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catena-Poly[[[aquacopper(**I**)]-μ-4,4′-bipyridyl-κ^2N:N'] hemi(isophthalate) monohydrate]

Yi-Hang Wen, Ye-Yan Qin, Jian Zhang, Zhao-Ji Li, Jian-Kai Cheng, Yao Kang and Yuan-Gen Yao*

The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China
Correspondence e-mail: yyg@ms.fjirsm.ac.cn

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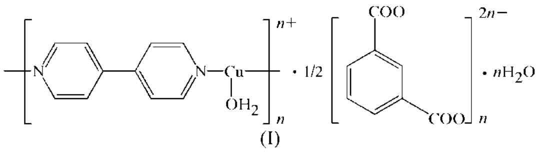
The title compound, $\{[Cu(C_{10}H_8N_2)(H_2O)](C_8H_4O_4)_{0.5}\cdot H_2O\}_n$, has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction. The compound consists of nearly linear one-dimensional chains of $[Cu(4,4'\text{-bipy})(H_2O)]_n^{n+}$ cations (4,4′-bipy is 4,4′-bipyridyl), surrounded by isophthalate anions and free water molecules. Hydrogen-bonding interactions involving cationic chains, isophthalate anions and free water molecules lead to the formation of a three-dimensional network structure.

Comment

Recently, much attention has been focused on metal-directed supramolecular complexes because of their potential applications as novel magnetic materials, microporous phases and catalysts (Chui *et al.*, 1999; Lo *et al.*, 2000). Usually, bi- or multidentate organic ligands containing N or O atoms are used to bind metal centers (Hagrman *et al.*, 1999). For example, 4,4′-bipyridyl (4,4′-bipy) is an excellent bridging ligand for coordination chemistry because of its rod-like shape, which allows the ligand to connect metal ions into an extended array (Park *et al.*, 2001); 4,4′-bipy is thus widely used in the construction of transition metal coordination complexes. A large number of one-, two- and three-dimensional extended metal–4,4′-bipy frameworks have been synthesized by hydrothermal methods (Noro *et al.*, 2002; Wang *et al.*, 1999), and this process has proved an efficient way to discover new coordination compounds, because it allows the formation of metastable phases. Additionally, 4,4′-bipy and benzenedicarboxylic acid have often been used simultaneously to construct metal-organic frameworks (Tao *et al.*, 2000; Lightfoot & Snedden, 1999; Ma *et al.*, 2003). In the present work, we chose isophthalic acid and 4,4′-bipy as ligands to react with a copper salt, resulting in the isolation of an unexpected novel three-coordinate copper(I) compound, *viz.* $[Cu(4,4'\text{-bipy})(H_2O)^+\cdot 0.5(\text{isophthalate})^{2-}\cdot H_2O]_n$, (I).



(I)

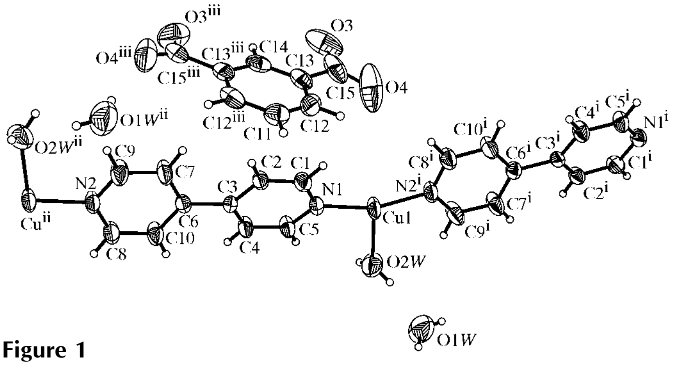


Figure 1
An ellipsoid plot of the title compound, showing the atom-numbering scheme for non-H atoms. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $-x, y, -\frac{1}{2}-z$.]

As shown in Fig. 1, the crystal structure of (I) reveals a coordinatively unsaturated, approximately T-shaped, copper(I) centre, trigonally coordinated by two N atoms from two 4,4′-bipy ligands [Cu—N = 1.920 (4) and 1.921 (4) Å, and N1—Cu1—N2 = 158.88 (18)°; Table 1] and by one O atom from a water molecule [Cu—O2*W* = 2.195 (5) Å, N1—Cu1—O2*W* = 99.65 (18)° and N2—Cu1—O2*W* = 101.47 (18)°]. The Cu^{I} centre is located in the plane defined by the three donor atoms. The dihedral angle between the two pyridine rings of 4,4′-bipy is 15.61°. The Cu^{I} centres are linked *via* 4,4′-bipy ligands to generate a one-dimensional cation chain propagating along the *a* axis, as shown in Fig. 2. The coordinated water molecules are alternately arranged on opposite sides of the cation chain, with the isophthalate anions interspersed between the chains.

There are extensive hydrogen-bonding interactions involving the isophthalate anions, coordinated water molecules and free water molecules (Table 2). Among these interactions, the distances for the O2*W*—H2*WB*···O3 and O2*W*—H2*WA*···O1*W* interactions are shorter than those for the other two interactions, implying that the coordinated water molecules may have stronger hydrogen-bonding interactions than the

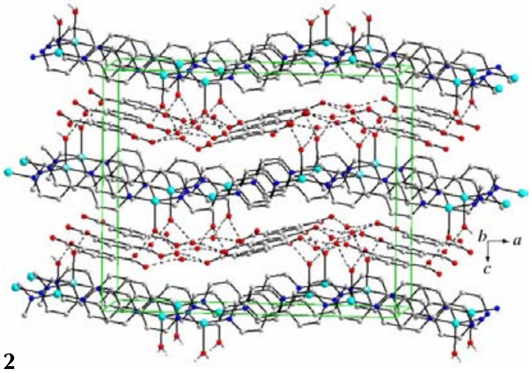


Figure 2
The packing of the title compound. Hydrogen bonds are depicted as dashed lines.

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free water molecules. As stated above, the structure contains a one-dimensional coordination polymer. However, there is hydrogen bonding through the coordinated water molecule in a second orthogonal direction and through the free water molecule in a third (Table 2), giving overall a three-dimensional framework structure.

The mechanism of hydrothermal reactions involves a shift from kinetic to thermodynamic control, in contrast to conventional solution synthetic systems, and this makes the structures produced more difficult to control. The successful synthesis of the title compound indicates that the copper(II) ion undergoes reduction through an unknown reaction mechanism. According to the literature (Yaghi & Li, 1995), it is accepted that Cu^{II} ions can be reduced to Cu^{I} by 4,4′-bipy or pyridine derivatives under hydrothermal conditions.

In summary, although the pyridine-3-carboxylic acid starting material is not incorporated into the product, its presence proved to be necessary in order to obtain the title compound. When this reagent was omitted, we obtained $[Cu_2(ipO)(4,4'\text{-bipy})]$ (ipOH is 2-hydroxyisophthalate), which has been reported previously (Tao *et al.*, 2002) as resulting from a reaction in which no pyridine-3-carboxylic acid was used. These results illustrate the point that the formation of a product can be greatly influenced by the reagents present, even if some of them do not appear in the product.

Experimental

A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.241 g, 1 mmol), 4,4′-bipyridyl (0.078 g, 0.5 mmol), pyridine-3-carboxylic acid (0.062 g, 0.5 mmol) and isophthalic acid (0.083 g, 0.5 mmol) in water (18 ml) was placed in a 25 ml Teflon-lined stainless steel reactor and heated to 453 K for 76 h. When the reactor was cooled to room temperature over a period of 3 d, pale-yellow prismatic single crystals suitable for X-ray diffraction were obtained.

Crystal data

$[Cu(C_{10}H_8N_2)(H_2O)]$-$(C_8H_4O_4)_{0.5}\cdot H_2O$
$M_r = 337.82$
Orthorhombic, *Pbcn*
$a = 21.6096$ (8) Å
$b = 7.2160$ (2) Å
$c = 17.6529$ (6) Å
$V = 2752.70$ (16) Å^3
$Z = 8$
$D_x = 1.630$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 2793 reflections
$\theta = 1.9$–25.0°
$\mu = 1.60$ mm^{-1}
$T = 293$ (2) K
Cubic prism, pale yellow
0.48 × 0.32 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.434$, $T_{max} = 0.730$
7492 measured reflections
2412 independent reflections
1585 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 25.0°$
$h = -17 \rightarrow 25$
$k = -8 \rightarrow 8$
$l = -20 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.164$
$S = 1.11$
2412 reflections
204 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 7.487P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0029 (4)

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.921 (4)	Cu1—O2*W*	2.195 (5)
Cu1—N2^{ii}	1.920 (4)		
N1—Cu1—N2^{ii}	158.88 (18)	N2^{ii}—Cu1—O2*W*	101.47 (18)
N1—Cu1—O2*W*	99.65 (18)		

Symmetry code: (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O4^{iv}	0.81 (5)	1.99 (4)	2.777 (9)	162 (11)
O1*W*—H1*WB*···O4^{v}	0.82 (5)	2.04 (4)	2.829 (8)	162 (10)
O2*W*—H2*WB*···O3^{vi}	0.82 (6)	1.87 (4)	2.634 (7)	156 (9)
O2*W*—H2*WA*···O1*W*	0.82 (7)	1.89 (7)	2.698 (8)	168 (8)

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

Water H atoms were located from difference maps and refined with the O—H distances restrained to 0.82 (1) Å and with $U_{iso}(H)$ values of $1.5U_{eq}(O)$. All other H atoms were positioned geometrically and treated as riding [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$].

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1570). Services for accessing these data are described at the back of the journal.

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