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# Coordination of Ce(III) and Nd(III) with pentaethylene glycol in the presence of picrate anion: Spectroscopic and X-ray structural studies

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#### ABSTRACT

<sup>1</sup>H NMR evidence for direct coordination between the Ln(III) ion and the oxygen atoms of the pentaethylene glycol (EO5) ligand and the picrate anion (Pic) in  $[Ln(Pic)_2(EO5)]$ [Pic] {Ln = Ce and Nd} complexes are confirmed by single X-ray diffraction. No dissociation of Ln–O bonds in dimethyl sulfoxide-*d* solution was observed in NMR studies conducted at different temperatures ranging 25–100 °C. The Ln(III) ion was chelated to nine oxygen atoms from the EO5 ligand in a hexadentate manner and the two Pic anions in each bidentate and monodentate modes. Both compounds are isostructural and crystallized in monoclinic with space group  $P2_1/c$ . Coordination environment around the Ce1 and Nd1 atoms can be described as tricapped trigonal prismatic and monocapped square antiprismatic geometries, respectively. The crystal packing of the complexes have stabilized by one dimensional (1D) chains along the [001] direction to form intermolecular O-H···O and C-H···O hydrogen bonding. The molar conductance of the complexes in DMSO solution indicated that both compounds are ionic. The complexes had a good thermal stability. Under the UV-excitation, these complexes exhibited the red-shift emission.

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#### 1. Introduction

In some examples lanthanide complexes with the series of polyethylene glycol (PEG) ligands, i.e. triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5), hexaethylene glycol (EO6) and heptaethylene glycol (EO7) have been previously reported [1–9], while complexes of PEG–Pic coordinated to the Ln(III) ions in the coordination sphere have yet to be described in the literature. The metal–organic coordination constructed by mixed ligand is more adjustive than those by single ligand [10]. Lanthanide formed various complexes in which higher coordination numbers, usually greater than 6 and often as high as 9–10 appear to dominate [11,12].

The use of PEG as a ligand coordinated to Ln(III) in the presence of Pic anion has been structurally characterized in our laboratory [13–17]. The light and heavy lanthanide ions effectively control the geometry of the inner-coordination sphere [17]. The EO5 molecule was chosen as ligand, based on the following considerations, i.e. (i) it is a flexible ligand and its donor oxygen atoms can be coordinated to the Ln(III) ion in a hexadentate mode, (ii) shielding the encapsulated Ln(III) ion from interaction with the surrounding atom or/and water molecules, and (iii) its terminal alcohol groups can act not only as donor oxygen atom but as a hydrogen-bond donor [13–16]. The Pic anion can minimize the water molecules involved in the inner-coordination spheres of the complexes [16,17].

This paper continues and completes previous research on crystal structure behavior in the light lanthanide ions Ce(III), and Nd(III) was chosen as coordination center with the EO5 ligand in the presence of Pic anion. In this paper, we report the systematic synthesis of two [Ln(Pic)\_2(EO5)][Pic] {Ln = Ce, Nd} complexes by using one-spot preparation. The structures of these complexes were characterized and their spectroscopic, molar conductance, luminescence and thermal stability were also investigated.

#### 2. Experimental

#### 2.1. Materials

All chemicals and solvents were of analytical grade and were used without further purification. Pentaethylene glycol, EO5 ( $C_{10}H_{22}O_6$ , >97% purity) was purchased from Fluka (Busch, Switzerland). Picric acid (HPic) [(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH, >98% purity] was purchased from BDH (Poole, England). Nd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (99.9% purity) from Aldrich (WI, USA). Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9% purity) was obtained from Johnson Matthey Electronic (NJ, USA).

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#### 2.2. Preparation of the complexes

EO5 ligand (0.60 g, 2.52 mmol) and each  $[Ln(NO_3)_3.6H_2O]$ {Ln = Ce, Nd} (0.43 g, 1 mmol) were added slowly to a HPic solution (0.91 g, 3.97 mmol) into 20 mL mixture acetonitrile:methanol (3:1, v/v) at room temperature under stirring for 5 min. The mixed solution was covered with aluminum foil to allow a slow evaporation at room temperature. Single crystals were grown after 1–5 days and were suitable for X-ray structure determination.

#### 2.2.1. [Ce(Pic)<sub>2</sub>(EO5)][Pic]

Yield: 75%. Colour: red. *Anal.* Calc.: C, 31.53; H, 2.53; N, 11.82. Found: C, 32.63; H, 2.46; N, 11.97%. Decomposition point: 253.8–280.6 °C. Molar conductivity:  $189(^{-1} \text{ mol}^{-1} \text{ cm}^3$ . Significant peaks IR (KBr),  $\nu/\text{cm}^{-1}$ : 3413, 3088, 2956, 1614, 1578, 1535, 1356, 1340, 1268, 1168, 1085, 1067, 937, 789.

#### 2.2.2. [Nd(Pic)<sub>2</sub>(EO5)][Pic]

Yield: 95%. Colour: brownish. *Anal.* Calc.: C, 31.36; H, 2.52; N, 11.76. Found: C, 31.66; H, 2.41; N, 11.52%. Decomposition point: 263.0–280.2 °C. Molar conductivity:  $152 (^{-1} \text{ mol}^{-1} \text{ cm}^3$ . Significant peaks IR (KBr),  $\nu/\text{cm}^{-1}$ : 3414, 3088, 2757, 1610, 1578, 1521, 1370, 1337, 1266, 1167, 1084; 1070, 939, 788.

#### 2.3. Physical measurements

Elemental analyses were performed on a Perkin-Elmer 2400II elemental analyzer. Conductivity measurements were carried out in DMSO solution at  $26.3 \pm 0.91$  °C using a Scan500 conductivity meter. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer in the region of 4000–400 cm<sup>-1</sup> by using the conventional KBr pellets method for solid samples. For liquid sample, i.e. the EO5 ligand, a thin layer of sample was applied on the surface of a KRS-5 (thallium bromoiodide). <sup>1</sup>H NMR spectra were measured on a Bruker 400 MHz spectrometer by using tetramethylsilane (TMS) as an internal standard in dimethyl sulfoxide-*d*. Thermogravimetric analysis was recorded on a Perkin-Elmer TGA-7 series thermal analyzer (under nitrogen atmosphere) with a heating rate of 20 °C/min.

Photoluminescence (PL) measurements were made at room temperature by using a Jobin Yvon HR800UV system, with the data collected and processed with Labspec Version 4 software source. A HeCd laser was used for excitation at 325 nm and the emission spectra were scanned from 330 to 1000 nm.

#### 2.4. X-ray crystallography analyses

X-ray diffraction data were collected from single crystals by using a Bruker APEX2 area-detector diffractometer with a graphite monochromated Mo-K $_{\alpha}$  radiation source and a detector distance of 5 cm. Data were processed using APEX2 software [18]. The collected data were reduced by using the SAINT program and the empirical absorption corrections were applied with the SADABS program [18]. The structures were solved by direct methods and refined by least-squares method on  $F_{obs}^2$  using the SHELXTL program [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from different Fourier maps and were isotropically refined. The final refinement converged well. Data for publication were prepared with SHELXTL [19] and PLATON [20]. Four oxygen atoms (O16, O23, O25, and O27) in the Ce complex are disordered over two positions with refined occupancies of 54:46, 70:30, 23:63, and 49:51. While for the Nd complex, four oxygen atoms (O16, O22, O24, and O27) are also disordered over two positions with refined occupancies of 68:32, 56:44, 38:62, and 58:42.

Table 1

 $^{1}$ H NMR chemical shift of the free EO5 ligand and the [Ln(Pic)<sub>2</sub>(EO5)][Pic] complexes.

Peak	Chemical shift (ppm)			
	Ligand	Compound		
	EO5	Ce	Nd	
(i) At 25 °C				
$-C(1)H_2-C(2)$	3.414	3.416	3.412	
$C(1)-C(2)H_2-$	3.491	3.475	3.484	
$-C(3)H_2-C(3)H_2$	3.51	3.516	3.511	
OH	4.142	3.660	3.333	
Pic	-	8.588	8.589	
(ii) At 50 °C				
$C(1)H_2-C(2)$	3.448	3.431	3.451	
$C(1)-C(2)H_2$	3.494	3.482	3.503	
$-C(3)H_2-C(3)H_2$	3.527	3.524	3.532	
OH	3.964	#	3.249	
Pic	-	8.558	8.574	
(iii) At 75 °C				
$C(1)H_2-C(2)$	3.457	3.465	3.476	
$C(1)-C(2)H_2$	3.523	3.525	3.511	
$C(3)H_2-C(3)H_2$	3.542	3.553	3.55	
OH	3.764	3.219	3.13	
Pic	-	8.559	8.56	
(iv) At 100 °C				
$C(1)H_2-C(2)$	3.476	3.451	3.495	
$C(1)-C(2)H_2$	3.540	3.496	3.528	
$C(3)H_2-C(3)H_2$	3.559	3.546	3.564	
OH	3.570	3.230	2.992	
Pic	-	8.525	8.555	

Note: (#) overlapping peak and (-) peak is lost.

#### 3. Results and discussion

#### 3.1. Properties of the complexes

Preparation of the complexes is carried out by reacting each lanthanide nitrate and HPic solution in acetonitrile–methanol, followed by adding the EO5 ligand, without previous synthesis of the

#### Table 2

Crystal data of the [Ln(Pic)2(EO5)][Pic] complexes.

Parameter	Compound	
Empirical formula	C <sub>28</sub> H <sub>28</sub> N <sub>9</sub> O <sub>27</sub> Ce	C <sub>28</sub> H <sub>28</sub> N <sub>9</sub> O <sub>27</sub> Nd
Formula weight	1062.71	1066.83
Volume (Å <sup>3</sup> )	3882.92(14)	3860.2(8)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Ζ	4	4
Unit cell dimensions		
a (Å)	18.8013(4)	18.7757(7)
b (Å)	9.0614(2)	9.0337(1)
c (Å)	24.1013(5)	24.094(3)
$\alpha = \gamma(\circ)$	90	90
$\beta(\circ)$	108.9750(10)	109.160(1)
$Dx(g/cm^3)$	1.818	1.836
$\mu ({\rm mm}^{-1})$	1.287	1.460
F(000)	2132	2140
Crystal size (mm)	$0.20\times0.50\times0.50$	$0.10 \times 0.20 \times 0.20$
$\theta$ range (°)	2.80-27.44	1.15-30.03
h, k, l	-24/24, -11/11, -31/31	-26/26, -12/12, -33/33
Reflections collected/unique	15120/8387	20074/11254
	[R(int) = 0.0258]	[R(int) = 0.029]
Refinement method	Full-matrix	Full-matrix least
	least squares of F <sup>2</sup>	squares of F <sup>2</sup>
Data/restraints/parameter	8387/0/626	11254/0/586
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0371,	R1 = 0.044,
	wR2=0.0899	wR2=0.122
R indices (all data)	R1 = 0.0608,	R1 = 0.075,
	wR2 = 0.1009	wR2=0.164
Goodness-of-fit on $F^2$	1.017	1.096



Fig. 1. Molecular structure of the [Ce(Pic)<sub>2</sub>(EO5)][Pic] complex with 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Ln–Pic salt such as in the close system 18C6–Ln–Pic complexes [17]. Because of the flexibility open chain from the EO5 ligand is easier compared to the cyclic 18C6 ligand in the formation of lanthanide complex. The EO5 molecule is chelated to the Ln(III) ion is easier compared to the 18C6 molecule. Analytical data for the synthesized compounds indicated that both compounds confirm to a 1:1:3 (Ln:EO5:Pic) compositions with salt-type compounds. And similar with our previous studies [13–16], both compounds are stable to air and moisture for long-period time. The complexes were soluble in dimethyl sulfoxide, slightly soluble in acetone, methanol, acetonitrile and water. However, neither was soluble in chloroform, ethyl acetate or toluene.

The solubility of the complexes in common solvents is low, which made solution studies difficult and prevented the measurement of conductivity. The molar conductivity values for the Ce and Nd complexes were at 189, and  $152(^{-1} \text{ mol}^{-1} \text{ cm}^3)$ , respectively, indicating that the complexes were electrolytes nature in a 1:3 ratio [21,22]. This means that the DMSO molecules have replaced the two Pic anions from the inner-coordination sphere of the complexes and the actual solution species are  $[\text{Ln}(\text{EO5})(\text{DMSO})_3]^{3+} \cdot 3[\text{Pic}]^{-}$  [22].

#### 3.2. IR spectra

The IR spectrum of the free EO5 ligand shows strong absorption bands at 3429, 2874, 1249–1067 cm<sup>-1</sup> which are assigned to the  $\nu$ (O–H),  $\nu$ (C–H) and  $\nu$ (C–C–O) stretching modes of the ether linkages in the respective order and have been reported by Saleh et al. [14–16]. On the basis of the similarity of their IR spectra, it may be assumed that both compounds have similar structures. The stretching band of  $\nu$ (C–O–C) in the Ce and Nd complexes were shifted higher frequencies by about 19 and 17 cm<sup>-1</sup>, respectively, relative to the frequency of free EO5 ligand. This shifting indicates that all of the donor oxygen atoms of the EO5 ligand were involved in coordination bonding with the Ln(III) ion. The absorption band due to the  $\nu$ (C–H) symmetric stretching at 2874 cm<sup>-1</sup> was signifi-

cantly shifted to the higher wavelength, namely 2956–2957 cm<sup>-1</sup>, indicating that the EO5 ligand rearranged to the pseudo-cyclic conformation [15,16,23].

The stretching bands from asymmetric and symmetric of nitro groups  $\nu(NO_2)$  were split into two bands, i.e. 1578, 1535; 1356, 1340 and 1578, 1521; 1370, 1337 cm<sup>-1</sup> for the Ce and Nd complexes, respectively. This splitting indicates that the Pic anion was coordinated to Ln(III) through the phenolic oxygen and the oxygen ortho-nitro group, forming a bidentate ligand [13-17,24-28]. The absorption band assigned to  $\nu$ (N–O) at 940–988 cm<sup>-1</sup> was shifted to 937–939 cm<sup>-1</sup>, indicating the coordination of Pic anion through the oxygen atoms [29]. In addition, the out-of-plane due to the phenolic bending vibration on the free HPic molecule at 1155 cm<sup>-1</sup> was shifted to higher frequencies of 1168 and 1167 cm<sup>-1</sup> for the Ce and Nd complexes, respectively. This shifting suggests that the hydrogen atom of the phenolic group in the HPic molecule was substituted by Ln(III) ion [13-17,24,25,27]. The vibration v(C-O) of HPic molecule at 1213 cm<sup>-1</sup> was shifted higher frequencies about  $\sim$ 54–56 cm<sup>-1</sup> in the IR spectra of both compounds. This suggested that the Ln-O<sub>phenolic</sub> bonds were stronger than those found in the  $Ln-O_{EO5}$  bonds [15].

#### 3.3. NMR studies

Because of poor solubility of the complexes in CD<sub>3</sub>CN or D<sub>2</sub>O, their <sup>1</sup>H NMR spectra were obtained in  $d_6$ -DMSO. The <sup>1</sup>H NMR spectrum suggested the coordination interaction between the Ln(III) ion and the EO5 ligand in the solid state and/or solution were observed. The <sup>1</sup>H NMR spectrum of the HPic molecule [15,16] shows two singlet peaks at 8.593 and 4.577 ppm assigned to the equivalents of two protons from the aromatic part and one proton from the phenolic group, respectively. The proton peak of the phenolic group in HPic molecule disappeared in both compounds, indicating that Ln(III) replaced the hydrogen atom via deprotonization or substitution [15–17].

(a)

In the lighter lanthanide complexes of Ce and Nd, all of the signals were found to be sharp and free from overlapping. At 25 °C, the singlet signal of the terminal alcohol groups in the complexes was shifted upfield (~0482 to 0.809 ppm) relative to the chemical shift of the free EO5 ligand (~4.142 ppm) (Table 1). This may reflect the conformation of the complex, causing the peak to be more shielded. Both the terminal alcohol groups were involved in coordination bonding and also to form a strong  $O-H\cdots O$  hydrogen bond. In addition, the terminal alcohol groups had a high mobility in the solution [30] and when more the donor atoms are present in the complex, they influenced each other and the chemical shift may even have an opposite change [31].

Small shifts were seen for the etheric protons from the EO5 ligand or the proton in the aromatic rings of Pic anions. Nevertheless, the EO5 and Pic ligands were still coordinated to the metal ion in solution. To investigate this phenomenon, a study was undertaken using <sup>1</sup>H NMR to measure chemical shifts at increasing temperature from 25 to 100 °C. Similar <sup>1</sup>H NMR spectra were obtained when the temperature was reduced from 100 to 25 °C. This indicates that the phenomenon study was reversible and no dissociation of bonds occurred in both compounds.

The terminal alcohol groups peak was shifted upfield when the temperature was raised and reached about 2.992–3.230 ppm at 100 °C. In addition, this peak signal became a broad at high temperature. This indicates that at high temperature, hydrogen bonding is weaker and may be broken [32,33]. At the same time, the peaks of etheric protons were splitted significantly and shifted downfield. We assume that the Ln–O<sub>etheric</sub> bond lengths are shorter than that found at room temperature because of decrease in the shield-ing effect. No splitting of the aromatic Pic peak in the complexes was observed. However, these peaks from 8.588 and 8.589 ppm at 25 °C were slightly shifted upfield by 8.525 and 8.555 ppm at 100 °C, respectively for the Ce and Nd complexes (Table 1). In these case, the strong  $\pi$ – $\pi$  interactions among the adjacent aromatic rings of the Pic anions was observed [34].

#### 3.4. X-ray studies

Single-crystal X-ray diffraction and elemental analysis that were performed on the Ce and Nd complexes reveal that they are identical in structure with formula [Ln(Pic)<sub>2</sub>(EO5)][Pic]. Both compounds are crystallized in monoclinic with space group  $P2_1/c$  (Table 2). The structure of complex Ce is similar with complex Nd, except the bond lengths and angles because of different ion radii of the lanthanide center. Single-crystal studies revealed the existence of interaction between the Ln(III) ion and the donor oxygen atoms of the EO5 ligand in the crystalline state. Fig. 1 shows that the Ln(III) metal center is coordinated to nine oxygen atoms from the EO5 ligand in hexadentate mode and the remaining three oxygen atoms from each bidentate and monodentate Pic anions. Additionally, due to the space obstacle of coordinated Pic anion, no coordinated solvent molecules are present in the complexes [16]. From these results, the Pic anions prevent that the water molecule does not involve in the inner-coordination sphere. The acyclic EO5 ligand wraps around Ln(III) with its donor oxygen atoms and forms a ring-like coordination structure such as 18-crown-6 [1,2,4,8,14-16].

The coordination geometry around the Ce1 atom is slightly distorted a tricapped trigonal prismatic with the O1, O3, and O5 atoms at the peak of the capping position of the three square planes was observed in the Ce complex (Fig. 2a). The coordination environment around the Nd1 atom can be described as a monocapped square antiprismatic geometry with the O2 atom at the peak of the capping position for one square O7–O8–O1–O3 plane (Fig. 2b).

The Ln–O<sub>EO5</sub> bond lengths in the inner-coordination sphere are of two types, i.e. Ln–O<sub>alcohol</sub> and Ln–O<sub>ether</sub>. The average of Ln–O<sub>ether</sub>



**Fig. 2.** Perspective view coordination polyhedron geometries around the Ce1 atom (a) and the Nd1 atom (b).

bond lengths are slightly longer than the Ln–O<sub>alcohol</sub> bond lengths. The Ce–O bond lengths range from 2.371(2) to 2.605(2) Å (Table 3). The Nd–O bond lengths range from 2.348(3) to 2.578(3) Å (Table 3). The averages of Ln–O<sub>ether</sub> bond lengths are 2.580(3) and 2.554(3) Å for the Ce and Nd complexes, respectively. The average of Ln–O<sub>alcohol</sub> bond lengths are 2.548(2) and 2.519(3) Å for the Ce and Nd complexes, respectively. The averages of Ln–O<sub>phenol</sub> bond lengths are the shortest, i.e. 2.370(2) and 2.352(3) Å for the Ce and Nd complexes, respectively. The shortness of these bond length is caused by a higher electron density of the phenolic oxygen of the Pic anion [14–17]. Both the coordinated Pic anions make a dihedral angle with the inner-coordination sphere of [Ln(Pic)<sub>2</sub>(EO5)] of about 89.4(2)° and 89.7(2)° for the Ce and Nd complexes, respectively.

Table 3	
Selected bond length (A	A) and bond angle (°) in the [Ln(Pic) <sub>2</sub> (EO5)](Pic) complexes.

Atom	Bond length	(Å)	Atom	Bond angle (°)		Atom	Torsion angle	(°)
	Ce	Nd		Ce	Nd		Ce	Nd
Ln1-01	2.522(2)	2.497(3)	01-Ln1-02	62.09(9)	62.23(10)	01-C1-C2-02	47.8(5)	48.6(6)
Ln1-02	2.589(3)	2.572(3)	02-Ln1-03	61.72(10)	61.92(12)	02-C3-C4-O3	-39.2(10)	-33.7(13)
Ln1-03	2.587(3)	2.567(3)	03-Ln1-04	61.83(10)	62.55(11)	03-C5-C6-O4	49.7(6)	48.8(7)
Ln1-04	2.538(3)	2.500(3)	04-Ln1-05	60.54(8)	61.04(9)	04-C7-C8-O5	-45.1(5)	-43.6(6)
Ln1-05	2.605(2)	2.578(3)	06-Ln1-05	62.25(7)	62.76(9)	05-C9-C10-O6	-50.0(5)	-51.4(6)
Ln1-06	2.573(2)	2.540(3)	01-Ln1-06	71.41(8)	71.67(9)	Average O-C-C-O	46.4(5)	45.2(8)
Ln1-07	2.371(2)	2.355(3)	Average C–O–C	113.5(4)	113.0(4)	C2-O2-C3-C4	169.7(6)	164.1(8)
Ln1-014	2.368(2)	2.348(3)	Average O–C–C	110.1(4)	110.1(5)	C3-O2-C2-C1	-171.8(5)	-173.8(6)
Ln1-08	2.603(2)	2.566(3)				C5-03-C4-C3	-171.0(6)	-171.8(8)
Average C–C	1.436(7)	1.446(8)				C4-03-C5-C6	-174.9(5)	-175.6(6)
Average C–O	1.430(5)	1.436(6)				C7-04-C6-C5	130.6(5)	126.1(6)
-						C6-O4-C7-C8	-164.5(4)	-163.1(5)
						C9-05-C8-C7	-86.6(5)	-82.8(5)
						C8-05-C9-C10	-179.2(4)	-179.9(4)
						Average C-O-C-C	156.0(5)	154.7(6)

One peculiarity of the coordinated Pic anion is the shortening of the C–O<sub>phenol</sub> bonds relative to these bonds in the acid structure of 1.322(3) Å [35]. The average C–O<sub>phenol</sub> bond lengths were 1.272(4) and 1.276(5) Å for the Ce and Nd complexes, respectively. These lengths result from the replacement of the hydrogen atom by Ln(III) and the increase in the  $\pi$ -bond due to the greater electron density of the phenol oxygen [14–17]. The average C–O<sub>phenol</sub> bond lengths of the coordinated Pic anion were quite similar to the C–O<sub>phenolic</sub> bond lengths in the Pic anion as a counteranion, i.e. 1.280(4) and 1.264(5) Å for the Ce and Nd complexes, respectively.

The averages of C–O and C–C bond lengths of the acyclic EO5 ligand are 1.430(5); 1.436(7) and 1.436(6); 1.446(8)Å for the Ce and Nd complexes, respectively. These distances were similar and comparable with the derivative EO5 complexes [13-16]. The average C-O-C and O-C-C bond angles of both compounds are similar and close to the tetrahedral angle (Table 3). The O-Ln-O bond angles between adjacent oxygen atoms in the acyclic EO5 ligand are slightly larger than 60° (Table 3). The O1–Ln–O6 bond angles between the oxygen atoms of terminal alcohol groups in the acyclic EO5 ligand are similar with the derivative [Ln(EO5)(Pic)<sub>2</sub>][Pic] complexes [14,15], except for the [La(EO5)(Pic)<sub>2</sub>][Pic][16]. The O-C-C-O torsion angles from the acyclic EO5 ligand use the same conformation patterns of  $g^+g^- g^+ g^- g^-$  with average values of 46.4(5)° and 45.2(8)° for the Ce and Nd complexes, respectively (Table 3). All the C-O-C-C torsion angles are anti, except C9-O5-C8-C7 that is close to the *gauche* conformation  $(g^{-})$  for both compounds.

Both terminal alcohol groups of the EO5 ligand are involved to form a strong intermolecular hydrogen bond, i.e.  $O1-H1C\cdots O21$  [1.835 Å, x, 1+y, z] and  $O1-H1C\cdots O21$  [1.855 Å, 1-x, 1/2+y, 1/2-z], thus producing the one-dimensional (1D) supramolecule network (Table 4). The crystal packing of the molecule units are linked by the intermolecular  $O-H\cdots O$  and  $C-H\cdots O$  hydrogen bonds to form 1D chain along *bc* plane with symmetry direction [001] (Fig. 3). Only one the terminal alcohol group of the EO5 ligand was involved to form bifurcated hydrogen bonds (Tables 4a and 4b). The Pic counteranion acts not only as hydrogen-bonds acceptor but also as hydrogen-bond donor, namely C25-H25A $\cdots$ O17 [2.465 Å, 1-x, -1/2+y, 3/2-z] and C27-H27A $\cdots$ O20 [2.476 Å, -1+x, y, z] for the Ce and Nd complexes, respectively.

Both compounds have no significant intermolecular  $\pi - \pi$  interactions between two aromatic rings of the Pic anion. In the Ce complex, between the aromatic rings of coordinated Pic anion and Pic counteranion formed the shortest  $\pi - \pi$  interaction with their centroids separation of 4.517(2)Å with a dihedral angle between two planes of 3.44° and symmetry code *x*, 1+*y*, *z*. In the Nd complex, between the aromatic rings of coordinated Pic anion and Pic counteranion formed the shortest  $\pi - \pi$  interaction with their centroids separation of 4.504(2) Å with dihedral angle of 3.63° and symmetry code 1 - x, 1/2 + y, 1/2 - z (Fig. 3). These values are longer than those found in the [La(Pic)<sub>3</sub>L] complex about of 3.774 and 4.019 Å [36] where L=*N*-phenyl-2-{2'-[(phenyl-ethyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-ethyl-acetamide.

The van der Waals interactions of O6–H6C···Cg2 [3.108 Å, x, y, z] with an angle of 129.03° where Cg2=aromatic ring of (C17–C22) also was observed in the Ce complex. In addition, the O···O interactions in the ranges of 2.648–2.728 Å was observed in both compounds. These interactions indicated that strong or moderate hydrogen bonds are present in the crystal packing of compounds.

Table 4			
Hydrogen bonding in the Ce and	Nd complexes	D = donor and	A = acceptor

D−H· · ·A	D–H (Å)	H···A (Å)	D· · · A (Å)	D−H···A (°)
(a) The Ce complex				
01-H1C021 <sup>i</sup>	0.930	1.835	2.642(4)	143.6
06-H6C···021 <sup>i</sup>	0.931	2.007	2.736(4)	133.9
06-H6C···022 <sup>i</sup>	0.931	2.346	2.987(4)	125.8
C1-H1B···O26 <sup>i</sup>	0.970	2.356	3.047(7)	127.6
C2-H2A···O10 <sup>ii</sup>	0.970	2.569	3.339(6)	136.4
C2-H2B···O26 <sup>iii</sup>	0.970	2.589	3.527(7)	162.8
C7−H7A···O18 <sup>iv</sup>	0.971	2.435	3.143(6)	129.5
C8-H8A···O23B <sup>v</sup>	0.970	2.493	3.38(3)	151.4
C9–H9A···O19 <sup>vi</sup>	0.971	2.599	3.315(6)	130.8
$C10\text{-}H10A \cdots O22^i$	0.971	2.481	3.098(5)	121.3
C21−H21A···O24 <sup>vii</sup>	0.929	2.568	3.495(6)	175.5
C25–H25A····O17 <sup>viii</sup>	0.930	2.465	3.383(5)	169.2
(b) The Nd complex				
$01-H1C\cdots 021^i$	0.930	1.847	2.637(5)	141.2
06-H6C···021 <sup>i</sup>	0.930	1.998	2.726(4)	133.8
06-H6C···026 <sup>i</sup>	0.930	2.352	2.983(5)	124.9
C1-H1B···O23 <sup>i</sup>	0.970	2.352	3.027(9)	126.2
C2-H2A···O11 <sup>ii</sup>	0.967	2.591	3.353(8)	135.6
C2-H2B···O23	0.971	2.572	3.509(9)	162.3
C5–H5A···O21 <sup>iii</sup>	0.970	2.593	3.501(9)	155.9
C7−H7A···O19 <sup>iv</sup>	0.970	2.485	3.155(7)	126.1
C9–H9A···O18 <sup>v</sup>	0.971	2.566	3.282(7)	130.6
C10-H10A···O26 <sup>i</sup>	0.970	2.439	3.066(6)	122.1
C19−H19A····O25 <sup>vi</sup>	0.930	2.565	3.493(7)	175.9
C27−H27A···O20 <sup>vii</sup>	0.929	2.478	3.391(8)	167.8

(a) Symmetry codes: (i) x, 1+y, z; (ii) x, 1/2 - y, -1/2 + z; (iii) -x, 1/2 + y, 3/2 - z; (iv) x, 1/2 - y, 1/2 + z; (v) 1 - x, -y, 2 - z; (vi) 1 - x, 1 - y, 2 - z; (vii) 1 - x, 1/2 + y, 3/2 - z; (viii) 1 - x, -1/2 + y, 3/2 - z.

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



Fig. 3. Packing diagram of [Nd(Pic)<sub>2</sub>(EO5)][Pic] complex viewed along *b*-axis. The dashed lines indicate the hydrogen bonds and the  $\pi$ - $\pi$  interactions.



Fig. 4. The photoluminescence of the Ce (a) and Nd (b) complexes.

#### 3.5. Photoluminescence studies

The emission spectra of the free EO5 ligand and its complexes were evaluated in the solid state at room temperature based on D2 filter measurement. The free EO5 ligand exhibits an intense broad emission bands at 412.1 and 492.8 nm ( $\lambda_{ex} = 325$  nm). Meanwhile, the HPic molecule had a broad band with the center peak at 537 nm. Comparison with the free EO5 ligand, the Ce and Nd complexes had red-shift emission peak, i.e. 414.1; 531.5 nm, and 414.0; 513.0 nm, respectively (Fig. 4). The red-shift emission peak is probably due to the intra-ligand fluorescent emission [37]. Meanwhile, the PL spectra of Ce and Ne complexes that had blue-shift emission are relative to the HPic molecule. The blue-shift emission of both compounds is attributed to the emission of ligand-to-metal charge transfer (LMCT).

#### 3.6. Thermal studies

Thermal analysis studies were carried out under  $N_2$  to evaluate complex dehydration and stability. Both compounds behave similarly (Fig. 5). The free EO5 ligand decomposed at 135–340 °C.

105 100 90 80 70 60 (%) Neight % 50 40 30 20 10 0+ 30 100 200 400 500 600 700 800 900 300 Temperature (°C)

**Fig. 5.** Thermogram of the free EO5 ligand (\_\_\_\_\_\_), the Ce complex (...) and the Nd complex (\_\_\_\_\_\_).

Based on this observation the melting point of the EO5 ligand is 187 °C. This ligand began to decompose at 190 °C, with decomposition going rapidly to completion at 260–290 °C due to the release of the EO5 ligand and the three Pic anions, with a corresponding weight loss of 94.7% and 94.3% (calc. 86.7% and 86.4%) for the Ce and Nd complexes, respectively.

Decomposition up to 600 °C and no mass loss is observed under this temperature. Further decomposition of the complexes at ~895 °C resulted in a lanthanide oxide as the final product. The complexes had good thermal stability due to the role of  $\pi$ - $\pi$  stacking interactions, the strong metal-oxygen bonds as well as hydrogen bonding. The Pic ligands are lost at more than 300 °C [30] after which there is no  $\pi$ - $\pi$  interaction. Similar pattern decomposition was seen with the lanthanide-picrate complexes [13,14,16,17,38].

#### 4. Conclusion

The  $[Ln(Pic)_2(EO5)][Pic]$  complexes have been synthesized by one-spot reaction of lanthanide nitrate, the EO5 and HPic molecules. The lighter lanthanide ions prefer to form the complexes with a nine-coordination number in which depending on the acyclic polyether chain length and number of donor oxygen atoms. Further investigations are in progress involving other lanthanides to get a reasonable explanation and deeper insight into this crystal structure behavior of the Ln–EO5 complexes and the luminescence properties.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2009.05.024.

#### References

- [1] R.D. Rogers, J. Zhang, C.B. Bauer, J. Alloys Compd. 49 (1997) 41.
- [2] Y. Hirashima, K. Kanetsuki, J. Shiokawa, N. Tanaka, Bull. Chem. Soc. Jpn. 54 (1981) 1567.
- [3] R.D. Rogers, R.D. Etzenhouser, Acta Crystallogr. C 44 (1988) 1400.
- [4] R.D. Rogers, A.N. Rollins, R.F. Henry, J.S. Murdoch, R.D. Etzenhouser, S.E. Huggins, L. Nunez, Inorg. Chem. 30 (1991) 4946.
- [5] R.D. Rogers, R.D. Etzenhouser, J.S. Murdoch, E. Reyes, Inorg. Chem. 30 (1991) 1445.
- [6] R.D. Rogers, R.D. Etzenhouser, J.S. Murdoch, Inorg. Chim. Acta 196 (1992) 73.
- [7] R.D. Rogers, R.F. Henry, Acta Crystallogr. C 48 (1992) 1099.
- [8] R.D. Rogers, A.N. Rollins, R.D. Etzenhouser, E.J. Voss, C.B. Bauer, Inorg. Chem. 32 (1993) 3451.
- [9] U. Casellato, G. Tomat, P. di Bernardo, R. Graziani, Inorg. Chim. Acta 61 (1982) 181.
- [10] D. Sun, W. Bi, X. Li, R. Cao, Inorg. Chem. Commun. 7 (2004) 683.
- [11] J.-G. Bünzli, N. André, M. Elhabiri, G. Muller, C. Piguet, J. Alloys Compd. 303–304 (2000) 66.
- [12] L.C. Thompson, in: K.A. Gschneidner, L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earth, vol. 3, Nort-Holland Publishing Company, Amsterdam, 1979, p. 209 (Chapter 25).

- [13] M.I. Saleh, E. Kusrini, R. Adnan, I.A. Rahman, B. Saad, A. Usman, H.-K. Fun, B.M. Yamin, J. Chem. Crystallogr. 35 (2005) 469.
- [14] M.I. Saleh, E. Kusrini, B. Saad, R. Adnan, A. Salhin, B.M. Yamin, J. Lumin. 126 (2007) 871.
- [15] M.I. Saleh, E. Kusrini, R. Adnan, B. Saad, H.-K. Fun, B.M. Yamin, J. Mol. Struct. 837 (2007) 169.
- [16] M.I. Saleh, E. Kusrini, B. Saad, H.-K. Fun, B.M. Yamin, J. Alloys Compd. 479 (2009) 428.
- [17] M.I. Saleh, E. Kusrini, H.-K. Fun, B.M. Yamin, J. Organomet. Chem. 693 (2008) 2561.
- [18] Bruker, APEX2, SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
- [19] G.M. Sheldrick, SHELXTL V5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998.
- [20] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
- [21] M.G. Abd El-Wahed, M.S. Řefat, S.M. El-Megharbel, J. Mol. Struct. 892 (2008) 402.
- [22] E. Kusrini, M.I. Saleh, Inorg. Chim. Acta, in press, 2009.
- [23] F. Vogtle, E. Weber, Angew. Chem. Int. Ed. Engl. 18 (1979) 753.
   [24] L.F. Delboni, G.O. Livia, F.E. Castellano, L.B. Zinner, S. Braun, Inorg. Chim. Acta
- [24] LF. DEIDOH, G.O. LIVIA, E.E. Castenano, L.B. Zhiner, S. Braun, morg. Chini. Acta 221 (1994) 169.
   [25] K.M. Janes, K. Anife, H. Minner, V. Janes, T. Halashi, B. Il. Chen. Soc. Jan. 60
- [25] K. Nakagawa, K. Amita, H. Mizuno, Y. Inoue, T. Hakushi, Bull. Chem. Soc. Jpn. 60 (1987) 2037.
- [26] C.V.P. de Melo, G. Vicentini, E.E. Castellano, J. Zukerman-Schpector, J. Alloys Compd. 255 (1995) 350.
- [27] A.G. Silva, G. Vicentini, J. Zukerman-Schpector, E.E. Castellano, J. Alloys Compd. 255 (1995) 354.
- [28] S.A. Jardino Filho, P.C. Isolani, G. Vicentini, J. Alloys Compd. 249 (1997) 91.
- [29] P.T. Maï, M.-H. Herzog-Cance, A. Potier, J. Potier, Can. J. Chem. 60 (1982) 2777.
   [30] S. Andrew, H.H. Clayton, M.K. Edward, in: F.C. Paul (Ed.), Introduction to Organic Chemistry, Macmillan Publishing Company, New York, 1992, pp. 358–467.
- [31] A. Bodor, I. Bányai, I. Tóth, Coord. Chem. Rev. 228 (2002) 175.
- [32] S.M. Reid, J.T. Mague, M.J. Fink, J. Organomet. Chem. 616 (2000) 10.
- [33] P.C. Andrews, R.E. Mulvey, W. Clegg, W. Reed, J. Organomet. Chem. 386 (1990) 287.
- [34] G.G. Talanova, N.S.A. Elkarim, V.S. Talanov, R.E. Hanes, H.-S. Hwang Jr., R.A. Bartsch, R.D. Rogers, J. Am. Chem. Soc. 121 (1999) 11281.
- [35] M.I. Saleh, E. Kusrini, M.R. Mustaqim, H.-K. Fun, Acta Crystallogr. E 64 (2008) 01318.
- [36] Y.-L. Guo, W. Dou, Y.-W. Wang, W.-S. Liu, D.-Q. Wang, Polyhedron 26 (2007) 1699.
- [37] L.-Q. Yu, R.-D. Huang, Y.-Q. Xu, T.F. Liu, W. Chu, C.W. Hu, Inorg. Chim. Acta 361 (2008) 2115.
- [38] J.C. Fernandes, J.R. Matos, L.B. Zinner, G. Vicentini, J. Zukerman-Schpector, Polyhedron 19 (2000)2315.