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A one-dimensional coordination polymer incorporating a less common bipyridine isomer: *catena*-poly[[bis(acetato-κO)aquacopper(II)]-μ-3,3′-bipyridine-$\kappa^2 N$:N']

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Key indicators

Single-crystal X-ray study
T = 94 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.079
Data-to-parameter ratio = 16.8

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

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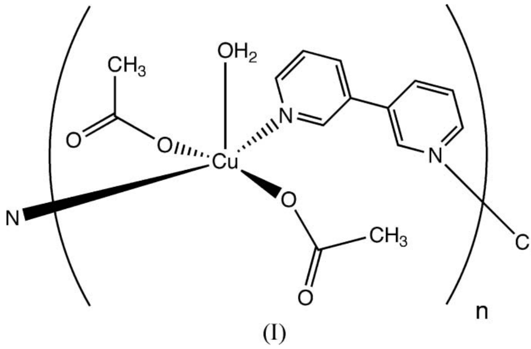
The title compound, $[Cu(CH_3COO)_2(C_{10}H_8N_2)(H_2O)]_n$, is a one-dimensional coordination polymer containing square-pyramidally coordinated Cu^{II} bound to two N atoms from two 3,3′-bipyridine molecules, two O atoms from two distinct monodentate acetate anions, and one O atom from an aqua ligand. *Anti*-conformation 3,3′-bipyridine units link the Cu^{II} atoms into chain motifs that run parallel to the *a* crystal axis. These arrange into layers parallel to the *ac* crystal plane through supramolecular hydrogen bonding.

Comment

Metal–organic framework materials (MOFs) have attracted significant attention due to their exciting potential in gas storage (Roswell & Yaghi, 2005) and small-molecule separation (Humphrey *et al.*, 2007). One of the most ubiquitous tethering ligands for the design and construction of MOFs is 4,4′-bipyridine (4,4′-bpy). Through its distal N donor atoms, 4,4′-bpy has been employed to create numerous functional coordination polymers with diverse structural chemistry (Yaghi *et al.*, 1998). We have been interested in probing the coordination chemistry of its less common isomer 3,3′-bipyridine (3,3′-bpy), focusing chiefly on bimetallic molybdates (LaDuca, Desciak *et al.*, 2000) and vanadates (LaDuca, Brodkin *et al.*, 2000). Here, we report the first extension of this work into a carboxylate system, with the structure of the title compound, (I).



(I)

Hydrothermal combination of copper(II) acetate with 3,3′-bpy afforded a high yield of (I) as blue blocks. The asymmetric unit (Fig. 1) consists of a Cu^{II} atom, two acetate ions, an aqua ligand, and one 3,3′-bpy molecule. Bond distance and angle data (Table 1) are consistent with square-pyramidal coordination about a Jahn–Teller active d^9 Cu^{II} ion. The basal plane of the [Cu^{II}N$_2$O$_3$] square-pyramidal coordination environment contains two mutually *trans* N donor atoms from two different 3,3′-bpy ligands and two *trans* O donors from two

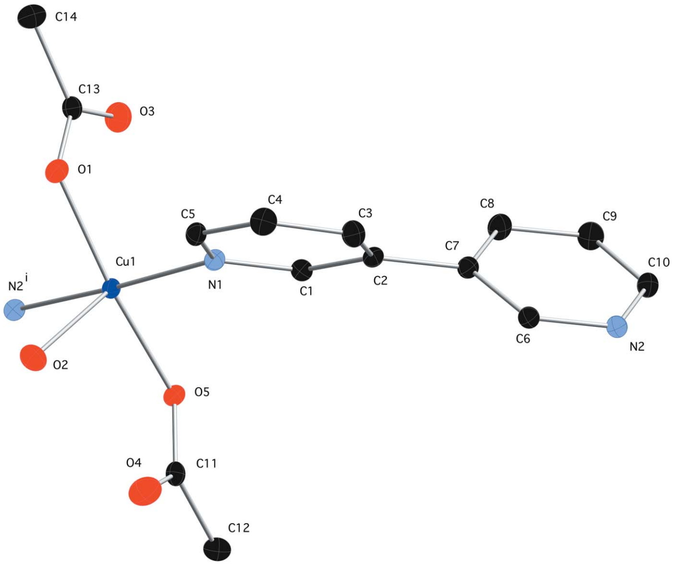


Figure 1
The asymmetric unit of the title compound, with the symmetry-equivalent N atom to complete the coordination environment, showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted. The symmetry code is as in Table 1.

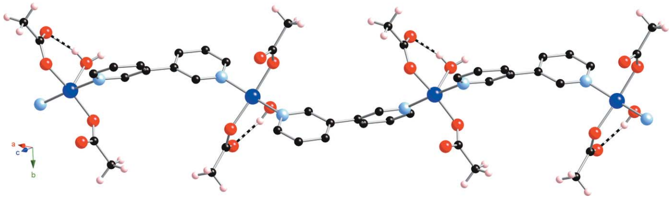


Figure 2
A single polymeric one-dimensional chain motif of (I), which lies parallel to the crystallographic *a* axis. Most H atoms have been omitted. Cu atoms are shown as dark blue, N atoms as light blue, O atoms as red, C atoms as black C and H atoms as pink. Hydrogen bonds are shown as dashed lines.

different monodentate acetate ligands. The apical position is occupied by an aqua ligand at a bond distance ~0.3 Å longer than those in the basal plane.

Neighboring Cu^{II} atoms are linked through tethering 3,3′-bpy molecules lying in a skewed *anti* conformation [133.4 (2)° inter-ring torsion angle] to form one-dimensional coordination polymer chains that run parallel to the *a* axis (Fig. 2). The Cu···Cu through-ligand separation is ~9.3 Å. Intrachain hydrogen bonding between the aqua ligands (*via* atom H2*B*) and unligated acetate O atoms (atom O4) enhances the covalent connectivity. Adjacent chain motifs form layer patterns, parallel to the *ac* crystal plane, through supramolecular hydrogen bonding between aqua ligands in one chain (*via* atom H2*A*) and unligated acetate O atoms (atom O3) in another (Fig. 3). Geometric parameters for the hydrogen-bonding interactions are given in Table 2. The interchain Cu···Cu through-space separation measures ~5.3 Å. These layers in turn stack through van der Waals and packing forces to afford the three-dimensional crystal structure of (I) (Fig. 4).

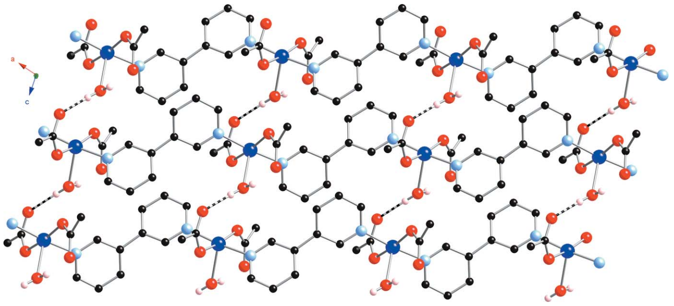


Figure 3
A diagram of (I), illustrating the supramolecular aggregation of chain motifs into layers that lie parallel to the *ac* crystal plane. Color code as in Fig. 2. Hydrogen bonds are shown as dashed lines.

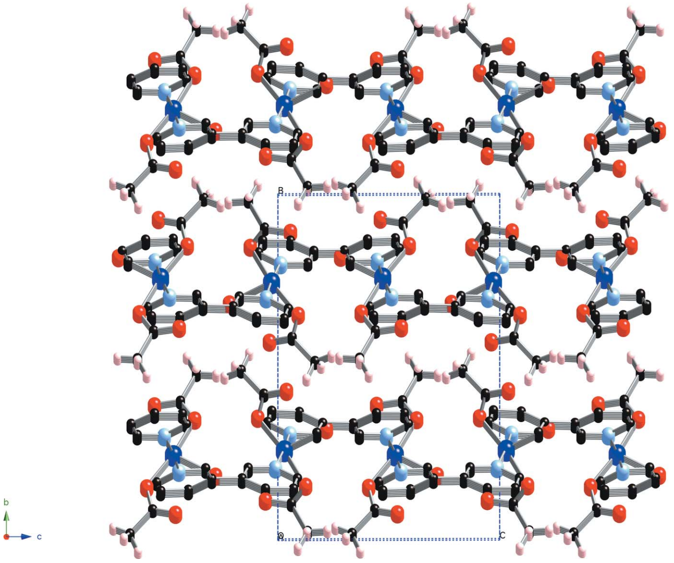


Figure 4
A packing diagram illustrating the stacking of slabs to form the three-dimensional crystal structure of (I). Color code as in Fig. 2.

Experimental

Copper(II) acetate monohydrate was obtained commercially. 3,3′-Bipyridine was prepared *via* a published procedure (Rarig *et al.*, 2002). A mixture of copper(II) acetate monohydrate (66 mg, 0.33 mmol), 3,3′-bipyridine (52 mg, 0.33 mmol), and water (6.0 g, 330 mmol) was flame-sealed into a borosilicate glass tube, which was then heated under autogenous pressure at 403 K for 72 h. Blue blocks (76 mg, 65% yield based on Cu) of the title compound, (I), were obtained after filtration, washing with water and acetone, and drying in air.

Crystal data

$[Cu(C_2H_3O_2)_2(C_{10}H_8N_2)(H_2O)]$
$M_r = 355.83$
Monoclinic, $P2_1/c$
$a = 9.1991$ (4) Å
$b = 15.7677$ (7) Å
$c = 10.5419$ (5) Å
$\beta = 105.6560$ (10)°
$V = 1472.36$ (12) Å^3
$Z = 4$
$D_x = 1.605$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 1.51$ mm^{-1}
$T = 94$ (2) K
Block, blue
0.32 × 0.24 × 0.18 mm

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Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.623$, $T_{\rm max} = 0.760$
9505 measured reflections
3508 independent reflections
3140 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\rm max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.06$
3508 reflections
209 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.6219P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.44$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.75$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O5	1.9551 (11)	O1—C13	1.277 (2)
Cu1—O1	1.9603 (12)	O3—C13	1.249 (2)
Cu1—N1	2.0162 (14)	O4—C11	1.244 (2)
Cu1—N2$^{\rm i}$	2.0172 (14)	O5—C11	1.286 (2)
Cu1—O2	2.3159 (13)		
O5—Cu1—O1	170.92 (5)	N1—Cu1—N2$^{\rm i}$	174.35 (5)
O5—Cu1—N1	91.08 (5)	O5—Cu1—O2	97.56 (5)
O1—Cu1—N1	89.48 (5)	O1—Cu1—O2	91.51 (5)
O5—Cu1—N2$^{\rm i}$	88.67 (5)	N1—Cu1—O2	90.54 (5)
O1—Cu1—N2$^{\rm i}$	89.88 (5)	N2$^{\rm i}$—Cu1—O2	95.09 (5)
C1—C2—C7—C6	133.39 (17)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O3$^{\rm ii}$	0.84 (2)	1.93 (2)	2.761 (2)	178 (2)
O2—H2*B*···O4	0.84 (2)	1.86 (2)	2.670 (2)	161 (2)

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

H atoms bound to aromatic C atoms were placed in calculated positions, with C—H = 0.93 Å, and refined in riding mode, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. H atoms bound to methyl C atoms within the acetate ligands were placed in calculated positions, with C—H = 0.96 Å, and refined in riding mode, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. The H atoms of the aqua ligand were found in a Fourier difference map, restrained with O—H = 0.85 (2) Å, and refined isotropically.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (Palmer, 2005); software used to prepare material for publication: *SHELXL97*.

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