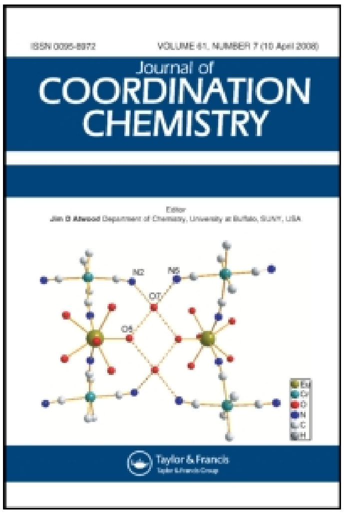

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Hydrothermal synthesis and structural characterization of three lanthanide coordination polymers with adipic acid and 1,10-phenanthroline

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Three new lanthanide coordination polymers, $[\mathrm{Ln(Ad)_{3/2}(Phen)}]_n \cdot 2n\mathrm{H_2O}$ (Ln = Eu, **1**; Pr, **2**; Ad = adipate; Phen = 1,10-phenanthroline) and $[\mathrm{Yb(Ad)_{3/2}(Phen)}]_n \cdot n\mathrm{H_2O}$ **3**, were prepared by hydrothermal reactions. The structures of **1**, **2** and **3** are reported. In compound **1**, Eu(III) ions are bridged by adipate ligands in two modes into 2-D polymeric layers. Adjacent layers are assembled by hydrogen bonding and π–π stacking between 1,10-phenanthrolines into a 3-D supramolecular structure. Compound **2** is isostructural with **1**. In compound **3**, the Yb(III) ions are connected by adipate ligands in three modes into a 3-D network.

Keywords: Lanthanide; Coordination polymer; Hydrothermal synthesis; Crystal structure

1. Introduction

Design and synthesis of metal-organic coordination polymers have received interest because supramolecular assembly is a route to new materials with unusual structures and properties [1–3]. Multifunctional rigid ligands such as 1,2,4,5-benzenetetracarboxylic acid [4], 1,3,5-benzenetricarboxylic acid [5], and 1,4-benzenedicarboxylic acid [6] are used as linkers in constructing coordination polymers. However, flexible ligands might construct more interesting structures by changing conformation to adapt to different environments [7]. Many lanthanide coordination polymers containing adipate have been reported [8], in which template molecules, such as 4,4′-dipyridyl and 1,3-di(4-pyridyl)propane, are used to fill the channels of porous structures or sensitize lanthanide ion emission. To the best of our knowledge, no lanthanide coordination polymer containing both adipic acid and 1,10-phenanthroline has been reported. Herein, we report the synthesis and crystal structures of three lanthanide coordination

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polymers, $[Ln(Ad)_{3/2}(Phen)]_n \cdot 2nH_2O$ (Ln = Eu, **1**; Pr, **2**; Ad = adipate; Phen = 1,10-phenanthroline) and $[Yb(Ad)_{3/2}(Phen)]_n \cdot nH_2O$ **3**, which have supramolecular architecture assembled via hydrogen bonding and π–π stacking.

2. Experimental

2.1. *Materials and apparatus*

$LnCl_3 \cdot nH_2O$ (Ln = Pr, $n = 7$; Ln = Eu and Yb, $n = 6$) were prepared by dissolving their oxides in dilute hydrochloric acid and then dried. All other chemicals were purchased and used as received without further purification. C, H and N data were obtained using a PE 2400II CHNS/O elemental analyzer. Infrared spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer.

2.2. *Preparation of compounds*

$Phen \cdot H_2O$ (0.3 mmol, 0.0595 g) and H_2Ad (0.3 mmol, 0.0438 g) were dissolved in 10 mL deionized water and the pH was adjusted to 4 with NaOH aqueous solution. Then the $LnCl_3 \cdot nH_2O$ (0.3 mmol; Eu, $n = 6$, 0.1099 g; Pr, $n = 7$, 0.1120 g; Yb, $n = 6$, 0.1162 g) was added. The mixture was placed in a Teflon-lined stainless steel vessel (23 mL), sealed and heated (Eu, at 180°C for 3d; Pr, at 150°C for 4d and Yb, at 140°C for 5d) under autogeneous pressure and then cooled to room temperature. After filtration, the product was washed with ethanol and then dried. Crystals of **1**, **2** and **3** were collected (0.0376 g, 32.19% for **1**; 0.0349 g, 30.45% for **2**; 0.0408 g, 33.69% for **3**).

$[Eu(Ad)_{3/2}(Phen)]_n \cdot 2nH_2O$ (1). Found (Calcd. %): C, 43.14(43.16); H, 3.88(4.14); N, 4.96(4.79). IR(KBr pellets, cm^{-1}): 3482(s, br), 3059(w), 2938(m), 2854(w), 1599(vs), 1588(vs), 1541(s), 1439(vs), 1426(vs), 1350(w), 1330(w), 1314(w), 1210(w), 1141(w), 1103(w), 1048(w), 852(s), 731(s), 723(s).

$[Pr(Ad)_{3/2}(Phen)]_n \cdot 2nH_2O$ (2). Found (Calcd. %): C, 44.28(43.99); H, 3.91(4.22); N, 5.04(4.89). IR(KBr pellets, cm^{-1}): 3463(s, br), 3060(w), 2937(m), 2854(w), 1578(vs), 1535(s), 1432(vs), 1350(w), 1312(w), 1299(w), 1272(w), 1142(w), 1102(w), 1047(w), 861(s), 731(s), 722(s).

$[Yb(Ad)_{3/2}(Phen)]_n \cdot nH_2O$ (3). Found (Calcd. %): C, 43.09(42.93); H, 3.96(3.77); N, 4.55(4.77). IR(KBr pellets, cm^{-1}): 3464(s, br), 3083(w), 3060(w), 2941(m), 2867(w), 1601(vs), 1545(vs), 1519(s), 1441(vs), 1425(vs), 1350(w), 1321(w), 1300(w), 1209(w), 1142(w), 1106(w), 925(w), 849(s), 730(s).

2.3. *Single-crystal X-ray diffraction*

Single-crystal X-ray data were collected on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied using the SADABS program. All calculations were carried out with SHELXS-97 and SHELXL-97 programs. The structures were solved by direct methods. All structures were refined on F^2 by full-matrix least-squares methods. The crystallographic data of the compounds are summarized in table 1 and the selected bond lengths and angles in tables 2 and 3.

Table 1. Crystallographic and experimental data for **1**, **2** and **3**.

	1	**2**	**3**
Empirical formula	$EuC_{21}H_{24}N_2O_8$	Pr $C_{21}H_{24}N_2O_8$	$YbC_{21}H_{22}N_2O_7$
Formula weight	584.38	573.33	587.445
Temperature (K)	273(2)	291(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)			
a	10.238(3)	10.294(2)	9.109(3)
b	11.384(4)	11.482(2)	10.539(3)
c	11.495(4)	11.573(2)	12.079(4)
α	98.386(5)	98.40(3)	99.320(5)
β	116.280(4)	116.11(3)	109.320(5)
γ	107.416(5)	107.57(3)	92.850(5)
Volume (Å^3)	1083.8(6)	1107.0(4)	99.320(5)
Z	2	2	2
Calculated density (Mg m^{-3})	1.791	1.720	2, 1.818
Absorption coefficient (mm^{-1})	2.944	2.250	4.403
$F(000)$	582	574	576
Crystal size (mm^3)	0.16 × 0.12 × 0.08	0.20 × 0.16 × 0.16	0.16 × 0.14 × 0.12
θ range for data collection	1.98–25.01	1.97–27.55	1.82–25.01
Limiting indices	$-12 \le h \le 11$, $-13 \le k \le 11$, $-12 \le 1 \le 13$	$-13 \le h \le 12$, $0 \le k \le 14$, $-15 \le l \le 14$	$-10 \le h \le 9$, $-12 \le k \le 12$, $-8 \le 1 \le 14$
Reflections collected/unique	5653/3818 [R(int) = 0.0211]	4338/4338 [R(int) = 0.0000]	5621/3771 [R(int) = 0.0240]
Completeness to $\theta = 25.01$	99.7%	84.8%	99.5%
Absorption correction	Semi-empirical from equivalents	None	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.793430	0.7147 and 0.6617	1.000000 and 0.746059
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3818/0/289	4338/0/290	3771/0/280
Goodness-of-fit on F^2	1.057	1.131	1.096
Final R indices [$I > 2\sigma$(I)]	$R_1 = 0.0268$, $wR_2 = 0.0608$	$R_1 = 0.0486$, $wR_2 = 0.1262$	$R_1 = 0.0264$, $wR_2 = 0.0648$
R indices (all data)	$R_1 = 0.0346$, $wR_2 = 0.0639$	$R_1 = 0.0558$, $wR_2 = 0.1322$	$R_1 = 0.0337$, $wR_2 = 0.0678$
Largest diff. peak and hole (e Å^{-3})	0.535 and −0.790	1.486 and −1.867	0.839 and −0.905

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Eu(1)–O(4)#1	2.338(3)	Pr(1)–O(2)#1	2.386(5)
Eu(1)–O(5)#2	2.352(3)	Pr(1)–O(5)#1	2.417(5)
Eu(1)–O(3)#3	2.415(3)	Pr(1)–O(1)	2.474(5)
Eu(1)–O(6)	2.438(3)	Pr(1)–O(6)	2.500(5)
Eu(1)–O(1)	2.489(3)	Pr(1)–O(3)#2	2.550(5)
Eu(1)–O(2)	2.519(3)	Pr(1)–O(4)#2	2.576(5)
Eu(1)–N(2)	2.587(3)	Pr(1)–N(2)	2.634(6)
Eu(1)–O(5)	2.614(3)	Pr(1)–O(5)	2.661(5)
Eu(1)–N(1)	2.649(4)	Pr(1)–N(1)	2.698(6)
O(4)#1–Eu(1)–O(5)#2	75.12(10)	O(2)#1–Pr(1)–O(5)#1	75.21(18)
O(4)#1–Eu(1)–O(3)#3	136.95(10)	O(2)#1–Pr(1)–O(1)	136.85(17)
O(5)#2–Eu(1)–O(3)#3	76.90(10)	O(5)#1–Pr(1)–O(1)	76.70(17)
O(4)#1–Eu(1)–O(6)	88.04(11)	O(2)#1–Pr(1)–O(6)	87.65(19)
O(5)#2–Eu(1)–O(6)	126.68(10)	O(5)#1–Pr(1)–O(6)	126.57(16)
O(3)#3–Eu(1)–O(6)	83.14(10)	O(1)–Pr(1)–O(6)	83.49(18)
O(4)#1–Eu(1)–O(1)	81.32(10)	O(2)#1–Pr(1)–O(3)#2	81.87(18)
O(5)#2–Eu(1)–O(1)	84.12(10)	O(5)#1–Pr(1)–O(3)#2	83.99(18)
O(3)#3–Eu(1)–O(1)	127.30(10)	O(1)–Pr(1)–O(3)#2	126.67(16)
O(6)–Eu(1)–O(1)	143.48(10)	O(6)–Pr(1)–O(3)#2	143.78(18)
O(4)#1–Eu(1)–O(2)	128.13(10)	O(2)#1–Pr(1)–O(4)#2	127.91(18)
O(5)#2–Eu(1)–O(2)	78.95(10)	O(5)#1–Pr(1)–O(4)#2	78.92(18)
O(3)#3–Eu(1)–O(2)	76.36(10)	O(1)–Pr(1)–O(4)#2	76.64(17)
O(6)–Eu(1)–O(2)	142.34(10)	O(6)–Pr(1)–O(4)#2	142.86(18)
O(1)–Eu(1)–O(2)	51.74(9)	O(3)#2–Pr(1)–O(4)#2	50.85(16)
O(4)#1–Eu(1)–N(2)	137.50(11)	O(2)#1–Pr(1)–N(2)	137.13(19)
O(5)#2–Eu(1)–N(2)	146.16(11)	O(5)#1–Pr(1)–N(2)	146.45(18)
O(3)#3–Eu(1)–N(2)	79.23(11)	O(1)–Pr(1)–N(2)	79.64(19)
O(6)–Eu(1)–N(2)	73.01(11)	O(6)–Pr(1)–N(2)	73.09(19)
O(1)–Eu(1)–N(2)	91.70(12)	O(3)#2–Pr(1)–N(2)	91.5(2)
O(2)–Eu(1)–N(2)	72.34(11)	O(4)#2–Pr(1)–N(2)	72.68(19)
O(4)#1–Eu(1)–O(5)	71.55(10)	O(2)#1–Pr(1)–O(5)	72.08(17)
O(5)#2–Eu(1)–O(5)	75.43(10)	O(5)#1–Pr(1)–O(5)	76.55(16)
O(3)#3–Eu(1)–O(5)	70.16(9)	O(1)–Pr(1)–O(5)	69.97(16)
O(6)–Eu(1)–O(5)	51.27(9)	O(6)–Pr(1)–O(5)	50.03(15)
O(1)–Eu(1)–O(5)	149.32(10)	O(3)#2–Pr(1)–O(5)	150.62(17)
O(2)–Eu(1)–O(5)	141.47(9)	O(4)#2–Pr(1)–O(5)	142.14(16)
N(2)–Eu(1)–O(5)	117.94(10)	N(2)–Pr(1)–O(5)	116.78(19)
O(4)#1–Eu(1)–N(1)	75.49(11)	O(2)#1–Pr(1)–N(1)	76.04(19)
O(5)#2–Eu(1)–N(1)	143.60(11)	O(5)#1–Pr(1)–N(1)	144.08(19)
O(3)#3–Eu(1)–N(1)	139.37(11)	O(1)–Pr(1)–N(1)	139.05(18)
O(6)–Eu(1)–N(1)	72.90(11)	O(6)–Pr(1)–N(1)	72.83(18)
O(1)–Eu(1)–N(1)	70.62(11)	O(3)#2–Pr(1)–N(1)	71.01(18)
O(2)–Eu(1)–N(1)	103.34(11)	O(4)#2–Pr(1)–N(1)	102.78(19)
N(2)–Eu(1)–N(1)	62.77(12)	N(2)–Pr(1)–N(1)	61.9(2)
O(5)–Eu(1)–N(1)	114.39(10)	O(5)–Pr(1)–N(1)	114.01(17)

Symmetry transformations used to generate equivalent atoms: **1** #1 $x+1$, y, z; #2 $-x+2$, $-y$, $-z$; #3 $-x+1$, $-y$, $-z$. **2** #1 $-x$, $-y+1$, $-z$; #2 $-x-1$, $-y+1$, $-z$.

3. Results and discussion

3.1. *Structural description of [Eu(Ad)$_{3/2}$(Phen)]$_n \cdot 2n$H$_2$O (1) and [Pr(Ad)$_{3/2}$(Phen)]$_n \cdot 2n$H$_2$O (2)*

Single crystal X-ray diffraction studies reveal that **1** and **2** are isostructural; **1** will be described in detail. The Eu(III) is nine-coordinate by two chelating bidentate adipates,

Table 3. Selected bond lengths (Å) and angles (°) for **3**.

Yb(1)–O(5)	2.180(4)	Yb(1)–O(2)	2.358(4)
Yb(1)–O(6)#1	2.254(4)	Yb(1)–O(4)	2.431(4)
Yb(1)–O(3)	2.340(4)	Yb(1)–N(1)	2.482(4)
Yb(1)–O(1)	2.348(4)	Yb(1)–N(2)	2.485(4)
O(5)–Yb(1)–O(6)#1	92.04(15)	O(2)–Yb(1)–O(4)	122.90(15)
O(5)–Yb(1)–O(3)	99.98(18)	O(5)–Yb(1)–N(1)	147.88(15)
O(6)#1–Yb(1)–O(3)	156.82(16)	O(6)#1–Yb(1)–N(1)	89.13(14)
O(5)–Yb(1)–O(1)	80.21(14)	O(3)–Yb(1)–N(1)	91.01(17)
O(6)#1–Yb(1)–O(1)	86.10(14)	O(1)–Yb(1)–N(1)	131.86(14)
O(3)–Yb(1)–O(1)	76.62(15)	O(2)–Yb(1)–N(1)	76.45(14)
O(5)–Yb(1)–O(2)	135.41(14)	O(4)–Yb(1)–N(1)	78.25(15)
O(6)#1–Yb(1)–O(2)	81.23(15)	O(5)–Yb(1)–N(2)	82.48(14)
O(3)–Yb(1)–O(2)	76.29(17)	O(6)#1–Yb(1)–N(2)	76.52(14)
O(1)–Yb(1)–O(2)	55.47(13)	O(3)–Yb(1)–N(2)	124.46(15)
O(5)–Yb(1)–O(4)	84.07(15)	O(1)–Yb(1)–N(2)	154.94(14)
O(6)#1–Yb(1)–O(4)	148.04(14)	O(2)–Yb(1)–N(2)	136.67(14)
O(3)–Yb(1)–O(4)	53.91(14)	O(4)–Yb(1)–N(2)	71.53(14)
O(1)–Yb(1)–O(4)	124.07(14)	N(1)–Yb(1)–N(2)	66.60(14)

Symmetry transformation used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+2$.

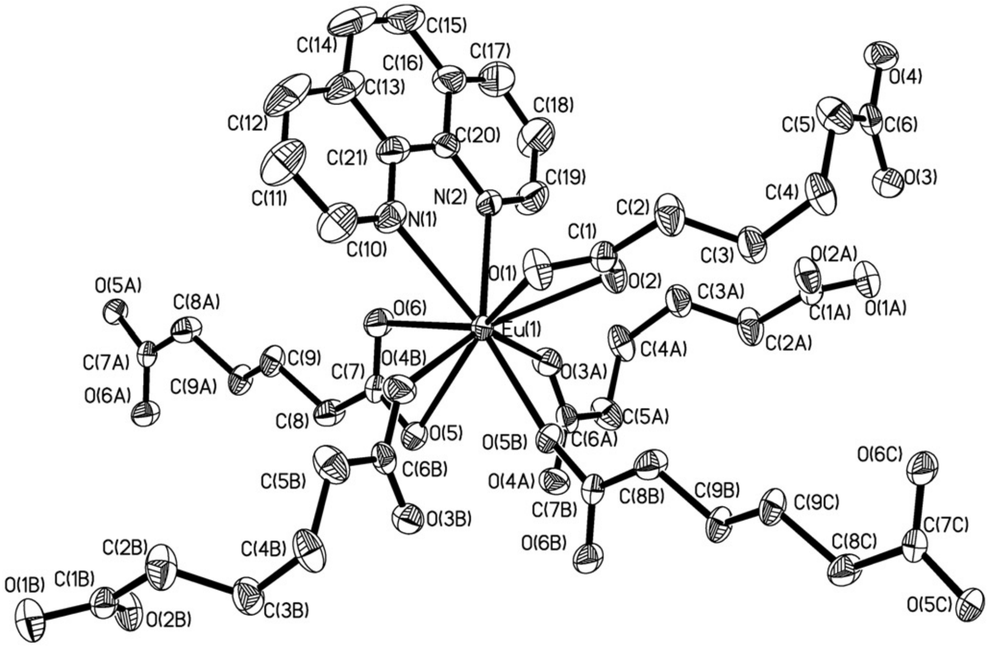

Figure 1. Coordination environment (50% probability ellipsoids) in **1**. All hydrogen atoms are omitted for clarity.

three monodentate adipates and one bidentate 1,10-phenanthroline (figure 1). There are two crystallographically dependent adipates in **1** (figure 2 **i** and **ii**). In **i**, one carboxylate group chelates one Eu(III) and the other bridges two Eu(III) ions. The aliphatic chain is ***gauche***-conformation. While in **ii**, two carboxylate groups coordinate to Eu(III) in

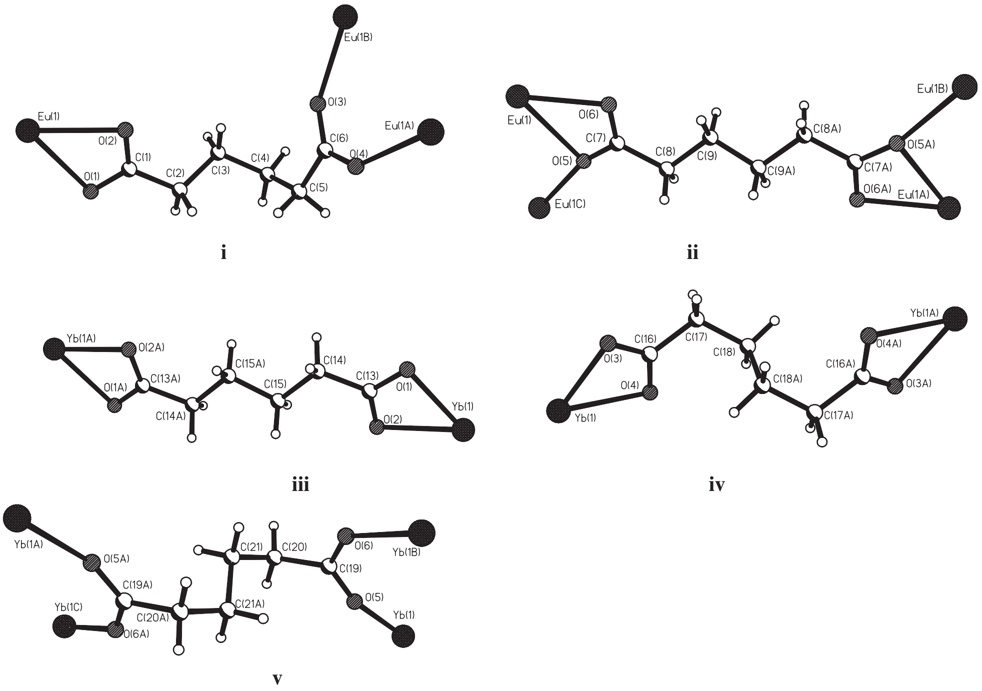

Figure 2. Coordination modes and stereo representations of conformations of five crystallographically dependent adipate ligands [(i), (ii) for **1** and (iii), (iv), (v) for **3**]: (i) anti-gauche-gauche [torsion angles: C(1)–C(2)–C(3)–C(4), 173.0°; C(2)–C(3)–C(4)–C(5), −74.7°; C(3)–C(4)–C(5)–C(6), −73.4°]; (ii) anti-anti-anti [torsion angles: C(7)–C(8)–C(9)–C(9A), 168.3°; C(8)–C(9)–C(9A)–C(8A), 180°; C(9)–C(9A)–C(8A)–C(7A), −168.3°]; (iii) anti-anti-anti [torsion angles: C(13)–C(14)–C(15)–C(15A), −174.2°; C(14)–C(15)–C(15A)–C(14A), −180°; C(15)–C(15A)–C(14A)–C(13A), 174.2°]; (iv) gauche-anti-gauche [torsion angles: C(16)–C(17)–C(18)–C(18A), −63.4°; C(17)–C(18)–C(18A)–C(17A), 180.0°; C(18)–C(18A)–C(17A)–C(16A), 63.4°]; (v) gauche-anti-gauche [torsion angles: C(19)–C(20)–C(21)–C(21A), −60.8°; C(20)–C(21)–C(21A)–C(20A), −180.0°; C(21)–C(21A)–C(20A)–C(19A), 60.8°].

Table 4. Hydrogen bond parameters (Å, °) for **1**.

D–H	d(D–H)	d(H···A)	DHA	d(D···A)	Position of A
O(7)–H(7A)	0.959	2.319	120.3	2.923	O(1) $[-x+1, -y+1, -z]$
O(7)–H(7B)	0.847	2.165	161.4	2.980	O(1) $[x-1, y, z]$
C(17)–H(17)	0.930	2.413	157.6	3.292	O(7) $[-x+1, -y+1, -z+1]$
O(8)–H(8C)	0.867	2.154	165.3	3.000	O(2) $[-x+1, -y, -z]$
O(8)–H(8D)	0.946	2.301	129.3	2.992	O(2)
C(14)–H(14)	0.930	2.431	165.9	3.341	O(8) $[-x+2, -y+1, -z+1]$

chelating and bridging tridentate mode and the aliphatic chain is ***anti***. Eu(III) ions are bridged by adipate ligands into 2-D coordination polymers. 1,10-Phenanthroline ligands locate at both sides of polymeric layers. Weak π–π stacking interactions exist between 1,10-phenanthroline ligands of adjacent layers with average distance of 3.71 Å. There are two crystallographically dependent lattice water molecules which are stabilized by three types of hydrogen bonds (table 4). Hydrogen bonding and π–π stacking interactions between layers result in a 3-D network (figure 3).

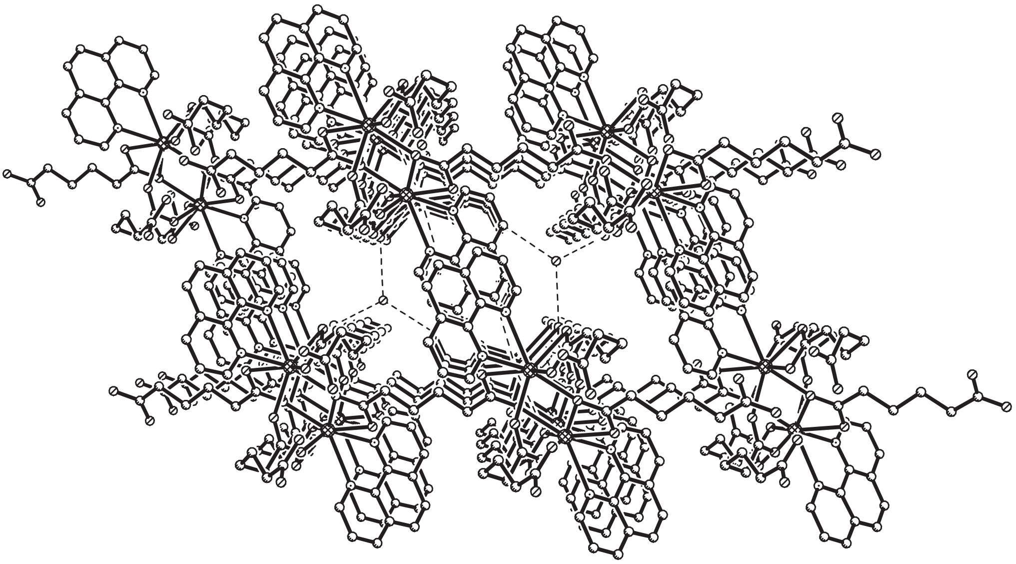

Figure 3. Packing diagram of $[Eu(Ad)_{3/2}(Phen)]_n \cdot 2nH_2O$ viewed along the *a*-axis. All hydrogen atoms are omitted for clarity.

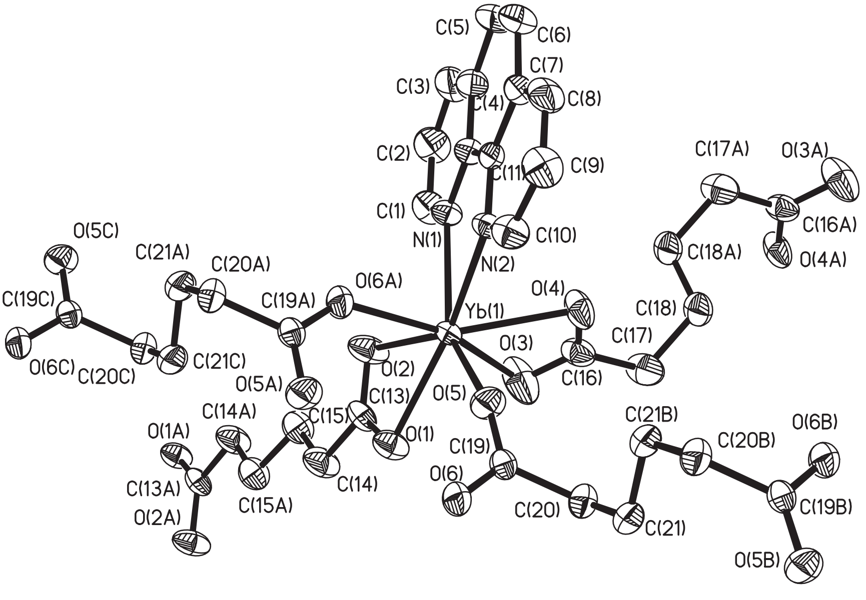

Figure 4. Coordination environment (50% probability ellipsoids) in **3**. All hydrogen atoms are omitted for clarity.

3.2. *Structural description of $[Yb(Ad)_{3/2}(Phen)]_n \cdot nH_2O$ (3)*

The crystal structure of **3** shows that the central Yb(III) ion is eight-coordinate by one bidentate 1,10-phenanthroline, two chelating bidentate and two monodentate adipates (figure 4). There are three types of crystallographically dependent adipate ligands

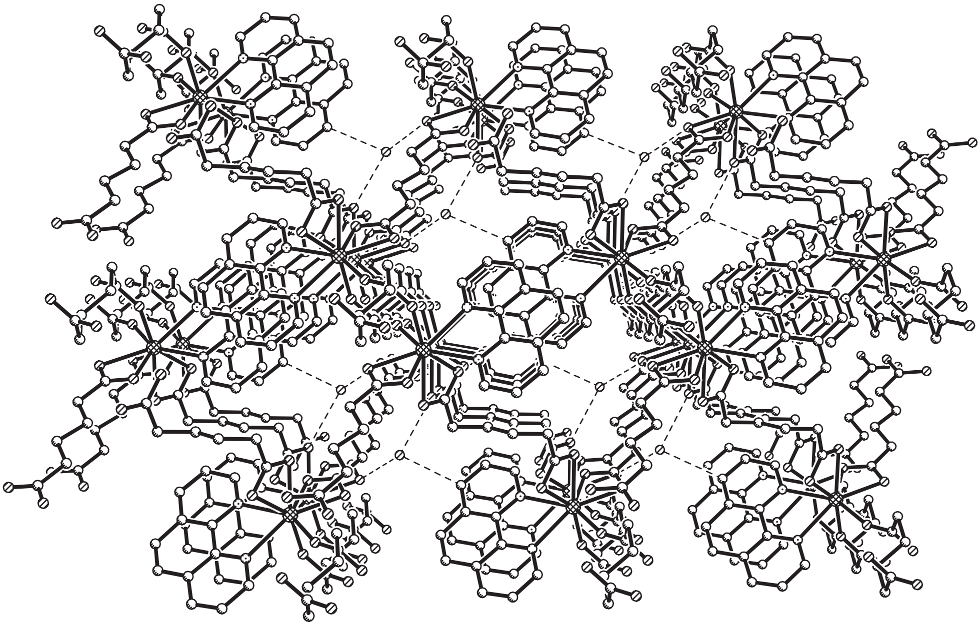

Figure 5. Packing diagram of **3** viewed along the *a*-axis. All hydrogen atoms are omitted for clarity.

Table 5. Hydrogen bond parameters (Å, °) for **3**.

D–H	d(D–H)	d(H···A)	DHA	d(D···A)	Position of A
O(7)–H(7A)	0.848	2.091	170.6	2.931	O(1) $[x, y, z-1]$
O(7)–H(7B)	0.853	2.122	162.4	2.946	O(3) $[-x+1, -y, -z+1]$
C(3)–H(3)	0.930	2.406	160.7	3.298	O(7) $[x-1, y, z]$

in **3** (figure 2 **iii**, **iv** and **v**). All carboxylate groups of **iii** and **iv** are chelating bidentate to Yb(III), but the conformations of their aliphatic chains are different. Aliphatic chain of **iii** is ***anti*** and that of **iv** is ***gauche***. The conformation of ligands **iv** and **v** are similar, both ***gauche***. The coordination mode of **v** is different from **iv** with two carboxylate groups coordinating to Yb(III) in bridging bidentate mode. The Yb(III) ions are connected by adipate ligands into a 3-D microporous structure (figure 5) with channels occupied by lattice water molecules, which form hydrogen bonds with coordinated oxygens of the adipate ligands and C–H bonds from 1,10-phenanthroline ligands (table 5), providing additional stability to the structure. 1,10-Phenanthroline ligands are parallel to each other with the average length of 3.46 Å, indicating π–π stacking interactions.

3.3. *IR spectra*

In IR spectra of the three compounds, characteristic bands of the carboxylate groups occur within the range 1545–1601 $\mathrm{cm^{-1}}$ for asymmetric stretching and 1425–1441 $\mathrm{cm^{-1}}$ for symmetric stretching [9]. C–H stretching vibrations appear above 3000 $\mathrm{cm^{-1}}$ and characteristic C–H out-of-plane bending vibrations are seen at about 731 and 850 $\mathrm{cm^{-1}}$, indicating the presence of phen [10]. The stretching bands of O–H (from the coordinated and lattice water molecules) centered at 3400 cm^{-1} are broadened by hydrogen bonding [11]. Asymmetric and symmetric stretching of CH_2 from adipate occur at about 2900 cm^{-1}. IR spectra of **1**, **2** and **3** support the results of the X-ray diffraction analysis.

Supporting information

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 642861 for **1**, 642862 for **2** and 642863 for **3**. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk; Fax: +44-1223-336033; http://www.ccdc.cam.ac.uk).

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