metal-organic compounds

Dipyridinium diaquabis(pyrazole-3,5-dicarboxylato-κ^2N,O)cuprate(II) dihydrate

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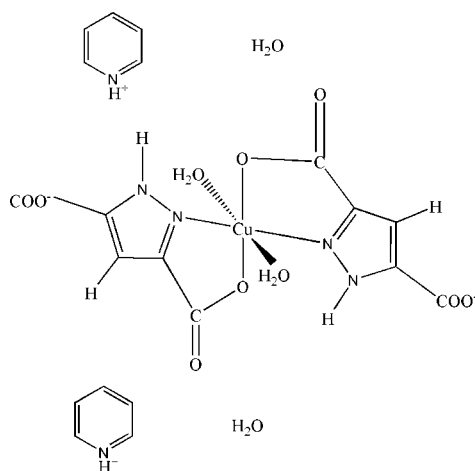Correspondence e-mail: siyoutao@hotmail.com

In the mononuclear title salt, $(C_5H_6N)_2[Cu(C_5H_2N_2O_4)_2(H_2O)_2]\cdot 2H_2O$, the Cu^{II} ion is located on an inversion centre and is coordinated by two chelating pyrazole-3,5-dicarboxylate anions and two water molecules, forming a Jahn–Teller-distorted CuN_2O_4 octahedron. O—H$\cdots$O and N—H$\cdots$O hydrogen bonds are formed between water molecules, complex anions and the pyridine counter-cations, leading to the formation of layers parallel to (100). The layers are held together by weak C—H$\cdots$O hydrogen bonds.

Related literature

For more information on ligands derived from pyrazole-3,5-dicarboxylic acid, see: King *et al.* (2004). For the bond-valence method, see: Brown (2002).

Experimental

Crystal data

$(C_5H_6N)_2[Cu(C_5H_2N_2O_4)_2(H_2O)_2]\cdot 2H_2O$	$\beta = 95.600$ (2)°
$M_r = 603.99$	$V = 1231.20$ (7) Å³
Monoclinic, $P2_1/c$	$Z = 2$
$a = 9.3531$ (4) Å	Mo $K\alpha$ radiation
$b = 7.3521$ (1) Å	$\mu = 0.96$ mm⁻¹
$c = 17.9903$ (7) Å	$T = 273$ K
	$0.34 \times 0.18 \times 0.06$ mm

Data collection

Bruker SMART CCD diffractometer	3386 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2106 independent reflections
$T_{min} = 0.735$, $T_{max} = 0.944$	1802 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.075$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.154$	
$S = 1.26$	
2106 reflections	$\Delta\rho_{max} = 0.50$ e Å⁻³
193 parameters	$\Delta\rho_{min} = -0.41$ e Å⁻³
5 restraints	

Table 1
Selected geometric parameters (Å, °).

Cu1—O4	1.959 (4)	Cu1—O5	2.539 (5)
Cu1—N2	2.006 (4)		
O4—Cu1—N2	81.99 (16)	N2—Cu1—O5	86.97 (17)
O4—Cu1—O5	90.92 (17)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O6[i]	0.86	1.99	2.783 (6)	154
O5—H3$A$$\cdots$O3[ii]	0.81 (4)	1.95 (4)	2.764 (6)	175 (8)
O5—H3$B$$\cdots$O2[iii]	0.82 (2)	2.04 (3)	2.845 (6)	170 (7)
O6—H4$A$$\cdots$O4	0.82 (5)	1.96 (5)	2.735 (7)	159 (7)
O6—H4$B$$\cdots$O1[ii]	0.82 (6)	2.01 (6)	2.801 (6)	162 (7)
N3—H5$\cdots$O1[iv]	0.87 (6)	1.81 (6)	2.665 (6)	171 (6)
C6—H6$\cdots$O5[v]	0.93	2.55	3.247 (9)	132
C8—H8$\cdots$O3[vi]	0.93	2.36	3.211 (8)	151
C10—H10$\cdots$O2[vii]	0.93	2.58	3.231 (8)	128

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

Data collection: *SMART* (Siemens, 1998); cell refinement: *SAINT* (Siemens, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *WinGX* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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References

Brown, I. D. (2002). In *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. Oxford University Press.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

King, P., Clérac, R., Anson, C. E. & Powell, A. K. (2004). *Dalton Trans.* pp. 852–861.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Siemens (1998). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Dipyridinium diaquabis(pyrazole-3,5-dicarboxylato-*κ²N,O*)cuprate(II) dihydrate

Youtao Si

S1. Comment

Pyrazole-3,5-dicarboxylic acid (H_3dcp) is a versatile ligand with six potential coordinating sites, namely two N atoms of the pyrazole ring and four O atoms of the carboxyl groups. Together with π—π interactions between neighbouring pyrazole rings, the coordination mode of H_3dcp can lead to different possibilities for creating supramolecular structures (King *et al.*, 2004). When trying to synthesize a copper-containing coordination compound involving H_3dcp, the title compound, $(C_5H_6N)^+_2[Cu(C_5H_2N_2O_4)_2(H_2O)_2]^{2-}\cdot2H_2O$, was obtained.

The Cu^{II} ion sits on an inversion center. One fully deprotonated pyrazole-3,5-dicarboxylic acid, one coordinating water molecule, one lattice water molecule and one pyridinium cation are also present in the asymmetric unit. The other half of the metal-containing moiety is generated by the inversion centre. Each pyrazole-3,5-dicarboxylate anion chelates the metal by one N atom and one O atom in the equatorial plane of an octahedron whereas the axial ligands are provided from water molecules at considerably longer distances (Fig. 1), in agreement with the tetragonal Jahn-Teller distortion (Table 1).

The BVS calculation (Brown, 2002) of the Cu ion gave a value of 1.88 valence units, which indicates that the Cu ion is divalent. Because pyrazole-3,5-dicarboxylic acid is a rather strong acid, the terminal non-coordinating carboxyl group also loses its proton to make the solvent pyridine molecules protonated. Besides four protonated pyridine molecules, four lattice water molecules are present in one unit cell as solvent molecules.
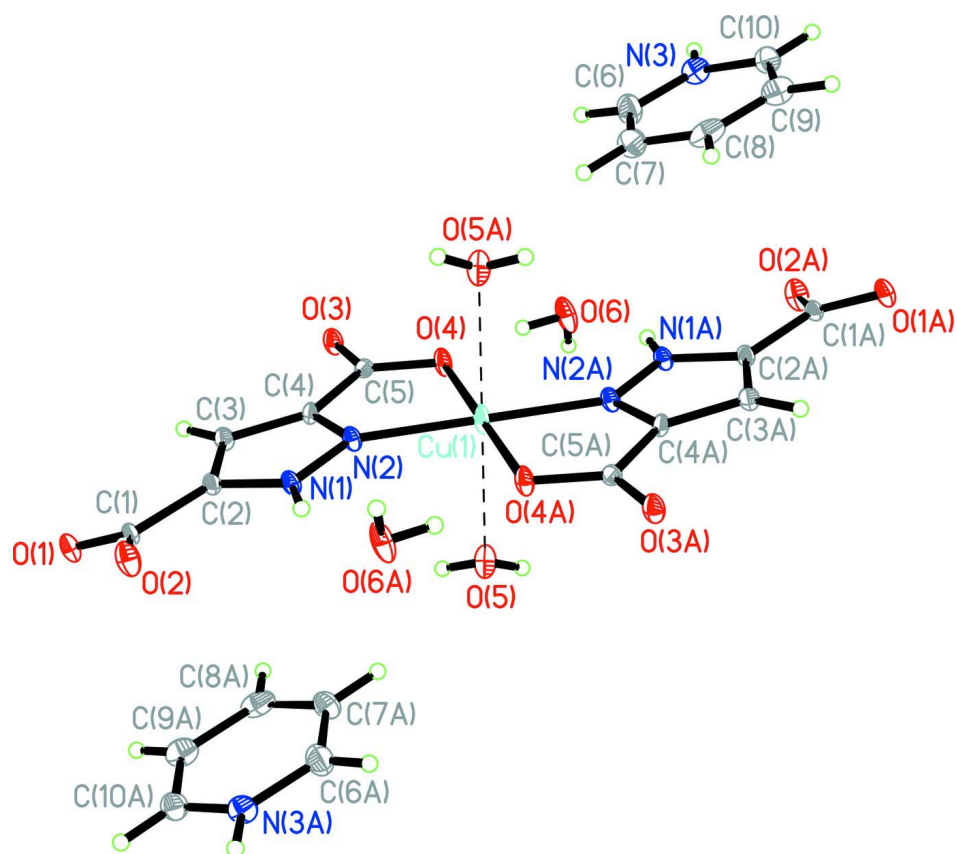
Classical O—H···O and N—H···O hydrogen bonding occurs between water molecules, pyridinium cations and complex anions to form a layer in (100), in which N1, N3, O5, O6 act as donor atoms, and O1, O2, O3, O4, O6 are acceptors (Table 2). The packing of adjacent layers along [100] is accomplished through non-classical weak C—H···O contacts, with the donor belonging to pyridine and acceptor being O atoms of the non-coordinating carboxylate groups.

S2. Experimental

0.5 mmol H_3dcp and 0.05 mmol CuCl were mixted in 10 ml H_2O to give a suspension. After addition of 0.5 ml pyridine, the suspension turned to solution, which was then stirred for 4 h and filtered. After standing in ambient conditions for about 3 days, the filtrate yielded blue crystals suitable for X-ray diffraction.

S3. Refinement

The H atoms on N3, O5 and O6 were found in the difference electron density map, and the corresponding N—H bond length was set at 0.86 Å, the O—H bond length at 0.82 Å. Other H atoms were placed at idealized positions and allowed to ride on their parent atoms, with C—H and N—H bonds being 0.930 Å and 0.86 Å, respectively. For all H atoms, $U_{iso}(H)=1.2U_{eq}(C, N \text{ or } O)$.

Figure 1

The molecular structure of the title compound, with atom labels and 20% probability displacement ellipsoids for all non-H atoms. [Symmetry code A: -x+1, -y+1, -z+1.]
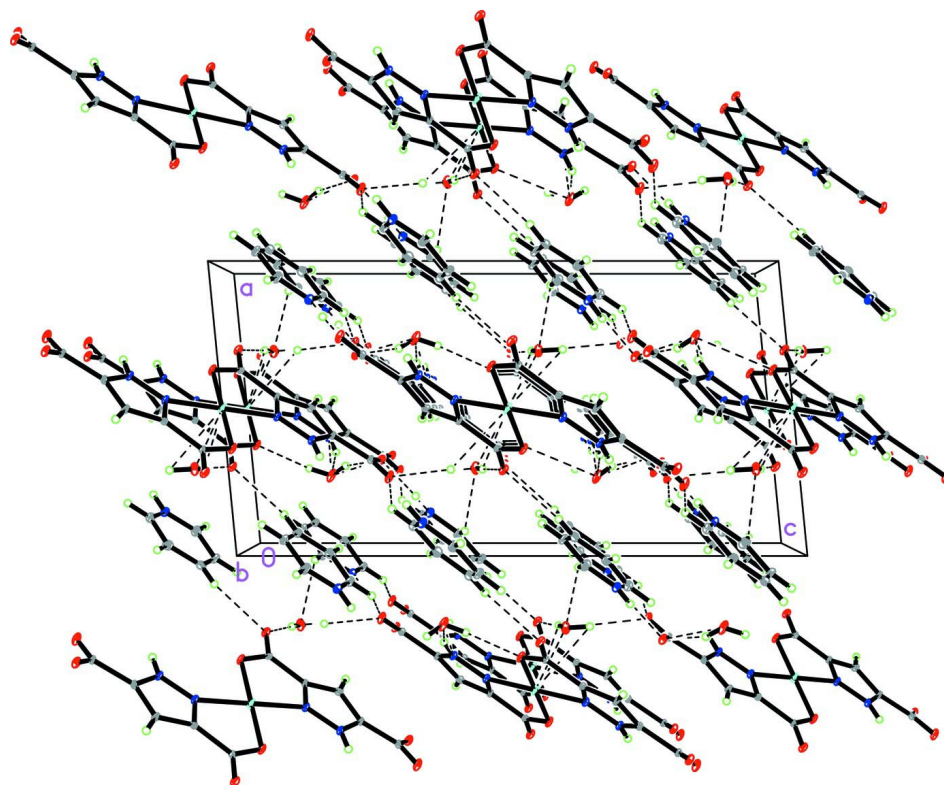
Figure 2

The packing diagram of the title compound, viewed down the **b** axis. Hydrogen bonding interactions are gived as dashed lines.

Dipyridinium diaquabis(pyrazole-3,5-dicarboxylato-κ^2N,O)cuprate(II) dihydrate

Crystal data

$(C_5H_6N)_2[Cu(C_5H_2N_2O_4)_2(H_2O)_2]\cdot 2H_2O$	$F(000) = 622$
$M_r = 603.99$	$D_x = 1.629$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1917 reflections
$a = 9.3531$ (4) Å	$\theta = 2.2$–25.0°
$b = 7.3521$ (1) Å	$\mu = 0.96$ mm^{-1}
$c = 17.9903$ (7) Å	$T = 273$ K
$\beta = 95.600$ (2)°	Prism, blue
$V = 1231.20$ (7) Å^3	$0.34 \times 0.18 \times 0.06$ mm
$Z = 2$	

Data collection

Bruker SMART CCD diffractometer	3386 measured reflections
Radiation source: fine-focus sealed tube	2106 independent reflections
Graphite monochromator	1802 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.038$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
	$h = -11 \rightarrow 9$
	$k = -8 \rightarrow 7$
$T_{min} = 0.735$, $T_{max} = 0.944$	$l = -21 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.075$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.154$	
$S = 1.26$	H atoms treated by a mixture of independent and constrained refinement
2106 reflections	
193 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0117P)^2 + 6.7689P]$
5 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.50$ e Å^{-3}
	$\Delta\rho_{min} = -0.41$ e Å^{-3}

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	0.5000	0.5000	0.5000	0.0307 (3)
O1	0.3159 (5)	1.0520 (5)	0.7574 (2)	0.0340 (10)
O3	0.7070 (4)	0.9725 (6)	0.5173 (2)	0.0334 (10)
N1	0.3911 (5)	0.6681 (6)	0.6461 (2)	0.0253 (11)
H1	0.3367	0.5826	0.6599	0.030*
O4	0.6331 (4)	0.6957 (5)	0.4799 (2)	0.0303 (10)
N2	0.4725 (5)	0.6559 (6)	0.5890 (2)	0.0250 (10)
C2	0.4060 (6)	0.8331 (8)	0.6791 (3)	0.0238 (12)
O2	0.2622 (5)	0.7604 (6)	0.7754 (2)	0.0405 (11)
C1	0.3205 (6)	0.8838 (8)	0.7425 (3)	0.0265 (13)
C4	0.5402 (6)	0.8162 (7)	0.5856 (3)	0.0220 (12)
O5	0.2915 (6)	0.6726 (6)	0.4319 (3)	0.0425 (11)
H3A	0.290 (8)	0.779 (4)	0.444 (4)	0.051*
H3B	0.287 (8)	0.679 (10)	0.3864 (12)	0.051*
C5	0.6349 (6)	0.8345 (7)	0.5240 (3)	0.0221 (12)
C3	0.5020 (6)	0.9310 (8)	0.6420 (3)	0.0270 (13)
H2	0.5345	1.0487	0.6523	0.032*
O6	0.7456 (6)	0.6665 (6)	0.3457 (3)	0.0482 (13)
H4A	0.719 (8)	0.703 (10)	0.385 (2)	0.058*
H4B	0.709 (8)	0.739 (9)	0.315 (3)	0.058*
N3	1.1229 (6)	0.2882 (8)	0.3354 (3)	0.0381 (13)
H5	1.185 (6)	0.350 (8)	0.313 (3)	0.046*
C9	1.0145 (7)	0.0054 (11)	0.3514 (4)	0.0479 (17)
H9	1.0028	−0.1166	0.3385	0.057*

C10	1.1080 (7)	0.1140 (9)	0.3174 (4)	0.0408 (16)
H10	1.1615	0.0649	0.2814	0.049*
C7	0.9545 (8)	0.2621 (13)	0.4227 (4)	0.056 (2)
H7	0.9016	0.3144	0.4583	0.067*
C8	0.9389 (7)	0.0817 (11)	0.4047 (4)	0.0496 (19)
H8	0.8760	0.0102	0.4291	0.059*
C6	1.0501 (8)	0.3639 (11)	0.3870 (4)	0.0512 (19)
H6	1.0637	0.4862	0.3989	0.061*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0437 (6)	0.0249 (5)	0.0268 (5)	−0.0106 (5)	0.0198 (4)	−0.0103 (5)
O1	0.042 (3)	0.029 (2)	0.033 (2)	0.0026 (19)	0.018 (2)	−0.0069 (18)
O3	0.038 (2)	0.031 (2)	0.034 (2)	−0.009 (2)	0.0175 (19)	−0.0081 (19)
N1	0.030 (3)	0.024 (2)	0.024 (2)	−0.001 (2)	0.013 (2)	−0.002 (2)
O4	0.040 (2)	0.027 (2)	0.027 (2)	−0.0115 (18)	0.0212 (19)	−0.0082 (17)
N2	0.031 (3)	0.024 (2)	0.021 (2)	−0.001 (2)	0.012 (2)	−0.001 (2)
C2	0.027 (3)	0.027 (3)	0.018 (3)	0.002 (2)	0.004 (2)	−0.003 (2)
O2	0.059 (3)	0.034 (2)	0.032 (2)	−0.004 (2)	0.024 (2)	0.002 (2)
C1	0.027 (3)	0.034 (3)	0.020 (3)	0.008 (3)	0.004 (2)	−0.007 (3)
C4	0.026 (3)	0.021 (3)	0.019 (3)	−0.004 (2)	0.004 (2)	−0.005 (2)
O5	0.068 (3)	0.030 (2)	0.030 (2)	−0.004 (2)	0.006 (2)	−0.002 (2)
C5	0.021 (3)	0.025 (3)	0.021 (3)	−0.001 (2)	0.003 (2)	−0.001 (2)
C3	0.028 (3)	0.025 (3)	0.029 (3)	−0.004 (2)	0.009 (3)	−0.004 (2)
O6	0.078 (4)	0.030 (3)	0.042 (3)	−0.004 (2)	0.037 (3)	−0.005 (2)
N3	0.037 (3)	0.046 (3)	0.033 (3)	−0.009 (3)	0.012 (2)	0.009 (3)
C9	0.045 (4)	0.049 (4)	0.050 (4)	−0.009 (4)	0.002 (3)	0.012 (4)
C10	0.042 (4)	0.046 (4)	0.035 (4)	0.000 (3)	0.008 (3)	0.001 (3)
C7	0.039 (4)	0.092 (6)	0.040 (4)	−0.002 (4)	0.019 (3)	−0.016 (4)
C8	0.037 (4)	0.076 (5)	0.035 (4)	−0.020 (4)	0.000 (3)	0.018 (4)
C6	0.051 (4)	0.051 (4)	0.054 (4)	−0.006 (4)	0.018 (4)	−0.013 (4)

Geometric parameters (Å, º)

Cu1—O4	1.959 (4)	O5—H3A	0.82 (2)
Cu1—O4ⁱ	1.959 (4)	O5—H3B	0.82 (2)
Cu1—N2	2.006 (4)	C3—H2	0.9300
Cu1—N2ⁱ	2.006 (4)	O6—H4A	0.82 (2)
Cu1—O5	2.539 (5)	O6—H4B	0.82 (2)
Cu1—O5ⁱ	2.539 (5)	N3—C10	1.325 (9)
O1—C1	1.267 (7)	N3—C6	1.325 (8)
O3—C5	1.230 (6)	N3—H5	0.87 (2)
N1—N2	1.341 (6)	C9—C8	1.367 (10)
N1—C2	1.351 (7)	C9—C10	1.371 (9)
N1—H1	0.8600	C9—H9	0.9300
O4—C5	1.292 (6)	C10—H10	0.9300
N2—C4	1.342 (7)	C7—C8	1.369 (11)

C2—C3	1.374 (8)	C7—C6	1.373 (10)
C2—C1	1.502 (7)	C7—H7	0.9300
O2—C1	1.239 (7)	C8—H8	0.9300
C4—C3	1.393 (7)	C6—H6	0.9300
C4—C5	1.491 (7)		
O4—Cu1—O4ⁱ	179.999 (1)	H3A—O5—H3B	102 (7)
O4—Cu1—N2	81.99 (16)	O3—C5—O4	124.5 (5)
O4ⁱ—Cu1—N2	98.01 (16)	O3—C5—C4	121.2 (5)
O4—Cu1—N2ⁱ	98.01 (16)	O4—C5—C4	114.3 (5)
O4ⁱ—Cu1—N2ⁱ	81.99 (16)	C2—C3—C4	105.2 (5)
N2—Cu1—N2ⁱ	179.999 (1)	C2—C3—H2	127.4
O4—Cu1—O5	90.92 (17)	C4—C3—H2	127.4
O4ⁱ—Cu1—O5	89.08 (17)	H4A—O6—H4B	103 (7)
N2—Cu1—O5	86.97 (17)	C10—N3—C6	121.9 (6)
N2ⁱ—Cu1—O5	93.03 (17)	C10—N3—H5	117 (5)
N2—N1—C2	110.8 (4)	C6—N3—H5	121 (5)
N2—N1—H1	124.6	C8—C9—C10	118.0 (7)
C2—N1—H1	124.6	C8—C9—H9	121.0
C5—O4—Cu1	116.0 (3)	C10—C9—H9	121.0
N1—N2—C4	106.3 (4)	N3—C10—C9	120.7 (7)
N1—N2—Cu1	141.0 (4)	N3—C10—H10	119.6
C4—N2—Cu1	111.6 (3)	C9—C10—H10	119.6
N1—C2—C3	107.6 (5)	C8—C7—C6	118.5 (7)
N1—C2—C1	121.1 (5)	C8—C7—H7	120.8
C3—C2—C1	131.3 (5)	C6—C7—H7	120.8
O2—C1—O1	126.0 (5)	C9—C8—C7	120.8 (7)
O2—C1—C2	118.2 (5)	C9—C8—H8	119.6
O1—C1—C2	115.8 (5)	C7—C8—H8	119.6
N2—C4—C3	110.1 (5)	N3—C6—C7	120.1 (7)
N2—C4—C5	115.5 (4)	N3—C6—H6	120.0
C3—C4—C5	134.4 (5)	C7—C6—H6	120.0
N2—Cu1—O4—C5	−5.9 (4)	Cu1—N2—C4—C5	−7.8 (6)
N2ⁱ—Cu1—O4—C5	174.1 (4)	Cu1—O4—C5—O3	−176.5 (4)
C2—N1—N2—C4	−0.1 (6)	Cu1—O4—C5—C4	3.3 (6)
C2—N1—N2—Cu1	−166.3 (5)	N2—C4—C5—O3	−176.9 (5)
O4—Cu1—N2—N1	173.2 (6)	C3—C4—C5—O3	4.2 (10)
O4ⁱ—Cu1—N2—N1	−6.8 (6)	N2—C4—C5—O4	3.3 (7)
O4—Cu1—N2—C4	7.4 (4)	C3—C4—C5—O4	−175.6 (6)
O4ⁱ—Cu1—N2—C4	−172.6 (4)	N1—C2—C3—C4	0.8 (6)
N2—N1—C2—C3	−0.5 (6)	C1—C2—C3—C4	−176.5 (6)
N2—N1—C2—C1	177.2 (5)	N2—C4—C3—C2	−0.9 (7)
N1—C2—C1—O2	16.6 (8)	C5—C4—C3—C2	178.0 (6)
C3—C2—C1—O2	−166.4 (6)	C6—N3—C10—C9	0.7 (11)
N1—C2—C1—O1	−163.7 (5)	C8—C9—C10—N3	−0.8 (10)
C3—C2—C1—O1	13.3 (9)	C10—C9—C8—C7	1.1 (11)
N1—N2—C4—C3	0.6 (6)	C6—C7—C8—C9	−1.3 (11)

| Cu1—N2—C4—C3 | 171.3 (4) | C10—N3—C6—C7 | −0.9 (11) |
| N1—N2—C4—C5 | −178.5 (5) | C8—C7—C6—N3 | 1.1 (12) |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O6ⁱ	0.86	1.99	2.783 (6)	154
O5—H3*A*···O3ⁱⁱ	0.81 (4)	1.95 (4)	2.764 (6)	175 (8)
O5—H3*B*···O2ⁱⁱⁱ	0.82 (2)	2.04 (3)	2.845 (6)	170 (7)
O6—H4*A*···O4	0.82 (5)	1.96 (5)	2.735 (7)	159 (7)
O6—H4*B*···O1ⁱⁱ	0.82 (6)	2.01 (6)	2.801 (6)	162 (7)
N3—H5···O1ⁱᵛ	0.87 (6)	1.81 (6)	2.665 (7)	171 (6)
C6—H6···O5ᵛ	0.93	2.55	3.247 (9)	132
C8—H8···O3ᵛⁱ	0.93	2.36	3.211 (8)	151
C10—H10···O2ᵛⁱⁱ	0.93	2.58	3.231 (8)	128

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) *x*, −*y*+3/2, *z*−1/2; (iv) *x*+1, −*y*+3/2, *z*−1/2; (v) *x*+1, *y*, *z*; (vi) *x*, *y*−1, *z*; (vii) *x*+1, −*y*+1/2, *z*−1/2.