

# A two-dimensional hydrogen-bonding supramolecular architecture of bis(2,2'-bipyridine)[(p-phenylenedioxy)diacetato]copper(II) tetrahydrate

Miao Du,\* Hua Cai and  
Xiao-Jun Zhao

College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, People's Republic of China

Correspondence e-mail:  
dumiao@public.tpt.tj.cn

## Key indicators

Single-crystal X-ray study

$T = 293$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å

$R$  factor = 0.054

$wR$  factor = 0.150

Data-to-parameter ratio = 15.0

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

Received 21 June 2004

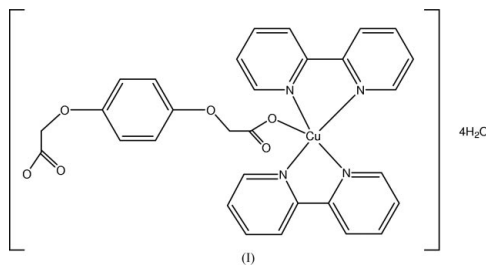
Accepted 13 July 2004

Online 17 July 2004

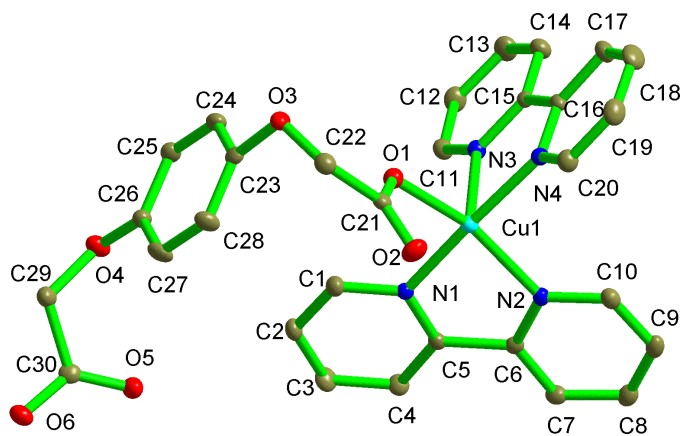
In the crystal structure of the title complex,  $[\text{Cu}(\text{bda})(\text{bipy})_2] \cdot 4\text{H}_2\text{O}$  [ $\text{H}_2\text{bda}$  = (*p*-phenylenedioxy)diacetic acid or benzene-1,4-dioxyacetic acid ( $\text{C}_{10}\text{H}_{10}\text{O}_6$ ) and  $\text{bipy}$  = 2,2'-bipyridine ( $\text{C}_{10}\text{H}_8\text{N}_2$ )], the  $\text{Cu}^{\text{II}}$  centre is pentacoordinated, with a square-pyramidal geometry comprising four N atoms from two chelating  $\text{bipy}$  ligands and one carboxylate O atom of the  $\text{bda}$  ligand. The other three uncoordinated carboxylate O atoms of the  $\text{bda}$  ligand act as the acceptors of four  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds from the water molecules, among which another four  $\text{O}-\text{H} \cdots \text{O}$  hydrogen-bonding interactions are also observed, resulting in a two-dimensional supramolecular pattern.

## Comment

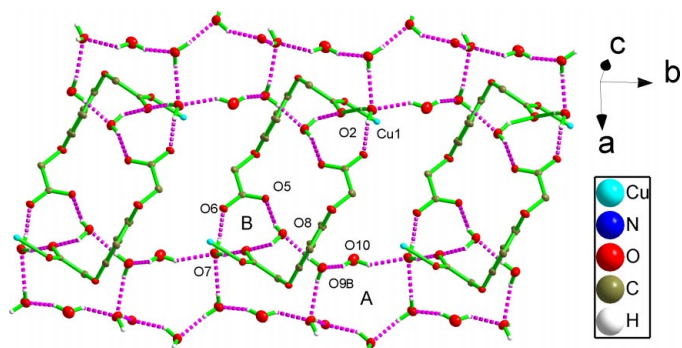
Self-assembly processes directed by either hydrogen-bonding interactions or metal coordination have been extensively utilized in crystal engineering to construct supramolecular systems with novel structures and properties due to their inherent strength and reliability (Braga *et al.*, 2003; Zhang *et al.*, 2004; Chen & Liu, 2002). Among synthetic strategies in the context of coordination supramolecules, one of the most fruitful approaches is to take advantage of suitable bridging ligands, such as aromatic carboxylic acids, which possess diverse coordination modes and favour the formation of hydrogen bonds (Yaghi *et al.*, 2003). Phenylenedioxydiacetic acids, especially (*p*-phenylenedioxy)diacetic acid (or benzene-1,4-dioxyacetic acid),  $\text{H}_2\text{bda}$ , could act as a family of flexible multidentate ligands with versatile binding abilities, the coordination chemistry of which has been documented very little to date. Curiously, according to results in recent reports on coordination supramolecular systems based on mixed ligands,  $\text{H}_2\text{bda}$  usually plays an uncoordinated anionic role in these complexes (Gao *et al.*, 2004) or is not involved in the final product (Liu *et al.*, 2004). In the present paper, we report the crystal structure of the title compound, (I), a new  $\text{Cu}^{\text{II}}$  complex based on the mixed ligands  $\text{bipy}$  and  $\text{H}_2\text{bda}$ , in which very interesting hydrogen-bonding interactions are observed.



The crystal structure of (I) consists of a neutral mononuclear  $[\text{Cu}(\text{bipy})_2(\text{bda})]$  molecule and four uncoordinated water molecules. Selected bond lengths and angles are listed in


**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the water molecules have been omitted for clarity.


**Figure 2**

A view of the two-dimensional supramolecular structure of (I), showing the hydrogen-bonding interactions (dashed lines) and the *A* and *B* ring motifs. The bipy molecules have been omitted for clarity.

Table 1. As shown in Fig. 1, the  $\text{Cu}^{\text{II}}$  centre is coordinated by four N atoms from two bipy ligands, with  $\text{Cu}-\text{N}$  bond lengths in the range 1.977 (3)–2.172 (4) Å, and by one additional O donor from the carboxylate group of the bda anion, with a  $\text{Cu}-\text{O}$  bond distance of 1.975 (3) Å. Thus, the coordination polyhedron around the  $\text{Cu}^{\text{II}}$  cation could be best described as a distorted square-based pyramid, with a  $\tau$  parameter of 0.21 (Addison *et al.*, 1984).

The  $\text{Cu}^{\text{II}}$  centre deviates from the least-squares basal plane of atoms N1/N2/O1/N4 by approximately 0.12 Å toward the apical N3 site. The bipy ligands combine with the  $\text{Cu}^{\text{II}}$  centre to give two five-membered chelate rings (N1–C5–C6–N2–Cu1 and N3–C15–C16–N4–Cu1), forming an N2–Cu1–N1 angle of 80.76 (15)° and an N3–Cu1–N4 angle of 79.28 (14)°.

It should be noted that only one (O1–C21–O2) of the two carboxylate groups is involved in coordination to the  $\text{Cu}^{\text{II}}$  cation, exhibiting the monodentate mode *via* atom O1; this is also reflected by the fact that the C21–O1 bond [1.259 (5) Å] is significantly longer than C21–O2 [1.237 (5) Å]. The two C–O bond distances of the other carboxylate group (O5–C30–O6) are almost equivalent [1.241 (6) and 1.243 (5) Å], agreeing with its uncoordinated structural feature and delocalized state.

Analysis of the crystal packing of (I) shows the existence of eight  $\text{O}-\text{H}\cdots\text{O}$  interactions between the water molecules and the complex molecules, resulting in a two-dimensional supramolecular network, as depicted in Fig. 2. All relevant hydrogen-bonding geometries are listed in Table 2. Water molecules O7 and O8 form two  $\text{O7}-\text{H7A}\cdots\text{O6}$  and  $\text{O8}-\text{H8A}\cdots\text{O5}$  hydrogen bonds with the two O atoms of the uncoordinated carboxylate group. The same two water molecules are also involved in the formation of  $\text{O7}-\text{H7B}\cdots\text{O2}^i$  and  $\text{O8}-\text{H8B}\cdots\text{O2}^i$  hydrogen bonds with the free atom O2 of the monodentate carboxylate subunit [symmetry code: (i)  $1-x, 1-y, 2-z$ ]. The resulting motif *B* (Fig. 2), in the formalism of graph-set analysis of hydrogen-bond patterns (Etter, 1990), is characterized as  $N_4 = R_3^3(10)$ . Furthermore, four other types of intermolecular  $\text{O}-\text{H}\cdots\text{O}$  interactions are observed among the water molecules (Table 2). Thus, a hydrogen-bonded ring *A*,  $N_7 = R_7^5(14)$ , is generated, which comprises six water molecules (two O7, two O9, one O8 and one O10) and one free O2 atom of the monodentate carboxylate group. In summary, eight types of  $\text{O}-\text{H}\cdots\text{O}$  interactions connect the water and complex subunits of (I) to form an infinite two-dimensional layered architecture (Fig. 2).

Examination of the structure of (I) with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids or  $\pi-\pi$  stacking interactions in the crystal structure.

## Experimental

A methanol solution (5 ml) of 2,2'-bipyridine (33 mg, 0.2 mmol) was added to a solution of  $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$  (42 mg, 0.2 mmol) in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (10 ml, 1:1) with vigorous stirring. A methanol solution (10 ml) of  $\text{H}_2\text{bda}$  (23 mg, 0.1 mmol) was then added and the mixture stirred for *ca* 30 min. The reaction solution was filtered and left to stand at room temperature. Blue block-like single crystals of (I) suitable for X-ray diffraction were obtained after several days by slow evaporation of the solvent (yield 45%). Spectroscopic analysis: IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 3384 (*b*), 3108 (*m*), 3070 (*m*), 3030 (*m*), 2953 (*m*), 2894 (*m*), 1619 (*vs*), 1597 (*vs*), 1509 (*s*), 1475 (*s*), 1445 (*s*), 1423 (*s*), 1342 (*s*), 1320 (*m*), 1287 (*m*), 1233 (*s*), 1162 (*m*), 1121 (*m*), 1055 (*s*), 1016 (*m*), 938 (*w*), 909 (*w*), 830 (*m*), 809 (*m*), 772 (*s*), 731 (*m*), 690 (*m*), 658 (*w*), 622 (*w*), 535 (*w*), 491 (*w*). Analysis calculated for (I): C 53.60, H 4.80, N 8.33%; found: C 53.97, H 4.55, N 8.28%.

### Crystal data

$[\text{Cu}(\text{C}_{10}\text{H}_8\text{O}_6)(\text{C}_{10}\text{H}_8\text{N}_2)_2]\cdot 4\text{H}_2\text{O}$   
 $M_r = 672.14$   
 Monoclinic,  $P2_1/n$   
 $a = 14.460$  (4) Å  
 $b = 10.112$  (3) Å  
 $c = 20.394$  (5) Å  
 $\beta = 91.459$  (5)°  
 $V = 2981.1$  (13) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.498$  Mg  $\text{m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 800 reflections  
 $\theta = 2.6-21.6^\circ$   
 $\mu = 0.80$   $\text{mm}^{-1}$   
 $T = 293$  (2) K  
 Block, blue  
 $0.16 \times 0.14 \times 0.10$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.796$ ,  $T_{\text{max}} = 0.923$   
 16 900 measured reflections

6108 independent reflections  
 3301 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.089$   
 $\theta_{\text{max}} = 26.4^\circ$   
 $h = -18 \rightarrow 18$   
 $k = -12 \rightarrow 9$   
 $l = -25 \rightarrow 25$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.150$   
 $S = 0.98$   
 6108 reflections  
 406 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

Table 1

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

Cu1—O1	1.975 (3)	O1—C21	1.259 (5)
Cu1—N1	1.977 (3)	O2—C21	1.237 (5)
Cu1—N4	1.990 (3)	O5—C30	1.241 (6)
Cu1—N2	2.032 (4)	O6—C30	1.243 (5)
Cu1—N3	2.172 (4)		
O1—Cu1—N1	93.94 (14)	N4—Cu1—N2	95.58 (14)
O1—Cu1—N4	91.00 (13)	O1—Cu1—N3	98.89 (13)
N1—Cu1—N4	173.98 (15)	N1—Cu1—N3	96.54 (14)
O1—Cu1—N2	161.33 (14)	N4—Cu1—N3	79.28 (14)
N1—Cu1—N2	80.76 (15)	N2—Cu1—N3	99.49 (14)

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O7—H7A $\cdots$ O6	0.85	1.83	2.661 (5)	165
O7—H7B $\cdots$ O2 <sup>i</sup>	0.85	2.07	2.908 (5)	170
O8—H8A $\cdots$ O5	0.85	1.87	2.681 (5)	160
O8—H8B $\cdots$ O2 <sup>i</sup>	0.85	2.08	2.834 (5)	148
O9—H9A $\cdots$ O8 <sup>ii</sup>	0.85	1.87	2.713 (6)	173
O9—H9B $\cdots$ O7 <sup>iii</sup>	0.85	2.16	2.930 (6)	151
O10—H10A $\cdots$ O7 <sup>iv</sup>	0.85	2.13	2.905 (6)	152
O10—H10B $\cdots$ O9 <sup>ii</sup>	0.85	2.04	2.839 (7)	156

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

Although all H atoms were visible in difference maps, they were finally placed in geometrically calculated positions, with C—H

distances in the range 0.93–0.97  $\text{\AA}$  and O—H distances of 0.85  $\text{\AA}$ , and included in the final refinement in the riding model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic and methylene H atoms, and  $1.5U_{\text{eq}}(\text{O})$  for water H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL97*.

This work was supported financially by the Starting Fund of Tianjin Normal University and the Natural Science Foundation of Tianjin (grant No. 043604011).

## References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Braga, D., Maini, L., Polito, M., Tagliavini, E. & Grepioni, F. (2003). *Coord. Chem. Rev.* **246**, 53–71.
- Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.
- Bruker (1998). *SMART* (Version 5.0), *SAINT* (Version 4.0) and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, X. M. & Liu, G. F. (2002). *Chem. Eur. J.* **8**, 4811–4817.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Gao, S., Liu, J.-W., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2004). *Acta Cryst.* **E60**, m620–m621, and references cited therein.
- Liu, J.-W., Gao, S., Huo, L.-H. & Ng, S. W. (2004). *Acta Cryst.* **E60**, m501–m503.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. & Kim, J. (2003). *Nature (London)*, **423**, 705–714.
- Zhang, J. P., Zheng, S. L., Huang, X. C. & Chen, X. M. (2004). *Angew. Chem. Int. Ed.* **43**, 206–209.