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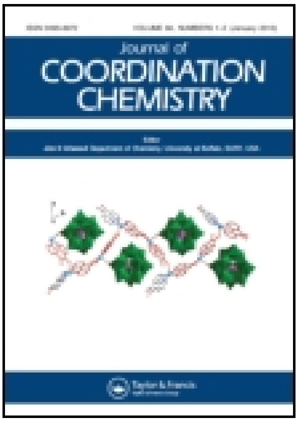

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Seven-, eight-, and ten-coordinated cerium(III) with highly connective pyridine-2,4,6-tricarboxylate, oxalate, and glycine ligands

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Two new 3-D Ce(III) coordination polymers, $[Ce_{1.3}(PTA)_2(Oxa)_2(Gly)(H_2O)_2]\cdot(Gly)4H_2O$ (**1**) and $[Ce_{2.6}(PTA)_4(Oxa)_2(H_2O)_{10}]\cdot(MeOH)7H_2O$ (**2**) (PTA = 2,4,6-pyridinetricarboxylate, oxa = oxalate and Gly = glycine), were synthesized. The oxalate in **1** and **2**, generated *in situ* from the cleavage and chemical rearrangement of $PTAH_3$, assembled into mixed-ligand networks to generate 3-D frameworks. Single crystal analysis reveals that in both complexes, Ce(III) shows coordination numbers of 7 and 10 in **1** and 8 and 10 in **2**. PTA adopts four kinds of coordination modes. These complexes were further characterized using elemental analysis, FTIR spectroscopy and thermogravimetric analysis.

Keywords: Pyridine-2,4,6-tricarboxylic acid; Ce(III) polymer; Mixed ligand; Oxalate; Glycine

1. Introduction

Discovery of architectures is the key for designing new functional materials due to their promising applications in storage, catalysis, and separation [1–3]. Metal–organic frameworks can be synthesized by the reactions between multidentate ligands containing N- or/and O-donors and lanthanide metals [4]. Most of these structures are generated by hydro(solvo)thermal techniques, while a substantial number of compounds are synthesized at room temperature [4–6]. However, to achieve desired topology is highly empirical. Many interesting final products were found involving substitution, oxidative coupling or hydrolysis. Oxalate has been generated *in situ* from the chemical rearrangement of isonicotinate [7] and pyridine-2,4,6-tricarboxylic acid ($PTAH_3$) [4c, 8] as well as oxidative coupling of methanol [9]. Such ligand transformations provide new routes for the construction of MOFs.

Studies of pyridine-2,4,6-tricarboxylate complexes with cerium are very rare [4c, 10]. By utilizing $PTAH_3$ as ligand, a ten-coordinate lanthanide environment is possible [4g, 11a]. In continuation of our studies [11] to explore coordination of $PTAH_3$ for the construction of

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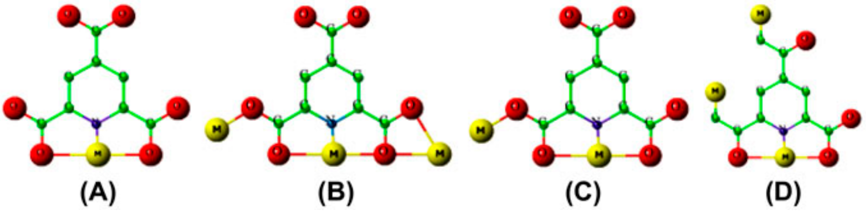

Figure 1. Coordination modes of PTA for **1** and **2**.

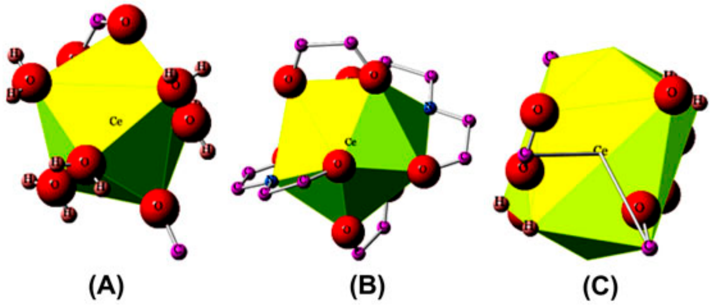

Figure 2. Coordination polyhedra around cerium in **1** and **2**.

coordination polymers, PTA has four coordination modes for **1** and **2** as shown in figure 1, while Ce(III) lies at the core of a surrounding set of 7, 8, and 10 donors as shown in figure 2. Coordination polymers were also characterized by FTIR, elemental, and thermogravimetric analysis.

2. Experimental

2.1. *Materials and measurements*

All reagents and solvents were commercially available and were used as received. Elemental analysis for C, H, and N were performed on a Vario Micro Cube, Elementar, Germany. IR spectra of the complexes were recorded on a Perkin-Elmer FTIR 180 spectrophotometer using KBr pellets from 4000 to 400 cm^{-1}. The crystal structure determination was performed on a Bruker KAPA APEX II CCD diffractometer equipped with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Thermal analysis (25–1200 °C) was recorded in a continuous nitrogen flow with a ramp rate of 10 °C min^{-1} by using a Differential Scanning Calorimeter/Thermo-gravimeter Analyzer (TGA) model SDT Q600, V8.3, TA Instruments, USA.

2.2. *Crystallographic analysis*

Suitable crystals of **1** and **2** were selected for data collection on a Bruker KAPA APEX II CCD diffractometer equipped with graphite-monochromated Mo-K$_\alpha$ radiation at 296 K.

Table 1. Details of crystals and experimental data for **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$C_{22}H_{28}Ce_{1.3}N_4O_{26}$	$C_{37}H_{50}Ce_{2.6}N_4O_{50}$
Formula weight	946.64	1715.12
Wavelength (Å)	0.71073, Mo–Kα	
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
a (Å)	11.7992(3)	11.9209(10)
b (Å)	11.8606(4)	14.5195(12)
c (Å)	13.6301(3)	17.7198(14)
α (°)	95.263(1)	102.145(4)
β (°)	108.5470(11)	100.577(5)
γ (°)	108.081(1)	91.647(4)
V (Å^3)	1680.28(7)	2940.2(4)
Z	2	2
μ (mm^{-1})	1.86	2.11
D_{Calcd} (Mg m^{-3})	1.871	1.937
Measured reflections	27,047	42,828
Independent reflections	6574	11,204
Refinement method	Full-matrix least-squares on F^2	
Final R indices [$I > 2\sigma(I)$]	$R_{\text{int}} = 0.019$	$R_{\text{int}} = 0.065$
$R[F^2 > 2\sigma(F^2)]$	0.022	0.060
$wR(F^2)$	0.058	0.152
Goodness of fit on F^2	1.04	1.09
Largest difference peak and hole (Å^{-3})	1.66; −1.16	3.12; −2.38

The structures were solved by direct methods using SHELXS-97 [12] and refined by full-matrix least-squares on F^2 using SHELXL-97 [12] within the WINGX [13] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Water and amino hydrogens were located in a difference map and refined subject to a DFIX restraint of O–H = 0.83(2) Å and N–H = 0.82(2) Å. All other hydrogens were located from difference maps and then treated as riding with C–H distances of 0.93–0.97 Å and O–H distances of 0.82 Å. The large su values and displacement parameters of carboxylate oxygen in **1** are caused by disorder. Refinement of the disorder was made anisotropically using PART restriction. This disorder was modeled as two different orientations (O3A and O3B) with occupancy factors of 0.742(8) and 0.258(8). Molecular diagrams were created using MERCURY [14]. Supramolecular and polyhedral analysis were performed and the diagrams were prepared with the aid of PLATON and CrystalMaker® [15, 16]. Details of data collection and crystal structure determinations are given in table 1.

2.3. *Synthesis*

2.3.1. Preparation of $C_{22}H_{28}Ce_{1.3}N_4O_{26}$ (1).

PTAH$_3$ was synthesized by the oxidization of pyridine-2,4,6-trimethyl with potassium permanganate following literature method [17]. To a solution of 106 mg (0.50 mM) of PTAH$_3$ in 10 mL water was slowly added a 5 mL aqueous mixture of cerium nitrate hexahydrate 54 mg (0.125 mM) and glycine 37 mg (0.50 mM). Stirring was continued to attain a clear solution and then a mixture was refluxed for 6 h. The transparent orange solution was filtered and left standing in a sealed vial at ambient temperature. Pale yellow needles suitable for single crystal analysis were directly obtained from the mother liquor after six weeks, separated from the mother liquor by decantation, washed with copious water, and dried at room temperature. IR (KBr; cm^{-1}): 3636–3247 (broad, strong) water O–H stretch; 1634 ν_{asym}(C=O); 1434, 1364 ν_{sym}(C=O). Yield *ca.* 70–75%. Anal. Calcd for $C_{22}H_{28}Ce_{1.3}N_4O_{26}$ (946.64): C, 27.89; H, 2.96; N, 5.92. Found: C, 27.68; H, 3.19; N, 5.73%.

2.3.2. Preparation of $C_{37}H_{50}Ce_{2.6}N_4O_{50}$ (2). To a solution of 106 mg (0.50 mM) of $PTAH_3$ in 10 mL water was slowly added a methanolic solution of cerium nitrate hexahydrate (54 mg, 0.125 mM). Stirring was continued to attain a clear solution and a mixture was refluxed for 6 h. The transparent yellow solution was filtered and left standing in a sealed vial at ambient temperature. Yellow plate-like crystals suitable for single crystal analysis were directly obtained from the mother liquor after four weeks, separated from the mother liquor by decantation, washed with copious water, and dried at room temperature. IR (KBr; cm^{-1}): 3646–3222 (broad, strong) water O–H stretch; 1635 ν_{asym}(C=O); 1437, 1364 ν_{sym}(C=O). Yield *ca.* 65-70%. Anal. Calcd for $C_{37}H_{50}Ce_{2.6}N_4O_{50}$ (1715.12): C, 25.89; H, 2.94; N, 3.26. Found: C, 25.71; H, 3.15; N, 3.11%.

3. Results and discussion

Oxalate was generated *in situ* in the presence of pyridine [4c, 8c] at room temperature, by hydrothermal [8a], as well as solvothermal [8b] processes. Herein, the presence of glycine and methanol may have similar effects as reported for pyridine and solvothermal, respectively. However, our results revealed that instead of hydrothermal process, reflux as well as controlled rate of evaporation led to the transformation of $PTAH_3$ to oxalate.

3.1. *Crystal structure of 1*

The molecular structure of **1** and the atom-labeling scheme are shown in figure 3. Selected bond lengths and angles are given in table 2. The asymmetric unit of **1** consists of two Ce (III), two coordinated waters, four non-coordinated waters, two glycines, two pyridine-2,4,6-tricarboxylates (PTA), and two half oxalates about an inversion center. The Ce(III) ions have two coordination types. Ce1 is a 10 coordinate by two nitrogens (N1 and N2) from two pyridine rings, four oxygens (O1, O6, O7, and O12) from four carboxylates and four oxygens (O17, $O18^{i}$, O19, and $O20^{ii}$) from two oxalates as shown in figure 2(B). Ce2 is seven-coordinate by O8, $O5^{ii}$, and $O4^{iv}$ from three carboxylates, O25 and $O23^{v}$ from two waters, and O13 and $O14^{vi}$ from two glycines as shown in figure 2(C).

Ce1 and oxalate form a coordination polymer running parallel to the [001] direction. The two tetradentate oxalates are located at a symmetry plane and bridge two symmetry-related cerium cations via bis-bidentate chelation. These *O,O*–chelate interactions are crystallographically equivalent with bite angles of 60.35(5)°–60.48(5)° with $Ce1\cdots Ce1^{i}$ and $Ce1\cdots Ce1^{ii}$ distances of 6.826 and 6.804 Å [symmetry operations: (i) $-x, -y, -z$; (ii) $-x, -y, -z+1$]. Ce2 generates eight-membered rings bonding to two glycines [18]. The $Ce2\cdots Ce2^{vi}$ separation is 5.582 Å (figure 4). PTA exhibit two distinct coordination modes, as depicted in figure 1(C) and 1(D), μ^2–bridging coordination and μ^3–bridging coordination. Ce1 and Ce2 are bridged by one μ^2–$O_{carboxylate}$ and two μ^3–$O_{carboxylate}$. $Ce2\cdots Ce1$ and $Ce2\cdots Ce1^{ii}$ separations are 6.005 and 5.696 Å, respectively. Ce(III) ions, carboxylates, oxalates, and glycines produce a 3-D coordination polymer (figure 5).

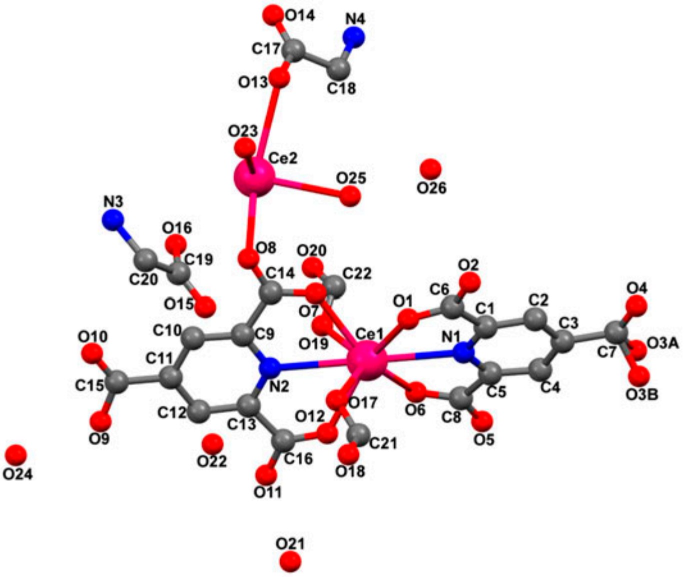

Figure 3. Molecular structure of **1** with atom-labeling scheme. For clarity, hydrogens have been omitted.

Each PTA is coordinated to Ce(III) in conventional *O,N,O*'–tridentate via nitrogen and two oxygens from each of the two carboxylates. The Ce–$O_{oxalate}$ distances are 2.6254 (16)–2.6851(16) Å [19], the Ce–O_{water} bond lengths are 2.774(3) and 2.865(3) Å and the Ce–$O_{glycine}$ bond lengths are 2.754(2) and 2.903(2) Å [20]. The Ce–$O_{carboxylate}$ bond distances are 2.5086(16)–2.8528(19) Å and the Ce–N bond lengths are 2.6815(18) and 2.6982(18) Å. These bond distances are comparable to reported corresponding bonds [21]. The pyridine rings' mean planes are approximately planar, with maximum deviations of 0.0215(15) Å for C1 and 0.0137(15) Å for C9, respectively.

Molecules of **1** are linked into sheets by the combination of O–H···O, N–H···O, and C–H···O hydrogen bonds (table 2). Water O3A and O3B at (x, y, z) are hydrogen-bond donors, via H3D and H3E, to O19 and O20 at ($x+1$, y, z), forming C(9) and C(11) chains [22] running parallel to the [100] direction. Similarly, O9 at (x, y, z) is a hydrogen-bond donor, via H9, to O17 and O18 at ($-1-x$, $-y$, $-z$), forming a C(9)C(11)[$R_2^2(4)$] chain of rings running parallel to the [100] direction (figure 6). Water O21 at (x, y, z) is a hydrogen-bond donor, via H21A and H21B, to O11 at (x, y, z) and O2 at ($-x$, $-y$, $-z$), forming a $R_2^2(14)$ ring. The combination of N3–H3A···O21^{ix}, N3–H3B···O24^{v}, O21–H21B···O2^{i}, N4–H4A···O24^{x}, and N4–H4B···O2^{xi} hydrogen bonds generates a chain of edge-fused $R_5^3(10)$ rings running parallel to the [010] direction. Finally, waters link neighboring polymeric chains via O–H···O hydrogen bonds into a 2-D framework parallel to the *bc* plane (figure 7).

3.2. *Crystal structure of 2*

The molecular structure of **2** with the atom labeling is shown in figure 8. Selected bond lengths and angles are collected in table 3. The asymmetric unit of **2** consists of four Ce (III) ions, 10 coordinated waters, seven non-coordinated waters, one methanol, four

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

Bond lengths (Å)			
Ce1–O12	2.5086(16)	Ce1–O18^{i}	2.6254(16)
Ce1–O6	2.5103(16)	Ce1–O19	2.6314(16)
Ce1–O7	2.5435(16)	Ce1–O20^{ii}	2.6636(16)
Ce1–O1	2.5479(16)	Ce1–N1	2.6815(18)
Ce1–O17	2.6851(16)	Ce1–N2	2.6982(18)
Ce2–O8	2.6511(18)	Ce2–O5^{ii}	2.7484(19)
Ce2–O4^{iv}	2.8528(19)	Ce2–O14^{vi}	2.754(2)
Ce2–O13	2.903(2)	Ce2–O23^{v}	2.865(3)
Ce2–O25	2.774(3)		
Angle (°)			
O18^{i}–Ce1–O17	60.35(5)	O19–Ce1–O20^{ii}	60.48(5)

D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
O3A–H3D···O20^{iii}	0.82	2.659(3)	166
O3A–H3D···O19^{iii}	0.82	3.159(3)	135
O3B–H3E···O19^{iii}	0.82	2.757(7)	159
O3B–H3E···O20^{iii}	0.82	3.054(8)	141
O9–H9···O17^{ix}	0.82	2.684(2)	164
O9–H9···O18^{iv}	0.82	3.237(2)	138
O26–H26A···O19^{ii}	0.86(2)	3.022(6)	143(8)
O26–H26A···O3B^{xi}	0.86(2)	2.990(8)	114(9)
O26–H26B···O22^{ii}	0.88(2)	2.703(5)	164(10)
O25–H25A···O7	0.82(2)	2.881(3)	159(4)
O25–H25B···O26	0.82(2)	2.673(5)	160(5)
O21–H21A···O11	0.81(2)	2.773(3)	126(4)
O21–H21B···O2^{i}	0.83(2)	2.790(3)	158(4)
O22–H22A···O25^{vii}	0.85(2)	2.779(4)	168(5)
O22–H22B···O11	0.84(2)	2.769(3)	172(4)
O23–H23A···O15^{ix}	0.83(2)	2.826(3)	172(4)
O23–H23B···O22	0.83(2)	2.866(4)	143(4)
O24–H24A···O23	0.81(2)	2.781(3)	167(4)
O24–H24B···O18^{iv}	0.81(2)	2.808(3)	172(3)
O13–H13···O5	0.82	2.566(3)	176
N4–H4A···O24^{x}	0.82(2)	2.829(3)	178(3)
N4–H4B···O2^{xi}	0.82(2)	2.824(3)	173(3)
O16–H16···O8	0.82	2.565(2)	160
N3–H3B···O24^{v}	0.82(2)	2.851(3)	167(3)
N3–H3A···O21^{ix}	0.81(2)	2.877(4)	157(3)
C18–H18B···O6^{xii}	0.97	3.364(3)	152
C20–H20B···O7^{xiii}	0.97	3.376(3)	144
C20–H20B···O8^{xiii}	0.97	3.387(3)	160

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, -z+1$; (iii) $x+1, y, z$; (iv) $x-1, y, z$; (v) $x, y-1, z$; (vi) $-1-x, -1-y, 1-z$; (vii) $x, y+1, z$; (ix) $-x-1, -y, -z$; (x) $-x, -y+1, -z+1$; (xi) $-x+1, -y, -z+1$; (xii) $-x+1, -y+1, -z+1$; (xiii) $-x-1, -y-1, -z$.

pyridine-2,4,6-tricarboxylates (PTA), one oxalate, and two half oxalates about an inversion center.

Ce(III) ions have two coordination types. In one, Ce1 and Ce2 are 10 coordinate by two nitrogens (N1, N2, N3, and N4) from two pyridine rings, four oxygens (O1, O6, O7, O12, O17, O22, O23, and O28) from four carboxylates and four oxygens (O13, O14, O15, O16, O29, O30^{i}, O36, and O37^{ii}) from two oxalates [symmetry operations: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+2, -z$] as shown in figure 2(B). In the second coordination, Ce3 and Ce4 are eight-coordinate by five oxygens (O31, O32, O33, O34, O35, O38, O39, O40,

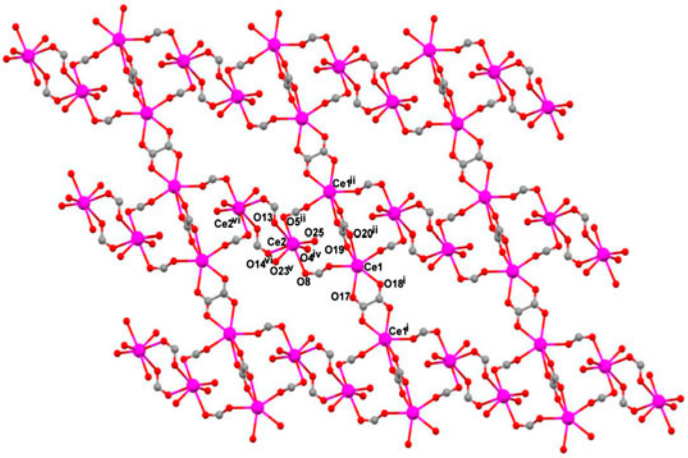

Figure 4. View of **1** showing the formation of a coordination polymer chain parallel to the [111] direction (symmetry codes as in table 2).

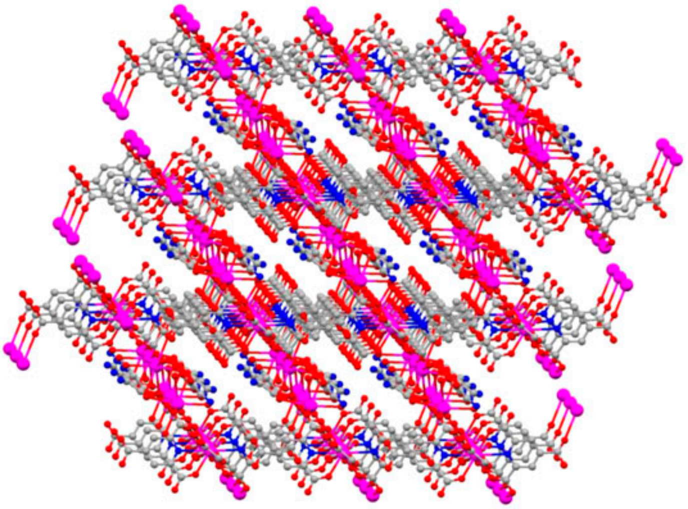

Figure 5. View of 3-D network of **1** (Ce, pink; N, blue; O, red)(see http://dx.doi.org/10.1080/00958972.2013.825719 for color version).

O41, and O42) from five waters and three oxygens (O23, O24, $O5^{iii}$, O1, O2, and $O27^{iv}$) from two carboxylates as shown figure 2(A). Ce1 and Ce2 and oxalate ligands form a coordination polymer running parallel to the [1–11] direction. The Ce1···Ce2, $Ce1\cdots Ce1^{ii}$, and $Ce2\cdots Ce2^{i}$ separations are 6.667, 6.608, and 6.745 Å, respectively (figure 9). PTA coordinates as depicted in figure 1(B) with μ^3–bridging. The Ce1, Ce3, and Ce4 are bridged by one μ^3–$O_{carboxylate}$. The Ce1···Ce4 and $Ce1\cdots Ce3^{iii}$ separations are 5.294 and 6.939 Å, respectively (figure 10). Similarly, Ce2, Ce3, and Ce4 are bridged by one μ^3–$O_{carboxylate}$, extending the 2-D chain into a 3-D network, as shown in figure 11. The Ce2···Ce3 and $Ce2\cdots Ce4^{iv}$ separations are 5.046 and 6.919 Å, respectively (figure 10).

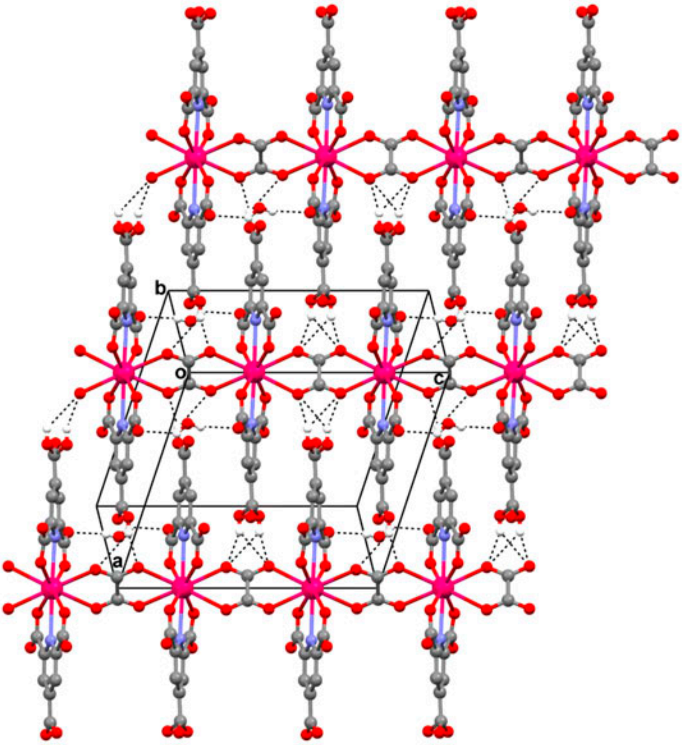

Figure 6. Complex **1** showing the formation of a chain along [100] generated by the O–H···O hydrogen bonds (dashed lines; see table 2). For clarity, hydrogens not involved in the motif have been omitted.

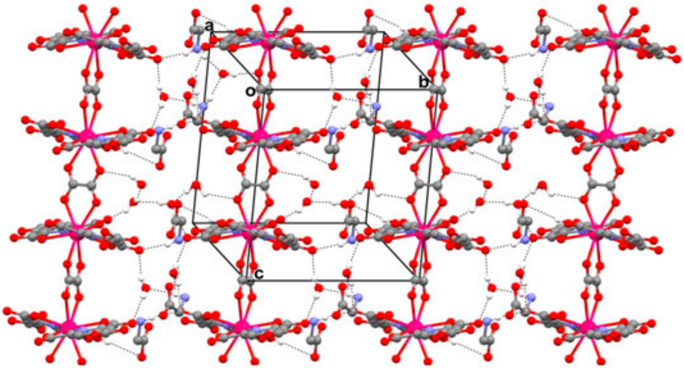

Figure 7. Complex **1** waters link neighboring polymeric chains via O–H···O hydrogen bonds into a 2-D framework parallel to the *bc* plane. For clarity, hydrogens are not involved in the motif have been omitted.

Each PTA is a coordinated tridentate via nitrogen and two oxygens, one from each carboxylate. The Ce–O$_{oxalate}$ bond distances are 2.550(5)–2.638(5) Å [23], Ce–O$_{water}$ bond lengths are 2.391(6)–2.537(7) Å [24] and Ce–O$_{carboxylate}$ bond lengths are 2.312(6)–2.899 (6) Å. The Ce–N distances are 2.666(6)–2.692(6) Å, also observed in other lanthanide complexes [25]. The pyridine ring mean planes are approximately planar with a maximum

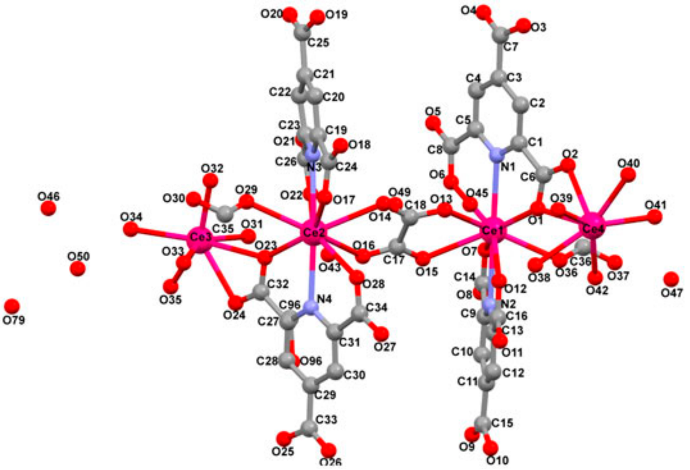

Figure 8. Molecular structure of **2** with atom-labeling scheme. For clarity, hydrogens have been omitted.

deviations of 0.0152(53) Å for C5, 0.0177(55) Å for C10, 0.0322(54) Å for C23, and 0.0074(53) Å for C31.

Molecules of **2** are linked into sheets by the combination of O–H···O and C–H···O hydrogen bonds (table 3). In the asymmetric unit, O38–H38A···O12, O32–H32B···O29, O45–H45A···O38, O45–H45B···O13, O42–H42B···O47, O41–H41A···O47, O31–H31A···O43, O43–H43A···O22, and O43–H43A···O16 produce S(4)S(6)S(8) motifs. O3 at (x, y, z) is a hydrogen-bond donor, via H3, to O37 at ($-x+1$, $-y+2$, $-z$), forming a centrosymmetric $R_2^2(18)$ ring centered at (1/2, 1, 0). O10 at (x, y, z) is a hydrogen-bond donor, via H10A, to O13 and O14 at ($x-1$, y, z), forming a $R_2^2(4)$ ring. Similarly, O19 at (x, y, z) is a hydrogen-bond donor, via H19, to O15 and O16 at ($x+1$, y, z), forming a $R_2^2(4)$ ring. O25 at (x, y, z) is a hydrogen-bond donor, via H25, to O30 at ($x-1$, y, z), forming a C(11) chain running parallel to the [100] direction. Water O39 and O40 at (x, y, z) is a hydrogen-bond donor, via H39A and H40A, to O18 at ($-x+1$, $-y+1$, $-z$), forming a $R_2^1(6)$ ring. The combination of O40–H40B···O24$^{\mathrm{ix}}$ and O35–H35B···O2$^{\mathrm{xii}}$ hydrogen bonds generates a $R_2^2(8)$ ring. Water O38 and O39 at (x, y, z) is a hydrogen-bond donor, via H38B and H39B, to O11 at ($-x$, $-y+1$, $-z$), forming a $R_2^1(6)$ ring. Strong hydrogen bonds are observed between water and oxygens of carboxyl groups, with the O···O distances from 2.828(8) to 3.139(9) Å (table 3). There are also weak hydrogen-bonding interactions between C4 and C96 and O35 and O20. Therefore, the packing diagram of **2** is a 3-D layer filled with crystal waters.

3.3. *Thermal analysis*

TGA experiments reveal weight loss consistent with the proposed stoichiometry. The decomposition pattern of **1** is illustrated in Supplementary material. At the first stage, water is released corresponding to weight loss of 11.1% (calculated value 11.4%) to 140 °C for two coordinated and four non-coordinated waters. The second weight loss of 66.1% to 860 °C results from the successive release of organic moieties (Calcd 65.5%) assuming 22.8% Ce_2O_3 as the final product (Calcd 23.1%).

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

Bond lengths (Å)			
N1–Ce1	2.692(6)	N2–Ce1	2.673(6)
N3–Ce2	2.685(6)	N4–Ce2	2.666(6)
O1–Ce1	2.568(6)	O6–Ce1	2.531(5)
O7–Ce1	2.536(5)	O12–Ce1	2.566(5)
O17–Ce2	2.535(5)	O28–Ce2	2.520(5)
O22–Ce2	2.591(6)	O23–Ce2	2.540(5)
Ce4–O27^{iv}	2.312(6)	O23–Ce3	2.750(5)
O24–Ce3	2.521(6)	O1–Ce4	2.899(6)
O27–Ce4	2.312(6)	O2–Ce4	2.413(6)
Ce3–O5	2.379(6)	O5^{iii}–Ce3	2.379(6)
O13–Ce1	2.571(5)	O14–Ce2	2.618(5)
O15–Ce1	2.632(6)	O16–Ce2	2.579(5)
O29–Ce2	2.608(5)	O36–Ce1	2.550(5)
O30^{i}–Ce2	2.638(5)	O37^{ii}–Ce1	2.606(6)
Ce3–O35	2.391(6)	Ce3–O31	2.399(7)
Ce3–O33	2.416(6)	Ce3–O32	2.425(7)
Ce3–O34	2.450(7)	Ce4–O38	2.407(7)
Ce4–O41	2.426(9)	Ce4–O39	2.439(7)
Ce4–O40	2.443(6)	Ce4–O42	2.537(7)
Angles (°)			
O13–Ce1–O15	61.61(16)	O36–Ce1–O37^{ii}	62.69(17)
O29–Ce2–O30^{i}	61.35(15)	O16–Ce2–O14	61.84(16)
Ce3–C32–O23–Ce2	174.1(5)	Ce4–C6–O1–Ce1	−179.7(5)
D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
O3–H3···O37^{v}	0.82	2.754(8)	157
O10–H10A···O14^{vi}	0.82	2.668(8)	162
O10–H10A···O13^{vi}	0.82	3.242(8)	141
O19–H19···O15^{vii}	0.82	2.674(9)	147
O19–H19···O16^{vii}	0.82	3.074(9)	143
O25–H25···O30^{vi}	0.82	2.646(8)	161
O49–H49B···O43	0.83(2)	3.078(14)	157(12)
O49–H49A···O6	0.83(2)	2.824(10)	163(16)
O40–H40A···O18^{viii}	0.82(2)	2.988(9)	140(8)
O40–H40B···O24^{ix}	0.82(2)	2.923(9)	154(9)
O45–H45A···O38	0.83(2)	3.092(15)	141(17)
O45–H45B···O13	0.83(2)	2.782(11)	139(17)
O39–H39A···O18^{viii}	0.83(2)	2.737(9)	173(13)
O39–H39B···O11^{iv}	0.83(2)	2.763(10)	149(12)
O42–H42A···O46^{x}	0.83(2)	2.958(12)	121(10)
O42–H42B···O47	0.83(2)	2.865(13)	159(13)
O38–H38A···O12	0.82(2)	2.751(9)	160(12)
O38–H38B···O11^{iv}	0.82(2)	2.787(10)	165(11)
O41–H41A···O47	0.83(2)	2.909(13)	136(11)
O31–H31A···O43	0.83(2)	2.872(11)	172(9)
O31–H31B···O9^{xi}	0.83(2)	3.139(9)	147(11)
O43–H43B···O20^{vi}	0.83(2)	3.035(13)	143(6)
O43–H43A···O22	0.84(2)	3.124(11)	139(14)
O43–H43A···O16	0.84(2)	2.948(10)	114(10)
O46–H46A···O28^{i}	0.83(2)	2.855(9)	164(14)
O46–H46B···O45^{i}	0.83(2)	2.935(14)	159(15)
O34–H34A···O3^{xii}	0.83(2)	3.129(10)	165(12)
O34–H34B···O50	0.84(2)	2.746(12)	133(13)
O47–H47B···O7^{ii}	0.83(2)	3.069(12)	122(12)
O32–H32A···O49^{iii}	0.83(2)	2.879(11)	172(11)
O32–H32B···O29	0.83(2)	2.856(8)	146(9)

(*Continued*)

Table 3. (*Continued*).

O35–H35A···O8^{xi}	0.83(2)	2.844(9)	174(10)
O35–H35B···O2^{xii}	0.83(2)	2.880(9)	175(8)
O33–H33A···O17^{i}	0.83(2)	2.828(8)	135(8)
O33–H33B···O26^{xiii}	0.83(2)	2.976(8)	155(11)
O50–H50A···O79	0.83(2)	2.69(2)	137(15)
O50–H50B···O18^{i}	0.83(2)	2.780(10)	174(15)
O79–H79A···O79^{xiv}	0.83(2)	2.74(3)	110(2)
O79–H79B···O45^{xii}	0.83(2)	2.68(2)	114(22)
C4–H4···O35^{iii}	0.93	3.329(9)	162(1)
C30–H30···O40^{iv}	0.93	3.280(9)	163(1)
C96–H96B···O43	0.96	2.722(17)	125
C96–H96C···O24	0.96	3.130(16)	131
C96–H96A···O20^{iii}	0.96	3.110(18)	157(1)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+2, -z$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x, -y+1, -z$; (v) $-x+1, -y+2, -z$; (vi) $x-1, y, z$; (vii) $x+1, y, z$; (viii) $-x+1, -y+1, -z$; (ix) $x, y, z-1$; (x) $x-1, y, z-1$; (xi) $-x, -y+2, -z+1$; (xii) $x, y, z+1$; (xiii) $-x, -y+1, -z+1$; (xiv) $-x+1, -y+1, -z+2$.

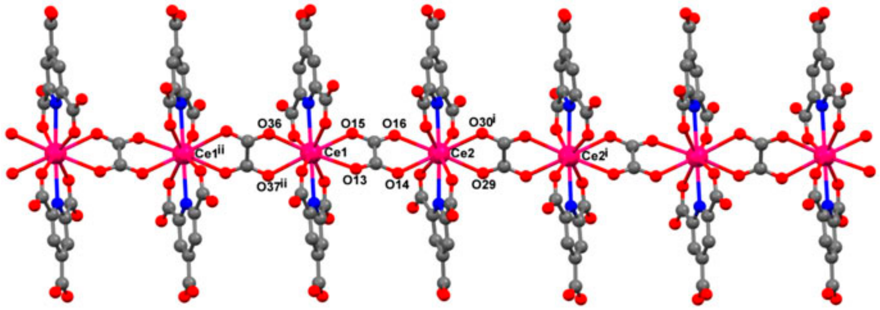

Figure 9. Complex **2** showing the formation of a coordination polymer chain parallel to the [1–11] direction (symmetry codes as in table 3).

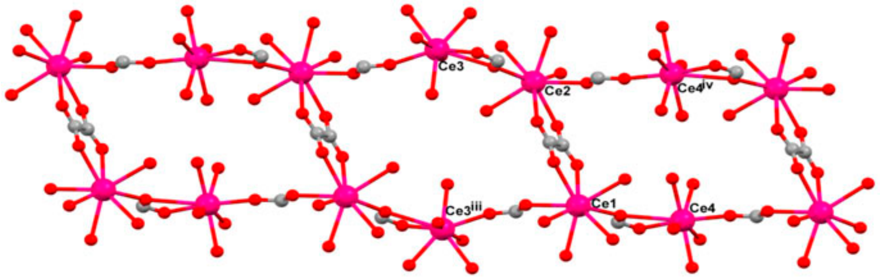

Figure 10. Complex **2** showing the formation of a coordination polymer chain parallel to the [111] direction (symmetry codes as in table 3).

The decomposition pattern of **2** is illustrated in Supplementary material. At the first stage, water is released corresponding to weight loss of 20.1% (calculated value 19.6%) to 190 °C for 10 coordinated and seven non-coordinated waters and one methanol. The second weight loss of 55.4% to 820 °C results from the successive release of organic moieties (Calcd 55.1%) assuming 24.6% Ce_2O_3 as the final product (Calcd 23.1%).

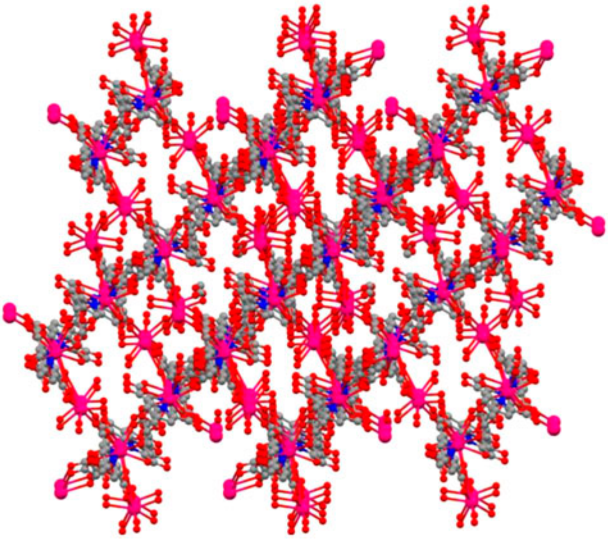

Figure 11. View of 3-D network of **2** (Ce, pink; N, blue; O, red) (see http://dx.doi.org/10.1080/00958972.2013.825719 for color version).

4. Conclusion

Two mixed-ligand cerium(III) coordination polymers were synthesized by applying reflux. Mixed-ligand approach as well as variable coordination modes of $PTAH_3$ have potential to design coordination polymers.

Supplementary material

CCDC 863355 and 863356 contain supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

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