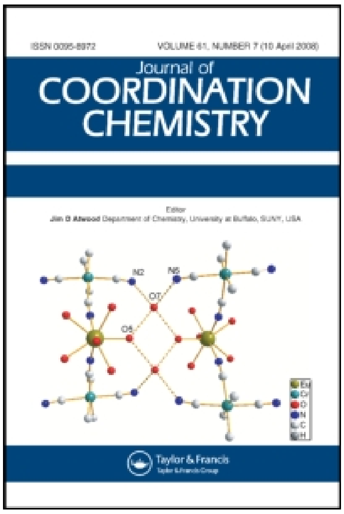

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Hydrothermal syntheses, and crystal structures of new lanthanide coordination polymers with nitrilotriacetic acid

Liang-Cai Yu[ab]; Zhen-Feng Chen[a]; Yan-Cheng Liu[a]; Hong Liang[ab]; Chun-Shan Zhou[b]; Yong Zhang[c]
[a] College of Chemistry & Chemical Engineering of Guangxi Normal University, Guilin 541004, People's Republic of China [b] College of Chemistry & Chemical Engineering of Central-South University, Changsha 410012, People's Republic of China [c] College of Chemistry & Chemical Engineering of Suzhou University, Suzhou 215006, People's Republic of China

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Hydrothermal syntheses, and crystal structures of new lanthanide coordination polymers with nitrilotriacetic acid

LIANG-CAI YU†‡, ZHEN-FENG CHEN*†, YAN-CHENG LIU†,
HONG LIANG†‡, CHUN-SHAN ZHOU‡ and YONG ZHANG§

†College of Chemistry & Chemical Engineering of Guangxi Normal University,
Guilin 541004, People's Republic of China
‡College of Chemistry & Chemical Engineering of Central-South University,
Changsha 410012, People's Republic of China
§College of Chemistry & Chemical Engineering of Suzhou University,
Suzhou 215006, People's Republic of China

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Hydrothermal reactions of $Nd(ClO_4)_3 \cdot 6H_2O$, $Gd(ClO_4)_3 \cdot 6H_2O$ and Er_2O_3 with H_3NTA (nitrilotriacetic acid) afford three new lanthanide coordination polymers, $\{[Nd(NTA)(H_2O)] \cdot 2H_2O\}_n$ (**1**), $\{[Gd(NTA)(H_2O)] \cdot 2H_2O\}_n$ (**2**) and $\{[Er(NTA)(H_2O)] \cdot H_2O\}_n$ (**3**), characterized by elemental analysis and IR spectroscopy. X-ray single crystal structural analyses showed that **1** and **2** are an isomorphous 2D-layered framework containing the nine-coordinated Nd(III) (or Gd(III)), and woven into a 3D suprastructure by interlayer hydrogen bonding while **3** is a 3D structure with eight-coordinate Er(III).

Keywords: Lanthanide complex; Nitrilotriacetic acid; Crystal structure

1. Introduction

Lanthanide complexation chemistry has been studied intensively over the past two decades and much progress has been made with well-defined, kinetically robust systems tailored to applications as bioactive probes for magnetic resonance and luminescence [1, 2]. Nitrilotriacetic acid (H_3-NTA) (scheme 1) is a multidentate complexing ligand that has attracted much attention [3]. The most common use of NTA is as a detergent builder, where it chelates magnesium and calcium ions, preventing the formation of scale. Other applications include the food, pharmaceutical, cosmetic, metal-finishing, photography, textile and paper industries, and also nuclear decontamination [4–14]. Nitrilotriacetate-based lanthanide complexes have been studied for a long time, and the crystal structures of a series of lanthanide complexes have been investigated,

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*Corresponding author. Email: chenzfgxnu@yahoo.com

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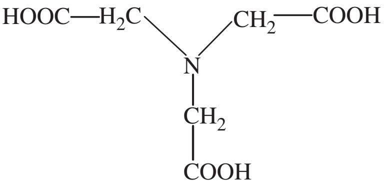

Scheme 1. Formula of nitrilotriacetic acid (H_3NTA).

some with multiple dimensional polymeric structures, such as $[Ln(NTA)(H_2O)]$ (Ln = La, Pr, Nd, Eu) [15], $[Pr(NTA)]\cdot 3H_2O$ [16], $[Dy(NTA)]\cdot 4H_2O$ [17], $[Tm(NTA)(H_2O)_2]\cdot 2H_2O$ [18], and $[Ln(NTA)(H_2O)]$ (Ln = Pr, Sm, Eu, Gd) [19], but in other cases, 1 : 2 monomers were also reported, such as $[Eu(NTA)_2\cdot H_2O]^{3-}$ and $[Tb(NTA)_2\cdot H_2O]^{3-}$ [10], $K_3[Nd(NTA)_2H_2O]\cdot 6H_2O$, $K_3[Er(NTA)_2(H_2O)]\cdot 5H_2O$ [20], $K_3[Y(NTA)_2(H_2O)]\cdot 6H_2O$ [21], $K_3[Ho(NTA)_2(H_2O)]\cdot 5H_2O$ [22]. Nonetheless, it is still worth investigating the structure diversity of such lanthanide coordination polymers with NTA. Therefore complexes $\{[Nd(NTA)(H_2O)]\cdot 2H_2O\}_n$ (**1**), $\{[Gd(NTA)(H_2O)]\cdot 2H_2O\}_n$ (**2**) and $\{[Er(NTA)(H_2O)]\cdot H_2O\}_n$ (**3**), were synthesized and their crystal and molecular structures are reported.

2. Experimental

2.1. *Materials and apparatus*

$Ln(ClO_4)_3\cdot nH_2O$ (Ln = Nd, Gd) were prepared by the reaction of Ln_2O_3 with $HClO_4$. All other chemicals were purchased and used as received without further purification. All solvents were of analytical grade. C, H and N data were obtained using a Perkin-Elmer 2400 II CHNS/O elemental analyzer. Infrared spectra were recorded in the range 4000–500 cm^{-1} with a Perkin-Elmer Spectroscopy One FT-IR spectrometer.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

2.2. *Synthesis of complexes 1–3*

2.2.1. $\{[Nd(NTA)(H_2O)_2]\cdot H_2O\}_n$ (1). An aqueous mixture (15 mL) containing $Nd(ClO_4)_3\cdot 6H_2O$ (0.5 mmol), H_3NTA (0.6 mmol), and KOH (0.5 mmol) was placed in a Teflon-lined stainless steel vessel (25 mL). Ethanol (5.0 mL) was added to the heterogeneous mixture and the vessel was sealed and heated to 130°C for 3 d. Upon cooling to room temperature, blue-purple crystals of **1** were obtained in 61% yield (0.1179 g). Anal. Calcd for $C_6H_{12}NNdO_9$: C, 18.65; H 3.10; N 3.62. Found: C, 18.74; H, 3.10; N, 3.52%. IR (KBr, cm^{-1}): 3547(m), 3421(s), 2957(w), 2910(w), 1646(s), 1589(s), 1557(s), 1469(m), 1448(w), 1412(m), 1353(w), 1318((m), 1258(m), 1117(m), 1022(m), 996(w), 970(w), 943(w), 930(w), 911(m), 760(m), 742(w), 669(w), 644(w), 621(w), 569(w), 550(w), 515(w), 473(w), 411(w).

2.2.2. $\{[Gd(NTA)(H_2O)_2]\cdot H_2O\}_n$ (2). The procedure was similar to that for **1**. Light-pink crystals of **2** were obtained in 65% yield (0.1298 g). Anal. Calcd for

$C_6H_{12}GdNO_9$: C, 18.03; H, 3.00; N, 3.51. Found: C, 18.14; H, 3.10; N, 3.45%. IR (KBr, cm^{-1}): 3556(s), 3248(s), 2963(w), 2914(w), 1646(s), 1598(m), 1560(s), 1563(s), 1473(m), 1452(w), 1430(w), 1406(m), 1352(m), 1318(m), 1300(m), 1254(m), 1116(m), 1024(w), 997(w), 971(w), 943.7(w), 912(m), 960(m), 743(w), 669(w), 644(w), 622(w), 570(w), 550(w), 517(w), 475(w), 414(w).

2.2.3. $\{[Er(NTA)(H_2O)]\cdot H_2O\}_n$ (3). The procedure was similar to that for **1** except that Er_2O_3 was used. Light-pink crystals of **3** were obtained in 58.3% yields (01141 g). Anal. Calcd for $C_6H_{10}ErNO_8$: C, 18.41; H, 2.55; N, 3.58. Found: C, 18.35; H, 2.50; N, 3.51%. IR (KBr, cm^{-1}): 3555(m), 3373(s), 3257(s), 2963(w), 2914(w), 1647(s), 1595(s), 1562(s), 1471(m), 1451(w), 1440(w), 1406(s), 1352(w) 1318(m), 1300((m), 1254(m), 1116(m), 1024(w), 997(w), 971(w), 943.7(w), 912(m), 960(m), 743(w), 669(w), 644(w), 622(w), 570(w), 550(w), 517(w), 475(w), 414(w).

2.3. *Single-crystal X-ray diffraction*

All measurements were made on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) at 193 K by using graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). Diffraction data were collected at ω mode with a detector distance of 55 mm to the crystal with CrystalClear Software [23]. Indexing was performed from 6 images, each of which was exposed for 15 s. The reflection data were reduced by using the program CrystalStructure 3.5.1 Package [24], and a semi-empirical absorption correction was applied which resulted in transmission factors ranging from 0.3234 to 0.6506 for **1**, from 0.1867 to 0.4584 for **2** and from 0.1302 to 0.3585 for **3**. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods. All structures were refined on F^2 by full-matrix least-squares methods. All calculations were carried out with SHELXS-97 and SHELXL-97 programs [25]. Complex **3** crystallizes in the non-centrosymmetric space group *P*2(1)2(1)2(1) with the Flack parameter value $\chi = 0.001(16)$. Figures 1 and 4 are generated by XP of SHELXS-97 [25]. Figures 2, 3, 5 and 6 are drawn using the Diamond program (2.1 version) of Crystal Impact. Details of the crystal structure solutions and refinements are listed in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Structures of 1–3*

Single-crystal X-ray diffraction studies reveal that complexes $\{[Nd(NTA)(H_2O)_2]\cdot H_2O\}_n$ (**1**) and $\{[Gd(NTA)(H_2O)_2]\cdot H_2O\}_n$ (**2**) are isomorphous; the structural characteristics of **1** are discussed in more detail. The asymmetric unit of **1** contains a nine-coordinate Nd(III) (figure 1) and differs from $[Nd(NTA)(H_2O)]_n$ [15]. Compound **1** belongs to orthorhombic *Pbca*, whilst $[Nd(NTA)(H_2O)]_n$ is monoclinic *P*2(1)/*n*. In $[Nd(NTA)(H_2O)]_n$ [15], the Nd(III) ion is eight-coordinate and possesses an NO_7 environment composed of one N and three O atoms from one NTA ligand, three O atoms from other surrounding NTA ligands and finally one O atom from the water ligand. In **1**, Nd(III) is nine-coordinate by one N and eight

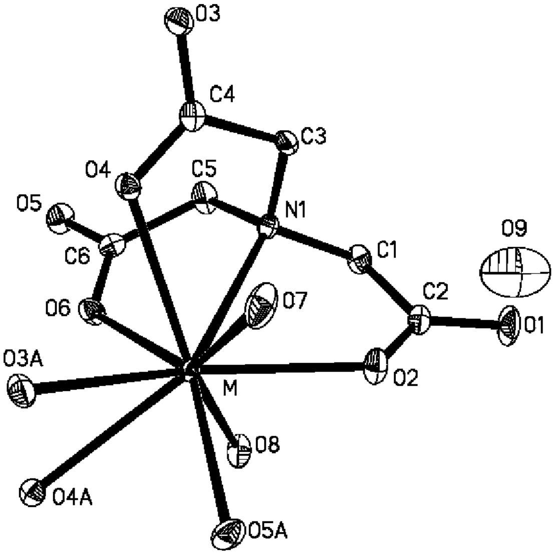

Figure 1. The asymmetric unit of $\{[Nd(NTA)(H_2O)_2]\cdot H_2O\}_n$ (**1**) (M = Nd) and $\{[Gd(NTA)(H_2O)_2]\cdot H_2O\}_n$ (**2**) (M = Gd) showing 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

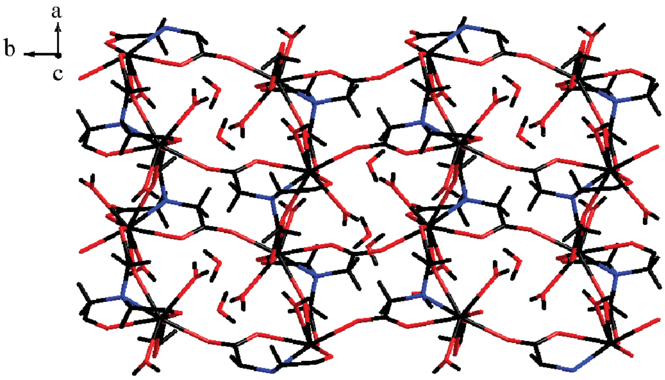

Figure 2. Drawing of complexes **1** and **2** showing 2D extended layer structure viewed along *c* axis.

O atoms, of which one N and three O atoms come from one NTA ligand, another three O atoms from two other coordianted NTA ligands and finally two O atoms from two aqua ligands. The Nd–O bond distances range from 2.363(3) to 2.670(3) Å. The average distance is 2.491 Å and longer than that of $[Nd(NTA)(H_2O)]_n$ [15]. The Nd–N bond length is 2.662(3) Å. The geometry around the Nd(III) can be best described as a capped square antiprism. As shown in figure 2, two of the three carboxylate groups of NTA bridge Nd(III) ions along *a*- and *b*-axes, respectively, with distances of 5.030 and 6.733 Å between two adjacent Nd(III) ions. The three types of carboxylate groups of NTA ligands link Nd(III) ions into a 2D-layered structure with monodentate, anti-anti-bridging bidentate and μ_3-bridging tridentate modes. In the 2D layer,

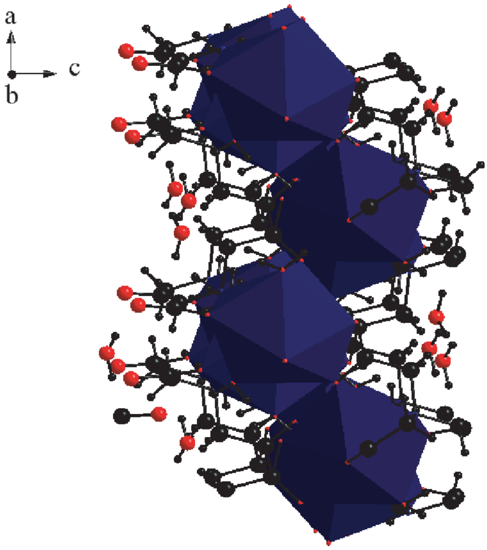

Figure 3. Polyhedron diagram of complexes **1** and **2** showing all Nd(III) or Gd(III) ions are not completely coplanar in the 2D layer structure viewed along *b* axis.

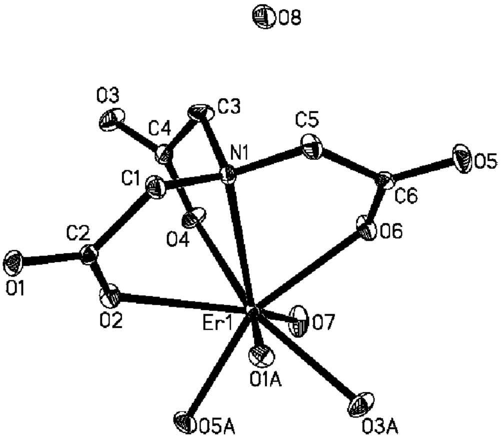

Figure 4. The asymmetric unit of $\{[Er(NTA)(H_2O)]\cdot H_2O\}_n$ (**3**) showing 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

all Nd(III) ions are not completely coplanar (figure 3), while in $[Nd(NTA)(H_2O)]_n$ [15], all Nd(III) ions are coplanar. Finally, a 3D supramolecular structure of **1** is formed through strong intermolecular hydrogen bonding interactions involving water molecules and carboxylate groups, while a 3D coordination polymer of $[Nd(NTA)(H_2O)]_n$ is formed via bridging NTA ligands [15].

The asymmetric unit of $\{[Er(NTA)(H_2O)]\cdot H_2O\}_n$ (**3**) contains an eight-coordinate Er(III) (figure 4) in a NO_7 environment composed of one N and three O atoms from one NTA, three O atoms from the other three surrounding NTA ligands and finally one O atom from a water molecule. The Er–O bond distances range from 2.242(3)

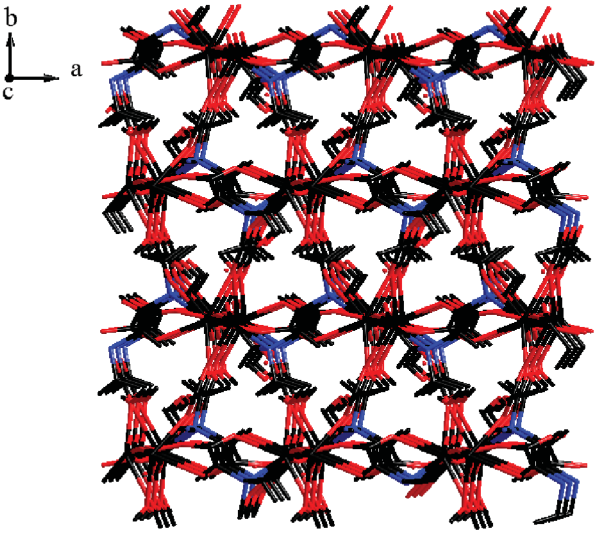

Figure 5. Drawing of complex **3** showing 3D extended layer structure viewed along the *c* axis.

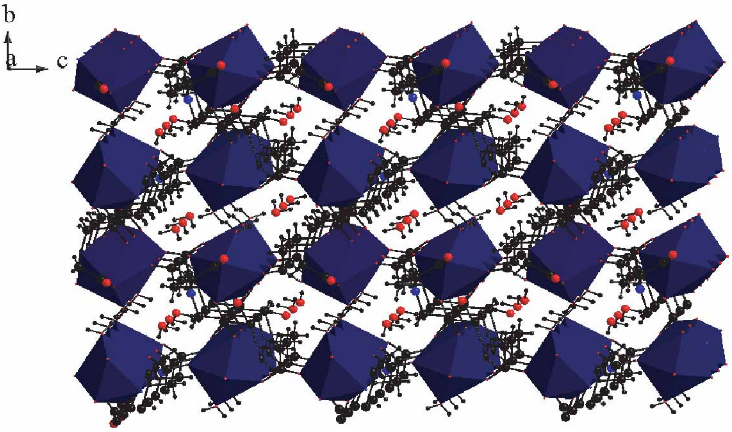

Figure 6. Polyhedral diagram of complex **3** showing the 3D framework with water-embedded in channels.

to 2.425(3) Å, with the average distance of 2.321 Å. The Er–N bond length is 2.589(3) Å. In $K_3[Er(NTA)_2(H_2O)] \cdot 5H_2O$ [20], Er(III) is coordinated with two N and six O atoms from two NTA ligands and one O atom from a H_2O molecule as a ninth ligand. The coordination mode of NTA in $[Er(NTA)_2(H_2O)]^{3-}$ [20] is similar to that of NTA in $K_3[Y(NTA)_2(H_2O)] \cdot 6H_2O$ [21]. Whilst in **3**, NTA is a heptadentate ligand (figure 4) and the three carboxylate groups of NTA adopt an anti-anti bridging bidentate mode. As shown in figure 5, two of the three carboxylate groups of NTA bridge Er(III) ions along the *b*- and *c*-axes, respectively, leading to a 2D layer with distances of 6.627 and 6.527 Å between two adjacent Er(III) ions. The third carboxylate group of NTA ligand bridges the 2D layer via coordination to Er(III) ions along the *a*-axis

Table 1. Summary of crystallographic data for compounds **1**, **2** and **3**.

Parameter	**1**	**2**	**3**
Empirical formula	$C_6H_{12}NNdO_9$	$C_6H_{12}GdNO_9$	$C_6H_{10}ErNO_8$
M	386.41	399.42	391.41
Crystal size (mm^3)	$0.310 \times 24 \times 0.10$	$0.41 \times 0.25 \times 0.15$	$0.40 \times 0.25 \times 0.15$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	*P2*(1)2(1)2(1)
a (Å)	8.0871(11)	8.0687(15)	6.5274(12)
b (Å)	13.2283(18)	13.049(3)	11.701(2)
c (Å)	20.813(3)	20.581(4)	12.816(2)
V (Å^3)	2226.6(5)	2166.9(7)	978.9(3)
Z	8	8	4
T (K)	193(2)	193(2)	193(2)
λ (Å)	0.71070	0.71070	0.71070
F(000)	1496	1528	740
D_{Calcd} (Mg m^{-3})	2.305	2.449	2.656
μ (mm^{-1})	4.703	6.161	8.604
Reflections collected	22936	22327	10843
Independent reflections	2546 [$R_{\text{int}} = 0.0417$]	2479 [$R_{\text{int}} = 0.0426$]	2236 [$R_{\text{int}} = 0.0404$]
Goodness-of-fit on F^2	1.44	1.42	1.164
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.033$, $wR_2 = 0.061$	$R_1 = 0.03$, $wR_2 = 0.071$	$R_1 = 0.022$, $wR_2 = 0.051$

Table 2. Selected bond distances (Å) and angles (°) for compounds **1**, **2** and **3**.

*Compound **1***					
Nd(1)–O(2)	2.437(3)	Nd(1)–O(3)#2	2.505(3)	Nd(1)–O(7)	2.492(3)
Nd(1)–O(6)	2.435(3)	Nd(1)–O(4)	2.563(3)	Nd(1)–O(4)#2	2.670(3)
Nd(1)–O(8)	2.461(3)	Nd(1)–N(1)	2.662(3)	Nd(1)–O(5)#1	2.363(3)
O(2)–Nd(1)–O(3)#2	148.16(10)	O(6)–Nd(1)–N(1)	65.55(10)	O(2)–Nd(1)–O(4)#	142.44(10)
O(2)–Nd(1)–O(4)	107.58(10)	O(2)–Nd(1)–N(1)	64.43(10)	Nd(1)–0(4)–Nd(1)#3	148.0(11)
*Compound **2***					
Er(1)–O(2)	2.425(3)	Er(1)–O(7)	2.370(3)	Er(1)–O(5)#1	2.242(3)
Er(1)–O(4)	2.281(2)	Er(1)#4–O(1)	2.304(3)	Er(1)#6–O(5)	2.242(3)
Er(1)–O(6)	2.304(3)	Er(1)#5–O(3)	2.323(3)	Er(1)–N(1)	2.589(3)
Er(1)–O(1)#2	2.304(3)	Er(1)–O(3)#3	2.323(3)		
O(1)#2–Er(1)–O(7)	148.57(10)	O (4)–Er(1)–O(2)	73.32(9)	O(1)#2–Er(1)–N(1)	73.30(10)
O(1)#2–Er(1)–O(2)	75.08(9)	O (6)–Er(1)–O(2)	130.80(10)		
*Compound **3***					
Gd(1)–O(2)	2.395(3)	Gd(1)–O(3)#2	2.430(3)	Gd(1)–O(5)#1	2.317(3)
Gd(1)–O(6)	2.386(3)	Gd(1)–O(4)	2.533(3)	Gd(1)#4–O(5)	2.317(3)
Gd(1)–O(7)	2.401(3)	Gd(1)–O(4)#2	2.648(3)	Gd(1)#3–O(3)	2.430(3)
Gd(1)–O(8)	2.429(4)	Gd(1)–N(1)	2.616(4)		
O(2)–Gd(1)–O(7)	73.05(12)	O(4)–Gd(1)#3	2.648(3)	O(2)–Gd(1)–O(3)#	148.01(12)
O(2)–Gd(1)–O(8)	71.21(12)	O(2)–Gd(1)–N(1)	65.50(11)	O(7)–Gd(1)–N(1)	80.06(12)

Symmetry code: #1: $-x+3/2$, $y+1/2$, z; #2: $x+1/2$, $-y+1/2$, $-z+1$; #3: $x-1/2$, $-y+1/2$, $-z+1$; #4: $-x+3/2$, $y-1/2$, z for **1**; #1: $-x+3/2$, $-y+1$, $z+1/2$; #2: $x+1/2$, $-y+3/2$, $-z+1$; #3: $x+1$, y, z; #4: $x-1/2$, $-y+3/2$, $-z+1$; #5: $x-1$, y, z; #6: $-x+3/2$, $-y+1$, $z-1/2$ for **2**; #1: $-x+3/2$, $y-1/2$, z; #2: $x+1/2$, $-y+1/2$, $-z+1$; #3: $x-1/2$, $-y+1/2$, $-z+1$; #4: $-x+3/2$, $y+1/2$, z for **3**.

resulting in a 3D coordination polymer with a third distance of 6.527 Å between two adjacent Er(III) ions (figure 5). The coordinated water molecules protrude from the polymeric layer and hydrogen-bond to the oxygen atoms of carboxylate groups from the neighboring layer. Interestingly, the lattice water molecules are intercalated in the 3D channel through hydrogen bonding interactions involving water molecules and carboxylate groups of NTA (figure 6).

The results show that Nd(III), Gd(III) and Er(III) complexes with NTA ligands exhibit a diversity of solid structures due to the variability of coordination modes of NTA, the differences of the ionic radius and electronic configuration of Nd(III), Gd(III) and Er(III), and importantly, the synthetic method [26].

3.2. *IR spectroscopy*

The ν(C–N) of **1**, **2** and **3** are at 1117, 1122 and 1116 cm^{-1}, undergoing red-shifts 83, 78 and 84 cm^{-1} compared with that of NTA (1200 cm^{-1}), respectively, indicative of coordination of the N atoms of NTA ligands to Nd(III), Gd(III) and Er(III). For the COOH group, the ν_{as}(COOH) of NTA at 1725 cm^{-1} disappeared in the complexes and ν_{as}(COO) at 1620 cm^{-1} of NTA red-shifts to 1589, 1598 and 1595 cm^{-1}, and ν_s(COO) at 1340 cm^{-1} of NTA blue-shifts to 1408, 1407 and 1406 cm^{-1} in complexes, respectively, confirming that the O atoms of COO^- also coordinate with Nd(III), Gd(III) and Er(III). There are broad ν(OH) bands of H_2O near 3550 cm^{-1} showing H_2O in complexes **1**, **2** and **3**.

Supplementary material

Crystallographic data for compounds **1**, **2** and **3** are deposited to the Cambridge Crystallographic Data center with deposition numbers CCDC 260190, 260191 and 260192, respectively.

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