

# Hydrothermal Synthesis and Structure of a New 3D Lanthanide-Carboxylate Framework, $[\text{La}(\text{btec})_{1/2}(\text{H}_2\text{btec})_{1/2}(\text{H}_2\text{O})]_n$ ( $\text{H}_4\text{btec} = 1,2,4,5\text{-Benzenetetra-carboxylic acid}$ )

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The title complex,  $[\text{La}(\text{btec})_{1/2}(\text{H}_2\text{btec})_{1/2}(\text{H}_2\text{O})]_n$  ( $\text{H}_4\text{btec} = 1,2,4,5\text{-benzenetetra-carboxylic acid}$ ) (1) was synthesized by the hydrothermal reaction of 1,2,4,5-benzenetetra-carboxylic dianhydride with  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , and crystallizes in the triclinic system, space group  $P\bar{1}$  with  $a = 0.64403(3)$  nm,  $b = 0.94500(4)$  nm,  $c = 0.96380(5)$  nm,  $\alpha = 88.535(2)^\circ$ ,  $\beta = 100.314(2)^\circ$ ,  $\gamma = 76.6470(10)^\circ$ ,  $V = 1.60968(10)$  nm<sup>3</sup>,  $Z = 2$ , and final  $R = 0.0274$ ,  $R_w = 0.0735$ . In 1, each La(III) ion is coordinated by eight oxygen atoms from six carboxylate groups and one coordinated water molecule. Two different coordination modes of  $\text{H}_4\text{btec}$  were present in the structure, one of which contains two protonated carboxylate groups to balance the charge.

**Keywords** hydrothermal synthesis, lanthanide polymer, 3D structure, 1,2,4,5-benzenetetra-carboxylic acid

## Introduction

Recently, the design and synthesis of materials with novel structure and unusual function have become an active research field.<sup>1,2</sup> Lanthanide complexes have attracted much attention of the chemists owing to their intriguing properties, such as molecular magnetization,<sup>3</sup> absorption,<sup>4</sup> heterogeneous catalysis. A series of lanthanide-carboxylate complex examples has been reported and all kinds of coordination models of the carboxylate group are found in those structures.<sup>5-8</sup> In our previous work and others, it was found that 1,2,4,5-benzenetetra-carboxylic acid is a versatile building block for the architectures of polymeric structures due to its variety of bridging abilities.<sup>9-12</sup> For example, some of the carboxyl groups may not lie in the phenyl ring plane upon complexation to metal ions owing to space hindrance, thus it may connect metal ions in different directions, and the high symmetry of  $\text{H}_4\text{btec}$  is also helpful for the growth of crystal. In this paper we will report a new lanthanum polymer,  $[\text{La}(\text{btec})_{1/2}(\text{H}_2\text{btec})_{1/2}(\text{H}_2\text{O})]_n$  (1), constructed by 1,2,4,5-benzenetetra-carboxylic acid. In 1, the completely deprotonated ( $\text{btec}^{4-}$ ) and the partially deprotonated ( $\text{H}_2\text{btec}^{2-}$ ) ligands

are present. The carboxylic groups, in four different coordination models, connect the lanthanum centers in different directions to give rise to the final 3D open framework, which is very rare in the structures of multi-carboxylate groups polymers.

## Experimental

### Preparation of $[\text{La}(\text{btec})_{1/2}(\text{H}_2\text{btec})_{1/2}(\text{H}_2\text{O})]_n$

A mixture of 1,2,4,5-benzenetetra-carboxylic dianhydride (0.065 g, 0.30 mmol) and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.130 g, 0.30 mmol) in 16 mL of  $\text{H}_2\text{O}$  was placed in a 25 mL stainless steel vessel and heated to 160 °C for 72 h, then cooled to room temperature during 8 h. The colorless prism crystals (m. p. > 300 °C) were obtained in 68% yield.

### Elemental analysis

Elemental analysis were carried out in the elemental analysis group of this institute. Anal. calcd for  $\text{C}_{10}\text{H}_5\text{LaO}_9$ : C 29.44, H 1.24; found C 29.49, H 1.21.

### Infrared spectrum

Infrared spectrum of the title complex was recorded with a Nicolet AVATAAR FT-IR Model 950 spectrophotometer (4000–400  $\text{cm}^{-1}$ ) using KBr pellets. IR  $\nu$ : 2853 (s), 2677 (brs), 1736 (s), 1695 (m), 1668 (s), 1583 (s), 1456 (s), 1425 (m), 1268 (s), 1366 (s), 769 (m), 722 (m)  $\text{cm}^{-1}$ .

### Crystal structure determination

A prism crystal of dimensions 0.50 mm × 0.26 mm × 0.18 mm of the title compound was mounted on a glass fiber

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Received August 8, 2002; revised October 8, 2002; accepted December 8, 2002.

Project supported by the National Natural Science Foundation of China (No. 29901005).

in a random orientation. Diffraction data were collected at room temperature (293 K) on a Siemens SMART-CCD area detector equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071073$  nm). A total of 2801 reflections were collected in the range of  $2.19^\circ < \theta < 24.98^\circ$  using  $\omega$ - $2\theta$  scan mode of which 1885 independent reflections with  $I > 2.50\sigma(I)$  were used in the succeeding refinement. The structure was solved by direct methods and refined by full-matrix least-squares method. The positions of H atoms were generated geometrically (C—H bond fixed at 0.096 nm), and allowed to ride on their parent carbon atoms before the final cycle of refinement. The final cycle of refinement included 189 variable parameters and converged to  $R = 0.0274$  and  $R_w = 0.0735$ . All calculations were performed on a Legend Pentium III computer with Shelex 97 program package. Crystal parameters and refinement results are summarized in Table 1.

## Results and discussion

The selected bond distances and angles are listed in Table 2. Complex **1** possesses a three-dimensional structure containing nine-coordination lanthanum centers. The observation of the absorption peak at  $1668\text{ cm}^{-1}$  for COOH in IR spectrum indicates the presence of protonated carboxylic groups in the complex, and structural data show that there are two kinds of carboxylate ligands,  $\text{H}_2\text{btec}^{2-}$  and  $\text{btec}^{4-}$ , in

**Table 1** Crystal data for  $\text{C}_{10}\text{H}_5\text{LaO}_9$

Chemical formula	$\text{C}_{10}\text{O}_9\text{H}_5\text{La}$
Crystal system	Triclinic
Space group	$P-1$
$a$ (nm)	0.64403(3)
$b$ (nm)	0.94500(4)
$c$ (nm)	0.96380(5)
$\alpha$ ( $^\circ$ )	88.535(2)
$\beta$ ( $^\circ$ )	74.757(2)
$\gamma$ ( $^\circ$ )	76.6470(10)
$V$ ( $\text{nm}^3$ )	0.55025(4)
$D_c$ ( $\text{g}/\text{cm}^3$ )	2.463
$Z$	2
$T$ (K)	293
Wavelength (nm)	0.071073
Absorption coefficient ( $\text{mm}^{-1}$ )	3.929
$F(000)$	388
Crystal size (mm)	$0.50 \times 0.26 \times 0.18$
$\theta$ range for data collection	$2.19^\circ$ to $24.98^\circ$
Total reflections	2801
Reflections with $I > 2.0\sigma(I)$	1885
$R$	0.0274
$R_w$	0.0735

**Table 2** Bond lengths (nm) and angles ( $^\circ$ ) for  $\text{C}_{10}\text{H}_5\text{LaO}_9$ <sup>a</sup>

La—O(7) <sub>D</sub>	0.2439(4)	La—O(4) <sub>C</sub>	0.2601(3)
La—O(8) <sub>E</sub>	0.2484(3)	La—O(3) <sub>C</sub>	0.2609(3)
La—O(9)	0.2514(4)	La—O(1)	0.2657(3)
La—O(1) <sub>B</sub>	0.2564(3)	O(5)—C(6)	0.1228(6)
La—O(2)	0.2569(3)	O(6)—C(6)	0.1310(6)
La—O(5)	0.2580(3)		
O(7) <sub>D</sub> —La—O(8) <sub>E</sub>	77.68(13)	O(1) <sub>B</sub> —La—O(4) <sub>C</sub>	73.59(11)
O(7) <sub>D</sub> —La—O(9)	140.46(14)	O(2)—La—O(4) <sub>C</sub>	122.39(11)
O(8) <sub>E</sub> —La—O(9)	66.79(13)	O(5)—La—O(4) <sub>C</sub>	70.07(11)
O(7) <sub>D</sub> —La—O(1) <sub>B</sub>	144.90(12)	O(7) <sub>D</sub> —La—O(3) <sub>C</sub>	73.43(13)
O(8) <sub>E</sub> —La—O(1) <sub>B</sub>	136.37(12)	O(8) <sub>E</sub> —La—O(3) <sub>C</sub>	137.98(11)
O(9)—La—O(1) <sub>B</sub>	69.93(13)	O(9)—La—O(3) <sub>C</sub>	145.89(13)
O(7) <sub>D</sub> —La—O(2)	81.88(12)	O(1) <sub>B</sub> —La—O(3) <sub>C</sub>	80.21(11)
O(8) <sub>E</sub> —La—O(2)	72.29(11)	O(2)—La—O(3) <sub>C</sub>	73.95(11)
O(9)—La—O(2)	102.37(14)	O(5)—La—O(3) <sub>C</sub>	120.01(11)
O(1) <sub>B</sub> —La—O(2)	112.81(10)	O(4) <sub>C</sub> —La—O(3) <sub>C</sub>	49.94(10)
O(7) <sub>D</sub> —La—O(5)	88.96(13)	O(7) <sub>D</sub> —La—O(1)	127.50(12)
O(8) <sub>E</sub> —La—O(5)	88.86(12)	O(8) <sub>E</sub> —La—O(1)	101.24(11)
O(9)—La—O(5)	74.02(15)	O(9)—La—O(1)	77.87(14)
O(1) <sub>B</sub> —La—O(5)	84.47(12)	O(1) <sub>B</sub> —La—O(1)	63.88(12)
O(2)—La—O(5)	160.38(12)	O(2)—La—O(1)	49.77(10)
O(7) <sub>D</sub> —La—O(4) <sub>C</sub>	71.76(12)	O(5)—La—O(1)	143.36(12)
O(8) <sub>E</sub> —La—O(4) <sub>C</sub>	142.74(12)	O(4) <sub>C</sub> —La—O(1)	114.10(11)
O(9)—La—O(4) <sub>C</sub>	130.41(14)	O(3) <sub>C</sub> —La—O(1)	74.34(11)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: D  $-x+1, -y+1, -z+1$ ; E  $x-1, y+1, z$ ; B  $-x+1, -y+2, -z$ ; C  $x, y-1, z$ .

the structure: (a) each of two *para*-protonated carboxylic groups coordinates to one lanthanum atom through carbonyl oxygen atom, while each of the other two *para*-deprotonated carboxylic groups bridges two lanthanum atoms ( $\text{H}_2\text{btec}^{2-}$ , Fig. 1a); (b) each of two *para*-carboxylate groups adopts bidentate chelating mode coordinating to one lanthanum atom and each of the other two *para*-carboxylate groups adopts bidentate chelating-bridging mode connecting two lanthanum atoms ( $\text{btec}^{4-}$ , Fig. 1b). As shown in Fig. 2, the central lanthanum ion is coordinated by nine oxygen atoms, five from three  $\text{btec}^{4-}$ , other three from three  $\text{H}_2\text{btec}^{2-}$ , with the length of  $\text{La}-\text{O}_{\text{btec}}$  bonds ranging from 0.2439(4) nm [ $\text{La}-\text{O}(7)_\text{D}$ ] to 0.2657(3) nm [ $\text{La}-\text{O}(3)_\text{C}$ ], while another coordination situation is occupied by a coordinated water molecule with the  $\text{La}-\text{O}_\text{w}$  distance being 0.2514(4) nm.

Each ligand has two co-planar carboxylic groups in *para*-orientation, which link the lanthanum atoms into a layer (as shown in Fig. 3). The other carboxylic groups, however, are

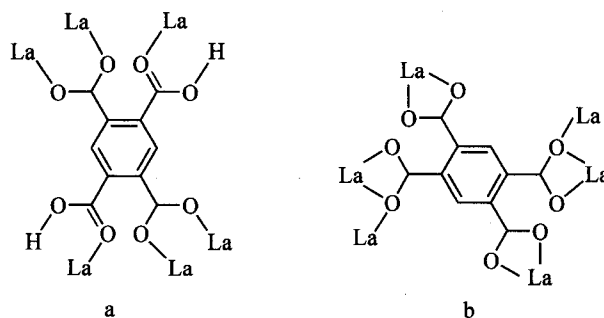


Fig. 1 Coordination models of the two ligands in the complex 1.

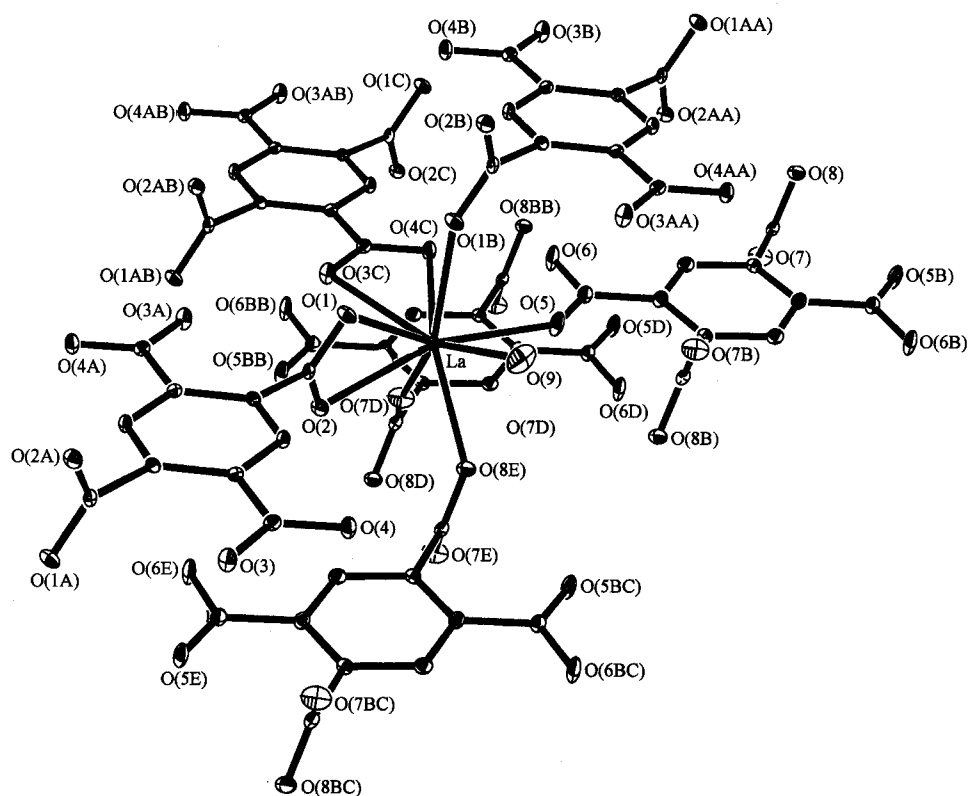


Fig. 2 Coordination environment of La(III) in 1.

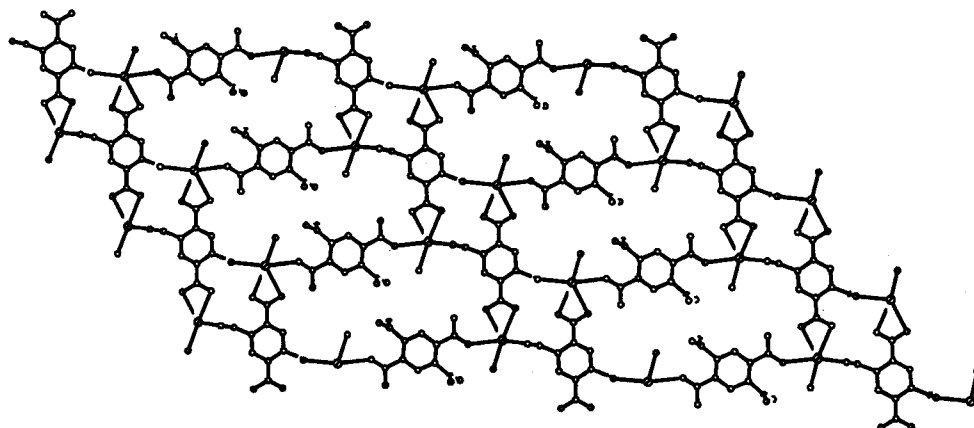
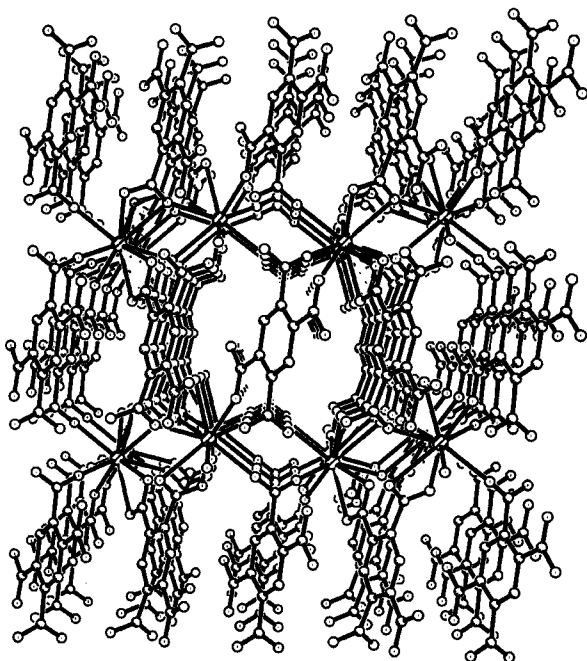


Fig. 3 Two-dimensional layer in 1.

**Table 3** Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{nm}^2 \times 10^5$ ) for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
La	3490(1)	9404(1)	2212(1)	10(1)
O(1)	3404(5)	11282(4)	116(4)	18(1)
O(2)	449(5)	11616(4)	1956(3)	17(1)
O(3)	1328(6)	18505(3)	604(4)	20(1)
O(4)	3522(6)	16772(4)	1463(4)	19(1)
O(5)	6103(7)	7543(4)	3357(4)	27(1)
O(6)	5890(7)	5252(4)	3031(5)	28(1)
O(7)	9651(6)	1320(4)	6154(4)	28(1)
O(8)	12663(6)	1071(4)	4338(4)	20(1)
O(9)	6630(7)	10547(6)	2257(5)	42(1)
C(1)	1527(7)	12030(5)	815(5)	11(1)
C(2)	708(7)	13547(5)	338(5)	12(1)
C(3)	1649(8)	14622(5)	699(5)	13(1)
C(4)	961(7)	16072(5)	385(5)	13(1)
C(5)	1994(8)	17182(5)	835(5)	13(1)
C(6)	6688(8)	6232(5)	3522(5)	16(1)
C(7)	8379(8)	5625(5)	4308(5)	15(1)
C(8)	8957(8)	4107(5)	4442(5)	17(1)
C(9)	10564(8)	3472(5)	5135(5)	13(1)
C(10)	11019(7)	1818(5)	5232(5)	12(1)

not in the plane of benzene ring. The dihedral angles of benzene ring and the carboxylic planes are  $80.3^\circ$  and  $79.0^\circ$  respectively. Those groups cross-link the layers to form the terminal three-dimensional framework (as shown in Fig. 4).

**Fig. 4** Three-dimensional packing structure of **1** along *a*-axis.

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