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Key indicators

Single-crystal X-ray study
 T = 295 K
 Mean $\sigma(C-C)$ = 0.003 Å
 R factor = 0.043
 wR factor = 0.111
 Data-to-parameter ratio = 15.9

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

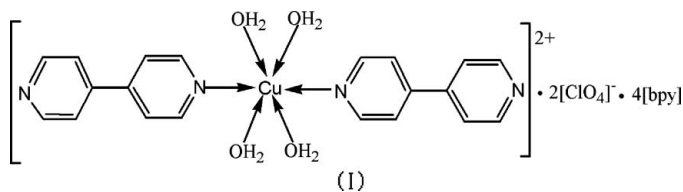
Tetraaquabis(4,4-bipyridine)copper(II) bis(perchlorate) bipyridine tetrasolvate

In the crystal structure of the title compound, $[Cu(C_{10}H_8N_2)_2(H_2O)_4](ClO_4)_2 \cdot 4C_{10}H_8N_2$, the asymmetric unit consists of one-half of a mononuclear $[Cu(bpy)_2(H_2O)_4]^{2+}$ cation (bpy is 4,4-bipyridine), one perchlorate ion and two solvent bpy molecules, the formula unit being generated by crystallographic inversion symmetry. A three-dimensional network with triangular channels is formed *via* O—H...N hydrogen bonds and π – π interactions.

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Comment

One-, two- and three-dimensional non-interpenetrating open network structures with variable cavities or channels of desired size, and well entangled structures through interpenetration, can be generated by both covalent and hydrogen bonding (Batten & Robson, 1998). Neutral *N,N'*-bidentate ligands, such as 4,4-bipyridine (bpy), pyrazine or 1,2-bis(4-pyridyl)ethane, are excellent bridging ligands. Until now, a large number of compounds with bpy as a ligand have been synthesized (Blake *et al.*, 1997; Carlucci *et al.*, 1997). Many of these complexes are constructed by coordination bonds or mixed coordination and hydrogen bond interactions. We report here the crystal structure of the title compound, (I), which is self-assembled by hydrogen-bonding and π – π interactions, and is isostructural with the manganese compound (Tong *et al.*, 1999).



Compound (I) consists of a mononuclear $[Cu(bpy)_2(H_2O)_4]^{2+}$ cation, two perchlorate ions and four solvent bpy molecules. As shown in Fig. 1, two N atoms from two different bpy and four water molecules complete the slightly distorted octahedral coordination environment for the Cu atom. The

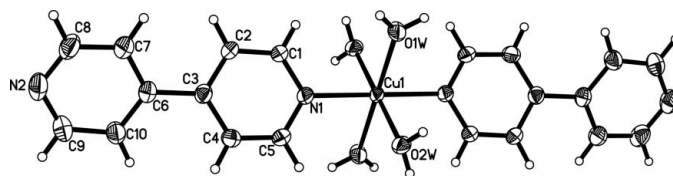


Figure 1 View of the cation of (I), with 35% probability displacement ellipsoids. The unlabeled atoms are related by the symmetry operator $(1 - x, 2 - y, -z)$.

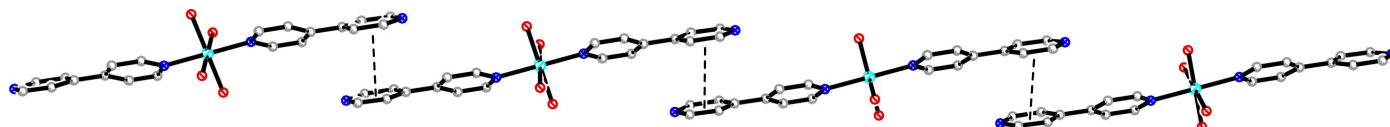


Figure 2
A view of the Cu–bpy...bpy–Cu chain formed by the π – π interactions (dashed lines).

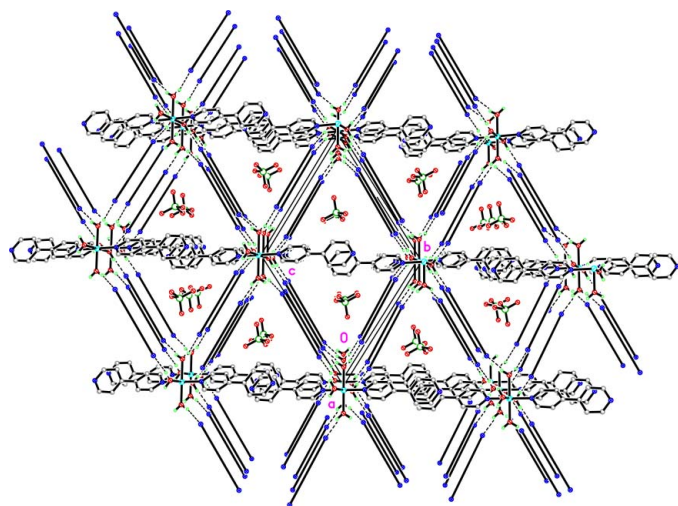


Figure 3
Packing diagram of (I), showing the triangular channels. The solvent bpy molecules are shown as single bold lines. Hydrogen bonds are shown as broken lines and ClO_4^- ions reside in the channels.

four water molecules form the equatorial plane and the axial positions are occupied by two coordinated bpy molecules. In the cation, each coordinated water molecule forms strong O–H...N hydrogen bonds with non-coordinated bpy molecules (Table 2). In addition, cations form extended one-dimensional chains (Fig. 2) through the π – π interactions between coordinated ligands related by inversion centers [with a centroid–centroid separation of 3.6960 (14) Å] in an off-set fashion with a face-to-face separation of *ca* 3.55 Å, which is the same as the value of 3.55 Å in the reported Mn^{II} compound (Tong *et al.*, 1999). The Cu...Cu separation of the Cu–bpy...bpy–Cu segment of this chain is 15.3286 (17) Å, which is longer than Cu–OH₂...bpy...H₂O–Cu [Cu...Cu = 14.951 (2) Å] *via* intermediate water molecules (Blake *et al.* 1997). As shown in Fig. 3, cations and the solvent bpy molecules are connected into a three-dimensional network with triangular channels by O–H...N hydrogen bonds and π – π interactions. The ClO_4^- anions occupy the triangular channels, making contacts with four adjacent bpy molecules through C–H...O hydrogen-bonding interactions (Table 2).

Experimental

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.5 mmol), NaClO_4 (0.5 mmol), an ethanol solution (2 ml) of bpy (0.5 mmol) and water (10 ml) was placed in a Parr Teflon-lined stainless steel vessel (25 ml), and the vessel was sealed and heated under autogenous pressure to 438 K. The temperature was held for six days, and then the reactant mixture was cooled at a rate of 0.5 K min^{-1} , leading to the formation of blue crystals of (I) (yield 50% based on Cu).

Crystal data

$[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_4] \cdot (\text{ClO}_4)_2 \cdot 4\text{C}_{10}\text{H}_8\text{N}_2$
 $M_r = 1271.62$
 Triclinic, $P\bar{1}$
 $a = 7.8728$ (5) Å
 $b = 14.1856$ (2) Å
 $c = 14.8321$ (4) Å
 $\alpha = 63.729$ (8)°
 $\beta = 88.073$ (10)°
 $\gamma = 81.464$ (10)°
 $V = 1467.95$ (15) Å³

$Z = 1$
 $D_x = 1.438$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3511 reflections
 $\theta = 6.5$ – 27.5 °
 $\mu = 0.54$ mm⁻¹
 $T = 295.2$ K
 Prism, blue
 $0.58 \times 0.55 \times 0.55$ mm

Data collection

Rigaku Mercury70 diffractometer
 ω scans
 Absorption correction: multi-scan (*CrystalClear*; Rigaku Corporation & Molecular Structure Corporation, 2004)
 $T_{\text{min}} = 0.729$, $T_{\text{max}} = 0.748$
 11148 measured reflections

6527 independent reflections
 5581 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 27.5$ °
 $h = -10 \rightarrow 10$
 $k = -18 \rightarrow 17$
 $l = -19 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.111$
 $S = 1.01$
 6527 reflections
 410 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.423P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–N1	2.1229 (15)	Cu1–O1W	2.1535 (13)
Cu1–O2W	2.1309 (14)		
N1 ⁱ –Cu1–N1	180.0	O2W–Cu1–O1W	90.78 (6)
N1–Cu1–O2W ⁱ	90.85 (6)	N1–Cu1–O1W ⁱ	89.40 (5)
N1–Cu1–O2W	89.15 (6)	O2W–Cu1–O1W ⁱ	89.22 (6)
O2W ⁱ –Cu1–O2W	180.0	O1W–Cu1–O1W ⁱ	180.0
N1–Cu1–O1W	90.60 (5)		

Symmetry code: (i) $-x + 1, -y + 2, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

D –H... A	D –H	H... A	D ... A	D –H... A
O1W–H1WB...N5 ⁱⁱ	0.83 (2)	2.03 (1)	2.841 (2)	166 (2)
O1W–H1WA...N3 ⁱⁱ	0.83 (2)	2.09 (1)	2.895 (2)	163 (2)
O2W–H2WB...N6 ⁱⁱⁱ	0.83 (2)	1.97 (1)	2.801 (2)	173 (2)
O2W–H2WA...N4 ^{iv}	0.83 (2)	2.05 (1)	2.876 (2)	176 (2)
C2–H2A...O4	0.93	2.47	3.336 (3)	155
C9–H9A...O3 ^v	0.93	2.56	3.211 (4)	128
C14–H14A...O2 ⁱⁱ	0.93	2.52	3.414 (3)	160
C32–H32A...O3 ^{vi}	0.93	2.36	3.283 (4)	175
C34–H34A...O1 ^{vii}	0.93	2.49	3.296 (3)	145

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

H atoms attached to C atoms were placed in calculated positions and treated using a riding-model approximation [$C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$]. The H atoms bonded to O atoms were visible in a difference map and were refined isotropically with an O–H distance restraint of $0.83(2) \text{ \AA}$.

Data collection: *CrystalClear* (Rigaku Corporation & Molecular Structure Corporation, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

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References

- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1460–1494.
- Blake, A. J., Hill, S. J., Hubberstey, P. & Li, W. S. (1997). *J. Chem. Soc. Dalton Trans.* pp. 913–914.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1801–1804.
- Rigaku Corporation & Molecular Structure Corporation (2004). *CRYSTAL-CLEAR*. Version 1.3. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan, and MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Tong, M. L., Lee, H. Y., Chen, X. M., Huang, R. B. & Mak, T. C. W. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3657–3659.