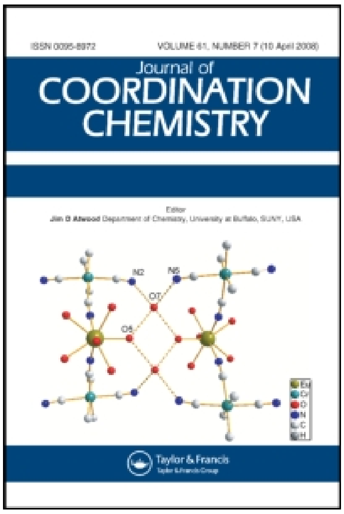

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Variation in coordination modes of aromatic *N*-oxides in lanthanum(III) coordination polymers

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Variation in coordination modes of aromatic *N*-oxides in lanthanum(III) coordination polymers

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Two new coordination polymers of lanthanum(III) benzoate having pyridine *N*-oxide and 4,4′-bipyridyl-*N*,*N*′-dioxide as ancillary ligands are synthesized and characterized. Different binding modes of the *N*-oxide are demonstrated; pyridine *N*-oxide binds as a bridging ligand, whereas 4,4′-bipyridyl-*N*,*N*′-dioxide is monodentate.

Keywords: Coordination polymer; Lanthanum(III) benzoate; Pyridine *N*-oxide; 4,4′-Bipyridyl-*N*,*N*′-dioxide; Crystal structure

1. Introduction

Coordination polymers have applications in catalysis, storage materials, luminescence, nonlinear optics, etc. [1–5]. Coordination polymers with transition metal ions are frequently studied, but less frequently with post-transition metals [6–13]. However, coordination polymers of lanthanides have enormous interest due to their important medicinal and luminescent properties [14–24]. The large size and variable coordination make lanthanides attractive for new supramolecular architecture. A number of reports on coordination networks of lanthanides with aromatic *N*-oxide-based ligands have appeared [25–28]. Herein, we report two coordination polymers of lanthanum(III) benzoate having aromatic *N*-oxide, pyridine *N*-oxide (Pno), and 4,4′-bipyridyl-*N*,*N*′-dioxide (BPNO) as ancillary ligands showing the varied coordination modes of *N*-oxides.

2. Results and discussion

Reaction of lanthanum(III) nitrate hexahydrate and sodium benzoate in the presence of pyridine *N*-oxide results in the formation of a 1-D coordination polymer (**1**) having composition $[La(Ben)_3(Pno)_{0.5}H_2O]_n$ (where Ben = Benzoate, Pno = pyridine *N*-oxide). Similar reaction with 4,4′-bipyridyl-*N*,*N*′-dioxide instead of pyridine *N*-oxide results

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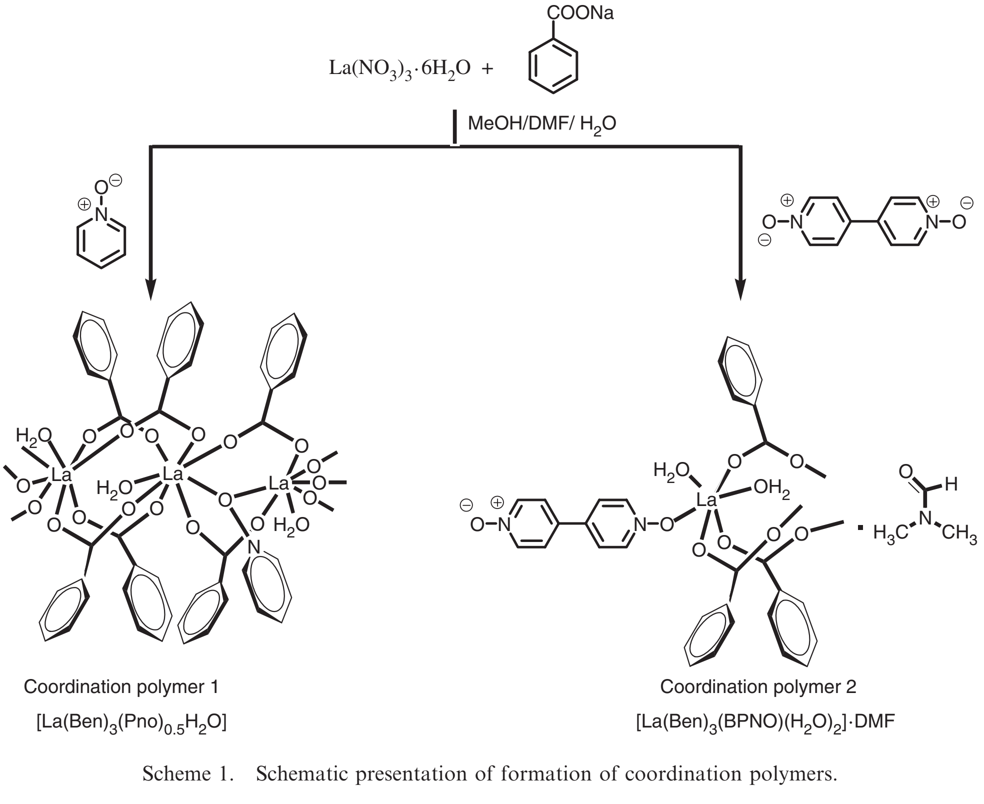
in the formation of coordination polymer **2** having composition $[La(Ben)_3(BPNO)(H_2O)_2]_n \cdot DMF$. The reactions are shown in scheme 1.

The crystal structures of both coordination polymers are determined. Coordination polymer **1** crystallizes in the triclinic space group *P-1* with a 1-D coordination backbone which self-assembles to 2-D through intermolecular O–H···O hydrogen bonds. Lanthanum(III) in **1** is eight coordinate with bridging benzoate providing six coordination sites, while the rest are satisfied by a bridging pyridine *N*-oxide and water. The structure of **1** is shown in figure 1(a) and smallest repeated units are shown in figure 1(b). Two different types of bridging exist between the lanthanum(III) centers. As shown in figure 1(a), La-1 centers are bridged by benzoate, whereas La-1 is connected to La-2 *via* benzoate as well as *N*-oxo bridges. All La–O bond distances in **1** are in the range 2.43–2.70 Å within reported La–O bond distances [16–18].

In **1**, O-5 (water) is involved in a hydrogen bond between two 1-D chains through O(5)–H···O(8) and O(5)–H···O(14) interactions, which propagate along the *a*-crystallographic axis leading to a hydrogen-bonded 2-D architecture (figure 2). The hydrogen bonding parameters are tabulated in table 1. The PXRD pattern of the bulk sample of **1** matches well with that obtained from the simulated one (Supplementary material), showing that only one product is formed in this reaction.

In the FT-IR spectra of **1**, the broad peak at $3445\,cm^{-1}$ is observed for water and at $1221\,cm^{-1}$ due to N–O stretching of pyridine *N*-oxide. The asymmetric and symmetric stretches of bridging carboxylate of the benzoate are at 1609 and $1464\,cm^{-1}$, respectively. ^{1}H NMR spectra for aromatic protons from pyridine *N*-oxide and



Scheme 1. Schematic presentation of formation of coordination polymers.

benzoate show appropriate integrations. The thermogram of **1** reveals three weight losses, the first at 120–240°C, with 2.8% of the total weight from the loss of water (theoretical weight loss 3.17%). The second loss occurs in the range 240–340°C, corresponding to 4.95% due to the loss of pyridine *N*-oxide molecule (theoretical weight loss 4.20%). After that the molecule undergoes a continuous degradation.

Coordination polymer **2** has absorption at 1230 cm^{-1} due to N–O stretching of 4,4′-bipyridyl-*N,N′*-dioxide and absorptions at 1594 and 1472 cm^{-1} due to asymmetric and symmetric stretches of carboxylate. The water absorption is at 3391 cm^{-1} and the peak at 1661 cm^{-1} is due to C=O of DMF. The C–H stretch of DMF is at 3104 cm^{-1} and the aromatic C–H stretches at 2928 cm^{-1}. Compound **2** has an uncoordinated N–O functionality showing a small peak at 1258 cm^{-1}. In the ^{1}H NMR spectra of **2**, the signals from the ring protons are observed.

Coordination polymer **2** is obtained as a solvate of DMF, crystallizing in the monoclinic space group $P2_1/c$. Similar to **1**, each lanthanum(III) is eight coordinated

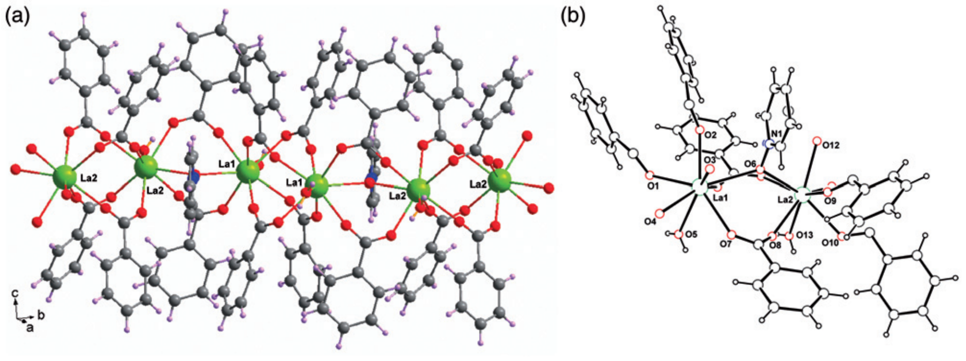


Figure 1. (a) The 1-D structure of **1** (drawn with Diamond software). (b) Smallest building block of **1** (drawn with PLUTO).

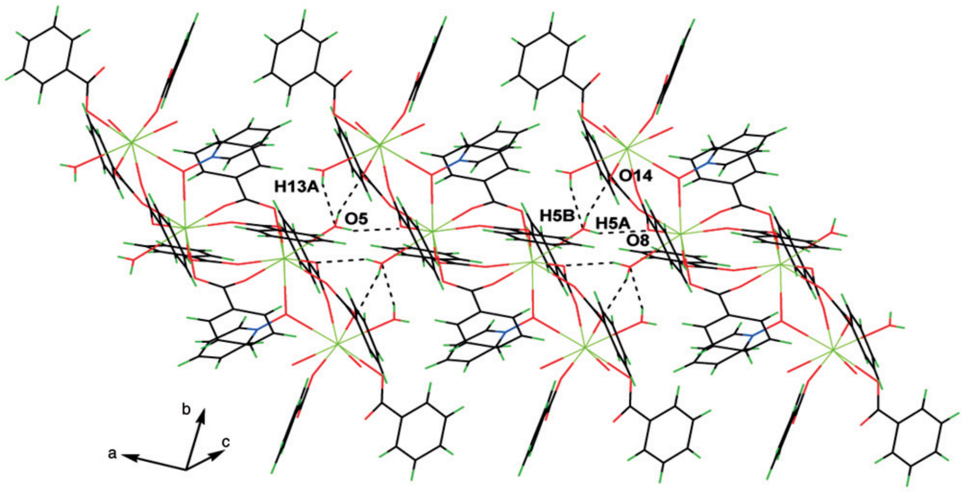


Figure 2. Self assemble of **1** to form a 2-D architecture (drawn with Rasmol).

Table 1. H-bonding parameters for **1** and **2**.

Donor–H ··· acceptor	Symmetry	D–H (Å)	H ··· A (Å)	D ··· A (Å)	D–H ··· A (°)
1					
O(5)–H(5A) ··· O(8)	$1-x,\ 1-y,\ 1-z$	0.98	1.93	2.88(3)	159
O(5)–H(5B) ··· O(14)	$1-x,\ 1-y,\ 1-z$	0.98	1.91	2.84(3)	156
O(13)–H(13A) ··· O(5)	$1-x,\ 1-y,\ 1-z$	0.98	2.37	2.83(4)	108
2					
O(9)–H(9A) ··· O(6)	$x,\ 1/2-y,\ 1/2+z$	0.98	1.80	2.74(4)	161
O(10)–H(10B) ··· O(11)	$-x,\ 1/2+y,\ 1/2-z$	0.98	1.86	2.81(7)	161
O(9)–H(9B) ··· O(5)	$1-x,\ -1/2+y,\ 1/2-z$	0.98	1.86	2.79(3)	157

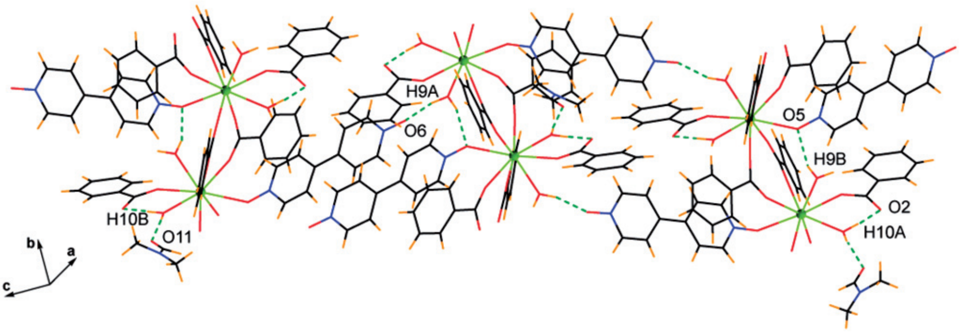


Figure 3. Hydrogen bonds between 1-D chains of **2**.

with benzoate: providing five of the eight and one BPNO and two waters completing coordination. In contrast to **1**, the *N*-oxide in **2** is monodentate. Generally, 4,4′-bipyridyl-*N*,*N*′-dioxide is a good spacer for syntheses of MOFs [16–18]. Unexpectedly, in **2** one end of this ligand remained uncoordinated. However, the free *N*–O is involved in H-bond interactions. DMF is H-bonded to water through O–H ··· O interactions. Unlike **1**, where all the benzoate groups are bidentate bridging, in **2** lanthanum(III) is coordinated by two different types of benzoates, two bidentate bridging and one monodentate. The monodentate benzoate is intramolecularly hydrogen bonded to H(10A) of water. The other hydrogen H(10B) on the same water is hydrogen bonded to DMF, O(10)–H ··· O(11). Both oxygens of BPNO are involved in O–H ··· O hydrogen bonds. O(6) of BPNO is intermolecularly hydrogen bonded with water on a nearby 1-D chain through O(9)–H ··· O(6), while O(5) is involved in O(9)–H ··· O(5). Some of these interactions are shown in table 1. The intermolecular interactions between the groups on the 1-D chains elongate the structure along the *c* crystallographic axis resulting in a 2-D network structure. The hydrogen-bonded structure is shown in figure 3 along with the asymmetric unit in figure 4(b). The purity of **2** is confirmed by analyzing the PXRD pattern (Supplementary material).

TGA of **2** shows three weight loss steps; the first step at 100–125°C corresponds to 11.18% of the total weight from loss of DMF and water (theoretical 11.3%). In the second step, from 250°C to 350°C weight loss of 18.7% accounts for the loss of water and a benzoate (theoretical 19.6%). In the third step, the compound undergoes complete degradation (Supplementary material).

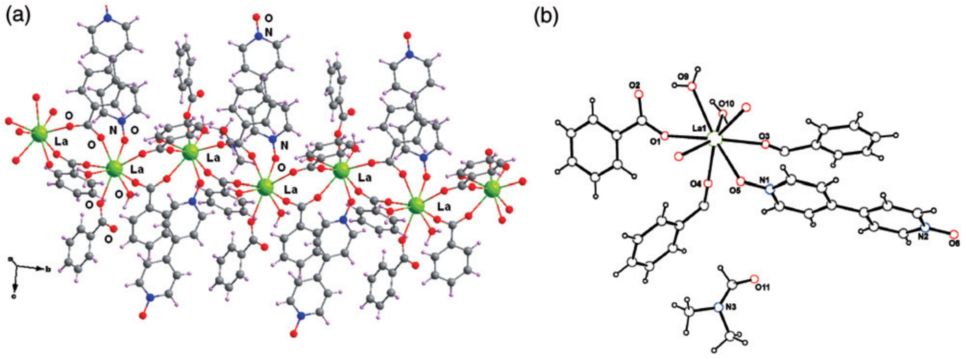


Figure 4. (a) 1-D structure of **2**. (b) Smallest building block of **2**.

In conclusion, different structures of coordination polymers of lanthanum benzoate can be brought about by using different aromatic *N*-oxide as ancillary ligands; such complexes enhance their dimensionality through hydrogen-bond interactions. There are lanthanum oxalate [14–17] coordination polymers which are expected to decompose at relatively low temperatures and need thorough examination as precursors for oxide materials. However, the ease of formation and the presence of oxide in *N*-oxides make their coordination polymers promising as advanced materials for future study.

3. Experimental

3.1. *Synthesis and characterization of the complexes*

3.1.1. Synthesis of 1. To a solution of sodium benzoate (0.363 g, 3 mmol) in methanol (10 mL), lanthanum(III) nitrate hexahydrate (0.433 g, 1 mmol) was added and stirred for 30 min. The white precipitate that appeared was dissolved by adding DMF and water (2 : 1) (10 mL). To this solution, pyridine *N*-oxide (0.095 g, 1 mmol) was added at room temperature and stirred. The resulting colorless solution was then kept for crystallization and colorless crystals of **1** were obtained after a week. Isolated yield, 65%. IR (KBr, cm^{-1}): 3445(b), 1609(m), 1596(w), 1536(s), 1464(m), 1419(s), 1221(m), 719(m). Anal. Calcd for $C_{47}H_{39}La_2NO_{15}$: C, 49.73; H, 3.46. Found: C, 49.47; H, 3.31%. ^{1}H NMR (DMSO-d_6, ppm): 8.21 (d, 1H, $J = 4$ Hz), 7.90 (d, 6H, $J = 4$ Hz), 7.4 (m, 10H). Molar conductance: 88.2 $S\,cm^2\,mol^{-1}$ in methanol. λ_{max} (methanol): 265 nm; $\epsilon = 22{,}570\ M^{-1}\,cm^{-1}$, 225 nm; $\epsilon = 79{,}000\ M^{-1}\,cm^{-1}$.

3.1.2. Synthesis of 2. To a solution of lanthanum(III) nitrate hexahydrate (0.433 g, 1 mmol) and sodium benzoate (0.363 g, 3 mmol) in DMF : methanol : water mixture (1 : 1 : 0.5 v/v; 25 mL), 4,4′-bipyridyl-*N,N*′-dioxide hydrate (0.188 g, 1 mmol) was added. The solution turned yellowish and was kept for crystallization for a week. Isolated yield, 54%. IR (KBr, cm^{-1}): 3391(b), 3104(w), 2928(w), 1661(m), 1594(s), 1536(s), 1472(m), 1402(s), 1258(w), 1230(m), 720(m). Anal. Calcd for $C_{34}H_{34}LaN_3O_{11}$: C, 51.07; H, 4.28. Found: C, 50.78; H, 4.06%. ^{1}H NMR (D_2O, ppm): 8.3 (d, 4H, $J = 8$ Hz),

Table 2. Crystallographic parameters for **1** and **2**.

	1	**2**
Emperical formula	$C_{47}H_{39}La_2NO_{15}$	$C_{34}H_{34}LaN_3O_{11}$
Formula weight	1135.61	799.55
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*P21/c*
Unit cell dimensions (Å, °)		
a	10.4412(17)	12.8949(4)
b	14.173(2)	10.3117(3)
c	15.401(3)	28.4092(8)
α	91.713(8)	90.00
β	98.092(8)	112.419(2)
γ	95.327(9)	90.00
Volume (Å^3), *Z*	2244.6(6), 2	3492.02(18), 4
Calculated density (mg m^{-3})	1.680	1.521
Absorption coefficient (mm^{-1})	1.949	1.286
F(000)	1124	1616
Total no. of reflections	20,794	30,581
Reflections collected	8077	8573
Max. θ (°)	25.50	28.26
Ranges (*h*, *k*, *l*)	$-12 \leq h \leq 12$; $-16 \leq k \leq 17$; $-18 \leq l \leq 18$	$-17 \leq h \leq 17$; $-11 \leq k \leq 13$; $-37 \leq l \leq 37$
Completeness to 2θ (%)	96.7	99.2
Data/restraints/parameters	8077/0/610	8573/0/512
Goodness-of-fit on (F^2)	0.990	1.050
R indices [$I > 2\sigma(I)$]	0.0240	0.0344
R indices (all data)	0.0309	0.0537

7.9 (d, 4H, $J = 8$ Hz), 7.8 (d, 6H, $J = 8$ Hz), 7.5 (t, 3H, $J = 8$ Hz), 7.4 (t, 6H, $J = 8$ Hz). Molar conductance: 101.8 S cm^2 mol^{-1} in methanol. λ_{max} (methanol): 330 nm; $\epsilon = 15{,}230$ M^{-1} cm^{-1}, 223 nm; $\epsilon = 21{,}700$ M^{-1} cm^{-1}.

3.2. *General experimental*

UV-Vis spectra were recorded in a Perkin-Elmer Lambda 750 UV-Vis spectrometer. Infrared spectra were recorded with a Perkin-Elmer FT-IR spectrometer from 4000 to 400 cm^{-1}. X-ray crystallographic data were collected at 296 K with Mo-Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXTL [19]. All non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H-atoms, except those attached to oxygen, were placed at their calculated positions and refined in the isotropic approximation; those attached to oxygen were located in the difference Fourier maps and refined with isotropic displacement coefficients. The crystal parameters of the two complexes are listed in table 2.

Supplementary materials

The CIF files (CCDC No. 729946 and 729947), UV spectra, thermograms, PXRD patterns, and the table with lengths and angles for the two coordination polymers are available.

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