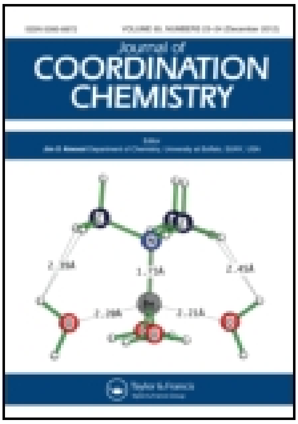

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Coordination polymers of lanthanides incorporating N,N′-ethylenebis(2-hydroxy-1-naphthylideneiminato): syntheses and crystal structures

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Coordination polymers of lanthanides incorporating *N*,*N*′-ethylenebis(2-hydroxy-1-naphthylideneiminato): syntheses and crystal structures

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Reaction of $Ln(NO_3)_3 \cdot 6H_2O$ with H_2napn (H_2napn = N,N′-ethylenebis(2-hydroxy-1-naphthylideneiminato)) and KSCN produces seven new coordination polymers, $[La(H_2napn)(SCN)(C_2H_5OH)_2(NO_3)_2]_n$ (**1**), $[La(H_2napn)_2(SCN)(NO_3)_2]_n$ (**2**), and $[Ln(H_2napn)_{1.5}(NO_3)_3]_n$ [Ln = La(**3**), Sm(**4**), Eu(**5**), Dy(**6**), Er(**7**)]. Crystal structure analysis reveals that H_2napn functions as a bridging ligand, forming a 1-D chain polymer (**1**) and 2-D open-frameworks (**2**–**7**) with lanthanides. Each metal center of **1**–**7** is nine-coordinate. Lanthanide contraction is observed in **3**–**7**.

Keywords: Schiff-base phthalen-ol; Lanthanide complexes; Crystal structure

1. Introduction

Lanthanide(III) coordination complexes attract attention because of their luminescence [1–4], magnetism [5–8], gas absorption [9], and sensor [10, 11] properties. However, the variable and high coordination numbers of lanthanides make rational design for lanthanide complexes challenging [12–17]. Selection of the polydentate ligand is crucial for the preparation of polymers. Lanthanides have a strong tendency to coordinate N-donors and O-donors, thus multidentate ligands containing N- and O-donors are ideal to assemble lanthanide polymers. We envisioned that the Schiff-base phthalen-ol, H_2napn (H_2napn = N,N′-ethylenebis(2-hydroxy-1-naphthylideneiminato)) [18], will be a good ligand for the construction of polymers. As an important multidentate acyclic ligand, H_2napn has played an essential role in tuning bioactivity and magnetic

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performances of transition-metal complexes [19–24]. A plethora of transition metal complexes supported by H_2napn were reported in [25–29], whereas its application in creating lanthanide coordination polymers has not been documented.

We carried out the reaction of H_2napn, lanthanide ions, and KSCN with seven coordination polymers, $[La(H_2napn)(SCN)(C_2H_5OH)_2(NO_3)_2]_n$ (**1**), $[La(H_2napn)_2(SCN)(NO_3)_2]_n$ (**2**), $[Ln(H_2napn)_{1.5}(NO_3)_3]_n$ [Ln = La(**3**), Sm(**4**), Eu(**5**), Dy(**6**), Er(**7**)] prepared. We describe here the syntheses and crystal structures of these complexes.

2. Experimental

2.1. *General considerations*

Materials and Instruments: All reagents used in the synthesis were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Carlo-Erba EA1110 CHNO-S microanalyzer. Infrared spectra (4000–400 cm^{-1}) were recorded using KBr pellets with a Nicolet MagNa-IR500 FT-IR spectrometer. Crystal structure determination was performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

2.2. *Syntheses*

2.2.1. Synthesis of 1. A mixture of $La(NO_3)_3 \cdot 6H_2O$ (0.0222 g, 0.05 mmol), H_2napn (0.0172 g, 0.05 mmol), KSCN (0.0048 g, 0.05 mmol), and ethanol (2 mL) was sealed in an 8 mL Pyrex-tube, which was heated at 70°C for 2 days and then cooled to room temperature at a rate of 5°C h^{-1}. Yellow needle-shaped crystals of **1** were collected in a yield of 30%. Anal. Calcd for $C_{29}H_{32}LaN_5O_{10}S$ (%): C, 44.57; H, 4.13; N, 8.96. Found (%): C, 44.75; H, 4.23; N, 8.44. Selected IR data (KBr, cm^{-1}): 3448 (m), 1636 (s), 1544 (m), 1511 (vw), 1475 (w), 1310 (vw), 1188 (w), 1114 (vw), 848 (w), 747 (vw), 727 (vw), 622 (vw), 457 (vw).

2.2.2. Synthesis of 2. This compound was synthesized by a procedure similar to that of **1**, except that the ratio of $Ln(NO_3)_3 \cdot 6H_2O$ to H_2napn was changed from 1 : 1 to 1 : 2. Yield = 19%. Anal. Calcd for $C_{49}H_{40}LaN_7O_{10}S$ (%): C, 55.63; H, 3.81; N, 9.27. Found (%): C, 54.94; H, 3.40; N 9.16. Selected IR data (KBr, cm^{-1}): 3426 (m), 1634 (s), 1545 (m), 1512 (vw), 1475 (w), 1371 (vw), 1311 (vw), 1260 (vw), 1189 (w), 1013 (vw), 847 (w), 747 (vw), 496 (vw).

2.2.3. Synthesis of 3–7. A mixture of $Ln(NO_3)_3 \cdot 6H_2O$ (0.05 mmol), H_2napn (0.0368 g, 0.1 mmol), and ethanol (2 mL) was sealed in an 8 mL Pyrex-tube. The tube was heated at 70°C for 2 days under autogenous pressure. Cooling of the resultant solution to room temperature at a rate of 5°C h^{-1} gave the product. The crystals were collected by filtration, washed with C_2H_5OH (3 mL), and dried in air.

[La(H$_2$napn)$_{1.5}$(NO$_3$)$_3$]$_n$ (3): Yield: 31%. Anal. Calcd for $C_{36}H_{30}LaN_6O_{12}$ (%): C, 49.27; H, 3.45; N, 9.58. Found (%): C, 48.76; H, 3.30; N, 9.54. Selected IR data (KBr, cm^{-1}): 3448 (w), 1636 (s), 1544 (m), 1511 (w), 1475 (m), 1403 (vw), 1310 (w), 1273 (vw), 1189 (w), 1114 (vw), 1012 (vw), 848 (w), 747 (w), 490 (vw), 457 (vw).

[Sm(H$_2$napn)$_{1.5}$(NO$_3$)$_3$]$_n$ (4): Yield: 24%. Anal. Calcd for $C_{36}H_{30}SmN_6O_{12}$ (%): C, 48.64; H, 3.40; N, 9.45. Found (%): C, 48.29; H, 3.43; N, 9.30. Selected IR data (KBr, cm^{-1}): 1635 (s), 1548 (m), 1478 (m), 1354 (w), 1264 (w), 1185 (w), 1030 (w), 971 (w), 737 (w), 498 (w).

[Eu(H$_2$napn)$_{1.5}$(NO$_3$)$_3$]$_n$ (5): Yield: 34%. Anal. Calcd for $C_{36}H_{30}EuN_6O_{12}$ (%): C, 48.55; H, 3.40; N, 9.44. Found (%): C, 48.17; H, 3.17; N, 9.27. Selected IR data (KBr, cm^{-1}): 3743 (m), 1634 (s), 1548 (w), 1476 (m), 1364 (w), 1309 (w), 1168 (w), 1142 (vw), 970 (w), 843 (w), 732 (vw), 499 (w).

[Dy(H$_2$napn)$_{1.5}$(NO$_3$)$_3$]$_n$ (6): Yield: 20%. Anal. Calcd for $C_{36}H_{30}DyN_6O_{12}$ (%): C, 47.98; H, 3.36; N, 9.33. Found (%): C, 47.42; H, 3.31; N, 9.13. Selected IR data (KBr, cm^{-1}): 3710 (m), 1636 (s), 1548 (m), 1512 (w), 1479 (m), 1364 (m), 1313 (w), 1262 (w), 1185 (w), 1034 (vw), 844 (vw), 741 (w), 505 (w).

[Er(H$_2$napn)$_{1.5}$(NO$_3$)$_3$]$_n$ (7): Yield: 27%. Anal. Calcd for $C_{36}H_{30}ErN_6O_{12}$ (%): C, 47.73; H, 3.34; N, 9.28. Found (%): C, 47.59; H, 3.23; N, 9.29. Selected IR data (KBr, cm^{-1}): 1635 (s), 1547 (m), 1478 (w), 1367 (w), 1186 (w), 1141 (m), 1029 (w), 845 (w), 763 (w), 498 (w).

2.3. *X-ray crystallography*

Single crystals of **1**–**7** were placed in a Bruker SMART APEX II CCD. The diffraction data were obtained using graphite-monochromated Mo-Kα radiation with a $\omega - 2\theta$ scan technique at room temperature. The structure was solved by direct methods with SHELX-97 [30]. A full matrix least-squares refinement on F^2 was carried out using SHELXL-97 [31].

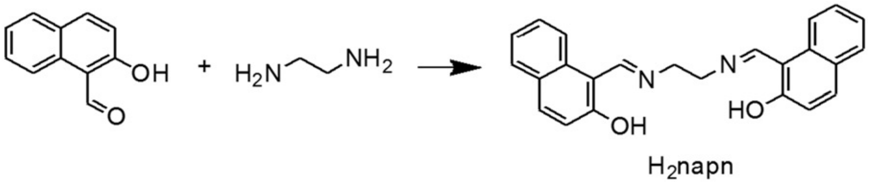
3. Results and discussion

3.1. *Syntheses*

The Schiff base H$_2$napn was prepared via condensation between naphthalen-2-ol and ethylene diamine (scheme 1).

Polymers **1**–**7** were prepared under solvothermal conditions in ethanol in sealed reaction vessels. The 1 : 1 : 1 reaction of $La(NO_3)_3 \cdot 6H_2O$: H$_2$napn : KSCN generates **1** in moderate yield. Changing the ratio of the reactants (1 : 2 : 1) affords **2** in lower yield. Excluding KSCN from the reaction mixture and by the treatment of $Ln(NO_3)_3 \cdot 6H_2O$ with one equiv of H$_2$napn produces **3**–**7**.

The most interesting feature regarding the synthesis of the complexes is that their structures could be tuned through adjusting the ratio of the reactants and introducing KSCN, which demonstrates the synthetic novelty of this work.



Scheme 1. Synthesis of H_2napn.

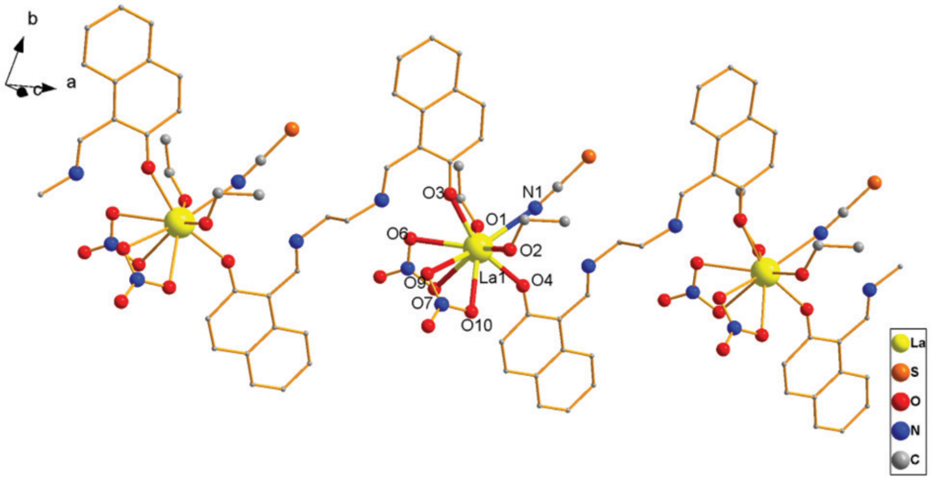


Figure 1. Coordination environment of La^{III} and the 1-D chain structure of **1** (hydrogen atoms are omitted for clarity).

3.2. *Structural descriptions of 1–7*

Partially labeled plots of **1**, **2**, and **3** are shown in figures 1, 3, and 4, respectively. Hydrogen bonding contacts of **1** are displayed in figure 2. View of the coordination polyhedra of La^{III} in **1**–**3** are presented in figure 5. The crystallographic data of the complexes are listed in table 1.

X-ray crystallographic analysis reveals that **1** crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit contains one La^{III}, one H_2napn, one SCN^-, two NO_3^-, and two ethanols. The central La^{III} was nine-coordinate by two phenol oxygens from two H_2napn, four oxygen atoms from two NO_3^- (bidentate), two oxygen atoms from two ethanols, and one nitrogen atom from SCN^-. The two imine nitrogens are not involved in coordination. Thus, the geometry around each La^{III} could be described as a distorted, capped square antiprism.

Adjacent La^{III} ions are linked by two phenol oxygens of two H_2napn, forming an infinite 1-D chain structure (figure 1). The distance between adjacent La^{III} ions is 11.069 Å. The distances of La–O (ethanol) are 2.5677(17) and 2.5491(16) Å, and the bond length of La–N (thiocyanate) is 2.581(2) Å. The average La–O (nitrate) bond length is 2.6601 Å. Longer La–O distances between the protonated phenol and La^{III} are 2.4279(16) and 2.4278(16) Å. The average C–O (phenol) bond length is notably shorter than that of H_2napn [32]. This is due to the coordination of phenol oxygen to

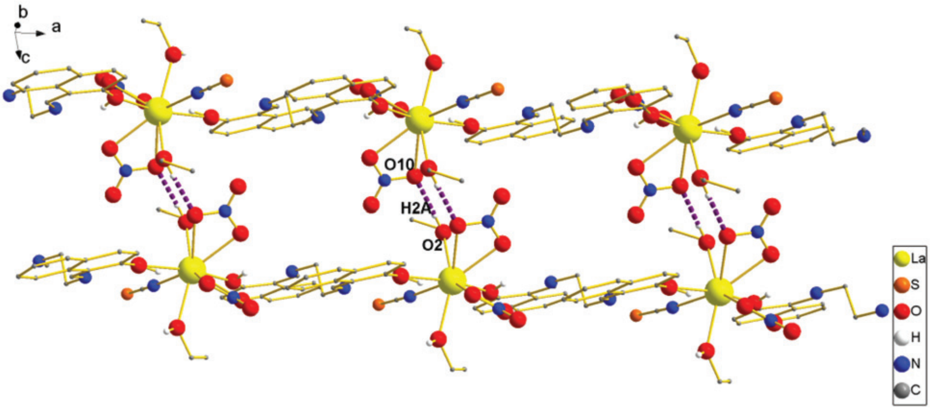


Figure 2. Crystal packing diagram of **1**. Hydrogen bonding contacts are represented by dotted lines.

lanthanide(III). As shown in figure 2, noticeable intermolecular O–H $\cdots$ O contacts (O2–H2A $\cdots$ O10 = 2.847(7) Å, O2–H2A $\cdots$ O10 = 177°) are present from the OH of ethanol (donor) to O10 of NO_3^- (acceptor). These hydrogen contacts connect the molecules to generate an infinite 2-D network (figure 2).

The X-ray single crystal diffraction analysis indicates that **2** crystallizes in the monoclinic *C2*/*c* space group. As shown in figure 3(a), the asymmetric unit contains one La^{III}, two H_2napn, one SCN^-, and two NO_3^-. Each La^{III} ion is nine-coordinate by four phenol oxygens from four different ligands, two bidentate nitrate oxygens, and one thiocyanate nitrogen. Nitrogen atoms of two imines remain uncoordinated. The geometry around each La^{III} is a distorted, capped square antiprism too.

The four H_2napn serve as bridging ligands to further connect four adjacent La^{III} ions, creating an infinite 2-D network (figure 3b). The distance of two adjacent La^{III} ions is 10.1462 Å, shorter than that of **1**. The distance of La–N (thiocyanate) is 2.614(5) Å. The average La–O (nitrate) bond length is 2.618 Å, which is slightly shorter than that of **1** (2.6601 Å). The average bond length of La–O (phenol) is 2.4687 Å. Four La^{III} ions are linked by four H_2napn, generating a 52-membered ring (figure 3c).

X-ray crystallographic analysis reveals that **3**–**7** crystallize in the monoclinic *C2*/*c* space group. The main diffraction peaks and the patterns of the main peaks for **3**–**7** are essentially similar, which indicate they are isomorphic and isostructural. Thus, only the structure of **3** is discussed here. As shown in figure 4(a), the asymmetric unit of **3** contains one La^{III}, 1.5 H_2napn, and three NO_3^-. Each La^{III} is nine-coordinate by three phenol oxygens from three different ligands and three bidentate nitrates. Nitrogen atoms of imines remain uncoordinated. The geometry around each La^{III} could be described neither as a tricapped trigonal prismatic arrangement nor as a distorted capped square antiprism arrangement. We describe it as a 1 : 5 : 3 (MFF) polyhedron [33].

Each ligand is a bidentate linker bridging two La^{III} ions through the two phenol oxygens, generating a 78-membered ring (figure 4b) and also affording an infinite 2-D network structure (figure 4c). Obviously, changing the ratio of the ligands and metal ions and introducing the ancillary ligands vary the final structure of these

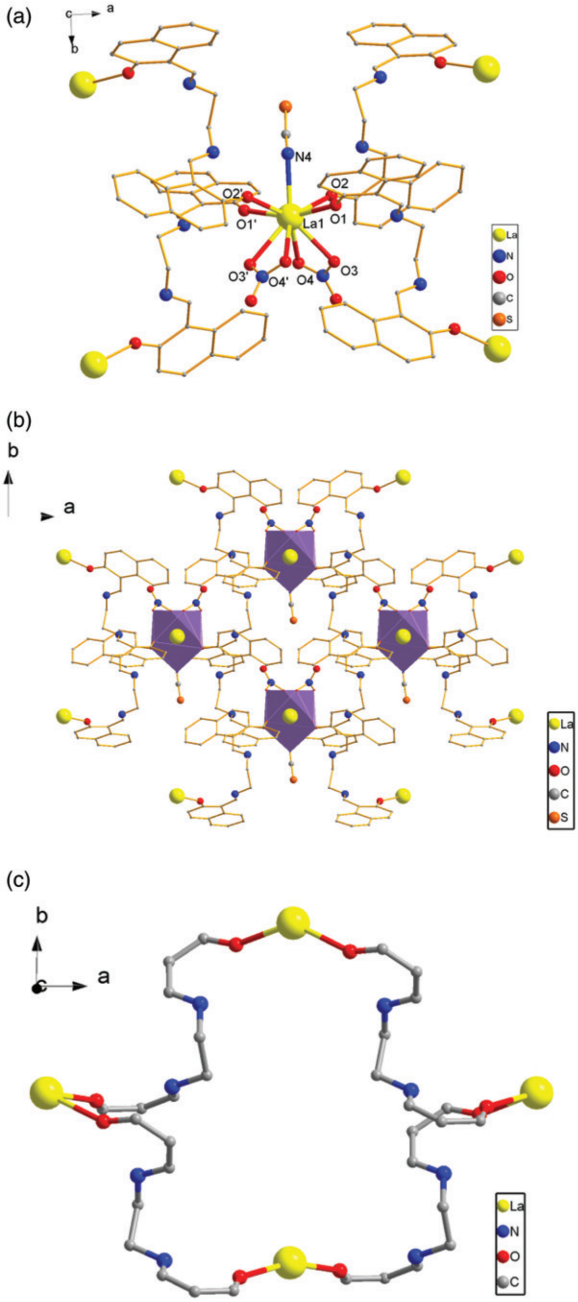


Figure 3. (a) Coordination environment of La^{III} in **2** (hydrogen atoms are omitted for clarity); (b) 2-D network of **2**; and (c) skeleton of the 52-membered ring.

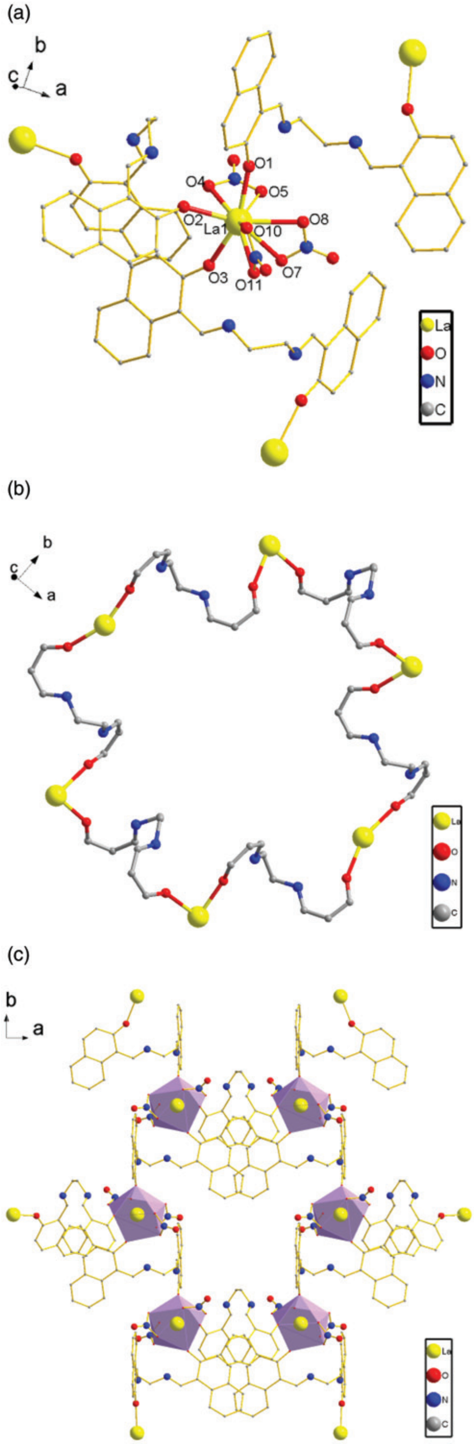


Figure 4. (a) Coordination environment of La^{III} in **3** (hydrogens are omitted for clarity); (b) skeleton of the 78-membered ring; (c) 2-D network of **3**.

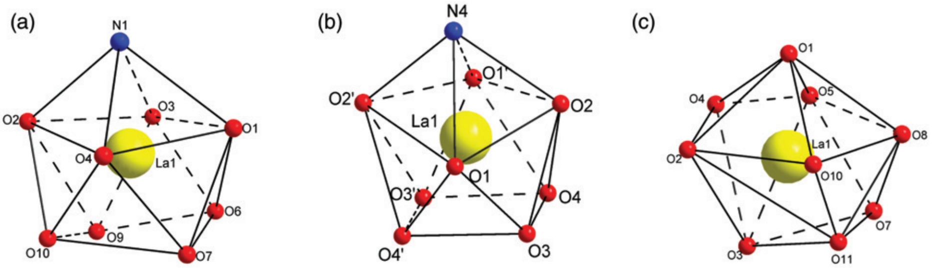


Figure 5. View of the coordination polyhedron of La^{III} ions in **1** (a), **2** (b), and **3** (c).

coordination complexes, and particularly their dimensionality [34, 35]. The La–La distance through the bridge is 9.784 Å, while Sm–Sm, Eu–Eu, Dy–Dy, and Er–Er distances are 9.610, 9.580, 9.471, and 9.448 Å, respectively, consistent with the lanthanide contraction.

The geometries of La^{III} are different in both **1** and **2** and are nine-coordinate, exhibiting distorted, capped square antiprisms. The nitrogen N1(N4) of SCN^- occupies the cap position. The La^{III} ion of **3** is also nine-coordinate, but geometry could be described as a 1 : 5 : 3 (MFF) polyhedron (figure 5) [33].

Metal organic frameworks (MOFS) of lanthanides are of interest owing to various topological networks and aesthetically pleasing crystal packing motifs. While MOFS of lanthanides supported by propylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid [36], 1,2,4,5-benzenetetracarboxylic acid [37], pyridine-2,4,6-tricarboxylic acid [38], 2-methyl imidazole dicarboxylate [39], benzene-1,3-dicarboxylic acid [40], (4,4-dicarboxy-1H-imidazol-2-yl)pyridine-1-oxide [41], etc., were widely investigated, no coordination polymers incorporating H_2napn have been reported. Similar to 1-D chain polymer or 2-D open-frameworks, **1**–**7** have luminescent properties. In-depth research to study the luminescent properties of these complexes is under investigation. Our studies, already well advanced, will be reported soon.

4. Conclusion

We present here a new family of lanthanide polymers generated from *N*,*N'*-ethylenebis(2-hydroxy-1-naphthylideneiminato) using the same reactants at different ratios. Structural analysis reveals that lanthanides serve as nine-coordinate connectors, generating a 1-D chain and 2-D network structures. Lanthanide contraction was shown for these complexes.

Supplementary material

Table S1 gives bond lengths and angles for **1**–**7**. Figure S1 gives the IR spectrum for the ligand. Figures S2–S8 give the IR spectra for **1**–**7**.

Table 1. Crystal data and structure refinements for **1–7**.

Complex	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{29}H_{32}N_5La_4O_{10}S$	$C_{49}H_{40}N_7LaO_{10}S$	$C_{36}H_{30}N_6LaO_{12}$	$C_{36}H_{30}N_6SmO_{12}$	$C_{36}H_{30}N_6EuO_{12}$	$C_{36}H_{30}N_6DyO_{12}$	$C_{36}H_{30}N_6ErO_{12}$
Formula weight	781.58	1057.85	877.57	889.02	890.64	901.16	905.92
Temperature (K)	293(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
Unit cell dimensions (Å, °)							
a	11.069(2)	16.6551(8)	27.649(6)	27.609(5)	27.671(6)	27.685(5)	27.652(6)
b	12.360(3)	11.5925(6)	17.204(3)	16.927(3)	16.791(8)	16.613(3)	16.626(3)
c	12.373(3)	24.4323(13)	17.841(4)	17.894(4)	17.753(4)	17.688(3)	17.754(4)
α	83.32(3)	90	90	90	90	90	90
β	74.95(3)	97.351(3)	111.85(3)	112.94(3)	111.93(3)	112.51 (3)	112.57(3)
γ	76.313(3)	90	90	90	90	90	90
Volume (Å^3), Z	1588.7(6), 2	4678.5(4), 4	7787(3), 8	7701(3), 8	7652(4), 8	7515(2), 8	7537(3), 8
Calculated density (g cm^{-3})	1.634	1.502	1.480	1.534	1.546	1.593	1.597
$F(000)$	788	2144	3528	3567	3575	3599	3616
Crystal size (mm^3)	0.32 × 0.16 × 0.11	0.25 × 0.20 × 0.13	0.31 × 0.26 × 0.22	0.35 × 0.28 × 0.22	0.35 × 0.26 × 0.22	0.36 × 0.27 × 0.21	0.34 × 0.28 × 0.22
θ range for data collection (°)	1.70–30.57	1.68–28.29	1.42–28.61	1.45–28.47	1.45–25.01	1.71–25.01	1.60–25.01
Limiting indices	$-15 < h < 15$; $-17 < k < 17$; $-17 < l < 17$	$-22 < h < 22$; $-15 < k < 8$; $-32 < l < 32$	$-34 \leq h \leq 37$; $-23 \leq k \leq 22$; $-23 \leq l \leq 23$	$-36 \leq h \leq 32$; $-22 \leq k \leq 1$; $-23 \leq l \leq 24$	$-32 \leq h \leq 32$; $-19 \leq k \leq 19$; $-20 \leq l \leq 20$	$-32 \leq h \leq 32$; $-19 \leq k \leq 15$; $-18 \leq l \leq 20$	$-28 \leq h \leq 32$; $-19 \leq k \leq 19$; $-21 \leq l \leq 21$
Reflections collected	39,936	21,252	37,965	36,896	2223,68	15,551	23,215
Independent reflection	9700	5805	9892	9656	6448	6453	6595
Data/restraints/parameters	9700/0/417	5805/7/317	9892/0/496	9656/14/493	6448/0/496	6453/0/496	6595/0/496
Goodness-of-fit on F^2	1.031	1.057	1.035	1.029	1.068	0.981	0.951
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0279$, $wR_2 = 0.0676$	$R_1 = 0.0307$, $wR_2 = 0.0748$	$R_1 = 0.0531$, $wR_2 = 0.1495$	$R_1 = 0.0370$, $wR_2 = 0.1025$	$R_1 = 0.0714$, $wR_2 = 0.2159$	$R_1 = 0.0540$, $wR_2 = 0.0998$	$R_1 = 0.0442$, $wR_2 = 0.0926$
R indices (all data)	$R_1 = 0.0330$, $wR_2 = 0.0703$	$R_1 = 0.0471$, $wR_2 = 0.0834$	$R_1 = 0.0935$, $wR_2 = 0.180$	$R_1 = 0.0591$, $wR_2 = 0.1138$	$R_1 = 0.1152$, $wR_2 = 0.2797$	$R_1 = 0.1320$ $wR_2 = 0.1333$	$R_1 = 0.0859$, $wR_2 = 0.1011$
Largest difference peak and hole (e Å^{-3})	0.694 and −0.554	0.771 and −0.719	1.162 and −0.921	1.011 and −0.533	1.740 and −1.715	0.683 and −0.567	0.687 and −0.388

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC numbers 805727, 798800, 872288, 805723, 872290, 881404, and 872 289 contain the supplementary crystallographic data for **1**–**7**. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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