

Han Xu, Ran Sun, Yi-Zhi Li* and
Jun-Feng BaiCoordination Chemistry Institute, State Key
Laboratory of Coordination Chemistry, Nanjing
University, Nanjing 210093, People's Republic
of China

Correspondence e-mail: llyyz@nju.edu.cn

Key indicators

Single-crystal X-ray study

T = 273 K

Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

R factor = 0.054

wR factor = 0.126

Data-to-parameter ratio = 11.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Poly[[diaqua- μ -1,2-benzene-1,2-dicarboxylato- μ -4,4'-bipyridine-copper(II)] dihydrate]: a
two-dimensional copper(II) polymer

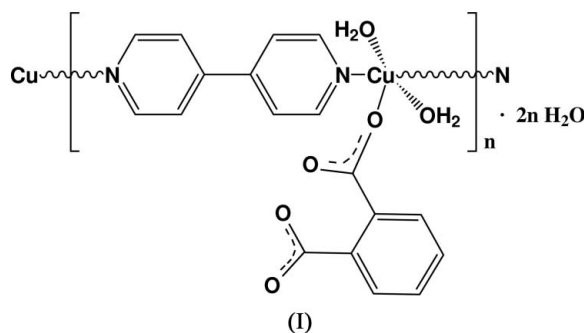
The title compound, $\{[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$, contains chains of copper(II) centres bridged by bipyridine ligands along the b axis. The chains are bridged by phthalate dianions, forming a rectangular grid complex. Each Cu^{II} atom adopts a slightly distorted octahedral geometry, being coordinated by two N atoms of 4,4'-bipyridine, two O atoms of phthalate dianions and two water molecules. Twofold axes are located along the copper–bipyridine chains and through the phthalate dianions.

Received 29 March 2006

Accepted 22 April 2006

Comment

Polycarboxylate ligands have attracted considerable attention and form a rapidly developing research area (Rao *et al.*, 2001), due not only to the easy synthesis of various carboxylates and their versatile coordination modes, but also to their potential properties, such as porosity, supramolecular architectures and applications (Chui *et al.*, 1999; Batten *et al.*, 1998; Yaghi *et al.*, 1996). Phthalate is one of the most commonly studied carboxylates in coordination polymer chemistry and this flexible dicarboxylate has been combined with the rigid spacer molecule 4,4'-bipyridine in a number of salts, such as Mn, Ni, Zn, Cd and Co complexes (Ma *et al.*, 2003; Yang *et al.*, 2003; Tang *et al.*, 2004; Wang *et al.*, 2005; Suresh *et al.*, 2001).



The title compound, (I) (Fig. 1), crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ and is isostructural with the Co and Cd complexes already reported by Suresh *et al.* (2001). The primary structure consists of chains of Cu^{II} centres bridged by bipyridine ligands along the b axis, linked by phthalate dianions, forming a rectangular grid complex. Each metal centre is thus coordinated by two *trans* μ -4,4'-bipyridine ligands in the equatorial positions and two *trans* μ -phthalate ions in the axial positions [$\text{Cu}-\text{O} = 2.413(3) \text{ \AA}$]. The equatorial coordination of two water molecules completes the slightly distorted octahedral Cu^{II} coordination (Table I). The pyridyl rings of the bridging 4,4'-bipyridine ligands are

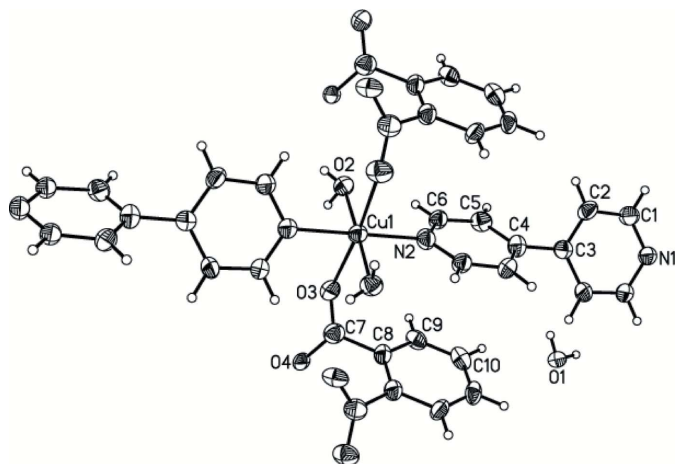


Figure 1

A segment of the polymeric structure of (I), with displacement ellipsoids drawn at the 30% probability level. Unlabelled atoms are generated from labelled atoms by twofold rotation symmetry and by translation along the *b* axis (symmetry codes as in Table 1).

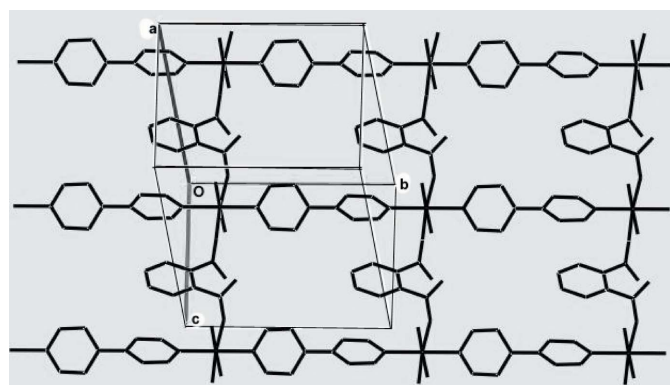


Figure 2

A view of the rectangular grid, with H atoms and solvent water molecules omitted for clarity.

twisted by $56.02(2)^\circ$. The rectangular grids run parallel to the crystallographic *ab* plane (Fig. 2). The intra-grid metal–metal separation, where the metal centre defines the corners of a rectangle, is $11.103(2) \times 7.696(2) \text{ \AA}$, similar to those observed in the Co and Cd complexes (Suresh *et al.*, 2001). These layers stack along the *c* axis and are staggered such that the metal ion of the first corresponds to the centre of the grid rectangle of the second, with distances between neighboring layers of $5.396(2) \text{ \AA}$. The layers are connected through H-bonds involving the solvent water molecules (Fig. 3 and Table 2).

Experimental

All manipulations were carried out in air. Cu^{II} hydroxide (0.020 g, 0.2 mmol), phthalic acid (0.033 g, 0.1 mmol) and 4,4'-bipyridine (0.0032 g, 0.02 mmol) were mixed in a water–methanol (1:1 *v/v*, 10 ml) solution. The mixture was sealed in a Teflon-lined stainless steel bomb and heated at 393 K for 48 h under autogeneous pressure. The resulting blue solution was filtered and left to evaporate at room temperature and pressure. After three weeks, blue crystals formed.

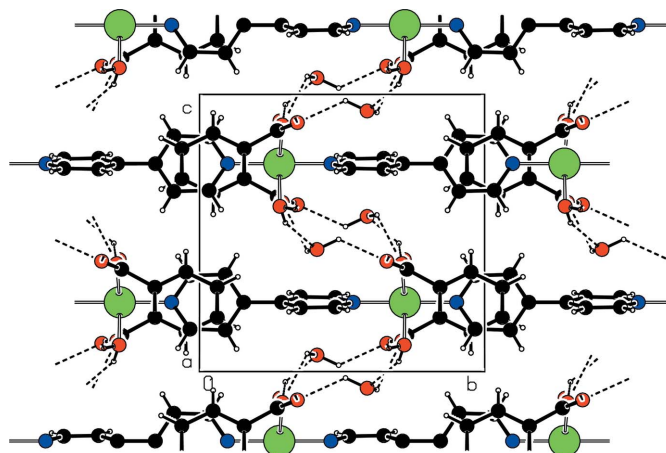
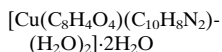


Figure 3

Packing diagram of the title compound, with intermolecular hydrogen bonds between neighboring layers drawn as dashed lines.

Crystal data



$M_r = 455.90$

Monoclinic, $P2_1/c$

$a = 7.6963(6) \text{ \AA}$

$b = 11.1028(8) \text{ \AA}$

$c = 12.9739(8) \text{ \AA}$

$\beta = 123.707(3)^\circ$

$V = 922.25(11) \text{ \AA}^3$

$Z = 2$

$D_x = 1.642 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\mu = 1.24 \text{ mm}^{-1}$

$T = 273(2) \text{ K}$

Prism, blue

$0.32 \times 0.26 \times 0.24 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2000)

$T_{\text{min}} = 0.69$, $T_{\text{max}} = 0.74$

4576 measured reflections

1626 independent reflections

1292 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.126$

$S = 1.10$

1626 reflections

146 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.63 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1–N1	1.334 (5)	Cu1–O2	2.010 (3)
C6–N2	1.346 (5)	Cu1–N1 ⁱⁱ	2.012 (5)
C7–O3	1.242 (6)	Cu1–N2	2.017 (5)
C7–O4	1.258 (5)	Cu1–O3	2.413 (3)
O2 ⁱ –Cu1–O2	178.57 (19)	O2–Cu1–O3 ⁱ	94.49 (12)
O2 ⁱ –Cu1–N1 ⁱⁱ	89.29 (9)	N1 ⁱⁱ –Cu1–O3 ⁱ	87.21 (8)
O2 ⁱ –Cu1–N2	90.71 (9)	N2–Cu1–O3 ⁱ	92.79 (8)
N1 ⁱⁱ –Cu1–N2	180	O3 ⁱ –Cu1–O3	174.42 (16)
O2 ⁱ –Cu1–O3 ⁱ	85.44 (12)		

Symmetry codes: (i) $-x + 2, y, -z + \frac{3}{2}$; (ii) $x, y + 1, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O4 ⁱⁱⁱ	0.93 (7)	2.10 (7)	2.777 (4)	128 (6)
O1—H1B \cdots O3 ^{iv}	0.86 (7)	2.25 (7)	2.724 (4)	115 (6)
O2—H2A \cdots O1 ^{iv}	0.92 (8)	1.84 (7)	2.684 (5)	150 (6)
O2—H2A \cdots O3	0.92 (8)	2.50 (7)	3.015 (5)	115 (5)
O2—H2B \cdots O4 ^v	0.71 (7)	2.17 (8)	2.635 (4)	124 (8)

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

The H atoms of water molecules O1 and O2 were located in difference maps and refined freely with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. All other H atoms were positioned geometrically (the distance to H atoms were in the range 0.93–0.98 Å) and refined as riding, with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the Nanjing University Talent Development Foundation (No. 0205005122).

References

- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
 Bruker (2000). *SMART, SAINT, SHELXTL, SADABS, XPREP* and *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chui, S. S.-Y., Lo, S. M.-F., Charmant, S. P. H., Orpen, A. G. & Williams, L. D. (1999). *Science*, **283**, 1148–1150.
 Ma, C.-B., Chen, C.-N., Liu, Q.-T., Liao, D.-Z., Li, L.-C. & Sun, L.-C. (2003). *New J. Chem.* **27**, 890–894.
 Rao, C. N. R., Natarajan, S., Choudhury, A., Neeraj, S. & Vaidhyanathan, R. (2001). *Acta Cryst.* **B57**, 1–12.
 Suresh, E., Boopalan, K., Jasra, R. V. & Bhadbhade, M. M. (2001). *Inorg. Chem.* **40**, 4078–4080.
 Tang, E., Dai, Y.-M. & Lin, S. (2004). *Acta Cryst.* **C60**, m433–m434.
 Wang, X.-L., Qin, C., Wang, E.-B. & Xu, L. (2005). *J. Mol. Struct.* **737**, 49–54.
 Yaghi, O. M., Li, H. & Groy, T. L. (1996). *J. Am. Chem. Soc.* **118**, 9096–9101.
 Yang, S.-Y., Long, L.-S., Huang, R.-B., Zheng, L.-S. & Ng, S. W. (2003). *Acta Cryst.* **E59**, m507–m509.