

## Poly[[diaquatris( $\mu_6$ -benzene-1,2,4,5-tetracarboxylato)tris( $\mu_2$ -4,4'-bipyridine)hexacopper(II)] dihydrate]

E. Yang, Jian Zhang, Yi-Hang Wen, Yu-Biao Chen, Yao Kang, Zhao-Ji Li and Yuan-Gen Yao\*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: yyg@ms.fjirsm.ac.cn

Received 18 March 2004

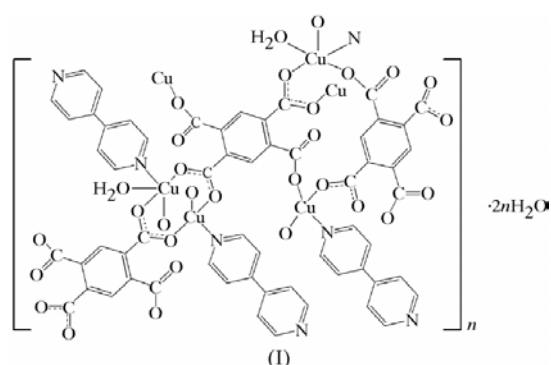
Accepted 5 April 2004

Online 22 May 2004

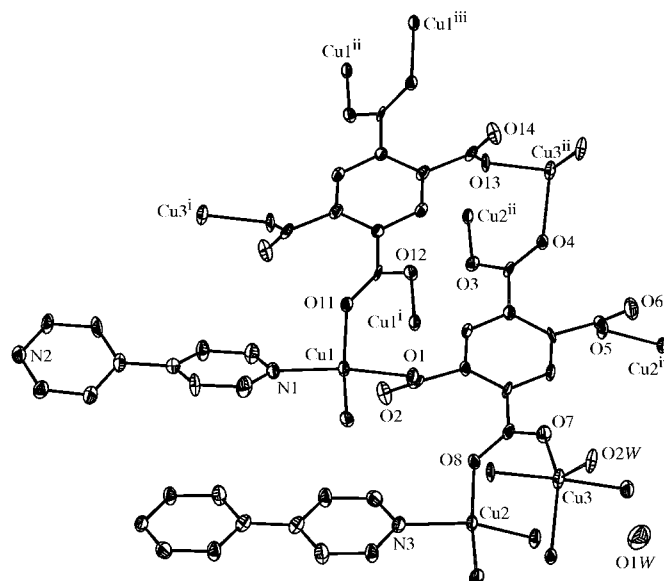
The hydrothermal reaction of an aqueous solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , 1,2,4,5-benzenetetracarboxylic acid and 4,4'-bipyridine gave rise to the interesting title three-dimensional polymer  $\{[\text{Cu}_6(\text{btec})_3(4,4'\text{-bpy})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (btec is 1,2,4,5-benzenetetracarboxylate,  $\text{C}_{10}\text{H}_2\text{O}_8^{4-}$ , and 4,4'-bpy is 4,4'-bipyridine,  $\text{C}_{10}\text{H}_8\text{N}_2$ ), in which each btec ligand links six copper(II) cations into a lamellar  $[\text{Cu}_6(\text{btec})_3(\text{H}_2\text{O})_2]_n$  subpolymer framework. There are two distinct diamine units and two distinct carboxylate units, with one of each lying across an inversion centre.

### Comment

The design of metal-organic materials with large tunnels and cavities has been extensively developed due to their intriguing structural diversities and potential applications as microporous solids for molecular adsorption, ion exchange and heterogeneous catalysis. Recent elaboration has shown that hydrothermal reaction at relatively low temperature and



autogenous pressure provides a powerful tool for the construction of such materials. In particular, multidentate benzenecarboxylate ligands and the rod-like 4,4'-bpy ligand have been shown to be good building blocks in the design of materials with the desired topologies under hydrothermal

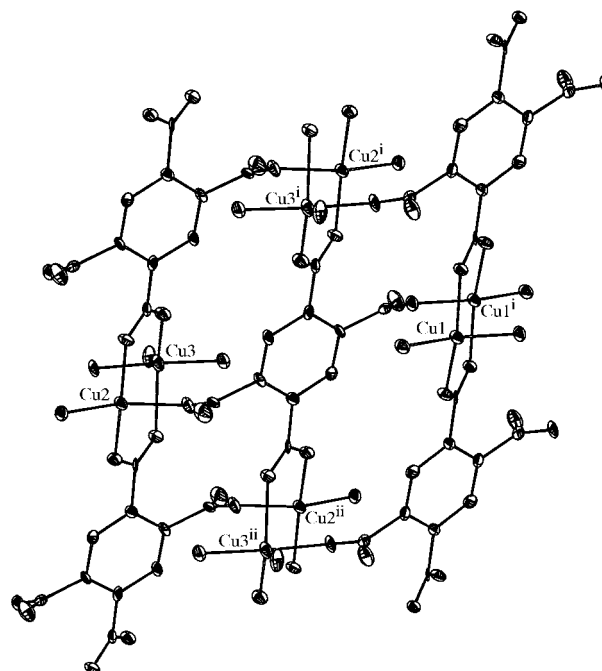


**Figure 1**

A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity [symmetry codes: (i)  $2 - x, 1 - y, 1 - z$ ; (ii)  $x, 1 + y, z$ ; (iii)  $2 - x, 2 - y, 1 - z$ ; (iv)  $2 - x, 1 - y, -z$ ].

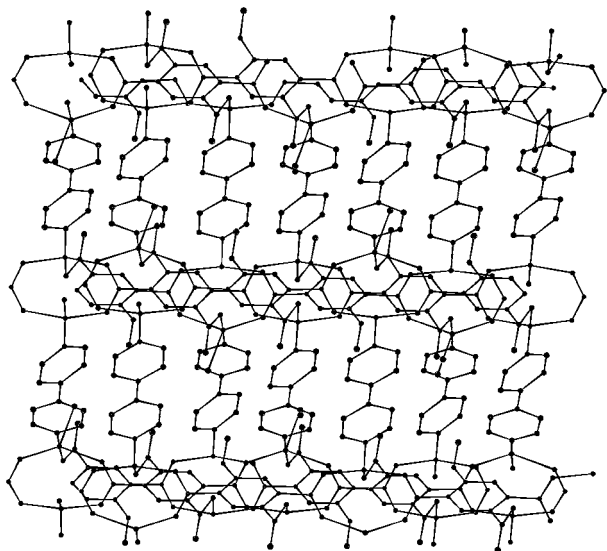
reaction. Recently, some compounds constructed from 1,2,4,5-benzenetetracarboxylic acid ( $\text{H}_4\text{btec}$ ) and 4,4'-bpy have been reported (Cao *et al.*, 2002; Wu *et al.*, 2001, 2002). We present here the title novel compound  $\{[\text{Cu}_6(\text{btec})_3(4,4'\text{-bpy})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (I).

The present crystal structure analysis reveals that (I) is a neutral three-dimensional polymer, which is very different from the structure of  $[\text{Cu}_2(\text{btec})_{4/4}\{\text{Cu}(\text{Hbtec})_{2/2}(4,4'\text{-Hbpy})(\text{H}_2\text{O})_2\}_2 \cdot 4\text{H}_2\text{O}]_n$  (Cao *et al.*, 2002). The hexanuclear species



**Figure 2**

A view of a lamellar sheet in (I), down the [100] face of the subpolymer. [Symmetry codes: (i)  $2 - x, 1 - y, 1 - z$ ; (ii)  $2 - x, -y, 1 - z$ ].



**Figure 3**  
The packing structure in (I), viewed along the [001] face.

$[\text{Cu}_6(\text{btec})_3(4,4'\text{-bpy})_3(\text{H}_2\text{O})_2]$  constitutes the basic building block (Fig. 1). There are two distinct diamine units and two distinct carboxylate units; the diamine unit containing N3 and the carboxylate unit containing O11 both lie across inversion centres.

The most interesting feature of (I) is that the btec ligands exhibit two different coordination modes. One mode is symmetric coordination, with two *para* carboxylate groups linking four Cu1 ions in a bidentate bridging coordination, with the  $\text{Cu1}\cdots\text{Cu1}$  distance being 2.8246 (14) Å [symmetry code: (i)  $2-x, 1-y, 1-z$ ], while the remaining two carboxylate groups link the two Cu3 ions in the axial positions in a monodentate bridging mode. The other mode is asymmetric coordination, with each *para* carboxylate group linking atoms Cu2 and Cu3 in a bidentate bridging coordination, with a  $\text{Cu2}\cdots\text{Cu3}$  distance of 3.0464 (10) Å, while the remaining two carboxylate groups link atoms Cu2 and Cu1 in the axial positions in a monodentate bridging mode (Figs. 1 and 2).

Atom Cu1 adopts a distorted tetrahedral coordination environment, consisting of one 4,4'-bpy N-atom donor and three carboxylate O atoms. Atom Cu2 has a coordination mode similar to that of Cu1, except that these three carboxylate O atoms are all from three asymmetrically coordinated btec ligands. Atom Cu3 has a square-pyramidal coordination, with the basal plane consisting of one N-atom donor and three O-atom donors from three carboxylate groups of three individual btec anions. The apical site is occupied by an O-atom donor from a coordinated water molecule.

As shown in Fig. 2, each btec ligand connects another four asymmetrically and two symmetrically coordinated ligands by six  $\text{Cu}^{\text{II}}$  cations into an infinite two-dimensional lamellar  $[\text{Cu}_6(\text{btec})_3(\text{H}_2\text{O})_2]_n$  subpolymer framework. These lamellae are integrated by 4,4'-bpy ligands to form a three-dimensional architecture, with vacancy dimensions of about  $5.8 \times 10.9$  Å (Fig. 3). These vacancies are filled with water molecules.

## Experimental

A mixture of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.303 g, 1.5 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.064 g, 0.25 mmol) and 4,4'-bpy (0.039 g, 0.25 mmol) was dissolved in water (18 ml) and kept at 418 K for 3 d in a 23 ml Teflon-lined bomb. After slow cooling of the reaction mixture to room temperature, blue crystals of (I) appeared.

### Crystal data

$[\text{Cu}_6(\text{C}_{10}\text{H}_2\text{O}_8)_3(\text{C}_{10}\text{H}_8\text{N}_2)_3 \cdot (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$   
 $M_r = 1672.20$   
 Triclinic,  $P\bar{1}$   
 $a = 10.2545$  (7) Å  
 $b = 10.8207$  (8) Å  
 $c = 13.7264$  (10) Å  
 $\alpha = 91.3050$  (10)°  
 $\beta = 90.461$  (2)°  
 $\gamma = 112.655$  (2)°  
 $V = 1404.97$  (17) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.976$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2833 reflections  
 $\theta = 1.5\text{--}25.1^\circ$   
 $\mu = 2.34$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, blue  
 $0.36 \times 0.20 \times 0.16$  mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.523$ ,  $T_{\text{max}} = 0.688$   
 7378 measured reflections

4938 independent reflections  
 3554 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.036$   
 $\theta_{\text{max}} = 25.1^\circ$   
 $h = -8 \rightarrow 12$   
 $k = -11 \rightarrow 12$   
 $l = -15 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.162$   
 $S = 1.04$   
 4938 reflections  
 463 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.86$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.55$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O1	1.939 (4)	Cu2—N3	2.017 (5)
Cu1—N1	1.963 (5)	Cu2···Cu3	3.0464 (10)
Cu1—O12 <sup>i</sup>	1.966 (4)	Cu3—O13 <sup>ii</sup>	1.955 (4)
Cu1—O11	1.993 (4)	Cu3—O7	1.979 (4)
Cu1···Cu1 <sup>i</sup>	2.8245 (14)	Cu3—N2 <sup>iv</sup>	1.994 (5)
Cu2—O3 <sup>ii</sup>	1.922 (4)	Cu3—O2W	2.102 (5)
Cu2—O8	1.945 (4)	Cu3—O4 <sup>ii</sup>	2.190 (4)
Cu2—O5 <sup>iii</sup>	1.961 (4)		
O1—Cu1—N1	163.4 (2)	O3 <sup>ii</sup> —Cu2—N3	93.51 (18)
O1—Cu1—O12 <sup>i</sup>	90.11 (16)	O13 <sup>ii</sup> —Cu3—O7	89.41 (16)
O1—Cu1—O11	88.98 (15)	O13 <sup>ii</sup> —Cu3—N2 <sup>iv</sup>	177.14 (19)
O3 <sup>ii</sup> —Cu2—O8	166.52 (18)	O13 <sup>ii</sup> —Cu3—O2W	95.20 (17)
O3 <sup>ii</sup> —Cu2—O5 <sup>iii</sup>	91.78 (16)	O13 <sup>ii</sup> —Cu3—O4 <sup>ii</sup>	84.77 (15)

Symmetry codes: (i)  $2-x, 1-y, 1-z$ ; (ii)  $x, y-1, z$ ; (iii)  $2-x, 1-y, -z$ ; (iv)  $1+x, y, z-1$ .

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1W—H1WA···O6 <sup>i</sup>	0.86 (8)	2.08 (9)	2.888 (8)	157 (8)
O1W—H1WB···O6 <sup>ii</sup>	0.76 (9)	2.07 (9)	2.831 (7)	175 (10)
O2W—H2WB···O14 <sup>iii</sup>	0.85 (7)	1.81 (7)	2.623 (6)	161 (7)
O2W—H2WA···O1W <sup>iv</sup>	0.80 (7)	1.98 (7)	2.768 (7)	166 (8)

Symmetry codes: (i)  $2-x, 1-y, -z$ ; (ii)  $x-1, y-1, z$ ; (iii)  $x, y-1, z$ ; (iv)  $1+x, y, z$ .

H atoms bonded to C atoms were located theoretically, with C–H distances of 0.93 Å, and treated as riding atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . H atoms bonded to O atoms were located in difference maps and refined isotropically (see Table 2).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve and refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

This work was financially supported by the State Key Basic Research and Development Plan of China (grant No. 001CB108906), the National Natural Science Foundation of China (grant Nos. 29733090 and 20173063), the Key Project in KIP of the Chinese Academy of Sciences (grant No. KJCX2-H3) and the Natural Science Foundation of Fujian Province (grant No. E0020001).

---

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1177). Services for accessing these data are described at the back of the journal.

---

## References

- Cao, R., Shi, Q., Sun, D. F., Hong, M. C., Bi, W. H. & Zhao, Y. J. (2002). *Inorg. Chem.* **41**, 6161–6168.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Siemens (1994). *SAINT* and *SHELXTL* (Release 5). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wu, C. D., Lu, C.-Z., Lu, S.-F., Zhuang, H.-H. & Huang, J.-S. (2002). *Inorg. Chem. Commun.* **5**, 171–174.
- Wu, C. D., Lu, C.-Z., Wu, D.-M., Zhuang, H.-H. & Huang, J.-S. (2001). *Inorg. Chem. Commun.* **4**, 561–564.