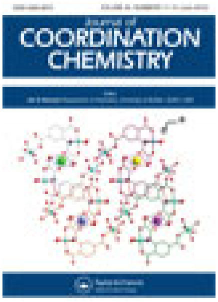

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

1-D and 2-D coordination polymers of cerium(III) with pyridine-2,4,6-tricarboxylic acid: synthesis and structural, spectroscopic, and thermal properties

Shahzad Sharif [a] [b] , Onur Sahin [c] , Islam Ullah Khan [a] & Orhan Büyükgüngör [c]

[a] Materials Chemistry Laboratory, Department of Chemistry , GC University , Lahore 54000 , Pakistan
[b] Chemical Crystallography, Chemistry Research Laboratory , 12 Mansfield Road, OX1 3TA Oxford , UK
[c] Department of Physics, Faculty of Arts and Sciences , Ondokuz Mayıs University , Samsun , Turkey

To cite this article: Shahzad Sharif , Onur Sahin , Islam Ullah Khan & Orhan Büyükgüngör (2012) 1-D and 2-D coordination polymers of cerium(III) with pyridine-2,4,6-tricarboxylic acid: synthesis and structural, spectroscopic, and thermal properties, Journal of Coordination Chemistry, 65:11, 1892-1904, DOI: 10.1080/00958972.2012.685165

To link to this article: http://dx.doi.org/10.1080/00958972.2012.685165

Journal of Coordination Chemistry
Vol. 65, No. 11, 10 June 2012, 1892–1904

1-D and 2-D coordination polymers of cerium(III) with pyridine-2,4,6-tricarboxylic acid: synthesis and structural, spectroscopic, and thermal properties

SHAHZAD SHARIF*†‡, ONUR SAHIN§, ISLAM ULLAH KHAN*† and ORHAN BÜYÜKGÜNGÖR§

†Materials Chemistry Laboratory, Department of Chemistry, GC University, Lahore 54000, Pakistan
‡Chemical Crystallography, Chemistry Research Laboratory, 12 Mansfield Road, OX1 3TA Oxford, UK
§Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey

(*Received 19 June 2011; in final form 12 March 2012*)

Two new Ce(III) complexes of pyridine-2,4,6-tricarboxylate (ptc), $[Ce_2(H_2O)_2(C_8H_3NO_6)_4(C_2O_4)Na_2(H_2O)_5]_n(H_2O)_4$ (**1**) and $[Ce(H_2O)_3(C_8H_2NO_6)]_n(H_2O)$ (**2**), were crystallized in the triclinic space group *P*-1 and the monoclinic space group $P2_1/c$, respectively. These polymers were also characterized by elemental analysis, FTIR spectroscopy, and thermogravimetric analysis. The latter shows high thermal stability for **1**. Each Ce(III) is ten-coordinate with two nitrogen atoms from two pyridine rings, five oxygen atoms from five carboxylic groups, two oxygen atoms from oxalate and one oxygen from water. Oxygen at the 2,6-position of ptc is a bridge to construct a 1-D polymer for **1**. Each Ce(III) is nine-coordinate with five oxygen atoms and one nitrogen from ptc and three water molecules, giving a tricapped trigonal prism for **2**. Each ptc bridges three Ce(III) ions with the formation of 2-D polymeric chains, and each carboxylic acid group at the 2,6-position of ptc is only bound to one Ce(III). The other carboxylate at the 6-position is bound to another Ce(III), and the carboxylates at the four-position adopt a chelating mode. Molecules are linked principally by OH···O hydrogen bonds involving water and carboxylate, forming R_1^2 (6), R_3^3 (14), and R_4^4 (27) rings, which link to give a 3-D network.

Keywords: Pyridine-2,4,6-tricarboxylic acid; Cerium(III); 2-D lanthanide polymers; Hydrogen bonds

1. Introduction

In supramolecular and materials chemistry, construction of inorganic–organic hybrid coordination polymers is of intense research activity owing to their fascinating structures and potential application as luminescent sensors, gas/chemical storage and separation, catalysts, and magnetic materials [1–11]. Multidentate ligands containing

---

*Corresponding authors. Email: mssharif@gcu.edu.pk; iukhan@gcu.edu.pk

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2012.685165

N-/O-donors are considered good candidates for building such complexes [12, 13]. Pyridine-2,4,6-tricarboxylate (ptc), having multidentate coordination modes, can link 3d, 4f, and 3d-4f metal ions to give supramolecular complexes. Much research has focused on 3d metal supramolecular architectures [14–22], while studies on lanthanide complexes are limited [23–27], and coordination polymers with cerium and H_3ptc have not been investigated. Herein, we report an easy synthesis of new 1- and 2-D cerium-based coordination polymers with diverse H_3ptc coordination, comprising 10 and 9 coordination numbers for **1** and **2**, respectively (figure 1). These polymers were characterized using single-crystal diffraction, elemental analysis, FTIR spectroscopy, and thermogravimetric analysis.

2. Experimental

2.1. *Materials and measurements*

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

2.2. *Synthesis*

2.2.1. Synthesis of 1, $C_{34}H_{34}Ce_2N_4Na_2O_{39}$. Pyridine-2,4,6-tricarboxylic acid was synthesized by the oxidization of pyridine-2,4,6-trimethyl with potassium permanganate following a literature method [28]. A mixture of H_3ptc (110 mg, 0.5 mmol) and $Ce(NO_3)_3 \cdot 6H_2O$ (110 mg, 0.25 mmol) in 15 mL H_2O followed by (45 mg, 0.3 mmol) sodium oxalate was heated in an autoclave at 160°C under autogenous pressure for 3 h. The resultant yellowish mixture was filtered and the filtrate was left for slow

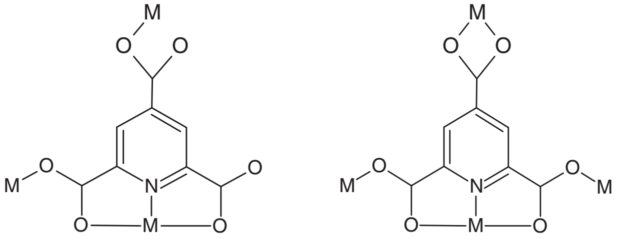

Figure 1. Coordination mode of H_3ptc for **1** and **2**.

evaporation to yield light yellow needles suitable for the analysis on a single-crystal diffractometer.

2.2.2. Synthesis of 2, $C_8H_{10}CeNO_{10}$. A mixture of H_3ptc (110 mg, 0.5 mmol) and $Ce(NO_3)_3 \cdot 6H_2O$ (110 mg, 0.25 mmol) in 15 mL H_2O followed by 200 µL of trifluoroacetic acid was heated in an autoclave at 160°C under autogenous pressure for 3 h. The resultant yellowish mixture was filtered and the filtrate was evaporated slowly to yield yellow plates suitable for the analysis by single-crystal diffraction.

2.3. *X-ray diffraction analysis*

Suitable crystals of **1** and **2** were selected for data collection which was performed on a Bruker KAPA APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation at 296 K. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [29] from within the WINGX [30] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Water hydrogen atoms were located in a difference map and refined subject to a DFIX restraint of O–H = 0.83(2) Å. All other hydrogen atoms were located from difference maps and then treated as riding with C–H distances of 0.93 Å and O–H distances of 0.82 Å. Molecular diagrams were created using MERCURY 1.4.1 [31]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [32]. Details of data collection and crystal structure determinations are given in table 1. The hydrogen bonds are characterized in table 2.

Table 1. Crystal and refinement data.

	1	**2**
Empirical formula	$C_{34}H_{34}Ce_2N_4Na_2O_{39}$	$_8H_{10}CeNO_{10}$
Formula weight	1448.87	420.29
Temperature (K)	296	296
Radiation, Wavelength (Å)	Mo-Kα; 0.71073	Mo-Kα; 0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
Unit cell dimensions (Å, °)		
a	11.5675(4)	12.1373(5)
b	11.7844(3)	7.4129(3)
c	19.4348(6)	13.6653(5)
α	97.7690(10)	90.00
β	103.8510(9)	96.508(2)
γ	99.4940(10)	90.00
Volume (Å^3), *Z*	2494.45(13), 2	1221.58(8), 4
Calculated density (g cm^{-3})	1.929	2.285
Crystal size (mm^3)	0.17 × 0.15 × 0.12	0.15 × 0.12 × 0.10
θ range for data collection (°)	2.3–28.2	3.0–28.3
Color	Orange	Yellow
Crystal shape	Block	Block
Reflections collected	37,149	10,562
Independent reflections	9230 [*R*(int) = 0.033]	2529 [*R*(int) = 0.033]
Parameters refined	796	213
Goodness-of-fit on F^2	1.10	1.05
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.030$, $wR_2 = 0.073$	$R_1 = 0.019$, $wR_2 = 0.046$
R indices (all data)	$R_1 = 0.045$, $wR_2 = 0.084$	$R_1 = 0.022$, $wR_2 = 0.047$
Largest difference peak and hole (e Å^{-3})	−0.63 and 1.86	−0.67 and 0.56

Table 2. Parameters of hydrogen bonds for **1** and **2**.

D–H···A	*d*(D–H)	D(H···A)	∠DHA	*d*(D···A)	Symmetry operations
1					
O(3)–H(3)···O(28)	0.82	1.85	2.623 (4)	158	$x-1, y-1, z$
O(3)–H(3)···O(30)	0.82	2.51	3.181 (4)	140	$x-1, y-1, z$
O(10)–H(10A)···O(39)	0.82	1.75	2.569 (5)	173	x, y, z
O(15)–H(15)···O(38)	0.82	1.84	2.625 (4)	160	$x, y+1, z$
O(22)–H(22)···O(40)	0.82	1.76	2.575 (5)	175	x, y, z
O(25)–H(25A)···O(7)	0.81 (2)	1.97 (2)	2.748 (4)	162 (5)	x, y, z
O(25)–H(25B)···O(33)	0.82 (2)	1.91 (2)	2.714 (5)	170 (5)	x, y, z
O(26)–H(26A)···O(19)	0.82 (2)	1.96 (2)	2.746 (5)	159 (5)	x, y, z
O(26)–H(26B)···O(37)	0.82 (2)	1.96 (2)	2.775 (5)	172 (5)	$-x+1, -y+1, -z$
O(31)–H(31A)···O(36)	0.84 (2)	2.17 (3)	2.989 (7)	165 (8)	$-x+1, -y+1, -z+1$
O(31)–H(31B)···O(24)	0.83 (2)	2.24 (4)	3.041 (6)	163 (8)	$-x+2, -y+1, -z+1$
O(31)–H(31B)···O(28)	0.83 (2)	2.59 (9)	3.028 (6)	114 (8)	$-x+2, -y+1, -z+1$
O(32)–H(32A)···O(36)	0.82 (2)	2.00 (3)	2.806 (7)	166 (7)	$x+1, y, z$
O(32)–H(32B)···O(2)	0.83 (2)	2.17 (5)	2.760 (6)	129 (6)	$-x+2, -y+1, -z+1$
O(33)–H(33A)···O(14)	0.84 (2)	1.95 (2)	2.763 (5)	165 (4)	$-x+2, -y+2, -z+1$
O(33)–H(33B)···O(2)	0.82 (2)	2.12 (2)	2.932 (5)	169 (6)	x, y, z
O(34)–H(34A)···O(29)	0.84 (2)	2.19 (4)	2.962 (5)	152 (6)	x, y, z
O(34)–H(34B)···O(12)	0.84 (2)	2.28 (4)	2.987 (5)	142 (5)	$x+1, y, z$
O(34)–H(34B)···O(35)	0.84 (2)	2.49 (5)	3.060 (6)	126 (6)	$x+1, y, z$
O(35)–H(35A)···O(17)	0.82 (2)	1.97 (3)	2.718 (5)	152 (6)	$x-1, y, z$
O(35)–H(35B)···O(16)	0.84 (2)	2.00 (2)	2.812 (5)	164 (6)	$-x+1, -y+2, -z$
O(36)–H(36A)···O(14)	0.84 (2)	2.07 (3)	2.870 (6)	159 (7)	$-x+2, -y+2, -z+1$
O(36)–H(36B)···O(1)	0.84 (2)	1.95 (2)	2.773 (5)	167 (6)	x, y, z
O(37)–H(37A)···O(5)	0.83 (2)	1.96 (3)	2.760 (5)	162 (7)	x, y, z
O(37)–H(37B)···O(17)	0.82 (2)	2.24 (4)	2.937 (6)	143 (6)	$-x+1, -y+1, -z$
O(39)–H(39A)···O(26)	0.81 (2)	2.14 (2)	2.934 (5)	167 (6)	$x, y+1, z$
O(39)–H(39B)···O(6)	0.82 (2)	1.95 (2)	2.759 (5)	168 (6)	$-x+1, -y+2, -z$
O(40)–H(40A)···O(25)	0.82 (2)	2.13 (3)	2.887 (5)	153 (6)	$x, y-1, z$
O(40)–H(40B)···O(13)	0.82 (2)	1.94 (2)	2.751 (5)	170 (6)	$-x+2, -y+1, -z+1$
C(2)–H(2)···O(32)	0.93	2.56	3.441 (7)	158	$-x+2, -y+1, -z+1$
C(12)–H(12)···O(37)	0.93	2.57	3.499 (6)	177	$x, y+1, z$
C(28)–H(28)···O(33)	0.93	2.47	3.400 (6)	174	$-x+2, -y+1, -z+1$
2					
O(7)–H(7B)···O(10)	0.82(2)	1.91(2)	2.729(4)	175(4)	x, y, z
O(8)–H(8A)···O(6)	0.79(2)	2.13(2)	2.898(3)	162(3)	$x, -y+1/2, z-1/2$
O(8)–H(8B)···O(2)	0.82(2)	1.87(2)	2.654(3)	162(4)	$-x, y+1/2, -z+1/2$
O(9)–H(9A)···O(5)	0.83(2)	1.97(2)	2.790(3)	175(4)	$x, y+1, z$
O(9)–H(9B)···O(3)	0.80(2)	2.10(2)	2.822(3)	150(3)	$-x+1, y+1/2, -z+1/2$
O(10)–H(10A)···O(1)	0.81(4)	2.31(4)	2.943(4)	135(5)	$x, -y+1/2, z-1/2$
O(10)–H(10B)···O(7)	0.82(5)	2.38(3)	3.120(4)	151(6)	$-x, -y, -z$
O(7)–H(7A)···O(2)	0.82(2)	2.05(2)	2.830(3)	158(3)	$-x, y+1/2, -z+1/2$

3. Results and discussion

3.1. *FTIR and elemental analysis*

FTIR spectra of **1** and **2** show vibrations at 3650–3159 cm^{-1} and 3671–3221 cm^{-1}, assigned as characteristic peaks of OH for water. Sharp ν(C = O) bands at 1629 cm^{-1} and 1634 cm^{-1} correspond to the asymmetric stretch, and 1419–1378 cm^{-1} and 1415–1383 cm^{-1} correspond to the symmetric stretch of carboxylates. The presence of ν(C = O) at lower frequency relative to characteristic value of 1684–1721 cm^{-1} indicates that the ligand is deprotonated. Anal. Calcd for $C_{34}H_{34}Ce_2N_4Na_2O_{39}$ (1448.47): N,

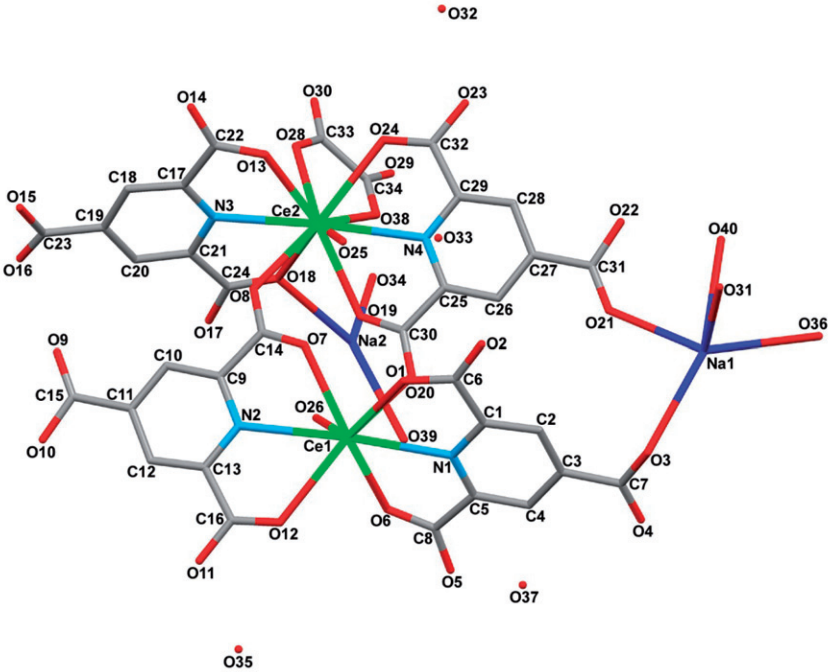

Figure 2. The molecular structure of **1** showing the atom numbering scheme.

3.86; C, 28.12; H, 2.35. Found (%): N, 3.60; C, 28.59; H, 2.67 and for $C_8H_{10}CeNO_{10}$ (420.29): N, 3.33; C, 22.88; H, 2.40. Found (%): N, 3.22; C, 22.54; H, 2.22.

3.2. *Crystal structure of 1*

The asymmetric unit consists of two Ce(III) ions, four non-coordinated water molecules, four ptc, two Na^+ and seven coordinated water molecules (figure 2). Each Ce(III) is ten-coordinate by two nitrogen atoms [N(1), N(2), N(3), and N(4)] from two pyridine rings, five oxygen atoms [O(1), O(6), O(7), O(8), O(12), O(13), O(18), O(19), O(20), and O(24)] from five carboxylates, two oxygen atoms [O(28), O(29), O(30), and O(38)] from oxalate, and one water molecule [O(25) and O(26)]. The ptc coordinates to Ce(III) O,N,O-tridentate. Ce(1) and Ce(2) form a centrosymmetric $[Ce_2(ptc)_4]$ dimer (figure 2). This connecting ring is formed by two ptc as bridging ligands. The Ce(1)$\cdots$Ce(2) distance in the $[Ce_2(ptc)_4]$ dimer is 5.820 Å, somewhat longer than the sum of the van der Waals radii. Each Ce(III) is surrounded by two neighboring Ce(III) connected *via* oxalate anions at 6.559 Å. Within the polymeric layer, Ce(1) and Ce(2) are alternately bridged by oxalate and ptc in the [100] direction (figure 3). Ce–O bond distances are 2.482(3) Å and 2.715(3) Å and that of Ce–N between 2.632(3) Å and 2.740(3) Å (table 3). The Ce–N and Ce–O distances found in $[Ce_2(ptc)_4]$ correlate well with those in other structurally characterized Ce(III) complexes with ptc [14, 33]. The pyridine ring mean planes are approximately planar, with maximum deviations of

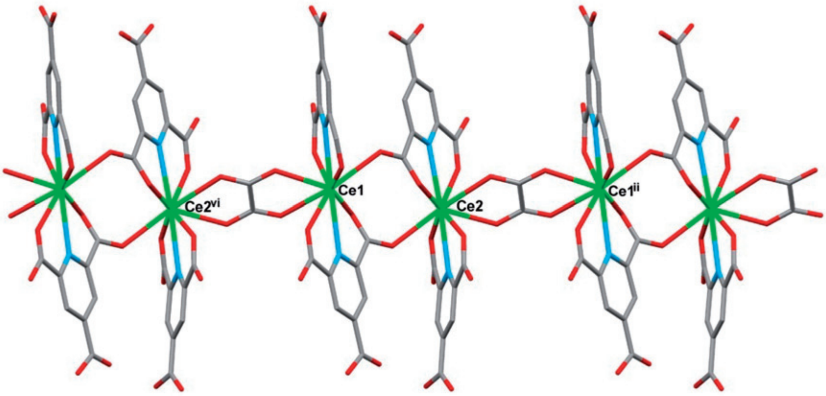

Figure 3. View of part of the crystal structure of **1** showing the formation of a coordination polymer chain parallel to the [100] direction. [Symmetry codes: (ii) $x+1$, y, z; (vi) $x-1$, y, z].

Table 3. Bond lengths (Å) and angles (°) for **1** and **2**.

1					
O(28)–Ce(2)	2.563(3)	Na(2)–O(34)^{xiv}	2.841(5)	O(1)–Ce(1)	2.533(3)
O(29)–Ce(1)	2.530(3)	O(6)–Ce(1)	2.482(3)	N(4)–Ce(2)	2.734(3)
O(26)–Ce(1)	2.619(3)	O(20)–Ce(1)	2.608(3)	N(3)–Ce(2)	2.632(3)
O(30)–Ce(1)	2.550(3)	O(8)–Ce(2)	2.619(3)	N(2)–Ce(1)	2.740(3)
N(1)–Ce(1)	2.642(3)	O(13)–Ce(2)	2.520(3)	O(19)–Ce(2)	2.537(3)
Na(1)–O(31)^{xiii}	3.016(6)	O(18)–Ce(2)	2.487(3)	O(38)–Ce(2)	2.565(3)
O(8)–Ce(2)–O(24)	141.30(11)	O(28)–Ce(2)–O(24)	68.40(10)	O(13)–Ce(2)–N(4)	120.00(10)
N(3)–Ce(2)–O(24)	124.64(10)	O(18)–Ce(2)–N(4)	117.32(10)	O(19)–Ce(2)–N(4)	59.52(10)
O(28)–Ce(2)–N(4)	114.97(10)	O(38)–Ce(2)–N(4)	67.28(10)	O(8)–Ce(2)–N(4)	115.26(10)
N(3)–Ce(2)–N(4)	175.96(11)	O(24)–Ce(2)–N(4)	58.84(10)	N(1)–Ce(1)–N(2)	174.20(11)
O(25)–Ce(2)–N(4)	64.69(10)	N(1)–Ce(1)–N(2)	174.20(11)	O(38)–Ce(2)–O(24)	73.11(10)
2					
C(6)–O(3)	1.252(3)	O(3)–Ce(1)	2.5217(19)	C(6)–O(4)	1.253(3)
O(4)–Ce(1)^{ii}	2.4129(19)	C(7)–O(2)	1.234(3)	O(5)–Ce(1)^{i}	2.6040(19)
C(7)–O(1)	1.262(3)	O(6)–Ce(1)^{i}	2.606(2)	C(8)–O(6)	1.251(3)
O(7)–Ce(1)	2.536(2)	C(8)–O(5)	1.258(3)	O(8)–Ce(1)	2.548(2)
N(1)–Ce(1)	2.589(2)	O(9)–Ce(1)	2.554(2)	O(1)–Ce(1)	2.474(2)
O(4)^{iii}–Ce(1)–O(1)	152.13(7)	O(1)–Ce(1)–O(9)	93.25(7)	O(4)^{iii}–Ce(1)–O(3)	75.61(6)
O(3)–Ce(1)–O(9)	71.44(7)	O(1)–Ce(1)–O(3)	124.56(6)	O(7)–Ce(1)–O(9)	144.39(8)
O(4)^{iii}–Ce(1)–O(7)	101.68(8)	O(8)–Ce(1)–O(9)	72.61(8)	O(1)–Ce(1)–O(7)	74.00(8)
O(4)^{iii}–Ce(1)–N(1)	131.56(7)	O(3)–Ce(1)–O(7)	142.96(7)	O(1)–Ce(1)–N(1)	62.33(7)
O(4)^{iii}–Ce(1)–O(8)	76.80(7)	O(3)–Ce(1)–N(1)	62.32(6)	O(1)–Ce(1)–O(8)	75.71(8)
O(7)–Ce(1)–N(1)	126.23(8)	O(3)–Ce(1)–O(8)	139.30(7)	O(8)–Ce(1)–N(1)	121.08(8)
O(7)–Ce(1)–O(8)	72.05 (8)	O(1)–Ce(1)–O(5)^{iv}	126.89(7)	O(4)^{iii}–Ce(1)–O(9)	74.15(7)

Symmetry operations: **1**: $^{(xiii)}$ $1-x$, $-y$, $1-z$; $^{(xiv)}$ $2-x$, $1-y$, $-z$. **2**: $^{(i)}$ x, $-y-1/2$, $z+1/2$; $^{(ii)}$ $-x+1$, $y-1/2$, $-z+1/2$; $^{(iii)}$ $-x+1$, $y+1/2$, $-z+1/2$; $^{(iv)}$ x, $-y-1/2$, $z-1/2$.

0.0057(31) Å for C(5), 0.0174(33) Å for C(11), 0.0108(33) Å for C(19), and 0.0136(28) Å for N(4).

The Na^+ cations are of two types. Na(1) coordinates by two equivalent water molecules [O(31) and O(31)^{xiii}; (xiii) $1-x$, $-y$, $1-z$], two other water molecules [O(36) and O(40)], and two oxygen atoms from two carboxylates [O(3) and O(21)]. The combination of Ce(1) and Na(1) and two ptc produce 15-membered chelate rings. In the

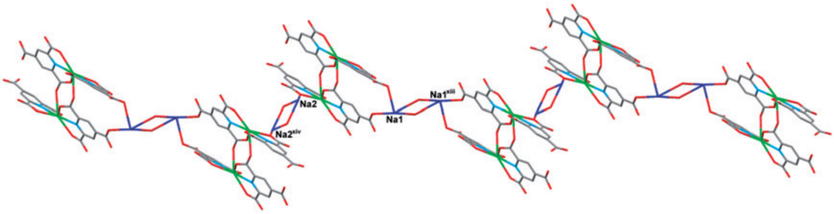

Figure 4. The molecular structure of **1** showing the formation of a coordination polymer chain parallel to the *ac* plane. (Symmetry operations as in table 3.)

second coordination, Na(2) is coordinated by two oxygen atoms from equivalent water molecules [O(34) and O(34)$^{\text{xiii}}$; (xiv) $2-x$, $1-y$, $-z$], two oxygen atoms from two carboxylates [O(5) and O(18)] and water molecule [O(39)]. Two adjacent Na^+ cations are linked by two H_2O bridges to form a four-membered ring with Na_2O_2 core. The Na(1)· · ·Na(1)$^{\text{xiii}}$ and Na(2)· · ·Na(2)$^{\text{xiv}}$ separations are 5.046 Å and 4.701 Å. Adjacent Na_2O_2 binuclear motifs are further joined by Ce(III) and ptc through carboxylates O(3), O(18), and O(21), generating a 2-D layer architecture in the crystallographic *ac* plane, with the Na(1)· · ·Na(2), Na(1)· · ·Na(1)$^{\text{xiii}}$, and Na(2)· · ·a(2)$^{\text{xiv}}$ separations of 10.648 Å, 5.046 Å, and 4.701 Å (figure 4).

The crystal packing is stabilized by intra and intermolecular C–H· · ·O and O–H· · ·O hydrogen bonds. The intramolecular O(22)–H(22)· · ·O(40), O(26)–H(26A)· · ·O(19), and O(25)–H(25A)· · ·O(7) hydrogen bonds produce S(6) motifs. Similarly, intramolecular O(34)–H(34A)· · ·O(29) hydrogen bonds produce S(8) motif. O(3) at (x, y, z) acts as a hydrogen-bond donor, *via* H(3), to O(28)$^{\text{viii}}$, and O(30)$^{\text{viii}}$, forming a R_1^2 (4) ring. Water O(31) in the molecule at (x, y, z) is a hydrogen-bond donor, *via* H(31B), to O(24)$^{\text{x}}$ and O(28)$^{\text{x}}$, forming a R_1^2 (4) ring. Strong intra-layer hydrogen bonds are observed between water molecules and carboxylates and water molecules, with O· · ·O distances from 2.569 to 3.181 Å (table 2). Furthermore, there are also weak hydrogen bonds between the carbon of pyridine rings [C(2), C(12), and C(28)] and oxygen of water [O(32), O(33), and O(37)] [C· · ·O distances range from 3.400 to 3.499 Å]. Therefore, the packing diagram of **1** contains a 3-D layer filled with crystal water molecules (figure 5).

3.3. *Crystal structure of 2*

The asymmetric unit of **2** consists of a Ce(III), three-coordinated water molecules, a non-coordinated water and one ptc (figure 6). The Ce(III) is coordinated by three water molecules [O(7), O(8), and O(9)], one ptc tridendate [through N(1) of the pyridine and two oxygen atoms O(1) and O(3) of two carboxylates]. Ce(III) has two coordination types. In the first running parallel to the [010] direction, Ce(1) is coordinated by O(4)$^{\text{iii}}$ of carboxylate from a symmetry-related ptc (figure 7). In the second running parallel to the [001] direction, Ce(1) is coordinated by O(5)$^{\text{iv}}$ and O(6)$^{\text{iv}}$ of carboxylate from a symmetry-related ptc (figure 8). The separations of Ce(III) ions bridged by carboxylates are 6.460 and 9.760 Å, respectively. Three coordination oxygen atoms [O(7), O(8), and O(9)] were from water with Ce–O bond lengths of 2.536(2), 2.548(2), and 2.554(2) Å, respectively; the other five [O(1), O(3), O(4)$^{\text{iii}}$, O(5)$^{\text{iv}}$, and O(6)$^{\text{iv}}$] were from the

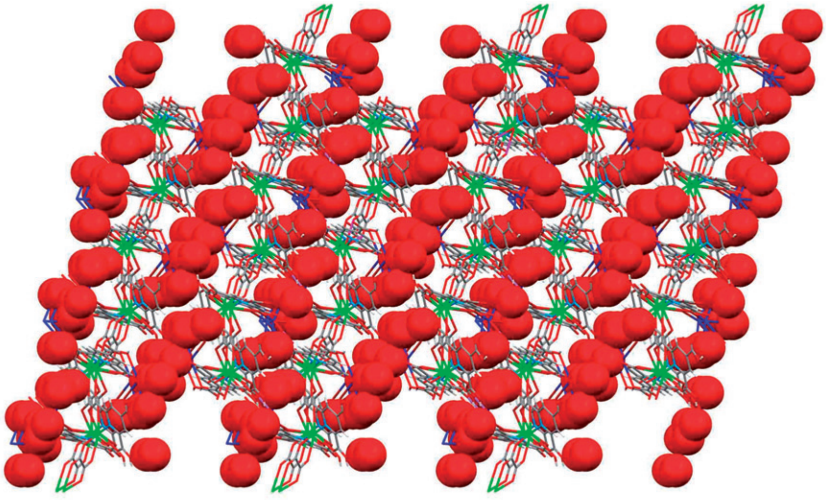

Figure 5. Ball and stick view of 3-D network of **1** showing solvent filled channels (hydrogen atoms are omitted for clarity, ● = water molecules).

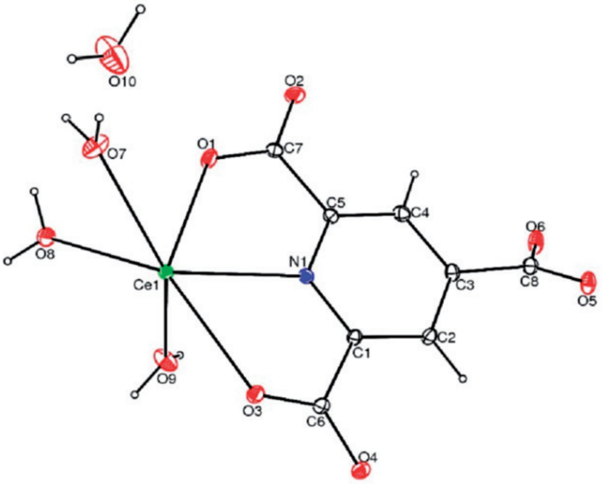

Figure 6. Independent part of the structure of $C_8H_{10}CeNO_{10}$.

carboxylates with Ce–O bond lengths of 2.474(2), 2.5217(19), 2.4129(19), 2.6040(19), and 2.606(2) Å, respectively; N(1) was from pyridyl ring with Ce–N bond length of 2.589(2) Å. This was also observed in other lanthanide complexes [34–38]. The bond angles of O–Ce–O are 71.44(7)°–152.13(7)° and O–Ce–N 62.32(6)°–131.56(7)°. The pyridine ring is planar with largest deviation from the mean plane being 0.0226(20) Å for C(4). Selected bond lengths and angles are given in table 3.

Molecules of **2** are linked into sheets by a combination of O–H···O hydrogen bonds (table 2). Water molecules O(7) and O(8) at (x, y, z) are hydrogen-bond donors,

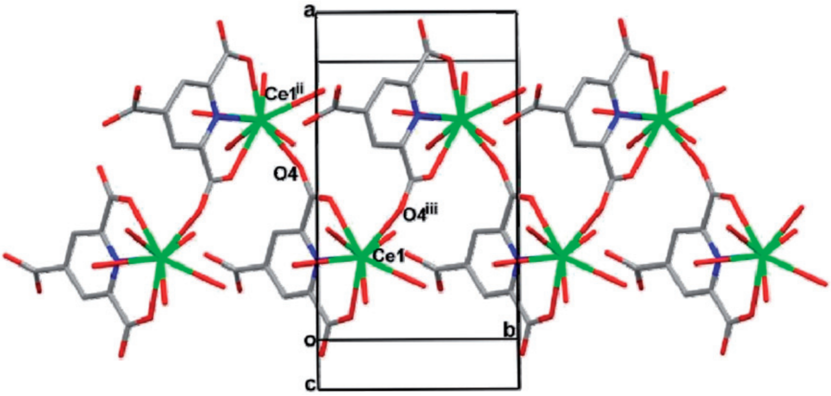

Figure 7. View of part of the crystal structure of **2** showing the formation of a coordination polymer chain parallel to the [010] direction. For the sake of clarity, the non-coordinated molecule and all hydrogen atoms have been omitted. (Symmetry operations as in table 3.)

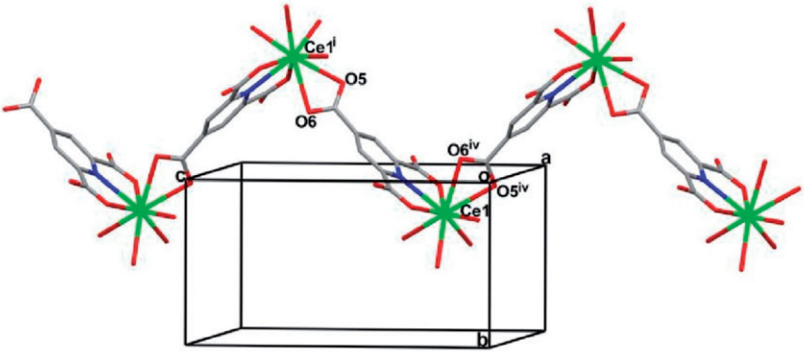

Figure 8. View of part of the crystal structure of **2** showing the formation of a coordination polymer chain parallel to the [001] direction. For the sake of clarity, the non-coordinated molecules and all hydrogen atoms have been omitted. (Symmetry operations as in table 3.)

via H(7A) and H(8B), to O(2) at ($-x$, $y+1/2$, $-z+1/2$), forming a C(6)C(6)[R_2^1 (6)] [39] chain of rings running parallel to the [010] direction. Similarly, water O(9) at (x, y, z) is a hydrogen-bond donor, *via* H(9A), to O(5) at (x, $y+1$, z), forming a C(9) chain running parallel to the [010] direction. The combination of C(6) and C(9) chains generates a chain of edge-fused R_4^4 (27) rings running parallel to the [010] direction (figure 9). Water O(8) at (x, y, z) is a hydrogen-bond donor, *via* H(8A), to O(6) at (x, $-y+1/2$, $z-1/2$), forming a C(9) chain running parallel to the [00$-$1] direction. The combination of O(7)–H(7B)···O(10), O(10)–H(10A)···(1)^{v}, and O(8)–H(8A)···O(6)^{v} hydrogen bonds generates a chain of edge-fused R_3^3 (14) rings parallel to the [001] direction (figure 10). Water O(9) at (x, y, z) is a hydrogen-bond donor, *via* H(9B), to O(3) at ($-x+1$, $y+1/2$, $-z+1/2$), forming a C(4) chain running parallel to the [010] direction. Finally, water molecules link neighboring polymeric chains *via* O–H···O hydrogen bonds into a 2-D framework parallel to the *ac* plane (figure 11).

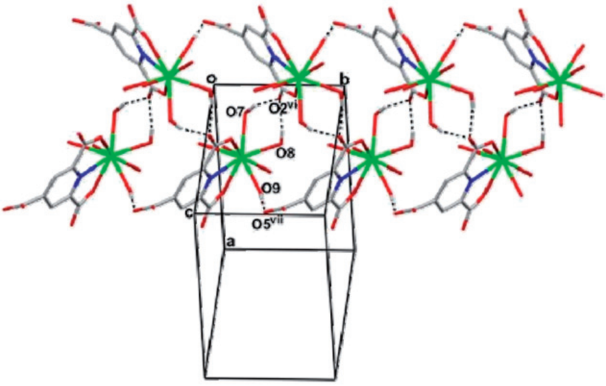

Figure 9. Part of the crystal structure of **2** showing the formation of R_2^1 (6) and R_4^4 (27) rings. For the sake of clarity, the non-coordinated water and hydrogen atoms not involved in the motif shown have been omitted. (Symmetry codes as in table 2.)

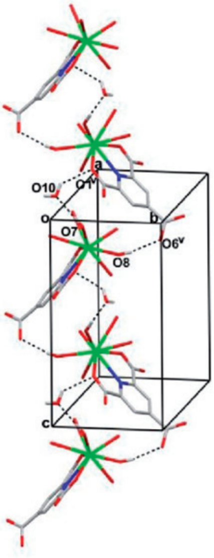

Figure 10. Part of the crystal structure of **2** showing the formation of R_3^3 (14) rings. For the sake of clarity, hydrogen atoms not involved in the motif shown have been omitted. (Symmetry code as in table 2.)

3.4. *Thermal analysis*

The results of the thermal analysis of **1** and **2** are consistent with the proposed stoichiometry. The decomposition pattern of **1** is illustrated in the "Supplementary material." At the first stage water is released in two steps, corresponding to the weight loss of 13.6% (calcd value 13.7%) for seven coordinated and four non-coordinated water molecules between 108°C and 218°C. The second weight loss of 6.9% is due to the removal of oxalate (calcd value 6.1%) and third weight loss of 51.2% to 1090°C results

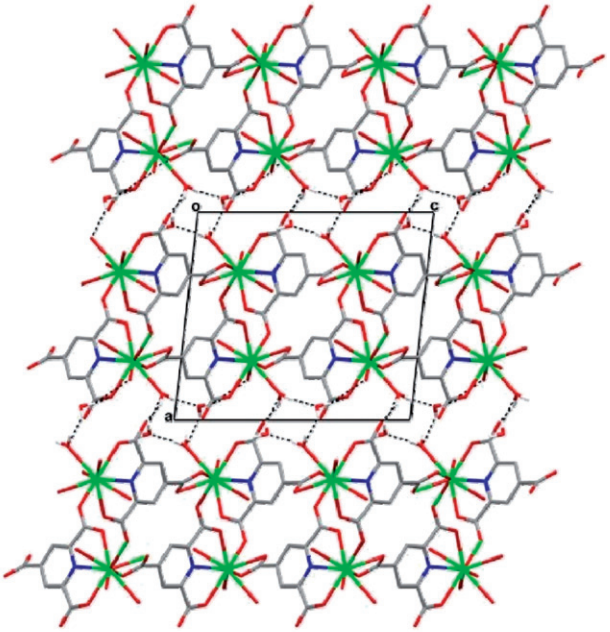

Figure 11. Part of the crystal structure of **2** showing the formation of a chain along [100] generated by the O–H···O hydrogen bonds (dashed lines; see table 2). For the sake of clarity, hydrogen atoms not involved in the motif shown have been omitted.

from the successive release of ptc (calcd 53.3%). The overall weight loss of 71.7% is in agreement with the calculated value (73.1%), assuming 28.3% is a mixture of Ce_2O_3 and Na_2O as the final product (Calcd 26.9%).

The decomposition pattern of **2** is illustrated in the "Supplementary material." At the first stage water is released, corresponding to 17.4% weight loss (Calcd 17.1% for three-coordinated water molecules and one non-coordinated water) between 65°C and 240°C. The second weight loss of 41.5% to 790°C results from the successive release of ptc (Calcd 41.9%). The overall weight loss of 58.9% is in agreement with the calculated value (59%), assuming 41.1% CeO_2 as the final product (calcd 40.9%). The residual mass also indicates the oxidation of Ce(III) to Ce(IV).

4. Conclusions

We describe a simple synthetic strategy using an autoclave to synthesize 1-D and 2-D coordination polymers derived from pyridine-2,4,6-tricarboxylic acid and Ce(III). The spectral studies and analytical data agree with the structure and composition of the polymers. The topology of the reported complex exhibits nine- and ten-coordination of Ce(III) and, thus, has potential for the design of supramolecular coordination networks.

Supplementary material

CCDC No. 804364 and 827607 contains the supplementary crystallographic data for **1** and **2** and can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

Acknowledgments

The author acknowledges the Higher Education Commission of Pakistan (HEC) for financing a visit to University of Oxford under IRSIP (HEC) and its financial support under “Strengthening of the Materials Chemistry Laboratory” at GC University, Lahore, Pakistan. The author also acknowledges Dr Richard Cooper, Chemical Crystallography, Chemistry Research Laboratory, Oxford, UK, for facilitating helpful discussions.

References

[1] B. Zhao, X.Y. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *J. Am. Chem. Soc.*, **126**, 15394 (2004).
[2] B. Zhao, H.L. Gao, X.Y. Chen, P. Cheng, W. Shi, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Chem. Eur. J.*, **12**, 149 (2006).
[3] B. Chen, D.S. Contreras, N.W. Ockwig, O.M. Yaghi. *Angew. Chem. Int. Ed.*, 4745 (2005).
[4] Q. Yue, J. Yang, G.H. Li, G.D. Li, W. Xu, J.S. Chen, S.N. Wang. *Inorg. Chem.*, **44**, 5241 (2005).
[5] L.J. Murray, M. Dinca, J.R. Long. *Chem. Soc. Rev.*, **38**, 1294 (2009).
[6] J.R. Li, R.J. Kuppler, H.C. Zhou. *Chem. Soc. Rev.*, **38**, 1477 (2009).
[7] J. Inanaga, H. Furuno, T. Hayano. *Chem. Rev.*, **102**, 2211 (2002).
[8] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk. *Chem. Soc. Rev.*, **38**, 1330 (2009).
[9] S. Tanase, J. Reedijk. *Coord. Chem. Rev.*, **250**, 2501 (2006).
[10] B.Q. Ma, S. Gao, G. Su, G.X. Xu. *Angew. Chem. Int. Ed.*, **40**, 434 (2001).
[11] Y.G. Huang, F.L. Jiang, M.C. Hong. *Coord. Chem. Rev.*, **253**, 2814 (2009).
[12] X.J. Kong, Y.P. Ren, L.S. Long, Z. Zheng, R.B. Huang, L.S. Zheng. *J. Am. Chem. Soc.*, **129**, 7016 (2007).
[13] G.B. Deacon, C.M. Forsyth, T. Behrsing, K. Konstas, M. Forsyth. *Chem. Commun.*, 2820 (2002).
[14] M.C. Das, S.K. Ghosh, E.C. Sanudo, P.K. Bharadwaj. *Dalton Trans.*, 1644 (2009).
[15] P.M. Xia, C.Z. Yun. *Chin. J. Chem.*, **25**, 1055 (2009).
[16] P. Ren, P.K. Chen, G.F. Xu, C. Zhi. *Inorg. Chem. Commun.*, **10**, 836 (2007).
[17] S.K. Ghosh, G. Savitha, P.K. Bharadwaj. *Inorg. Chem.*, **43**, 5495 (2004).
[18] H.L. Gao, B. Ding, L. Yi, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Inorg. Chem. Commun.*, **8**, 151 (2005).
[19] R.Q. Zhong, R.Q. Zou, S.D. Pandey, T. Kiyobayashi, Q. Xu. *Inorg. Chem. Commun.*, **11**, 951 (2008).
[20] S.K. Ghosh, F.E.M. Salah, J. Ribas, P.K. Bharadwaj. *Inorg. Chim. Acta*, **359**, 468 (2006).
[21] X.W. Wang, Y.R. Dong, Y.Q. Zheng, J.Z. Chen. *Cryst. Growth Des.*, **7**, 4 (2007).
[22] L. Wang, J. Wang, C. Xie. *J. Coord. Chem.*, **61**, 3401 (2008).
[23] C.Z. Yun, P.M. Xia. *Chem. Res. Chin. Univ.*, **25**, 79 (2009).
[24] H.S. Wang, B. Zhao, B. Zhai, W. Shi, P. Cheng, D.Z. Liao, S.P. Yan. *Cryst. Growth Des.*, **7**, 1851 (2007).
[25] S.K. Ghosh, P.K. Bharadwaj. *Eur. J. Inorg. Chem.*, 488 (2005).
[26] H.L. Gao, L. Yi, B. Ding, H.S. Wang, P. Cheng, D.Z. Liao, S.P. Yan. *Inorg. Chem.*, **45**, 481 (2006).
[27] Y.Y. Ren, B.L. An, Q. Xu. *J. Alloys Compd.*, **501**, 42 (2010).
[28] L. Syper, K. Kloc, J. Mlochowski. *Tetrahedron*, **36**, 123 (1980).
[29] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
[30] L.J. Farrugia. *J. Appl. Cryst.*, **32**, 837 (1999).

[31] I.J. Bruno, J.C. Cole, P.R. Edgington, M.K. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor. *Acta Cryst.*, **B58**, 389 (2002).

[32] A.L. Spek. *PLATON-A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht (2005).

[33] J. Hamacek, S. Zebret, G. Bernardinelli. *Polyhedron*, **28**, 2179 (2009).

[34] T. Zhu, K. Murokawa, K. Uematsu, T. Ishigaki, K. Toda, H. Okawa, M. Sato. *Polyhedron*, **28**, 2196 (2009).

[35] M.N. Tahir, D. Ulku, C. Unaleroglu, E.M. Movsumou. *Acta Cryst.*, **C52**, 1449 (1996).

[36] H.S. Wang, B. Zhao, B. Zhai, W. Shi, P. Cheng, D.-Z. Liao, S.-P. Yan. *Cryst. Growth Des.*, **7**, 1851 (2007).

[37] J. Bernstein, R.E. Davis, L. Shimoni, N.L. Chang. *Angew. Chem. Int. Ed. Engl.*, **34**, 1555 (1995).

[38] S. Shabnam, D.K. Parvaneh, A. Hossein, S. Ardeshir, K. Guido, S. Mojtaba, R. Farshid, M. Abolghasem. *Z. Anorg. Allg. Chem.*, **631**, 3058 (2005).

[39] P.Z. Jian, L.L. Sheng, J.L. Ming, H.T. Xin, J.X. Qiu, P. Qiang, C.G. Guo. *Polyhedron*, **29**, 2674 (2010).