

# A nanoporous three-dimensional metal coordination polymer $\{(\text{NH}_4)_2\text{Zn}[\text{C}_6\text{H}_2(\text{COO})_4]\cdot 8\text{H}_2\text{O}\}_n$

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**Key indicators**

Single-crystal X-ray study  
 $T = 293 \text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
 H-atom completeness 39%  
 Disorder in solvent or counterion  
 $R$  factor = 0.032  
 $wR$  factor = 0.097  
 Data-to-parameter ratio = 13.5

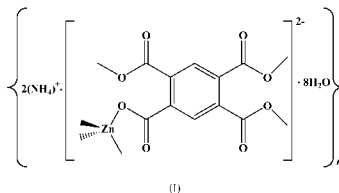
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, poly[ammonium zinc- $\mu$ -benzene-1,2,4,5-tetracarboxylate octahydrate]  $\{(\text{NH}_4)_2\text{Zn}[\text{C}_6\text{H}_2(\text{COO})_4]\cdot 8\text{H}_2\text{O}\}_n$ , forms a three-dimensional network containing one-dimensional nanoporous rhomboid channels along the  $c$  axis, accommodating guest water molecules and the ammonium cations. The dimensions of the large channel are  $11.555(2) \times 15.00(1) \text{ \AA}$ . The network consists of  $[\text{Zn}(\text{C}_6\text{H}_2(\text{COO})_4)]^{2-}$  anions containing tetrahedral Zn atoms bonded to four carboxylate groups. The  $\text{Zn}\cdots\text{O}$  distances range from  $1.974(2)$  to  $1.978(2) \text{ \AA}$ . The ammonium cations and the water molecules are associated in a centrosymmetric network by intermolecular hydrogen bonds. The hydrogen bonding is essential to stabilize the crystal structure.

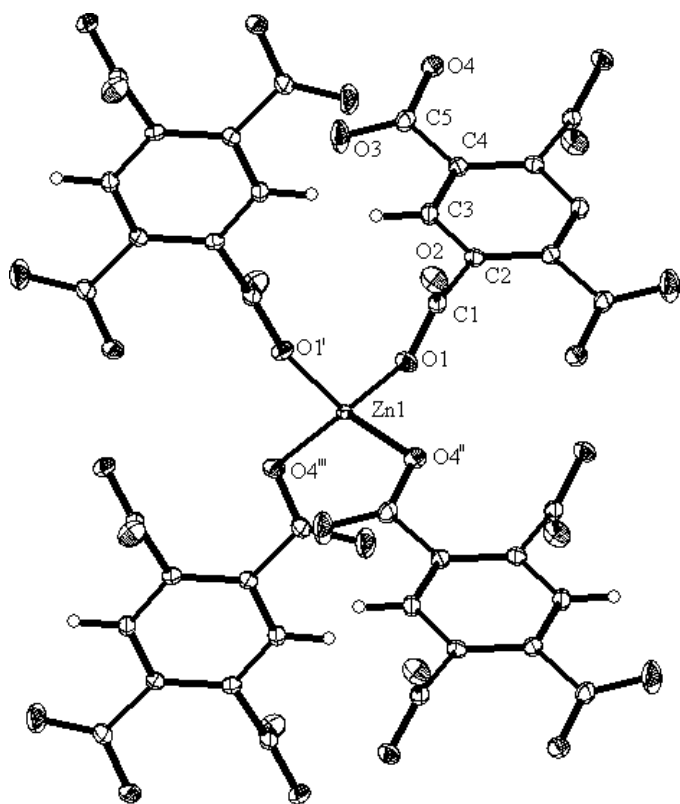
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**Comment**

Aromatic polycarboxylate ligands have versatile coordination modes as they can form bridges between metallic centers, generating various molecular topologies and architectures, as well as having potential application as functional materials. They find widespread application in heterogeneous catalysis, chemical absorption and magnetism. Owing to their widespread utility (Yaghi & Li, 1996), a considerable number of reports based on metal–aromatic polycarboxylate coordination polymers have appeared over the past few years (Yaghi *et al.*, 1997). 1,2,4,5-Benzenetetracarboxylic acid ( $\text{H}_4\text{btec}$ ) has four carboxyl groups, with eight O-donor atoms that may be completely or partly deprotonated, inducing rich coordination modes and allowing novel structures with up to three-dimensional networks. It has been reported that an increase in pH results in a higher connectivity level of the ligands, which in turn leads to a higher dimensionality of the crystal structure (Pan *et al.*, 2001). We adjusted the pH value to 9–10 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  and obtained the title compound, (I).



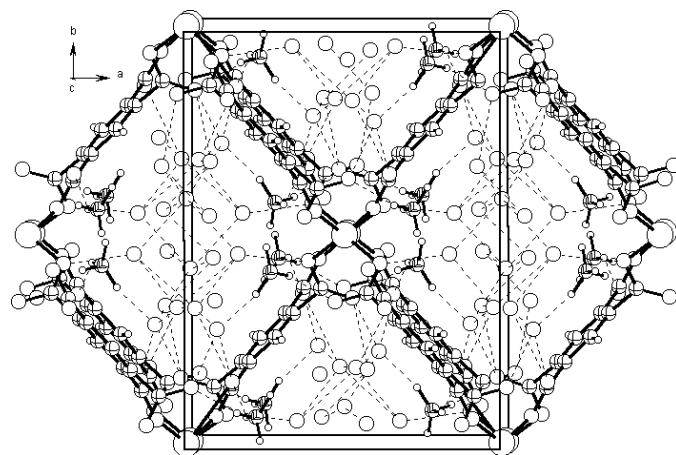
$\{(\text{NH}_4)_2\text{Zn}[\text{C}_6\text{H}_2(\text{COO})_4]\cdot 8\text{H}_2\text{O}\}_n$  is a three-dimensional polymer containing one-dimensional nanoporous channels along the  $c$  axis, accommodating guest water molecules and the ammonium cation. All the carboxyl groups of  $\text{H}_4\text{btec}$  are deprotonated, in agreement with the IR data, in which no absorption peaks are observed around  $1700 \text{ cm}^{-1}$  for COOH. There is a strong absorption peak at  $1603 \text{ cm}^{-1}$  for  $\nu_{\text{as}}(\text{CO})$ .



**Figure 1**

The  $\text{Zn}^{2+}$  coordination environment in the title compound and the atom-labeling scheme. Displacement ellipsoids are shown at the 30% probability level [symmetry codes: (i)  $1-x, y, -z+\frac{1}{2}$ ; (ii)  $x+\frac{1}{2}, y-\frac{1}{2}, z$ ; (iii)  $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$ ].

Only one type of coordination mode of  $\text{btec}^{4-}$  is present in the structure. Each carboxylate group adopts a monodentate mode, coordinating one Zn atom. Therefore, each  $\text{btec}^{4-}$  acts as an  $\mu_4$ -bridge, linking four Zn centers, and each Zn atom attaches to four  $\text{btec}^{4-}$  ligands, forming a slightly distorted tetrahedron around  $\text{Zn}^{2+}$ , with Zn–O bond lengths ranging from 1.974 (2) to 1.978 (2) Å, similar to other related Zn–O distances (Robl, 1992).  $\text{Zn}^{2+}$  is situated on the twofold axis and the four coordinated O atoms are related to each other in pairs by the twofold axis; the  $\text{btec}^{4-}$  phenyl ring is centrosymmetric. The closest Zn $\cdots$ Zn distance is 5.538 (1) Å, indicating the lack of any direct metal–metal interaction. The macrocyclic unit  $[\text{Zn}_4(\text{btec})_4]^{12-}$ , which forms a rhomboid sheet, with a Zn $\cdots$ Zn distance of 9.587 (1) Å, constitutes the basic building block of the structure. Every building block is linked together through Zn–O bonds to generate a three-dimensional structure with a nanoporous rhomboid channel along the *c* axis. The dimensions of this large channel are 11.555 (2)  $\times$  15.100 (3) Å. It accommodates ammonium cations and water molecules associated into a centrosymmetric network by intermolecular hydrogen bonds. Different kinds of hydrogen bonding are observed in the structure: (a) hydrogen bonding among water molecules [O $\cdots$ O distance: 1.845 (2)–3.039 (2) Å]; (b) hydrogen bonding of water molecules and carboxylate O atoms [O $\cdots$ O distance: 2.725 (8)–3.028 (1) Å]; (c) hydrogen bonding between the ammonium cations and



**Figure 2**

Packing diagram, viewed down *c* axis, showing hydrogen-bond interactions.

carboxylate O atoms [N $\cdots$ O distance: 2.847 (2)–3.016 (2) Å]; (d) hydrogen bonding between the ammonium cations and water molecules [N $\cdots$ O distance: 2.894 (2)–3.058 (2) Å]. The guest water molecules and ammonium cations are obviously essential to stabilize the crystal structure.

## Experimental

A mixture of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  (0.043 g, 0.2 mmol), 1,2,4,5-benzenetetracarboxylic dianhydride (0.043 g, 0.2 mmol),  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (1 ml) and  $\text{H}_2\text{O}$  (6 ml) with a molar ratio of 1:1:278:1667 (solution pH = 8–9) was heated in a stainless steel reactor with a Teflon liner at 433 K for three days. It produced a colorless solution. After evaporation for several days at room temperature, colorless rhomboidal crystals were obtained.

### Crystal data

$[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)](\text{NH}_4)_2 \cdot 8\text{H}_2\text{O}$   
 $M_r = 495.70$   
 Monoclinic,  $C2/c$   
 $a = 11.555$  (2) Å  
 $b = 15.300$  (3) Å  
 $c = 11.072$  (2) Å  
 $\beta = 91.97$  (3)°  
 $V = 1956.4$  (7) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.683$  Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 50 reflections  
 $\theta = 2.2$ –27.5°  
 $\mu = 1.34$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Rhomboidal, colorless  
 0.20  $\times$  0.19  $\times$  0.10 mm

### Data collection

Siemens SMART CCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.762$ ,  $T_{\max} = 0.877$   
 4233 measured reflections

2242 independent reflections  
 2015 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.010$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -14 \rightarrow 14$   
 $k = -19 \rightarrow 18$   
 $l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.097$   
 $S = 0.98$   
 2242 reflections  
 166 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2 + 1.4324P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.66$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.59$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Zn1—O4 <sup>i</sup>	1.9744 (14)	O2—C1	1.235 (3)
Zn1—O1	1.9789 (14)	O3—C5	1.237 (3)
O1—C1	1.276 (2)	O4—C5	1.268 (2)
O4 <sup>ii</sup> —Zn1—O4 <sup>i</sup>	123.02 (9)	O1 <sup>iii</sup> —Zn1—O1	117.40 (8)
O4 <sup>ii</sup> —Zn1—O1	103.79 (6)	O2—C1—O1	124.74 (17)
O4 <sup>i</sup> —Zn1—O1	104.91 (6)	O3—C5—O4	123.50 (18)

Symmetry codes: (i)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (ii)  $\frac{1}{2} + x, y - \frac{1}{2}, z$ ; (iii)  $1 - x, y, \frac{1}{2} - z$ .

The phenyl ring and ammonium H atoms were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. Atom O3w is equally disordered over two positions (O3w—O3w' distance: 1.523 Å). The occupancy of atom O5w refined to 0.496 and was fixed at 0.5. The refinement is unstable if the occupancy of O5w is set to 1. The H atoms of the water O atoms were not located in the difference Fourier map, and were not included, owing to the complexities of the structure.

Data collection: *SMART* (Bruker, 1999); data reduction: *SAINT* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97*

(Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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