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Coordination of trivalent lanthanum with polyethylene glycol in the presence of picrate anion: Spectroscopic and X-ray structural studies

Muhammad I. Saleh^{a,*}, Eny Kusrini^a, Bahruddin Saad^a, Hoong-Kun Fun^b, Bohari M. Yamin^c

^a School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

^b School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia

^c School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

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ABSTRACT

The effect of polyethylene chain length on molecular structures of lanthanum–picrate–polyethylene glycol (PEG) complexes has been studied. The change in the ability of the inner coordination sphere to accommodate the largest size of La³⁺ has been investigated in complexes with the ligands triethylene glycol (EO3), tetraethylene glycol (EO4), and pentaethylene glycol (EO5). The X-ray studies demonstrated that the complexes [La(Pic)₂(EO3)₂]⁺(Pic)⁻ (I and II), [La(Pic)₂(OH₂)(EO4)]⁺(Pic)⁻·H₂O (III), and [La(Pic)₂(EO5)]⁺(Pic)⁻ (IV) crystallized in the monoclinic system in space groups P2₁/c (I and IV), Pn (II), and C2/c (III). Compounds I and II are polymorphs. The La³⁺ coordination with the PEG ligand in the presence of picrate anion (Pic) showed a coordination number of 10. The number of oxygen donor atoms dictated the geometry of the inner coordination sphere and the formation of additional inner-sphere ligands through the incorporation of water molecules, especially in III. The result with III is due to the availability of free space in the complex and to the lack of saturation of the inner coordination sphere. All crystals were further stabilized by $\pi - \pi$ interactions stacking along the *a*-axis. No dissociation of La–O bonds in solution was observed in NMR studies conducted at different temperatures.

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1. Introduction

The study of coordination and structural chemistry of trivalent lanthanide (Ln^{3+}) complexes with oxygen donor atoms of polyether ligands has attracted interest in recent decades due to their unique structural characteristics as well as their ability to adopt different geometries and thereby give rise to structural diversity [1–3]. The physical and chemical properties of the host–guest complexes are determined not only by the nature of the $Ln-O_{ligand}$ coordination but also by the geometrical arrangement of the ligands around the Ln^{3+} ion. The Ln^{3+} ion forms various complexes with a high coordination number, usually >6 and sometimes as high as 9–10; with small donor atoms, such as oxygen and nitrogen, a coordination number of 12 can be achieved [4].

The effecton the structure of different polyethylene glycol (PEG) chain lengths and counteranion such as Cl^- , SCN^- , and NO_3^- has been reported by Rogers et al. [1] for the series of lanthanide complexes. The use of PEG as a ligand coordinated to Ln^{3+} in the presence of picrate anion (Pic) has been structurally characterized in our laboratory [5–8]. The light and heavy rare-earth elements

effectively control the geometry of the coordination sphere [8]. In addition, the Pic anion dictates the structure of the complexes through strong steric effects [7,8]. Lanthanide complexes with PEG have previously been reported [1,9–19], while complexes of PEG–Pic coordinated to the lanthanides in the coordination sphere have yet to be described in the literature. Previous work emphasized the structure of lanthanide complexes with PEG but did not report any studies on the spectroscopic and luminescence properties of the compounds.

To gain deeper understanding into the coordination behavior of the PEG acyclic polyether system, this paper reports the structural and spectral characterization of lanthanum complexes with different ether linkages and therefore different numbers of oxygen donor atoms. Lanthanum was chosen because it has the largest ionic radius in the series. The thermal properties of the complexes in relation to their crystal structure is also discussed and correlated with the structural arrangement and chemical bonding.

2. Experimental

2.1. Materials

All chemicals and solvents were of analytical grade and were used without further purification. Triethylene glycol (EO3, 99% purity) and tetraethylene glycol (EO4, 99.5% purity) were purchased from Acros (NJ, USA). Pentaethylene glycol (EO5, >97%

^{*} Corresponding author. Tel.: +60 4 6533888x3108; fax: +60 4 656646. *E-mail address:* midiris@usm.my (M.I. Saleh).

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Table 1
Elemental analysis for the lanthanum complexes and their molar conductivity

Compound	Colour	Decomposition (°C)	Found (calculated)) (%)	Molar conductivity ($\Omega^{-1} \operatorname{mol}^{-1} \operatorname{cm}^3$)	
			С	Н	N	
I	Red	128.4-202.7	31.26 (32.07)	2.81 (3.05)	11.08 (11.22)	133
II	Yellow	117.3-173.2	32.02 (32.07)	2.73 (3.05)	11.50 (11.22)	181
Ш	Yellow	244.2-289.7	30.25 (29.53)	2.37 (2.37)	11.79 (11.93)	124
IV	Yellow	262.6-290.1	31.49 (31.56)	2.56 (2.54)	11.93 (11.84)	140

purity) and La(NO₃)₃·7H₂O (98% purity) were purchased from Fluka (Buchs, Switzerland). Picric acid (HPic) [(NO₂)₃C₆H₂OH, >98% purity) was purchased from BDH (Poole, England).

2.2. Apparatus

The percentages of carbon, hydrogen, and nitrogen were determined using a PerkinElmer 2400II elemental analyzer. Conductivity measurements were carried out in DMSO solution at 26.3 ± 0.91 °C using a Scan500 conductivity meter. IR spectra were recorded on a PerkinElmer 2000 FTIR spectrophotometer in the region of 4000–400 cm⁻¹ using the conventional KBr pellet method for solid samples. For liquid samples, i.e. PEG ligands, a thin layer of sample was applied to the surface of a KRS-5 (Thallium bromoiodide). ¹H and ¹³C NMR spectra were recorded on a Bruker 400 and 300 MHz spectrometer, respectively. Thermogravimetric analysis was performed on a PerkinElmer TGA-7 series thermal analyzer under a nitrogen atmosphere, with a heating rate of $20 \, ^{\circ}$ C/min.

Photoluminescence (PL) measurements were made at room temperature using a Jobin Yvon HR800UV system. The data were collected and processed with Labspec Version 4 software. An HeCd laser was used for excitation at 325 nm, and the emission spectra were scanned from 330 to 1000 nm. An incident laser (20 mW) was used as the excitation source. The microscope objective lens of UV40 was used to focus the laser on the sample surface. The emitted light was dispersed by a double grating monochromator (0.8 m focal length) equipped with an 1800 grove/mm holographic plane grating. Signals were detected with a Peltier-cooled CCD4 array detector.

2.3. X-ray crystallographic study

X-ray diffraction data were collected from single crystals using a Bruker APEX2 area-detector diffractometer with a graphite monochromated Mo K α radiation source and a detector distance of 5 cm. Data were processed using APEX2 software [20]. The collected data were reduced using the SAINT program and the empirical absorption corrections were applied using the SADABS program [20]. The structures of **I**, **III**, and **IV** were solved by direct methods and refined by XL command with the full-matrix least-squares method on F^2_{obs} using the SHELXTL program [21]. Meanwhile, the structure of **II** was solved using similar methods and refined using XH command. Due to the very large atoms in **II**, the usual refinement XL command could not be used. 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 using SHELXTL [21] and PLATON [22].

2.4. Synthesis of the [La(Pic)₂(EO3)₂]⁺(Pic)⁻ complex, I

The preparations of the complexes were carried out as described previously [5–8]. A mixture of EO3 (0.454g, 3.0 mmol), HPic (0.917g, 4 mmol), and [La(NO₃)₃:7H₂O] (0.434g, 1 mmol) was dissolved in 30 mL acetoni-trile:methanol:water (3:3:1, v/v). The solution mixture was stirred for 5–10 min. The clear yellow solution was filtered into a 100 mL beaker. The beaker was covered with aluminum foil to enable slow evaporation at room temperature. The red crystalline complex was obtained by recrystallization from acetonitrile after 6 months with 75% yield.

hot CH₃CN, hot CH₃OH and CH₃OH. Single crystals were obtained from CH₃OH with 90% yield after 11 months.

2.6. Synthesis of the $[La(Pic)_2(OH_2)(EO4)]^+(Pic)^- \cdot H_2O$, III and $[La(Pic)_2(EO5)]^+(Pic)^-$, IV complexes

2.5. Synthesis of the [La(Pic)₂(EO3)₂]⁺(Pic)⁻ complex, II

Compounds III and IV were synthesized in a manner similar to I, except that the solution mixture was acetonitrile:methanol (3:1, v/v).

The preparation of **II** was carried out using a method similar to that used to

make I. Acetonitrile was the solvent used, followed by reflux for 10 h. Precipitate was obtained after 3 days. Yellow crystalline complex was recrystallized in CH₃CN,

For **III**, a light yellow single crystal was observed after 2 days with 80% yield, while for **IV**, a yellow single crystal was visible after 5 days with 85% yield. Both compounds were isolated and characterized.

3. Results and discussion

3.1. Preparation and spectral analysis

The elemental analysis of the lanthanum complexes is consistent with the molecular formula obtained from single-crystal X-ray diffraction (Table 1). All complexes are stable when exposed to the atmosphere and are also thermally stable. While they are almost insoluble in many common solvents, such as methanol, acetonitrile, ethyl acetate, and ethanol, they are very soluble in dimethyl sulfoxide.

The solubility of **I–IV** in common solvents is low, which made solution studies difficult and prevented the measurement of conductivity. Measurement of the molar conductance of the complexes in DMSO solution (see Table 1) indicates that the lanthanum complexes are ionic [23], suggesting that only two Pic ions are in the inner coordination sphere, whereas the third Pic ion is a counteranion.

The infrared spectra of the free PEG ligands showed broad bands stretching from ν (O–H) at 3368, 3402, and 3429 cm⁻¹ and ν (C–O–C) at 1115, 1102, and 1102 cm⁻¹ (Table 2). The stretching vibration of ν (O–H) was shifted to higher frequency (~12 cm⁻¹) for **III**; for **I**, **II**, and **IV**, in contrast, the band shifted to the lower frequency (~21, 19, and 17 cm⁻¹, respectively). This indicates the existence of free OH groups from water molecules in **III**. The OH groups in **I**, **II**, and **IV** were involved in the formation of hydrogen bonding that originated from the terminal alcoholic group. The stretching band of ν (C–O–C) was shifted toward lower frequency by about 35, 37, 31,

Table 2	
IR data of the free PEG ligands and their lanthanum complexes	

Compound	Wavenumber (cm ⁻¹)										
	v(O-H)	v(C–H) Ar	ν(C–H) Met	δ (O–H)	$v_{as}(NO_2)$	$\nu_{s}(NO_{2})$	v(C-O)	δ (C–O) Ar	ν(C-O-C)	ν(C–N)	
EO3	3368b	-	2879s	1651s	-	-	1247s	-	1115b	-	
EO4	3402b	-	2873st	1633s	-	-	1248s	-	1102b	-	
EO5	3429b	-	2874st	1650st	-	-	1249s	-	1102b	-	
I	3347b	3086w	2956m	1630st	1562s; 1551s	1370s; 1330s	1270s	1163s	1080s	936s; 795m	
II	3349b	3092w	2954s	1613st	1576s; 1540s	1367s; 1333s	1276s	1165s	1078s	937m, 795s	
Ш	3414b	3087w	2954w	1615st	1573s; 1536s	1349s; 1335s	1277s	1169s	1071s	945b; 789w	
IV	3412b	3095m	2949w	1611s	1576s; 1533s	1354s; 1342s	1278s	1167s	1064s	938s; 788s	

Note: b = broad, st = strong, s = sharp, m = medium, and w = weak, ν = stretching, δ = deformation (bending), Ar = aromatic, and Met = methylene.

Table 3

Summary of crystallographic data and refinement for the lanthanum complexes

Parameter	Compound						
	I	И	III	IV			
Formula	C ₃₀ H ₃₄ N ₉ O ₂₉ La	C ₃₀ H ₃₄ LaN ₉ O ₂₉	C ₂₆ H ₂₈ N ₉ O ₂₈ La	C ₂₈ H ₂₈ N ₉ O ₂₇ La			
Formula weight	1123.57	1123.57	1053.48	1061.50			
Temperature (K)	293(2)	100	293(2)	293(2)			
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic			
Space group	$P2_1/c$	Pn	C2/c	P2 ₁ /c			
Unit cell dimensions							
a (Å)	9.33250(10)	9.4974(2)	38.658(9)	17.9505(9)			
<i>b</i> (Å)	19.1971(3)	37.5821(7)	8.755(2)	9.0440(5)			
<i>c</i> (Å)	23.6383(3)	22.7915(4)	23.887(6)	23.5433(12)			
$\alpha = \gamma (\circ)$	90	90	90	90			
β(°)	90.4900(10)	91.8140(10)	107.890(6)	93.3540			
Volume (Å ³)	4234.81(10)	8130.9(3)	7694(3)	3815.6(3)			
Ζ	4	8	8	4			
F(000)	2264	4528	4208	2128			
Dx (g/cm ³)	1.762	1.836	1.819	1.848			
μ (mm ⁻¹)	1.123	1.169	1.227	1.236			
Crystal size (mm)	$0.38 \times 0.41 \times 0.50$	$0.50 \times 0.38 \times 0.37$	$0.50 \times 0.43 \times 0.38$	$0.20\times0.20\times0.10$			
θ range (°)	1.71-32.50	1.05-40.00	1.79-26.00	2.41-28.30			
Completeness to theta (%)	99.8	98.4	99.7	98.3			
h, k, l	-15/15, -28/30, -38/38	-17/17, -67/66, -41/41	-47/47, -10/10, -29/29	-21/23, -11/12, -30/20			
Reflections collected/unique	104,668/15,302	465,489/95,739	37,805/7540	23,165/9300			
R(int)	0.0288	0.0590	0.0181	0.0502			
Data/restraints/parameters	15,302/0/604	95,739/2/2321	7540/0/656	6916/0/586			
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0618$, w $R_2 = 0.1753$	$R_1 = 0.0767, wR_2 = 0.1292$	$R_1 = 0.0343$, w $R_2 = 0.0916$	R = 0.0682, wR = 0.1186			
R indices (all data)	$R_1 = 0.0749$, w $R_2 = 0.1998$	$R_1 = 0.1015$, w $R_2 = 0.1414$	$R_1 = 0.0372$, w $R_2 = 0.0938$	$R_1 = 0.0974$, w $R_2 = 0.1283$			
Goodness of fit	1.078	1.091	1.103	1.113			
Largest difference peak and hole, $e(\acute{A}^{-3})$	4.086 and -2.269	3.492 and -2.822	0.862 and -0.589	0.994 and -2.278			

and 38 cm⁻¹, indicating that all the ether oxygen atoms of the PEG ligands were involved in the coordination of the La³⁺ ion.

The absorption band due to the ν (C–H) symmetric stretching at 2879–2874 cm⁻¹ was significantly shifted to the higher wavelength, namely 2954–2949 cm⁻¹, indicating that the PEG ligands rearranged to the cyclic conformation [5–8,24]. The stretching bands from ν_s (NO₂) were split into two bands, which indicates that the Pic anion was coordinated to La³⁺ through the phenolic oxygen and the oxygen of one *ortho*-nitro group, forming a bidentate ligand [5–8,25–27]. The absorption band assigned to ν (C–N) at 920–940 cm⁻¹ was shifted to 936–945 cm⁻¹, indicating that the coordinated Pic anion affected the C–N bonds. In addition, the out-of-plane due to the phenolic bending vibration on the free HPic molecule at 1155 cm⁻¹ was shifted to 1163, 1165, 1169, and 1167 cm⁻¹ for **I–IV**, respectively. This suggests that the hydrogen atom of the phenolic group in the Pic anion was substituted by La³⁺ [28–30].

3.2. X-ray studies

The coordination of La³⁺ with the PEG ligands in the presence of Pic anion involved a coordination number of 10. All of the complexes crystallized in a monoclinic system with different space groups, i.e. P2₁/c (I and IV), Pn (II), and C2/c (III) (Table 3). Molecular structures of the complexes reported here are unique because of the different inner coordination spheres and outer spheres. As a result, the lanthanum complexes have different crystal structures. In virtually all cases the change in cell type or crystal system are due to the insertion of a specific ligand or guest, as well as the changing of the central metal ion [31]. The differences in space group of these complexes are not due to the differences in chain length of the PEG ligands, but are instead governed by the point symmetry and the crystal system. The space group is determined by the chemical moiety and the orientation of the atoms around each point of a Bravais lattice [32]. The low symmetry for the primitive unit cell and centered unit cell were observed for space groups $P2_1/c$ and C2/c with moieties of symmetry 2/m at Wyckoff position *a* in the coordinates of equivalent positions (0, 0, 0), compared to space group Pn with moiety of symmetry *m* at Wyckoff positions *n*. The space group of $P2_1/c$ is symmorphic, whereas C2/c is non-symmorphic [32].

Compound I forms on slow evaporation of the solution within a relatively short time (6 months), whereas compound II crystallizes on slow evaporation after a long time (11 months), suggesting that the latter is thermodynamically more stable than compound I. Consistent with this idea, compound II has higher density (1.836 g/cm³ vs. 1.762 g/cm³ for compound I), thus suggesting more efficient packing. The calculated density of I is the smallest. Meanwhile the calculated density of II–IV are almost similar, namely 1.836, 1.819, and 1.848 g/cm³, respectively (Table 3).

As the polyethylene chain length of the PEG ligand increases, the number of oxygen donor atoms of the PEG ligand also increases, leading to a structural change to accommodate the largest ionic radius of La^{3+} in the ring PEG ligand to form a stable complex. Nevertheless, the coordination number of the complex does not depend on the PEG ligand: all of the lanthanum complexes examined here maintain a coordination number of 10.

All of the complexes studied here are mononuclear and the PEG ligands are coordinated to La^{3+} in the bi-, tetra-, penta-, and hexadentate modes. This pattern may be due to the presence of a second large ligand, i.e. the picrate anion, which coordinates to La^{3+} in a bidentate chelating mode, making it difficult to form a polymer or a dimer. There is an uncoordinated picrate anion in the lattice as a counteranion. The results also indicate that the picrate ligand maintains a coordination number of 10 in the lanthanum complexes. This contrasts with the La–PEG–chloride and La–PEG–nitrate complexes, where the coordination polyhedron is inconsistent with a coordination number of 10, but instead a coordination number of 9–12 [1,9–18].

Both polymorphs of **I** and **II** have similar molecular structures, even though the crystals differ in space group, unit cell dimensions, unit cell volume, and number of molecules in one unit cell (Z) (Table 3). Meanwhile for the $[Ce(Pic)(NO_3)(H_2O)_2(EO3)]^+(Pic)^-$

complexes isolated from the same preparation we observed slight difference in the crystal parameters, significant difference was in the coordination of the Pic anion one was monodentate and the other one was bidentate [33]. It may be that the method of preparation, the central metal ion, the type of solvent (protic or aprotic), and length of the complexation reaction affect the formation of complex. In this way, the use of aprotic solvents seems to favor the formation of compounds in hydrophobic conformations.

The La³⁺ ion can form a sandwich complex with short ether linkages and four oxygen donor atoms, which is the situation with the EO3 ligand. In our study, the La³⁺ ion was coordinated to two EO3 ligands and two Pic anions and was neutralized by one Pic anion as counteranion. One of the EO3 ligands was coordinated to La³⁺ through all four oxygen donor atoms in a tetradentate manner; the second EO3 ligand was chelated to La³⁺ in a bidentate manner via the terminal alcoholic oxygen (O5) and the adjacent etheric oxygen (O6) atoms, leaving the remaining chain like a hanging tail (Fig. 1(a) and (b)). Both the EO3 ligands surround the La1 atom with their side chains pointing directly in each other's direction (Fig. 2(a)). Positioned across from each other, the two Pic anions were coordinated to La^{3+} in a bidentate manner, and the inner coordination sphere had a dihedral angle of $83.5(2)^{\circ}$ for I. This unusual sandwich complexation involving an EO3 ligand has also been observed in the complexes [LaCl(OH₂)(EO3)₂]Cl₂ [15] and [La(ClO₄)₃(EO3)₂]·xH₂O [19].

Supramolecular materials that contain two or more components linked weakly by non-covalent interactions exhibit remarkable structural adaptability [31]. Compound **II** was shown to have greater chances of forming a supramolecular complex through abundant non-covalent interactions, namely intra- and intermolecular hydrogen bonds and also π - π interactions. Formation of polymeric chain complex was not observed. One asymmetric unit of the monoclinic structure comprises four crystallographically independent molecules A–D, whereas the asymmetric unit in **I** contains only one molecule (Fig. 1(a) and (b)). Changes in crystal packing and complex structure may take place even without a



Fig. 1. Molecular structure of compounds I (a), II (b), III (c), and IV (d) with the atomic numbering schemes of 30, 80, 50, and 50%, respectively. All the hydrogen atoms have been omitted for clarity.





Fig. 1. (Continued).

change in composition [31]. The aromatic ring of the bidentate Pic anion between (C13–C18) and (C19–C24) formed dihedral angles of 77.7(2)°, 80.2(3)°, 75.7(3)°, and 80.1(2)° in the structures of A–D, respectively. Both aromatic rings of the coordinated Pic anion were planar with maximum deviations, respectively, on the order of -0.046(5), -0.056(5), -0.030(6), and -0.035(5) Å for the C19A, C19B, C17C, and C23D atoms.

The lack of saturation of the La-EO4 inner coordination sphere enables easy reactions, either with a donor solvent or with a nucleophilic impurity such as water, which ultimately leads to a poorly volatile or non-volatile hydroxo-complex. The fact that the inner coordination sphere in **III** is less crowded, allows the coordinated water molecule and a solvated water molecule to participate in complex formation. This coordination results from the favorable matching between the coordinated as an inner-sphere ligand. Thus, the outer sphere of the complex is obtained and the necessary coordination number is reached with one water molecule. The inner coordination sphere of $[La(Pic)_2(OH_2)(EO4)]^+$ is hydrophilic. To complete the formation of **III**, the La³⁺ ion was coordinated to the EO4 ligand in a pentadentate mode, with the two picrates coordinating in a bidentate manner and one water molecule also participating (Fig. 1(c)). The coordinated water molecule positioned itself centrally between O1 and O5 of the terminal alcoholic groups (Fig. 2(b)). Complex formation is easier with long-chain PEG ligands than with short-chain ones. The aromatic part of the coordinated Pic anion, i.e. the aromatic rings of (C9–C14) and (C15–C20), was planar and showed a maximum deviation of 0.022(4) Å for the C9 atom. Both the aromatic rings of the coordinated Pic anion formed a dihedral angle of 87.6(2)°. This is in contrast to **I**, **II** and **IV** where water molecules were not involved in **III**. This may reflect the overlapping orbital between the central metal ion and the PEG ligand, which reduced the space available in these complexes.

As expected, the PEG ligand has a profound effect on the inner coordination sphere in complex formation. In contrast to the five donor atoms of EO4, the six donor atoms of EO5 formed a complex with a hydrophobic environment (**IV**) such as **I** and **II**. La³⁺ was chelated to ten oxygen donor atoms from the EO5 ligand in a



Fig. 2. The inner coordination spheres of I (a), III (b), and IV (c).

hexadentate manner and the two picrates in a bidentate manner, and the positive charge was balanced by one Pic as counteranion (Fig. 1(d)). Both aromatic rings of the coordinated Pic anions were planar, with a maximum deviation of 0.037(5)Å for C11 atom and forming a dihedral angle of $85.7(3)^{\circ}$ in the opposite direction. The conformation in the inner coordination sphere of [La(Pic)₂(EO5)]⁺ (Fig. 2(c)) is similar to that of the 18-crown-6 complexes [1,5–8,17]. The acyclic PEG ligand was coordinated to La³⁺ in **I–IV**, which exhibited pseudo-cyclic behavior (Fig. 2(a–c)) [5–7,9–19]. The flexibility of the PEG ligand and the characteristics of its coordination with La³⁺ make it very suitable for the formation of complexes.

All of the complexes had a bicapped square antiprismatic geometry around La³⁺. This geometry was slightly distorted due to the bond angle nearly equal to 180° for pairs of etheric oxygens at the top in the capping position, i.e. (O3, O5), (O2, O5), (O2, O5), and (O3, O6) atoms for **I–IV**, respectively. The lanthanum complexes showed point symmetry C_{2h} with two-element symmetries, i.e. C_2 and σ_h . This symmetry is typical of the monoclinic crystal system [32].

Increasing the number of oxygen donor atoms in PEG slightly increased the average La $-O_{PEG}$ bond length by 2.608(3), 2.610(2), and 2.623(4)Å for I, III and IV, respectively (Table 4). In contrast, the average bond lengths in II of La-O_{EO3A}, La-O_{EO3B}, La-O_{EO3C}, and La-O_{EO3D} were approximately 2.608(4), 2.608(4), 2.611(5), and 2.606(5)Å, respectively. This bond was significantly longer than those reported in the complexes $[Pr(Pic)_2(EO5)]^+(Pic)^- [2.557(4) Å]$ [5] and $[Ho(Pic)_2(EO5)]^+(Pic)^-$ [2.432(3)Å] [7]. The La–O_{PEG} bonds in the inner coordination sphere were of two types: La-O_{alcoholic} and La-O_{etheric}. As expected, the La-O_{alcoholic} bond lengths were shorter than the La-O_{etheric} bond lengths (Table 4). The average La-O_{alcoholic} bond length in I, III, and IV was 2.557(3), 2.588(3), and 2.594(4)Å. Meanwhile, the average La-O_{etheric} bond length in these three compounds was 2.659(3), 2.625(2), and 2.637(4)Å. In IV, the difference of 0.045 Å between the average $La-O_{etheric}$ and La-O_{alcoholic} bond lengths was similar to the corresponding difference in the chloride complex of [LaCl₂(OH₂)(EO5)]Cl·H₂O, reported to be 0.042 Å [17]. The difference in La-O_{etheric} and La-O_{alcoholic} bond lengths for I and III, ~0.11-0.12 Å, was greater than in IV, but similar to that reported in [LaCl₃(EO4)]₂ [14] and [LaCl(OH₂)(EO3)₂]Cl₂ [15]. However, the difference between the average La-O_{etheric} and La-O_{alcoholic} bond lengths in the three La-PEG complexes was shorter by 0.106, 0127, 0.104, and 0.125 Å, respectively, compared to the difference in the thiocyanate and nitrate complexes in the $[La(NCS)_3(OH_2)_2(EO3)].0.5(H_2O)$, [La(NCS)₃(OH₂)(EO4)], [La(NCS)₃(EO5)] [1], and [La(NO₃)₃(EO4)] [18]. Thus, bidentate ligands such as Pic and NO₃⁻ coordinate La³⁺ more tightly than monodentate ligands such as Cl⁻ and SCN⁻.

The average La–O_{phenolic} bond lengths were the shortest, i.e. 2.426(3), 2.410(4), 2.431(2), and 2.470(4)Å for **I–IV**, respectively. The shortness of these bond length is caused by the higher electron density of the phenolic oxygen of the Pic anion [6–7,29]. However, the average La–O_{nitro} bond length was the longest, growing longer from **I** to **IV**: 2.741(4), 2.745(4), 2.802(3), and 2.686(4)Å. The same trend was observed in the analogous complexes [Pr(Pic)₂(EO5)]⁺(Pic)⁻ [2.582(4)Å] [5], [Sm(Pic)₂(EO5)]⁺(Pic)⁻ [2.519(3)Å] [7], and [Eu(Pic)₂(EO5)]⁺(Pic)⁻ [2.496(2)Å] [6]. The La–O_{nitro} bond length was the longest, reflecting the fact that the electron density of the *ortho*-nitro group is lower than that of the phenolic group of the Pic anion.

Along the chain of the acyclic PEG ligand, the bond lengths of C–C and C–O, and the bond angles in C–O–C and O–C–C were unchanged and were comparable to the values seen in the other La–PEG complexes. For **I–IV**, bond angles between the adjacent terminal alcoholic groups in the complexes were significantly reduced, i.e. $145.7(1)^{\circ}$, $148.0(1)^{\circ}$, $123.8(8)^{\circ}$, and $66.4(1)^{\circ}$, respectively (Table 4). However, the O–La–O bond angle between the adjacent oxygen atoms in the inner coordination sphere of all of the complexes was approximately the same, slightly larger than 60° . The O6-La–O1 bond angle in **IV** was quite close to the other bond angles because its inner coordination sphere was more symmetrical than that of complexes **I–III**.

One particularity of the coordinated Pic anion structure is the shortening of the C–O_{phenolic} bonds relative to these bonds in the acid structure of 1.322(3)Å [34]. The average C–O_{phenolic} bond lengths of the coordinated Pic anion were in the order 1.270(6),

Table 4

Bond length (Å), bond angle, and torsion angle (°) of all the complexes

Bond	Compound							
	I	II.,	III	IV				
Length (Å)								
La1-01	2.570(3)	2.563(4)	2.591(3)	2.539(4)				
La1-02	2.646(3)	2.686(5)	2.642(2)	2.659(4)				
La1-03	2.657(3)	2.640(4)	2.636(2)	2.641(4)				
La1-04	2.563(3)	2.558(4)	2.598(3)	2.656(4)				
La1-05	2.538(3)	2.557(4)	2.584(2)	2.592(4)				
La1-06	2.675(3)	2.644(4)	_	2.649(4)				
La1-Onbenolic	2.418(3)	2.423(4)	2.429(2)	2.471(4)				
La1-O _{phenolic}	2.434(3)	2.396(4)	2.433(2)	2.468(4)				
La1-O _{nitro}	2.744(4)	2.703(3)	2.709(3)	2.708(4)				
La1-O _{nitro}	2.737(3)	2.786(4)	2.894(3)	2.667(4)				
La1–Owater	_	_	2.537(2)	_				
Average C–O	1.431(6)	1.436(7)	1.442(8)	1.432(7)				
Average C–C	1.485(8)	1.511(9)	1.449(8)	1.439(10				
	(-)							
Angle (°)								
01-La1-02	62.3(9)	59.5(1)	60.3(8)	62.4(1)				
02-La1-03	59.6(9)	59.2(1)	60.8(8)	61.0(1)				
03-La1-04	60.2(9)	62.4(1)	61.0(8)	61.1(1)				
04-La1-05	-	-	61.7(8)	61.3(1)				
05-La1-06	61.2(1)	62.9(1)	-	62.6(1)				
04-La1-01	145.7(1)	148.0(1)	-	-				
05-La1-01	-	-	123.8(8)	-				
06-La1-01	-	-	-	66.4(1)				
Average C-O-C	112.4(3)	111.4(5)	113.1(4)	114.3(5)				
Average O-C-C	107.7(6)	107.3(5)	108.0(6)	110.3(6)				
Torsion angle (°)								
01-C1-C2-02	54.0(5)	-51.6(8)	-54.1(5)	-51.6(8)				
02-C3-C4-03	-53.5(5)	48.7(6)	56.7(4)	-31.8(2)				
03-C5-C6-04	49.1(8)	-53.4(5)	-50.4(7)	55.9(7)				
04-C7A-C8A-05	_	_	51.7(12)	-				
O4-C7B-C8B-O5	-	_	-58.9(11)	_				
04-C5-C6-05	_	_	_	-57.2(6)				
05-C5-C6-O6	_	_	_	-54.5(7)				
Average O-C-C-O	52.2(6)	51.2(6)	54.4(8)	50.2(6)				
Average C–O–C–C	173.6(4)	169(5)	161.2(6)	152.6(5)				
The second EO3 ligand								
Average C-O	1.427(5)	1.419(7)	-	-				
Average C-C	1.488(2)	1.522(9)	-	-				
Average C-O-C	112.4(7)	114.3(5)	-	-				
Average O-C-C	109.2(6)	109.5(5)	-	-				
Average O-C-C-O	59.1(5)	59.4(7)	-	-				
Average C-O-C-C	132.0(11)	139.5(6)	-	-				

Note: (*) for molecular structure of A in II.

1.268(4), and 1.264(6) Å for **I**, **III**, and **IV**. This is due to the replacement of the hydrogen atom by La³⁺ and the increase in the π -bond due to the greater electron density of the phenolic oxygen. In **II**, the C–O_{phenolic} bond lengths of the coordinated Pic anion, i.e. 1.273(6), 1.331(9), 1.345(10), and 1.271(7) Å were longer than the C–O_{phenolic} bond lengths in the Pic counteranion, which measured 1.212(8), 1.319(8), 1.300(7), and 1.215(8) Å in the structures of A–D.

The C and N atoms of the Pic anions were coplanar with a maximum deviation of 0.117(8) Å for N8 (I); -0.107(4), -0.122(7), -0.133(6), -0.130(7), -0.105(7), and 0.120(7) Å for N1B, N2C, N5A, N6B, N4D, and N7A (II); 0.121(4) Å for N2 (III); -0.140(6) and 0.119(5) Å for N1 and N5 (IV), respectively. The *para*-nitro groups of all the Pic anions were coplanar with their aromatic ring. The distances from the oxygen of the phenolic group to the adjacent coordinated oxygen atoms of the *ortho*-nitro groups in the coordinated Pic anion (2.650–2.662 Å) were significantly shorter than those between the free oxygen atoms of the *ortho*-nitro groups of the Pic anion (2.835–3.029 Å). In contrast, the free and coordinated forms of the Pic counteranion showed similar distances between the oxygen of the phenolic group atoms of the *ortho*-nitro groups of the *ortho*-nitro groups, i.e. 2.706 and 2.725 Å, respectively.

The acyclic polyether stand of the molecule displayed a series of anti and gauche torsion angles for C–O and C–C bonds. In I, the average O-C-C-O torsion angle was 52.2(6)° and the first EO3 ligand showed a geometric conformational pattern of g⁺ g⁻ g⁺ in a tetradentate mode. However, the O-C-C-O torsion angle of the second EO3 ligand in a bidentate mode took on a different conformation, namely g⁻ g⁺ g⁻ or g⁺, due to the disorder in the positions of the C7 and C8 atoms. For II, the structures A-D showed the following average O-C-C-O torsion angles and conformation patterns in the first EO3 ligand in a tetradentate mode: $g^- g^+ g^- [51.3(6)^\circ]$, $g^- g^+ g^- [51.5(6)^\circ]$, $g^+ g^- g^+ [54.1(6)^\circ]$, and $g^+ g^- g^+ [55.2(7)^\circ]$, respectively. In contrast, the average O-C-C-O torsion angles for the second EO3 ligand in a bidentate mode for structures A-D was larger, and the geometric conformational patterns different, compared to the first EO3 ligand: $g^+ g^+ g^+ [59.4(7)^\circ]$, $g^+ g^+ g^+ [61.7(7)^\circ]$, $g^ g^ g^-$ [61.4(8)°], and $g^ g^ g^-$ [61.5(7)°]. In III, the average O-C-C-O torsion angle and conformation pattern of g⁻ g⁺ g⁻ g⁺ or g⁻ is due to the disorder in the position of the C7 and C8 atoms. In **IV**, the O–C–C–O torsion angle with conformation patterns of g⁻ g⁻ g⁺ g⁻ g⁻ occurred. The O–C–C–O torsion angles for overall compounds showed minor differences less than 60° (Table 4). However,

Table 5

Geometrical parameter of intra- and intermolecular hydrogen bonding involved in supramolecular construction of the lanthanum complexes

D−H···A	D–H (Å)	$H{\cdot}{\cdot}{\cdot}A({\rm \AA})$	D···A (Å)	D−H· · · A (°)
(a) I				
04–H4C···07 ^a	0.850(3)	1.810	2.639(5)	168(6)
01-H1C···025	0.840(5)	1.800(5)	2.629(6)	165(5)
05–H5C···08 ⁱ	0.840(5)	1.87(5)	2.706(6)	175(9)
08–H8C···024 ⁿ	0.850(6)	2.480(7)	3.116(10)	132(8)
08–H8C···025 ⁿ	0.850(6)	2.080(8)	2.861(7)	152(8)
C1–H1B···O10 ^a	0.970	2.490	3.043(7)	116
C6–H6A···O26	0.970	2.420	3.151(11)	132
C4-H4A011ª	0.970	2.590	3.153(7)	117
C9-H9A···012	0.970	2.470	3.216(11)	133
	0.910	1.040	2 (5(7)	170 1
	0.819	1.842	2.656(7)	1/3.1
	0.820	2.405	3.217(0)	170.4
$04A - H4AC \cdot 027C$	0.820	1 802	2.389(0)	104.9
08A-H8AC05A ⁱⁱⁱ	0.820	1.883	2.698(6)	107.2
01B-H1BC···08B ⁱ	0.821	2 279	3 090(6)	169.3
O1B-H1BC···O27B ^{iv}	0.821	2.315	2.589(6)	100.2
O4B-H4BC···O7B ^a	0.820	1.856	2.670(7)	170.9
O5B-H5BC···O8B ⁱ	0.821	1.914	2.722(7)	167.8
O8B-H8BC···O5B ⁱⁱⁱ	0.819	1.924	2.722(7)	164.5
01C-H1CC···07Ca	0.820	1.786	2.600(7)	171.6
O4C−H4CC···O8C ⁱⁱⁱ	0.819	2.444	3.252(8)	168.9
04C−H4CC···027A ^v	0.819	2.288	2.630(7)	105.7
05C−H5CC···08C ⁱⁱⁱ	0.819	1.995	2.800(8)	167.8
08C−H8CC···05C ⁱ	0.820	1.984	2.800(8)	173.5
01D−H1DC···08D ⁱⁱⁱ	0.821	2.366	3.175(7)	168.6
O1D−H1DC···O27D ^v	0.821	2.305	2.627(6)	104.0
04D-H4DC···07D ^a	0.821	1.785	2.599(6)	170.6
O5D−H5DC···O8D ^m	0.821	2.000	2.808(6)	168.0
08D-H8DC···05D ⁴	0.820	1.993	2.808(6)	1/2./
CIIB-HIID····OI9D ^{**}	0.970	2.533	3.227(10)	128.5
CIER LIER OI2R	0.970	2.539	3.122(11)	101.6
C15B_H15B_01/Ba	0.930	2.400	2.800(13) 2.772(0)	101.0
C15C_H15C09Cª	0.930	2,300	2.772(9)	104.7
C2A_H2AB015D	0.971	2.500	2.034(3) 3.251(9)	146.0
$C21D-H21D\cdots O18D^{a}$	0.930	2.315	2.642(7)	100.1
C6A-H6AA···O10A ^a	0.972	2.501	3.036(6)	114.6
C27A–H27A····O24A ^a	0.931	2.322	2.662(10)	101.0
C27C-H27C···023C ^a	0.931	2.322	2.653(10)	100.5
C6A-H6AB···O24C ⁱⁱ	0.969	2.452	3.155(8)	129.2
C29B−H29B····O23B ^a	0.931	2.304	2.634(9)	100.3
C8A–H8AA···O12C ⁱⁱ	0.971	2.575	3.177(8)	120.3
C9A–H9AB···O12A ^a	0.971	2.552	3.300(8)	133.9
C1B–H1BA O11B ^a	0.970	2.566	3.104(9)	115.0
C1B–H1BA···O21C ¹	0.970	2.593	3.220(7)	122.5
C1B−H1BB····O29B ^{IV}	0.969	2.533	3.189(10)	125.0
C4B−H4BB····O10B ^a	0.970	2.495	3.062(7)	117.2
C5B-H5BB····O8B"	0.970	2.521	3.206(7)	127.6
COB-HOBA····UI3B···	0.970	2.304	3.297(8)	101.4
C7B_H7BB_011Ba	0.909	2.435	3.104(0)	115 5
C9B_H9BBO10Bª	0.970	2.330	3.061(8)	118.3
C3C-H3CA016Ca	0.969	2,510	3,099(7)	110.5
C6C-H6CB023AV	0.971	2.468	3 137(10)	125.9
C8C-H8CB019B ^{viii}	0.972	2.589	3 146(11)	116.6
C1D-H1DA····O24D ^v	0.970	2.519	3.101(10)	118.5
C4D-H4DA···O10D ^a	0.971	2.408	2.983(8)	117.5
C5D-H5DA···O14A ^a	0.971	2.377	3.200(10)	142.1
C5D-H5DB···O10D ^a	0.970	2.479	3.001(11)	114.0
C5D-H5DB····O13D ⁱ	0.970	2.259	3.151(13)	152.5
C6D-H6DA···O12D ⁱ	0.970	2.476	3.241(10)	135.6
C9D−H9DA···O10D ^a	0.970	2.575	3.140(9)	117.3
(c) III				
01-H1C···O2W ⁱ	0.850	2.448	2.798(10)	105.5
01-H1C···09 ⁱⁱ	0.850	2.237	2.997(5)	148.9
05-H5C···020 ⁱ	0.850	1.938	2.709(4)	150.2
05-H5C···026A ⁱ	0.850	2.478	3.067(17)	127.2
$05-H5C\cdots O26B^i$	0.850	2.328	2.94(2)	129.5
02W−H12W···02W ⁱⁱⁱ	0.851	1.900	2.465(12)	122.5
02W-H12W010 ^{iv}	0.851	2.429	2.833(10)	109.0

Table 5 (Continued)

D)−H···A	D–H (Å)	$H{\cdots}A({\mathring{A}})$	$D{\cdots}A({\mathring{A}})$	$D-H\cdots A(^{\circ})$
	$01W\text{-}H21W\text{-}\cdot020^{i}$	0.850	2.236	2.633(4)	108.5
	$O1W-H21W\cdots O21A^{i}$	0.850	2.300	2.84(3)	121.7
	$O1W-H21W\cdots O21B^{i}$	0.850	2.254	2.92(3)	135.6
	O2W−H22W···O18 ^v	0.849	2.331	3.061(11)	144.4
	C5−H5B···O23 ^{vi}	0.970	2.591	3.240(6)	124.4
	C8A–H8A···O26A ⁱ	0.972	2.587	3.21(2)	122.2
	C8A–H8A···O26B ⁱ	0.972	2.267	2.97(3)	128.8
	C13−H13A····O19B ^{vi}	0.930	2.530	3.16(3)	124.9
	C19–H19A· · · O12A ^{viii}	0.930	2.569	3.08(3)	114.8
	C19−H19A····O12B ^{viii}	0.930	2.569	3.22(3)	127.7
	C23−H23A· · ·O16A ^{ix}	0.930	2.434	3.27(3)	150.3
	$C8A-H81\cdots O26B^i$	0.843	2.519	2.97(3)	114.9
(d) IV				
	01-H1C···021 ^a	0.931	1.767	2.669(6)	162.3
	01–H1C···027 ^a	0.931	2.346	2.884(7)	116.5
	O6-H6C···O21 ^a	0.929	2.087	2.778(6)	130.0
	C1−H1A···O27 ^a	0.970	2.472	3.092(10)	121.5
	C5−H5A···O7 ^a	0.971	2.550	3.091(8)	115.3
	C7−H7B···O25 ⁱ	0.969	2.552	3.167(8)	121.3
	C8−H8B···O8ª	0.970	2.552	3.213(6)	125.4
	C15-H15A···O16 ⁱⁱ	0.929	2.465	3.039(7)	120.1
	$C25\text{-}H25A \cdots O11^{\text{iii}}$	0.929	2.451	3.059(8)	123.0

 $\begin{array}{l} \mathsf{D}= \mathsf{donor} \text{ and } \mathsf{A}= \mathsf{acceptor.} (a) \text{ Symmetry codes: } (i) 1+x, y, z; (ii) x-1, y, z; (iii) -x, 2-y, 1-z; (b) \text{ symmetry codes: } (i) -1+x, y, z; (ii) -1/2+x, 1-y, -1/2+z; (iii) 1+x, y, z; (iv) -1+x, y, -1+z; (vi) 1/2+x, 1-y, -1/2+z; (vii) x, y, -1+z; (viii) 1/2+x, 2-y, 1/2+z; (c) \text{ symmetry codes: } (i) x, -1+y, z; (ii) -x, -y, 1-z; (i) -x, y, 1/2-z; (iv) -x, 1-y, 1-z; (v) x, 1+y, z; (vi) x, 1-y, 1/2+z; (vii) x, -y, 1/2+z; (vii) x, 1-y, -1/2+z; (vii) x, 1/2-y, -1/2+z; (ii) x, -1/2-y, 1/2+z; (iii) 1-x, 1/2+y, 1/2-z. \end{array}$

^a Intramolecular hydrogen bonding.

the O–C–C–O torsion angle patterns in **IV** were different from those measured in the other derivative complexes involving Pr [5], Eu [6] and Sm, Dy, and Ho [7]. Among the different lanthanide ion complexes, the inner coordination sphere and geometrical arrangement also influence the torsion angle sequence [7,8,17].

All of the C–O–C–C torsion angles were *anti*, except for C8–O6–C9–C10, and they measured $58.7(6)^{\circ}$, $60.8(6)^{\circ}$, $-63.4(8)^{\circ}$, and $-65.1(7)^{\circ}$, respectively, for structures A–D. The angle was very close to the *gauche* (g) conformation in **II**. For **I**, **III**, and **IV**, the torsion angles C8A–O6-C9-C10 [$-62.5(16)^{\circ}$], C8B-O6-C9-C10 [$-92.6(12)^{\circ}$], C6–O4–C7B-C8B [$-101.1(9)^{\circ}$], and C8–O5-C9-C10 [$-87.5(6)^{\circ}$] were not *anti* and were close to the g⁻ conformation, respectively.

The supramolecular architectures of the complexes were built in different ways. In general, hydrogen bonding is possible with highly electronegative atoms such as oxygen, nitrogen, and fluorine, with the limitation that the distance between these atoms and hydrogen must be less than 2.8 Å. In C–H \cdots O hydrogen bonding, the C \cdots O bond length must have a distance less than 3.3 Å (Table 5(a-d)). In I, despite the disorder in the positions of C7 and C8 atoms in the second EO3 ligand, there was one strong intramolecular O4-H4C...O7 hydrogen bond interaction, with the O4-H4C···O7 angle close to 170°. Generally, the strength of the hydrogen bond is greatest when the D–H···A angle is 180°, where D = donor atom and A = acceptor atom [35,36]. In addition, the nitro group in I accepted a few weak intermolecular O-H···O and C-H···O hydrogen bonds with D-H···A angles of 132–152°. Some weak intramolecular C-H···O contacts were also observed, but they seemed to be insignificant and more or less repulsive in nature (Table 5(a)). The dominant packing feature of both polymorphs of I and II was hydrogen bonding between the terminal alcohol groups of the EO3 ligand and the oxygen atoms of the Pic anion and the bidentate EO3 ligand. For I and II, the intra- and intermolecular hydrogen bonding stabilized the crystal packing of the complexes in the one-dimensional (1D) network with a symmetry direction of [100] parallel to the *bc* plane along the *b*-axis (Fig. 3(a) and (b)). In **II**, only one terminal alcohol group was involved in the intramolecular hydrogen bonding, i.e. 01A-H1AC···O7A [1.842 Å], O4B-H4BC···O7B [1.856 Å], O1C-H1CC···O7C [1.786 Å], and O4D-H4DC···O7D [1.785 Å] in the structures A–D, respectively (Table 5(b)).

The number of hydrogen bonds formed in the complex was greater when water molecules were involved either in the inner or outer coordination spheres forming the intermolecular hydrogen bonding in 1D chain along symmetry direction of [0 0 1] (Table 5(c)). The crystal structure consisted of a layer of molecules parallel to the *bc* plane. The disordered positions of the C7, C8, O12, O16, O19, O21, O25, and O26 atoms in **III** were stabilized by intermolecu-

lar O-H···O and C-H···O hydrogen bonds along the *b*-axis. Also observed in **III** were the four bifurcated and one trifurcated hydrogen bond along the long *b*-axis with channels occupied by water molecules. The bifurcated and trifurcated hydrogen bonds required a very high electron density in the acceptors or at least locally in the hydrogen bond itself [36]. The solvated water molecules linked together between two layers in the stacks of the molecules (Fig. 3(c)). One strong intramolecular O1-H1C···O21 hydrogen bond was observed in **IV** with a distance of 1.767 Å and the O1-H1C···O21 angle of 162.3° (Table 5(d)). Two molecules in adjacent layers of **IV** were linked by two hydrogen bonds, i.e. C25-H25A···O11-N2 [2.451 Å] and C1-H1A···O17-N6 [2.582 Å] (Fig. 3(d)). For **IV**, the intra- and intermolecular hydrogen bonding stabilized the crystal



Fig. 3. 1D network of compounds I (a), II (b), III (c), and IV (d) view down the b-axis. Hydrogen bonds are shown in dashed lines (---).



Fig. 3. (Continued).

packing of the complex in the 1D chains with a symmetry direction of [001].

In **II**, van der Waals interactions were observed as follows: C1A-H1AA···Cg5 [2.799 Å], C5B-H5BA···Cg6 [2.635 Å], C1C-H1CB···Cg3 [3.026 Å], and C6D-H6DB···Cg8 [2.866 Å] with symmetry code *x*, *y*, and *z*, where Cg5 corresponds to (C19A–C24A), Cg6 to (C19B–C24B), Cg3 to (C13C–C18C), and Cg8 to (C19D–C24D). For **IV**, a van der Waals interaction was observed between C3-H3A···Cg2 [3.242 Å] with symmetry code -x, -y, and -z and Cg2 = aromatic ring of (C17–C22). The presence of O···O interactions in the complexes, with distances ranging from 2.463 to 2.908 Å, was taken to indicate hydrogen bonding situations. In addition, a long contact length of N···O in the range of 2.876–2.945 Å was observed for **II–IV**. Based

on our studies in one asymmetric unit, the Pic counteranion occupied different positions in the complexes, reflecting the influence of π - π interactions. The stacking layer between aromatic Pic rings caused π - π interactions in the absence of the coplanarity of all three nitro groups with their aromatic ring. Similar interactions have been reported in picrate complexes with other metal ions [37].

In **I**, the aromatic ring of the Pic counteranion was exactly coplanar and packed in a face-to-face orientation with the aromatic ring of the coordinated Pic anion; the centroids of the two rings were separated by 3.825 Å (Fig. 3(a)). The Pic counteranion was not coplanar with the inner coordination sphere of $[\text{La}(\text{EO3})_2(\text{Pic})_2]^+$ in **II**. Thus, it was separated by a long distance from the inner coordi-

	8	1				
Compound	δ[OH]	$\delta[C(1)H_2-C(2)]$	δ [C(1)–C(2)H ₂]	$\delta[C(3)H_2-C(3)H_2]$	$\delta[H_2O]$	$\delta[Ar]$
EO3	4.557	3.417	3.486	3.520	-	-
EO4	4.425	3.430	3.494	3.516	-	-
E05	4.142	3.414	3.491	3.510	-	-
I	4.567	3.414	3.481	3.527	-	8.592
II	3.813	3.411	3.486	3.512	-	8.589
III	4.510	3.430	3.477	3.518	3.340	8.597
IV	4.560	3.414	3.480	3.514	-	8.593

 Table 6

 ¹H NMR data of the free PEG ligands and their complexes at 25 °C

nation sphere and the distance between the free and coordinated Pic rings was 11.059 Å. In I and II, the adjacent aromatic rings of the Pic counteranion and the coordinated Pic anion were separated by 3.851(3)Å with symmetry codes x, y, and z and -1 + x, y, -1 + z, respectively, with stacking along the *a*-axis. In **III** and **IV**, the aromatic ring of the Pic counteranion was coplanar and positioned relative to the aromatic ring of the coordinated Pic anion with a centroid distance of 4.207 and 5.449 Å, respectively. In **IV**, the oxygen of the phenolic group from the Pic counteranion was slightly coplanar with the La^{3+} and situated at a distance of 4.280 Å from the ion. The π - π interaction in III was longer than those found in I, II, and IV with a centroid separation of 4.189(3)Å; in addition, a symmetry code x, y, and z stack along the *a*-axis was observed. The crystal structure of **IV** was also stabilized by $\pi - \pi$ interactions of 4.134(3)Å along the *a*-axis and symmetry code x, -1 + y, z. These values were longer than those found in the [La(Pic)₃L] complex of 3.774 and 4.019 Å [38], where L = N-phenyl-2-{2'-[(phenyl-ethyl-carbamoyl)methoxy]-biphenyl-2-yloxy}-N-ethyl-acetamide.

3.3. ¹H and ¹³C NMR studies

The ¹H NMR study on the lanthanum complexes verified the coordination of La^{3+} in the PEG ligands. NMR spectra were taken of the free PEG ligands and their complexes in dimethyl sulfoxide-*d* (DMSO-*d*₆) using tetramethylsilane (TMS) as an internal standard (Table 6). The ¹H NMR spectrum of the Pic molecule [7] shows two singlet peaks at 8.593 and 4.577 ppm assigned to the equivalents of two protons from the aromatic ring and one proton from the phenolic group in HPic disappeared in all of the complexes, indicating that La^{3+} replaced the hydrogen atom via deprotonization or substitution [7].

At 25 °C, the peak for the terminal alcoholic groups in I, III and **IV** was shifted downfield by 0.01, 0.385, and 0.437 ppm relative to the chemical shift of each free PEG ligand. This indicates that the terminal alcoholic groups were coordinated to La³⁺ and their bond lengths were shorter than that of the La-O_{etheric} bond. ¹H NMR data suggesting direct coordination of Ln(III) to the oxygen atoms of the acyclic PEG and the Pic ligands in the complexes were consistent with the X-ray studies carry out in this paper. In II, the peak of the terminal alcoholic group of the EO3 ligand was shifted upfield by 0.744 ppm relative to the chemical shift of the free EO3 ligand. This may reflect the conformation of the supramolecular sandwich complex (2:1 = ligand:metal), causing the peak to be more shielded. Meanwhile, small or no shifts were seen for the etheric proton from the PEG ligand or the proton in the aromatic Pic anion. Nevertheless, the PEG ligand and the Pic anion were still coordinated to La^{3+} in the DMSO- d_6 solution. To investigate this phenomenon, a study was undertaken using ¹H NMR to measure chemical shifts at increasing temperature from 25 to 100 °C. Similar ¹H 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 the complexes.

For I and II, the terminal alcoholic group peak was shifted upfield, and its signal broadened when the temperature was raised the shifts reached 4.033 and 3.293 ppm at 100 °C, respectively. At the same time, the etheric protons were significantly split and shifted downfield to 3.568 and 3.567 ppm at 100 °C. No splitting of the aromatic peak of the Pic anion was observed in the complexes, but the peak was shifted upfield (to \sim 8.545 and 8.540 ppm) at 100 °C for I and II, respectively. In contrast, the signal of the aromatic Pic anion in III and IV was shifted upfield due to the stronger interaction between the adjacent aromatic Pic anions. The peak of the terminal alcoholic group was shifted upfield at a high temperature, causing the chemical shift in I to exceed that in IV (Fig. 4). This indicates that at high temperature, hydrogen bonding is weaker and may be broken [39,40]. In III, the signal of the terminal alcoholic groups disappeared at 50-100 °C, even though the signal of the water molecules was shifted upfield to about 2.949 ppm at 100 °C. The peak for the terminal alcoholic group in **IV** was shifted upfield as a triplet signal and it reached ~3.951 ppm at 100 °C. The etheric proton peaks of lanthanum complexes were shifted slightly downfield. The results show that the La-O_{etheric} bond lengths are shorter at higher temperatures than at room temperature because of a decrease in the shielding effect. Interestingly, the aromatic peak of Pic anion was shifted significantly upfield by 0.05 ppm for the lanthanum complexes, indicating stronger $\pi - \pi$ interactions due to the rearrangement of three Pic anions in the crystal packing of the complexes [41].

The ¹³C NMR spectra of the complexes showed no significant change compared to the free PEG ligand and HPic molecule (Table 7), because the coordination bonding did not directly affect the carbon atoms. However, the *ipso* aromatic carbon (*ipso* C) from the Pic anion was shifted downfield (1.17–1.32 ppm), probably due to the deprotonation and coordination bonding. In contrast, the *ortho* C and *meta* C from the Pic anion were shifted upfield (1.69–1.80 ppm) and (1.24–1.57 ppm), respectively, relative to the free HPic molecule.



Fig. 4. Effect variable temperatures on the terminal alcoholic groups at 25-100 °C.

	8	I					
Compound	C1	C2	C3	meta C	ortho C	para C	ipso C
EO3	60.04	69.95	72.48	-	-	-	-
EO4	60.40	69.95	72.48	-	-	-	-
EO5	60.39	69.93	72.44	-	-	-	-
I	60.39	69.95	72.48	124.40	125.32	142.03	160.96
II	60.45	70.04	72.59	124.71	125.44	142.03	161.05
III	60.23	69.78	72.35	124.07	125.21	141.86	160.81
IV	60.22	69.81	72.35	124.27	125.22	141.86	160.81

Table 7 ^{13}C NMR data of the free PEG ligands and their complexes at 25 $^\circ\text{C}$

3.4. Photoluminescence studies

Photoluminescence spectra of the diamagnetic lanthanum complexes produced similarly broad bands with the center at 534.6 nm resulting from only the PEG ligand and the Pic anion [7]. Thus, the emission peak in La³⁺, which has no electron in the 4f orbital, occurred due to relaxation. This observation suggests that the nitro electron withdrawing groups of the Pic anion acts as a quencher [42]. Usually, the non-luminescent lanthanides such as La³⁺, Gd³⁺, and Y³⁺ can show increased emission intensity in the presence of the activator Eu³⁺, in what is termed the "co-fluorescence effect" [43].

3.5. Thermal analysis

Only thermograms of III and IV were obtained because of the explosive nature of the Pic anion due to the presence of the nitro groups. These complexes showed a decomposition pattern similar to that reported for the other Ln–Pic complexes [5,7,8,44,45]. In III, a gradual decomposition of the two water molecules occurred at 100–200 °C with a weight loss of 3.6% (calc. 3.4%), followed by decomposition of the EO4 ligand and the three Pic anions between 225 and 300°C, with a corresponding weight loss of 87.9% (calc. 86.6%). However, compound IV was more thermally stable than III. It began to decompose at 180°C, and decomposition rapidly went to completion at 290 °C due to loss of the EO5 ligand and the three Pic anions, with a corresponding weight loss of 89.1% (calc. 87.2%). Further decomposition of the complexes at \sim 895 °C resulted in lanthanum oxide as the final product. Both compounds exhibit good thermal stability due to the high coordination number of the complexes, the strong metal-oxygen bonds, and π - π interactions.

4. Conclusion

Compounds I-IV crystallized in a monoclinic form with different space groups: $P2_1/c$ (I and IV), Pn (II), and C2/c (III). The presence of the terminal alcoholic groups provide the possibility of the formation of strong and weak hydrogen bonds to confer high stability on the complexes through formation of an infinite, 1D chain via hydrogen bonds. The formation of a pseudo-cyclic conformation makes it easier for the PEG ligands to wrap around the La³⁺ ion, in comparison to coordination by rigid cyclic ligands such as crown ethers. The La³⁺ ion prefers a coordination number of 10 independent of the PEG chain length and number of oxygen donor atoms, even though the inner coordination sphere in the different complexes is not the same. The bond angle between the oxygen atoms of terminal alcoholic groups is greater in I and II because of the shorter PEG chain length. The thermal stability of the framework can be attributed to the high coordination number of the complexes, the strong La-O bonds, and π - π interactions. Photoluminescence studies indicate that relaxation takes place. The reversible and dynamic properties of the lanthanum complexes as shown by ¹H NMR studies are evident.

5. Supplementary material

CCDC 295232, 667496, 667497, and 247724 supplementary crystallographic data for compounds **I**, **II**, **III**, and **IV**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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