

A novel copper(II) coordination polymer with 2,2'-bipyridyl-3,3'-dicarboxylic acid

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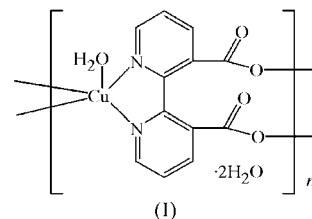
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A novel copper(II) coordination polymer, poly[[[aqua-copper(II)]- μ_3 -2,2'-bipyridyl-3,3'-dicarboxylato- $\kappa^4 N, N': O: O'$] dihydrate], $\{[\text{Cu}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$, was obtained by the reaction of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ and 2,2'-bipyridyl-3,3'-dicarboxylic acid (H_2L) in water. In the molecule, each Cu^{II} atom is five-coordinated and lies at the centre of a square-pyramidal basal plane, bridged by three L ligands to form a two-dimensional (4,4)-network. Each L moiety acts as a bridging tetradentate ligand, coordinating to three Cu^{II} atoms through its two aromatic N atoms and two O atoms of the two carboxyl groups. The two-dimensional square-grid sheets superimpose in an off-set fashion through the inorganic water layer.

Comment

In recent years, research on coordination polymers has expanded rapidly, because of their fascinating structural diversity and potential application as functional materials (Batten & Robson, 1998; Moulton & Zaworotko, 2001). To date, a number of one-, two- and three-dimensional infinite frameworks have been generated with linear N, N' -bidentate spacers (Tong *et al.*, 2002). Much of the work has so far been focused on coordination polymers with rigid ligands, such as 4,4'-bipyridine, and pyrazine and its analogues. However, flexible ligands such as 2,2'-bipyridyl-3,3'-dicarboxylic acid (H_2L) have not been explored as much and only a few examples have been reported to date (Goddard *et al.*, 1990; Kovalev *et al.*, 1989; Memon *et al.*, 1997; Perkovic, 2000; Xie *et al.*, 1999, 2000; Yoo *et al.*, 1997; Zhang *et al.*, 2002, 2003; Zhong *et al.*, 1994). In these known structures based on the 2,2'-bipyridyl-3,3'-dicarboxylate anion, most are one-dimensional polymeric chains, such as $[\text{M}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$ (M is Co, Cu or Mn) and $\{[\text{Ni}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_3]\cdot \text{H}_2\text{O}\}_n$. These one-dimensional chains extend into two-dimensional sheets *via*

$\text{O}\cdots\text{H}-\text{O}$ hydrogen-bonding interactions. Two- or three-dimensional structures of this type based on covalent linkages are rare. In the present work, we report the preparation and crystal structure of the title novel two-dimensional coordination polymer, (I), formulated as $\{[\text{Cu}L(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$.



Single-crystal X-ray diffraction reveals that the molecules of (I) form an extended two-dimensional network involving coordination frameworks of (4,4)-topology. In these layers, all the metal centres are five-coordinated. As shown in Fig. 1, each Cu^{II} atom is coordinated by two N atoms of an L ligand,

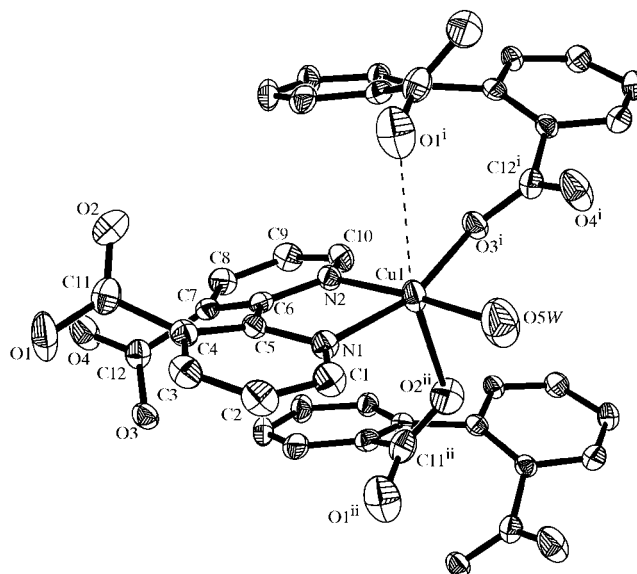


Figure 1
A view of the local coordination of the Cu^{II} atom in (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

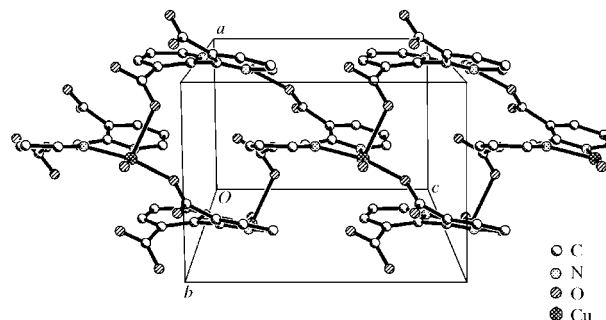
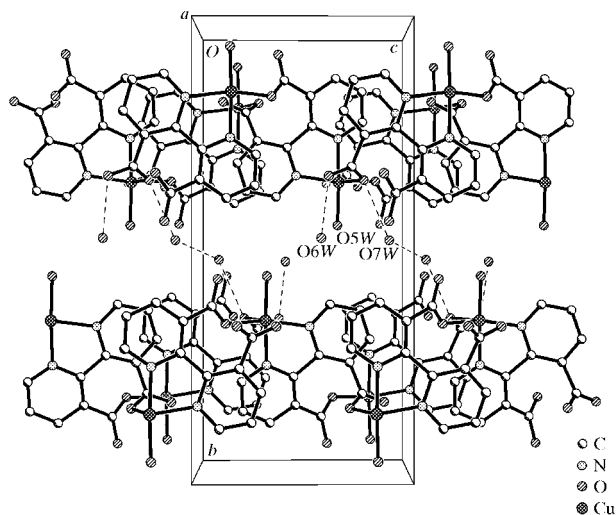


Figure 2
The two-dimensional single-layer (4,4)-network in (I). Water molecules have been omitted for clarity.


Figure 3

A view perpendicular to the two-dimensional sheets, showing the stacking of these layers in the *b* direction. Hydrogen-bonding contacts are indicated by dashed lines.

two O atoms of two carboxyl groups from another two *L* ligands and one O atom of a water molecule, giving a square-pyramidal geometry (Table 1). An additional carboxyl O atom occupies the sixth coordination site at a distance [Cu1...O1 = 3.060 (1) Å] which is beyond the sum of the van der Waals radii of Cu and O (1.40 Å for Cu and 1.52 Å for O) and which is therefore too long to be considered a significant interaction.

Each *L* moiety, acting as a tetradentate ligand, coordinates to three Cu^{II} atoms. As a result, three Cu^{II} centres are bridged by three *L* ligands to form a grid (Fig. 2). Within this grid, the Cu...Cu distances are 6.767 (5), 6.908 (5) and 6.967 (1) Å. One Cu atom with one organic ligand constructs a node and these nodes connect to each other to form an extended layer structure with (4,4)-topology in the *ac* plane. As illustrated in Fig. 3, the water molecules occupy channels formed by parallel stacking of two layers.

There are a number of significant contacts between the oxo groups of the two-dimensional layers and the water molecules. These include O5W...O4ⁱ = 2.819 (5), O5W...O3ⁱ = 2.880 (4), O6W...O1ⁱⁱ = 2.769 (4), O6W...O5Wⁱⁱⁱ = 3.094 (4), O6W...O6W^{iv} = 3.199 (5), O7W...O2ⁱⁱ = 2.915 (5), O7W...O4ⁱⁱ = 2.971 (4) and O7W...O7^v = 2.800 (6) Å [symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, 1 - y, 1 - z$; (vi) $2 - x, 1 - y, 1 - z$; (v) $1 - x, 1 - y, 2 - z$]. Therefore, the extended structure of (I) has the metal-organic layers and inorganic water layers arranged alternately along the *b* axis.

Experimental

A mixture of CuCl₂·2H₂O (0.168 g, 1 mmol) and H₂L (0.244 g, 1 mmol) in water (30 ml) was refluxed for 20 min and then filtered while hot. Dark-green crystals of (I) were obtained by evaporating the filtrate at room temperature for a period of three weeks. The compound is insoluble in common organic solvents and dissolves in water very slowly. Analysis found: C 40.1, H 3.2, N 8.0%; C₁₂H₁₂CuN₂O₇ requires: C 40.0, H 3.3, N 7.8%.

Crystal data

[Cu(C₁₂H₆N₂O₄)(H₂O)]·2H₂O
M_r = 359.78
 Monoclinic, *P*₂₁/*n*
a = 6.7680 (9) Å
b = 19.989 (3) Å
c = 9.4923 (12) Å
 β = 90.717 (2)°
V = 1284.0 (3) Å³
Z = 4

D_x = 1.861 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6856 reflections
 θ = 3.2–25.5°
 μ = 1.77 mm⁻¹
T = 293 (2) K
 Prism, dark green
 0.24 × 0.23 × 0.11 mm

Data collection

Rigaku R-Axis RAPID area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
*T*_{min} = 0.628, *T*_{max} = 0.812
 7065 measured reflections

2498 independent reflections
 1871 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.045
 θ _{max} = 26.0°
h = -8 → 7
k = -24 → 20
l = -11 → 11

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.039
wR(*F*²) = 0.094
S = 0.95
 2498 reflections
 199 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 $\Delta\rho$ _{max} = 0.47 e Å⁻³
 $\Delta\rho$ _{min} = -0.31 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O3 ⁱ	1.966 (2)	Cu1—N1	2.034 (3)
Cu1—O5W	1.979 (3)	Cu1—O2 ⁱⁱ	2.411 (2)
Cu1—N2	1.999 (3)		
O3 ⁱ —Cu1—O5W	93.74 (10)	N2—Cu1—N1	79.75 (10)
O3 ⁱ —Cu1—N2	90.27 (9)	O3 ⁱ —Cu1—O2 ⁱⁱ	92.60 (9)
O5W—Cu1—N2	175.79 (11)	O5W—Cu1—O2 ⁱⁱ	91.49 (11)
O3 ⁱ —Cu1—N1	162.38 (10)	N2—Cu1—O2 ⁱⁱ	87.05 (9)
O5W—Cu1—N1	96.68 (11)	N1—Cu1—O2 ⁱⁱ	101.27 (10)

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

All H atoms on C atoms were generated geometrically and refined as riding atoms, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The H atoms of the two solvate water molecules and the water ligand could not be located.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1177). Services for accessing these data are described at the back of the journal.

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