV spectra of the reported complexes. The NMR spectrum of the free HL ligand was recorded from DMSO-d_6. The aromatic protons of the pyridine rings exhibit signals of multiplets in the region 8.54 - 6.52 ppm, while the H-N proton was located at 11.18 ppm. The H-C=N proton shows a singlet at 8.14 ppm. The total number of carbon atoms present in the HL Schiff base exhibited signals in their expected regions. The unique non-aromatic C=N carbon atom is located at ~140 ppm while the aromatic carbon atoms show signals in the range 106-156 ppm. Upon coordination all signals are very slightly shifted. These small shifts are probably due to the orbital involved in the bonds. In addition the spectra of the complexes show new broad signal at ~5 ppm attributable to protons of the water molecules.

Table 2. Selected bond lengths (Å) and bond angles (°) for complex Y^{3+} and complex Er^{3+}.

Atom-Atom	Bond lengths (Å)	Atom-Atom	Bond lengths (Å)
Y1-O6W	2.320 (3)	Er1-O6W	2.316 (2)
Y1-O5W	2.330 (2)	Er1-O5W	2.321 (2)
Y1-O2	2.366 (2)	Er1-O1	2.360 (2)
Y1-O4	2.424 (3)	Er1-O3	2.417 (3)
Y1-O3	2.453 (2)	Er1-O4	2.443 (2)
Y1-O1	2.455 (2)	Er1-O2	2.455 (2)
Y1-N2	2.522 (3)	Er1-N1	2.507 (3)
Y1-N1	2.554 (3)	Er1-N3	2.540 (3)
Y1-N3	2.557 (3)	Er1-N2	2.543 (3)
Atom-Atom-Atom	**Bond angles (°)**	**Atom-Atom-Atom**	**Bond angles (°)**
O2-Y1-O4	142.58 (10)	O1-Er1-O3	142.71 (10)
O2-Y1-O3	146.04 (9)	O1-Er1-O4	145.74 (9)
O4-Y1-O1	146.09 (9)	O3-Er1-O2	146.14 (9)
O3-Y1-O1	137.89 (9)	O4-Er1-O2	137.41 (8)
O6W-Y1-N2	137.83 (11)	O6W-Er1-N1	137.72 (11)
O5W-Y1-N2	137.12 (11)	O5W-Er1-N1	137.21 (11)
O1-Y1-N2	113.41(12)	O4-Er1-N1	109.07 (11)
O3-Y1-N2	108.69(12)	O2-Er1-N1	113.51 (11)

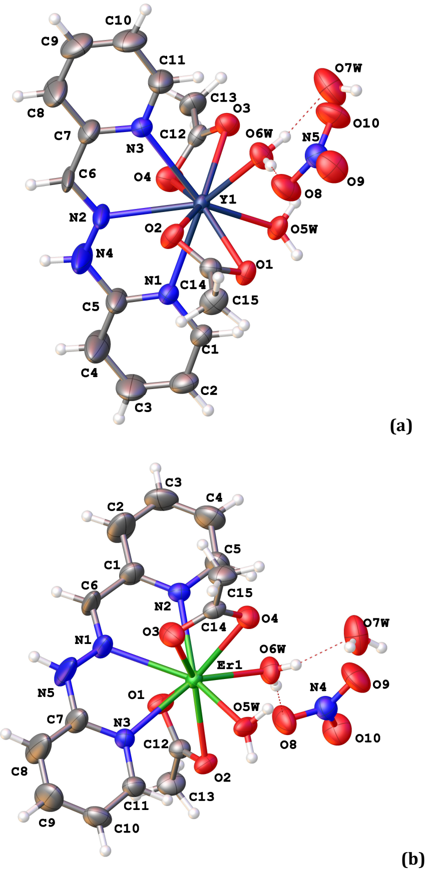


Figure 1. Crystal structure of mononuclear Y^{3+} (a) and Er^{3+} (b) showing the atom-numbering scheme. Displacement ellispsoids are drawn at the 30% probability level and H atoms are shown as small sphere.

Signals due to the methyl groups of the acetate moieties are probably obscured by the intense signal of the DMSO-d_6 solvent.

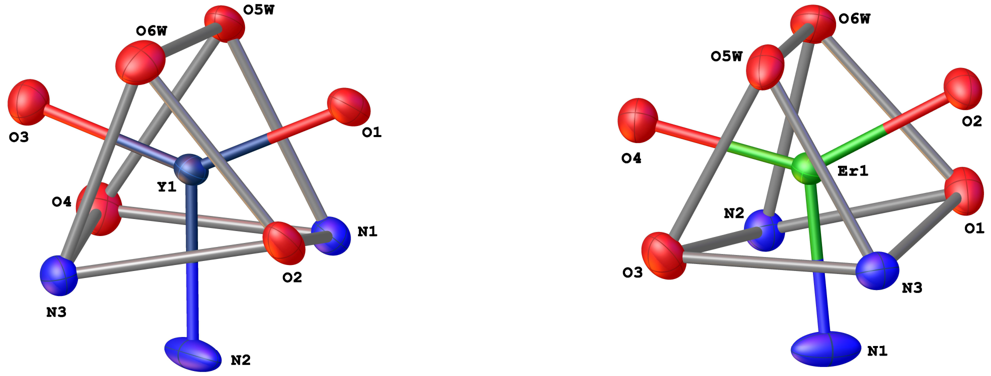
3.2. Structure description of $Y^{3+}$and Er^{3+}complex

Single-crystal X-ray diffraction analysis reveals that {$[Ln(HL)(OAc)_2(H_2O)_2]\cdot NO_3\cdot H_2O$} (Ln = Y for complex Y^{3+} and Er for complex Er^{3+}) complexes have similar structures. Perspective views of the complex Y^{3+} and Er^{3+} with the atomic labeling system are showed in Figure 1a and b, respectively. Both complexes crystallize in the triclinic crystal system with space group $P\bar{1}$. Each complex shows in asymmetric unit one nine-coordinated Ln^{3+} ion with a distorted tricapped trigonal prism geometry as reported in Figure 2a and b. The lanthanide atom is coordinated by one azomethine nitrogen atom and two pyridine nitrogen atoms from the Schiff base **HL** ligand, four oxygen atoms from the two bidentate chelating acetate groups and two oxygen atoms from coordinated water molecules. The bonds lengths of Ln-N of the two complexes are Y1-N2 = 2.522(3) Å, Y1-N1 = 2.554(3) Å, Y1-N3 = 2.557(3) Å for complex Y^{3+} and Er1-N1 = 2.507(3) Å, Er1-N3 = 2.540(3) Å, Er1-N2 = 2.543(3) Å for complex Er^{3+} (Table 2). The bond lengths of Er-N are little longer than those of Y-N.

Table 3. Geometrical parameters for hydrogen bonds for complex Y^{3+} and Er^{3+} complex.

D-H···*A* *	*D*-H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*-H···*A* (°)
Complex Y^{3+}				
O5W-H5WA···O9^{a}	0.82	2.04	2.852(4)	171
O5W-H5WA···O8^{a}	0.82	2.60	3.195(4)	130
O5W-H5WB···O1^{b}	0.82	1.90	2.710(3)	169
O6W-H6WA···O8	0.83	1.94	2.769(4)	176
O6W-H6WB···O7W	0.82	1.84	2.661(4)	171
O7W-H7WA···O10^{c}	0.85	2.21	2.988(5)	152
O7W-H7WB···O9^{a}	0.85	2.08	2.914(5)	168
N4-H4N···O4^{d}	0.91	2.22	3.009(6)	145
Complex Er^{3+}				
O5W-H5WA···O10^{e}	0.81	2.08	2.855(4)	162
O5W-H5WB···O2^{f}	0.81	1.91	2.716(3)	174
O6W-H6WA···O7W	0.81	1.87	2.659(5)	165
O6W-H6WB···O8	0.82	1.95	2.771(4)	175
O7W-H7WA···O10^{e}	0.81	2.12	2.923(5)	174
O7W-H7WB···O9^{g}	0.81	2.19	2.984(5)	167
N5-H5N···O3^{h}	0.91	2.14	3.004(5)	158

Symmetry transformation used to generate equivalent atoms: (a) $x+1, y, z$; (b) $-x+1, -y+1, -z+2$; (c) $-x, -y+2, -z+2$; (d) $-x+2, -y+1, -z+1$; (e) $x-1, y, z$; (f) $-x+1, -y+1, -z$; (g) $-x+2, -y, -z$; (h) $-x, -y+1, -z+1$.



(a) **(b)**

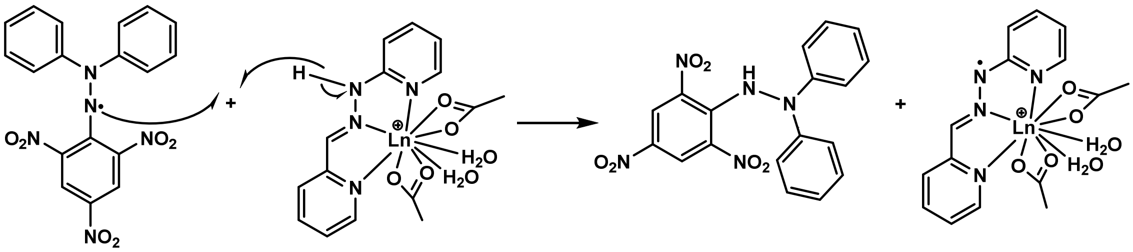
Figure 2. Plot showing the coordination sphere of (**a**) Y^{3+} and (**b**) Er^{3+} complexes.

This fact can be explicated by the radii contraction of the lanthanide ions ($r_{Y^{3+}}$ = 90 pm and $r_{Er^{3+}}$ = 89 pm). For both complexes the Ln-O, when the oxygen atom is from carboxylate, bond lengths are comparable and vary in the range 2.360(2)-2.455(2) Å. The mean values of these Ln-O bond lengths are 2.424(3) Å and 2.419(2) Å for Y^{3+} and Er^{3+} complexes, respectively. The average of the Ln-O distances for both complexes suggests that the character of the Er-O bond is slightly more covalent than for Y-O. These values are slightly smaller than the mean distances value found in carboxylate complex for Sm-O lengths (2.462(5) Å) [28] and are longer than the value found for Yb-O lengths (2.378(2) Å) [29]. These observations can be correlated with the ions radii values of Sm^{3+} (96 pm) and Yb^{3+} (87 pm) which are respectively greater and smaller than those of Y^{3+} (90 pm) and Er^{3+} (89 pm). The Ln-Ow distances for complex Y^{3+} and complex Er^{3+} are in the range 2.316(2)-2.330(2) Å and are comparable to those found for mononuclear complexes of [Ln(L)(NO_3)(H_2O)] where H_2L is 2,6-diacetylpyridine-*bis*-(benzoylhydrazone) [30].

The nitrate anion acts as counter ion as found in the infrared study of the complexes. The environments of Y^{3+} as well as Er^{3+} are best described by a distorted tricapped trigonal prism geometry with the tree caps position occupied, in each complex, by two oxygen atoms from two chelating acetate moieties and the azomethine nitrogen atom of the tridentate ligand. The angles sum subtended by the three capping atoms at Y^{3+} and Er^{3+} are respectively 359.93° and 359.99°. The crystal structures are stabilized by intermolecular hydrogen bonds interactions resulting in three dimensional networks as shown in Figure 3. The H-bond donors are the H-N of the hydrazine function and the H-O from both coordinated and uncoordinated water molecules while the acceptors are the free nitrate anion oxygen atoms, acetate oxygen atoms and oxygen atom of the uncoordinated water molecule (Table 3).

3.3. Antioxidant activities study

The antioxidant activities of the ligand 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene)hydrazine and its two new mononuclear yttrium(III) and erbium(III) complexes have been studied. Percentage scavenging activities of the test samples are calculated as per standard procedure. The percentage antioxidant activity of the novel compounds compared with ascorbic acid (AA) is represented in Figure 4. IC_{50} value of the ascorbic acid is 0.980±0.005 μM while the synthesized compounds scavenge the DPPH$^{\bullet}$ radical with IC_{50} values of 82.38±0.01, 10.65±0.02 and 8.01±0.01 μM for the ligand **HL** and complexes Y^{3+} and Er^{3+}, respectively. These data imply that the ascorbic acid has a larger ability to scavenge the DPPH$^{\bullet}$ than the **HL** ligand and its two Ln(III) complexes. In screening these results it becomes clear that the inhibitory effect of the ligand and its complexes increases rapidly with the concentration in the range 0-50 μM as shown in Figure 4. The DPPH$^{\bullet}$ inhibitory effect of the complexes is stronger than that of the ligand. Indeed, after the complexation, the metal bonded to the azomethine nitrogen atom of the chromophore group C=N-NH exerts an electron-draining effect which makes the N-H bond more polarized [31].



Scheme 2

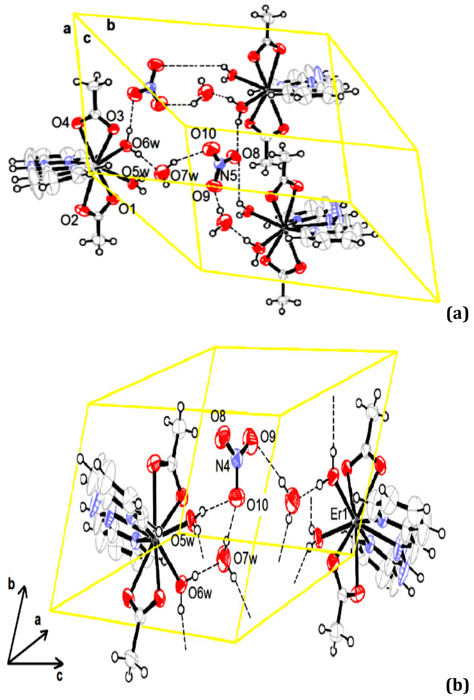


Figure 3. Three dimensional network of the Y^{3+} and Er^{3+} complexes.

Therefore, the hydrogen atom of the N-H moiety will tend to more readily undergo the H-abstraction reaction to neutralize DPPH• to DPPH as shown in Scheme 2. The resulting radical complex is stabilized by the possibility of a strong delocalization of the single electron.

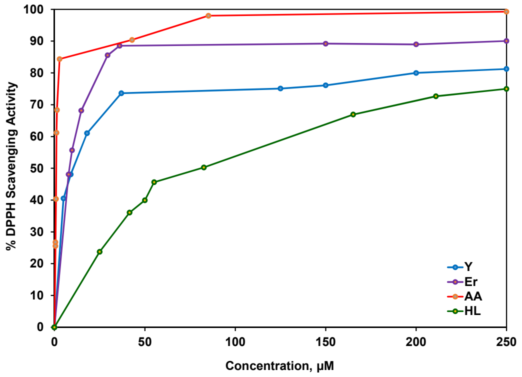


Figure 4. Antioxidant activity of ascorbic acid (AA), the ligand **HL** and its Y^{3+} and Er^{3+} complexes.

4. Conclusion

The mononuclear complexes of the ligand **HL** are synthesized and characterized as $\{[Ln(HL)(OAc)_2(H_2O)_2]\cdot NO_3\cdot H_2O\}$. The structures of these complexes are established by single-crystal X-ray diffraction showing similar kinds of coordination geometry for each lanthanide ion. In these complexes, the metal atoms are bonded to the ligand by two nitrogen atoms from two pyridine rings and the azomethine of the C=N-NH chromophore. They are also bound in bidentate fashion to two acetate groups. Two water molecules complete the sphere of coordination forming Ln(III) complexes with a coordination number of nine. The environment around the metal center is best described as a distorted tricapped trigonal prism. The antioxidant activities of the two mononuclear complexes are greater than that of the free ligand HL.

Acknowledgements

The authors thank the FONDATION SONATEL for his financial support.

Supplementary material

CCDC-1511898 (Complex Y^{3+}) and 1511902 (Complex Er^{3+}) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

References

[1]. Biswas, S.; Diaz, C.; Ghosh, A. *Polyhedron* **2013**, *51*, 96-101.
[2]. Kaabi, I.; Sibous, L.; Douadi, T.; Chafaa, S. *J. Mol. Struct.* **2015**, *1084*, 216-222.
[3]. Bhattacharjee, C. R.; Goswami, P.; Mondal, P. *Inorg. Chim. Acta* **2012**, *387*, 86-92.
[4]. Wang , W. M.; Ren, Y. H.; Wang, S.; Zhang, C. F.; Wu, Z. L.; Zhang, H.; Fang, M. *Inorg. Chim. Acta* **2016**, *453*, 452-456.
[5]. Gu, Z. G.; Pang, C. Y.; Qiu, D.; Zhang, J.; Huang, J. L.; Qin, L. F.; Sun, A. Q.; Li, Z. *Inorg. Chem. Commun*. **2013**, *35*, 164-168.
[6]. Gorczynski, A.; Zaranek, M.; Witomska, S.; Bocian, A.; Stefankiewicz, A. R.; Kubicki, M.; Patroniak, V.; Pawluc, P. *Catal. Commun*. **2016**, *78*, 71-74.
[7]. Al Zoubi, W.; Ko, Y. G. *J. Organomet. Chem.* **2016**, *822*, 173-188.
[8]. Sarıoglu, A. O.; Ceylan, U.; Yalcin, S. P.; Sonmez, M.; Ceyhan, G.; Aygun, M. *J. Lumin.* **2016**, *176*, 193-201.
[9]. Hui, Y.; Feng, W.; Wei, T.; Lu, X.; Song, J.; Zhao, S.; Wong, W. K.; Jones, R. A. *Inorg. Chem. Commun*. **2011**, *14*, 200-204.
[10]. Cristovao, B.; Hnatejko, Z. *J. Mol. Struct*. **2015**, *1088*, 50-55.
[11]. Cristovao, B.; Klak, J.; Pelka, R.; Miroslaw, B.; Hnatejko, Z. *Polyhedron* **2014**, *68*, 180-190.
[12]. Anacona, J. R.; Rincones, M. *Spectrochim. Acta A* **2015**, *141*, 169-175.
[13]. Soliman, A. A.; Amin, M. A.; El-Sherif, A. A.; Ozdemir, S.; Varlikli, C.; Zafer, C. *Dyes Pigm.* **2013**, *99*, 1056-1064.
[14]. Sarkar, A.; Pal, S. *Polyhedron* **2006**, *25*, 1689-1694.
[15]. Meng, Z.; Liu, J. L.; Leng, J. D.; Guo, F. S.; Tong, M. L. *Polyhedron* **2011**, *30*, 3095-3099.
[16]. Baraniak, E.; Bruce, R. S. L.; Freeman, H. C.; Hair, N. J.; James, J. *Inorg. Chem*. **1976**, *15*, 2226-2228.
[17]. Ito, M.; Hamada, D.; Ono, H.; Matsumoto, N.; Sunatsuki, Y.; Re, N. *Inorg. Chim. Acta*, **2016**, *443*, 274-278.
[18]. Kaczmarek, M. T.; Jastrząb, R.; Kubicki, M.; Gierszewski, M.; Sikorski, M. *Inorg. Chim. Acta* **2015**, *430*, 108-113.
[19]. Sheldrick, G. M. SHELXTL Version 5. 10, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
[20]. Sheldrick, G. M. SHELXTL-97, University of Göttingen, Göttingen, Germany, 1997.
[21]. Farrugia, L. J. *J. Appl. Cryst*. **1997**, *30*, 565.
[22]. Geary, W. J. *Coord. Chem. Rev*. **1971**, **7**, 81-122.
[23]. Vleck, J. H. V.; Frank, A. *Phys. Rev*. **1929**, *34(11)*, 1494-1496.
[24]. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Wiley-Interscience, New York, 1978.
[25]. Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227-250.
[26]. Xie, Q. L.; Li, S. H.; Zhang, D. K.; Zhang, Z. G.; Hu, J. M. *Acta Chim. Sin*. **1991**, *49*, 723-728.
[27]. Sonmez, M.; Levent, A.; Sekerci, M. *Russ. J. Coord. Chem*. **2004**, *30*, 655-660.
[28]. Fomina, I. G.; Dobrokhotova, Z. V.; Ilyukhin, A. B.; Aleksandrov, G. G.; Kazak, V. O.; Gehman, A. E.; Efimov, N. N.; Bogomyakov, A. S.; Zavorotny, Y. S.; Gerasimova, V. I.; Novotortsev, V. M.; Eremenko, I. L. *Polyhedron* **2013**, *65*, 152-160.
[29]. Oliveira, C. A. F.; Silva, F. F.; Malvestiti, I.; S. Malta, V. R.; Dutra, J. D. L.; Costa, N. B.; Freire, R. O.; Alves, S. *J. Mol. Struct.* **2013**, *1041*, 61-67.
[30]. Tamboura, F. B.; Haba, P. M.; Gaye, M.; Sall, A. S.; Barry, A. H.; Jouini, T. *Polyhedron* **2004**, *23*, 1191-1197.
[31]. Ajlouni, A. M.; Taha, Z. A.; Al-Hassan, K. A.; Anzeh, A. M. A. *J. Lumin.* **2012**, *132*, 1357-1363.