catena-Poly[[aquadipyridinecopper(II)]-μ-fumarato]

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The title compound, $[Cu(C_4H_2O_4)(C_5H_5N)_2(H_2O)]_n$, is a one-dimensional coordination polymer based on pyridine and fumarate ligands. Each Cu^{II} cation is coordinated by two carboxylate O atoms belonging to two fumarate anions, two N atoms from two pyridine molecules and one water molecule, in a square-based pyramidal geometry. Each fumarate anion bridges two Cu^{II} cations through the two carboxylate groups in a bis-monodentate fashion to form a one-dimensional polymeric chain along the c axis. Neighbouring chains are linked together to form a two-dimensional network parallel to the ac plane *via* hydrogen bonding interactions between uncoordinated carboxylate O atoms and coordinated water molecules of adjacent chains.

Related literature

For related literature, see: Barthelet *et al.* (2002); Che *et al.* (2006); Dalai *et al.* (2002); Rao *et al.* (2004); Yaghi *et al.* (1998).
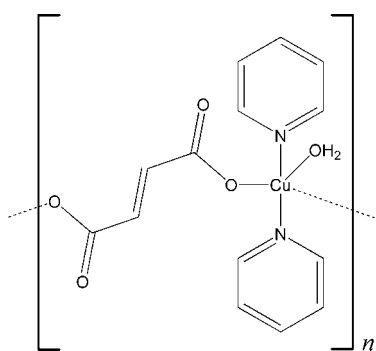
Experimental

Crystal data

$[Cu(C_4H_2O_4)(C_5H_5N)_2(H_2O)]$	V = 1502.4 (3) Å³
M_r = 353.81	Z = 4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 5.6238 (6) Å	μ = 1.48 mm⁻¹
b = 15.3174 (16) Å	T = 273 (2) K
c = 17.4404 (16) Å	0.32 × 0.32 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer	9106 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3330 independent reflections
T_{min} = 0.648, T_{max} = 0.732	2520 reflections with $I > 2\sigma(I)$
	R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046	$\Delta\rho_{max}$ = 0.70 e Å⁻³
$wR(F^2)$ = 0.116	$\Delta\rho_{min}$ = −0.33 e Å⁻³
S = 1.02	Absolute structure: Flack (1983), 1347 Friedel pairs
3330 reflections	Flack parameter: 0.50 (2)
199 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.925 (2)	Cu1—N1	2.030 (4)
Cu1—O4ⁱ	1.931 (2)	Cu1—O5	2.210 (3)
Cu1—N2	2.031 (3)		
O1—Cu1—O4ⁱ	179.45 (15)	N2—Cu1—N1	173.11 (17)
O1—Cu1—N2	89.83 (13)	O1—Cu1—O5	88.78 (12)
O4ⁱ—Cu1—N2	89.86 (12)	O4ⁱ—Cu1—O5	90.80 (12)
O1—Cu1—N1	90.30 (13)	N2—Cu1—O5	95.07 (15)
O4ⁱ—Cu1—N1	90.06 (12)	N1—Cu1—O5	91.82 (15)

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O5—H5B⋯O2ⁱⁱ	0.91	1.82	2.718 (4)	167
O5—H5A⋯O3ⁱⁱⁱ	0.88	1.86	2.700 (4)	158

Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x + \frac{3}{2}, -y + 2, z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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supporting information

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S1. Comment

Recently, the design and construction of coordination polymers have attracted great attention due to their rich network topologies and potential applications (Yaghi *et al.*, 1998). Organic O– and N-donors are often chosen to fabricate these complexes. A number of metal-organic frameworks with extended structures and novel adsorption and magnetic properties have been synthesized based on aromatic dicarboxylate ligands (Barthelet *et al.*, 2002; Rao *et al.*, 2004). Compared with benzenedicarboxylic acid, the alkenedicarboxylic acid is also regarded as an excellent candidate for the self-assembly of coordination polymers. Fumaric acid ligand is the typical example of alkenedicarboxylic acid ligand. As far as we know, several coordination polymers based on fumaric acid have been obtained (Che *et al.*, 2006; Dalai *et al.*, 2002). We report here the crystal structure of the title coordination polymer, $[Cu(C_4H_2O_4)(C_5NH_5)_2(H_2O)]_n$.

   The asymmetric unit of the title compound consists of one Cu^{II} cation, one fumarate dianion, two pyridine ligands and one water molecule (Fig. 1). The Cu^{II} cation has a square-based pyramidal geometry formed by two carboxylate O atoms from two fumarate ligands, two N atoms from two pyridine molecules and one water molecule. The four basal coordination sites are filled by the atoms O1, N1, N2 and O4[i], while the axial position is occupied by the atom O5. The Cu—O distances are in the range 1.925 (2)–2.210 (3) Å and the Cu—N distances are 2.030 (4) and 2.031 (3) Å. These values are in good agreement with those found in other extended structures (Dalai *et al.*, 2002). The angles subtended at the metal centre are listed in Table 1. Each fumarate dianion acts as a μ_2-bridging ligand to connect two Cu^{II} centers to form a chain structure along the *c* axis, with a Cu···Cu distance of 8.743 (4) Å. The chains are further packed into a two-dimensional network parallel to the *ac* plane through O—H···O hydrogen bonding interactions between the water molecule and uncoordinated carboxylate O atoms of fumarate ligands of adjacent chains (Fig. 2). Each pyridine, as a terminal ligand, occupies two coordination positions of Cu^{II} cation and decorates alternately at two sides of chains (Fig. 3).

S2. Experimental

A solid mixture of $Cu(NO_3)_2\cdot6H_2O$ (0.120 g, 0.5 mmol) and fumaric acid (0.06 g, 0.5 mmol) was dissolved in a 25 ml vial containing DMF (10 ml). The solution was stirred in air for 50 min and the vial was placed in a 80 ml beaker containing pyridine (3 ml) and DMF (5 ml). The reaction mixture was sealed by parafilm and kept at 333 K. Block-shaped blue crystals of the title compound were obtained after 5 d.

S3. Refinement

C-bound H atoms were placed in calculated positions (C—H = 0.93 Å) and refined in the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$. O-bound H atoms were located in a difference map and refined in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(O)$. Flack parameter refined to 0.50 (2) indicating that the crystal used was a racemic twin (Flack, 1983).
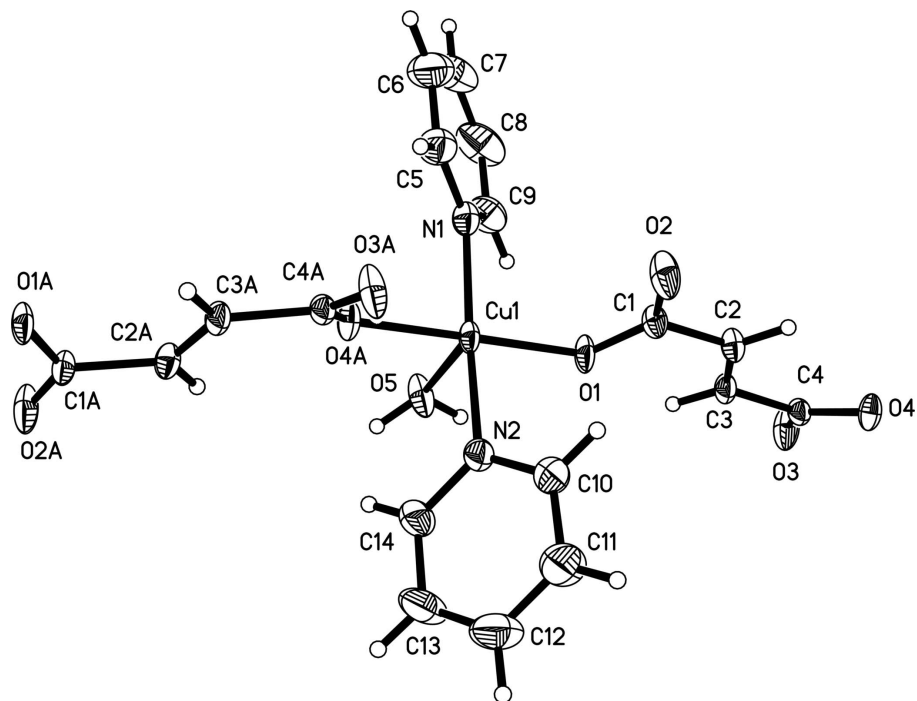
Figure 1

View of a fragment of polymeric title compound, showing the coordination environment of the metal center and atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [symmetry code: (A) -x + 1/2, -y + 2, z + 1/2].
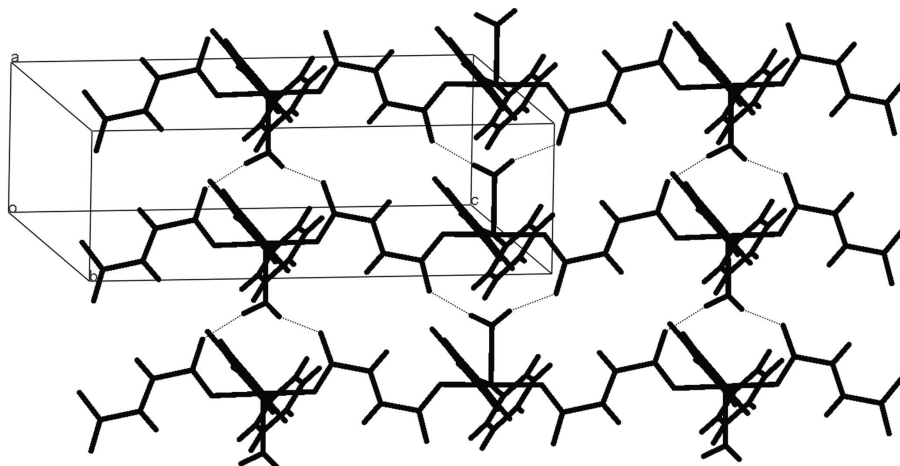
Figure 2

View of a hydrogen-bonded (dashed lines) two-dimensional network in the title compound.
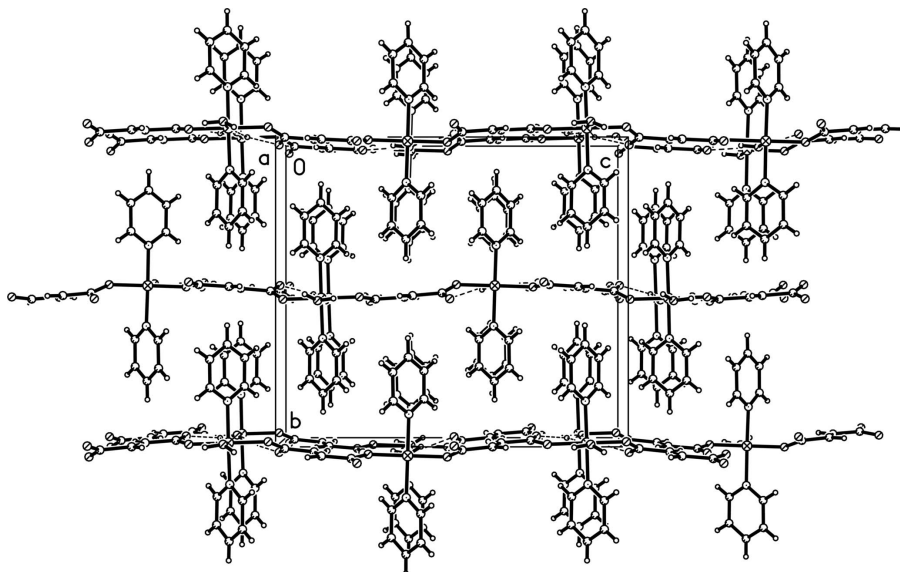
Figure 3

The crystal packing of the title compound, viewed down the *a* axis.

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Crystal data

[Cu(C₄H₂O₄)(C₅H₅N)₂(H₂O)]	$F(000) = 724$
$M_r = 353.81$	$D_x = 1.564$ Mg m⁻³
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2169 reflections
$a = 5.6238$ (6) Å	$\theta = 2.3–27.5°$
$b = 15.3174$ (16) Å	$\mu = 1.48$ mm⁻¹
$c = 17.4404$ (16) Å	$T = 273$ K
$V = 1502.4$ (3) Å³	Block, blue
$Z = 4$	0.32 × 0.32 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer	$T_{min} = 0.648$, $T_{max} = 0.732$
	9106 measured reflections
Radiation source: fine-focus sealed tube	3330 independent reflections
Graphite monochromator	2520 reflections with $I > 2\sigma(I)$
Detector resolution: Bruker SMART CCD area-detector pixels mm⁻¹	$R_{int} = 0.034$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
φ and ω scans	$h = -7 \rightarrow 7$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$k = -18 \rightarrow 19$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.046$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.116$	
$S = 1.03$	Hydrogen site location: inferred from neighbouring sites
3330 reflections	
199 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.6209P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}

$\Delta\rho_{min} = -0.33$ e Å^{-3}
Absolute structure: Flack (1983), with 1347
   Friedel pairs
Absolute structure parameter: 0.50 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.25711 (11)	0.97944 (3)	0.87637 (2)	0.03127 (15)
O1	0.2678 (6)	0.9836 (2)	0.76609 (13)	0.0420 (7)
O2	−0.1160 (6)	0.9684 (3)	0.74117 (16)	0.0595 (10)
O3	0.6212 (6)	0.9782 (3)	0.50624 (16)	0.0573 (9)
O4	0.2510 (6)	1.02406 (18)	0.48704 (12)	0.0404 (6)
O5	0.6495 (5)	0.9721 (2)	0.87740 (15)	0.0526 (8)
H5B	0.7218	0.9792	0.8313	0.063*
H5A	0.7522	0.9928	0.9109	0.063*
N1	0.2274 (7)	0.8475 (2)	0.87281 (18)	0.0414 (8)
N2	0.2434 (7)	1.1119 (2)	0.87979 (17)	0.0411 (7)
C1	0.0911 (8)	0.9761 (3)	0.7220 (2)	0.0338 (9)
C2	0.1466 (8)	0.9824 (3)	0.6380 (2)	0.0356 (10)
H2	0.0221	0.9820	0.6030	0.043*
C3	0.3656 (9)	0.9883 (3)	0.6126 (2)	0.0345 (10)
H3	0.4903	0.9872	0.6476	0.041*
C4	0.4217 (9)	0.9968 (2)	0.5281 (2)	0.0320 (11)
C5	0.0718 (10)	0.8032 (4)	0.9141 (3)	0.0586 (14)
H5	−0.0377	0.8337	0.9438	0.070*
C6	0.0664 (13)	0.7118 (4)	0.9146 (4)	0.083 (2)
H6	−0.0454	0.6822	0.9440	0.100*
C7	0.2251 (13)	0.6674 (4)	0.8719 (4)	0.087 (2)
H7	0.2249	0.6067	0.8716	0.105*
C8	0.3846 (13)	0.7123 (4)	0.8294 (4)	0.086 (2)
H8	0.4958	0.6827	0.7998	0.103*
C9	0.3818 (11)	0.8019 (4)	0.8303 (3)	0.0606 (14)
H9	0.4911	0.8320	0.8003	0.073*
C10	0.0860 (10)	1.1570 (3)	0.8377 (3)	0.0581 (15)
H10	−0.0264	1.1269	0.8088	0.070*
C11	0.0874 (12)	1.2476 (4)	0.8363 (4)	0.080 (2)
H11	−0.0234	1.2776	0.8067	0.095*
C12	0.2507 (12)	1.2924 (3)	0.8781 (3)	0.0804 (17)

H12	0.2544	1.3530	0.8771	0.096*
C13	0.4077 (11)	1.2468 (4)	0.9211 (4)	0.0752 (19)
H13	0.5201	1.2761	0.9505	0.090*
C14	0.4004 (9)	1.1567 (3)	0.9211 (3)	0.0538 (13)
H14	0.5091	1.1262	0.9511	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0335 (2)	0.0455 (3)	0.01487 (19)	0.0008 (4)	−0.0003 (2)	−0.0007 (2)
O1	0.0401 (18)	0.0715 (17)	0.0145 (11)	−0.003 (2)	−0.0026 (13)	0.0035 (12)
O2	0.039 (2)	0.115 (3)	0.0241 (14)	−0.006 (2)	0.0066 (13)	−0.0059 (19)
O3	0.0350 (19)	0.108 (3)	0.0286 (15)	0.009 (2)	0.0072 (13)	0.0122 (18)
O4	0.0478 (18)	0.0552 (15)	0.0180 (11)	0.010 (3)	0.0002 (15)	0.0010 (12)
O5	0.0291 (14)	0.101 (3)	0.0279 (15)	−0.0031 (16)	−0.0005 (12)	−0.013 (2)
N1	0.046 (2)	0.0493 (19)	0.0295 (16)	0.001 (2)	−0.002 (2)	−0.0013 (15)
N2	0.0424 (18)	0.0470 (19)	0.0340 (16)	−0.007 (2)	−0.001 (3)	0.0016 (15)
C1	0.034 (2)	0.047 (2)	0.0204 (17)	0.001 (2)	0.0036 (15)	−0.005 (2)
C2	0.033 (2)	0.050 (2)	0.023 (2)	0.004 (2)	−0.0031 (16)	−0.003 (2)
C3	0.041 (2)	0.042 (3)	0.020 (2)	−0.0003 (19)	−0.0036 (16)	0.0008 (17)
C4	0.033 (3)	0.041 (3)	0.0226 (19)	−0.0061 (16)	−0.0010 (16)	0.0006 (15)
C5	0.060 (4)	0.053 (3)	0.063 (3)	−0.001 (3)	0.000 (3)	0.000 (3)
C6	0.078 (5)	0.065 (4)	0.107 (5)	−0.016 (4)	−0.013 (4)	0.020 (4)
C7	0.067 (4)	0.047 (3)	0.147 (7)	0.005 (3)	−0.043 (6)	−0.008 (4)
C8	0.072 (5)	0.063 (4)	0.122 (6)	0.015 (4)	−0.014 (4)	−0.037 (4)
C9	0.058 (4)	0.056 (3)	0.068 (4)	0.003 (3)	−0.002 (3)	−0.015 (3)
C10	0.070 (4)	0.045 (3)	0.059 (3)	−0.001 (3)	−0.018 (3)	0.005 (2)
C11	0.085 (5)	0.052 (4)	0.102 (5)	0.010 (3)	−0.031 (4)	0.007 (3)
C12	0.082 (4)	0.046 (3)	0.114 (5)	−0.008 (4)	−0.008 (6)	0.001 (3)
C13	0.070 (4)	0.050 (3)	0.106 (5)	−0.010 (3)	−0.027 (4)	−0.015 (3)
C14	0.045 (3)	0.057 (3)	0.059 (3)	−0.006 (2)	−0.014 (2)	−0.002 (3)

Geometric parameters (Å, º)

Cu1—O1	1.925 (2)	C3—H3	0.93
Cu1—O4ⁱ	1.931 (2)	C5—C6	1.400 (8)
Cu1—N2	2.031 (3)	C5—H5	0.93
Cu1—N1	2.030 (4)	C6—C7	1.347 (9)
Cu1—O5	2.210 (3)	C6—H6	0.93
O1—C1	1.262 (5)	C7—C8	1.351 (9)
O2—C1	1.218 (5)	C7—H7	0.93
O3—C4	1.219 (5)	C8—C9	1.372 (8)
O4—C4	1.268 (5)	C8—H8	0.93
O4—Cu1ⁱⁱ	1.931 (2)	C9—H9	0.93
O5—H5B	0.91	C10—C11	1.388 (8)
O5—H5A	0.88	C10—H10	0.93
N1—C5	1.321 (6)	C11—C12	1.358 (8)
N1—C9	1.338 (6)	C11—H11	0.93

N2—C14	1.330 (6)	C12—C13	1.352 (8)
N2—C10	1.342 (6)	C12—H12	0.93
C1—C2	1.501 (5)	C13—C14	1.381 (7)
C2—C3	1.312 (6)	C13—H13	0.93
C2—H2	0.93	C14—H14	0.93
C3—C4	1.513 (5)		
O1—Cu1—O4^i	179.45 (15)	O4—C4—C3	114.9 (4)
O1—Cu1—N2	89.83 (13)	N1—C5—C6	122.1 (6)
O4^i—Cu1—N2	89.86 (12)	N1—C5—H5	119.0
O1—Cu1—N1	90.30 (13)	C6—C5—H5	119.0
O4^i—Cu1—N1	90.06 (12)	C7—C6—C5	119.2 (7)
N2—Cu1—N1	173.11 (17)	C7—C6—H6	120.4
O1—Cu1—O5	88.78 (12)	C5—C6—H6	120.4
O4^i—Cu1—O5	90.80 (12)	C6—C7—C8	119.0 (6)
N2—Cu1—O5	95.07 (15)	C6—C7—H7	120.5
N1—Cu1—O5	91.82 (15)	C8—C7—H7	120.5
C1—O1—Cu1	125.5 (3)	C7—C8—C9	119.7 (7)
C4—O4—Cu1^{ii}	124.9 (3)	C7—C8—H8	120.1
Cu1—O5—H5B	115.7	C9—C8—H8	120.1
Cu1—O5—H5A	130.0	N1—C9—C8	122.4 (6)
H5B—O5—H5A	104.5	N1—C9—H9	118.8
C5—N1—C9	117.6 (5)	C8—C9—H9	118.8
C5—N1—Cu1	123.3 (3)	N2—C10—C11	121.4 (5)
C9—N1—Cu1	118.9 (4)	N2—C10—H10	119.3
C14—N2—C10	117.9 (4)	C11—C10—H10	119.3
C14—N2—Cu1	120.4 (3)	C12—C11—C10	120.0 (6)
C10—N2—Cu1	121.6 (3)	C12—C11—H11	120.0
O2—C1—O1	126.5 (4)	C10—C11—H11	120.0
O2—C1—C2	118.2 (4)	C13—C12—C11	118.6 (6)
O1—C1—C2	115.2 (4)	C13—C12—H12	120.7
C3—C2—C1	122.0 (4)	C11—C12—H12	120.7
C3—C2—H2	119.0	C12—C13—C14	119.8 (5)
C1—C2—H2	119.0	C12—C13—H13	120.1
C2—C3—C4	122.1 (4)	C14—C13—H13	120.1
C2—C3—H3	119.0	N2—C14—C13	122.4 (5)
C4—C3—H3	119.0	N2—C14—H14	118.8
O3—C4—O4	126.7 (4)	C13—C14—H14	118.8
O3—C4—C3	118.4 (4)		

Symmetry codes: (i) −x+1/2, −y+2, z+1/2; (ii) −x+1/2, −y+2, z−1/2.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O2^{iii}	0.91	1.82	2.718 (4)	167
O5—H5A···O3^{iv}	0.88	1.86	2.700 (4)	158

Symmetry codes: (iii) x+1, y, z; (iv) −x+3/2, −y+2, z+1/2.