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Poly[[diaquadi-μ_2-cyanido-bis(μ_2-pyrazine-2-carboxylato)dicopper(I)copper(II)] dihydrate]

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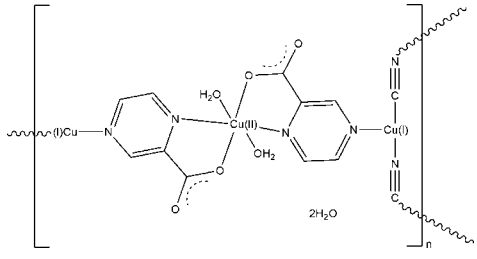
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; R factor = 0.029; wR factor = 0.095; data-to-parameter ratio = 11.1.

In the title compound, $\{[Cu^{II}Cu^{I}_2(C_5H_3N_2O_2)_2(CN)_2(H_2O)_2]\cdot 2H_2O\}_n$, the Cu^{II} atom lies on an inversion centre and is octahedrally coordinated by two N atoms and two O atoms from opposing pyrazine-2-carboxylate (2-pac) ligands and two water O atoms. The Cu^{I} atom has a triangular geometry, coordinated by one N atom and one C atom from two bridging cyanide ligands, and another N atom from the 2-pac ligand. The three-dimensional structure features a succession of two-dimensional sheets containing $[Cu(CN)]_n$ chains linked by $Cu(2\text{-pac})_2(H_2O)_2$ groups. The coordinated and free water molecules are involved in an extended three-dimensional hydrogen-bond network with the 2-pac ligands.

Related literature

For applications of metal-organic frameworks (MOFs), see: Klein *et al.* (1982); Li *et al.* (2004); Plater *et al.* (2001); Thomas (1978). For a related structure, see: Fan *et al.* (2006).



Experimental

Crystal data

$[Cu_3(C_5H_3N_2O_2)_2(CN)_2(H_2O)_2]\cdot 2H_2O$
M_r = 560.91
Monoclinic, $P2_1/c$
a = 13.8297 (4) Å
b = 9.4906 (3) Å
c = 7.1272 (3) Å
β = 100.768 (3)°
V = 918.99 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.50 mm^{-1}
T = 296 K
0.10 × 0.08 × 0.05 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.721, T_{max} = 0.845
4141 measured reflections
1615 independent reflections
1269 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.095
S = 0.99
1615 reflections
145 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O1	1.978 (2)	Cu2—C6	1.865 (3)
Cu1—N1	2.003 (3)	Cu2—N3^{i}	1.886 (4)
Cu1—O3	2.378 (3)	Cu2—N2	2.163 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O2	0.86 (2)	2.08 (3)	2.910 (5)	160 (7)
O3—H3B···O1^{ii}	0.82 (2)	2.11 (2)	2.883 (3)	156 (4)
O3—H3A···O2^{iii}	0.84 (2)	1.94 (2)	2.783 (4)	172 (4)

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VN2007).

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supporting information

Acta Cryst. (2011). E**67**, m822–m823 [doi:10.1107/S1600536811019453]

Poly[[diaquadi-μ_2-cyanido-bis(μ_2-pyrazine-2-carboxylato)dicopper(I)copper(II)] dihydrate]

Guang Fan, Jia-juan Sun, Min-yan Zheng, San-ping Chen and Sheng-Li Gao

S1. Comment

Single crystal diffraction has revealed that complex (I) crystallizes in the monoclinic space group $P2_1/c$ featuring two-dimensional networks through chain-like $[Cu(CN)]_n$ units linked by $Cu(2\text{-pac})_2(H_2O)_2$. As shown in Fig. 1, there are two crystallographic inequivalent copper atoms. The Cu(1) atom is divalent and Cu(2) is monovalent. Cu(1) adopts a distorted octahedral geometry by two N and two O atoms from the 2-pac ligands in the equatorial plane whereas the axial positions are occupied by two water molecules with 1.9781 (17)Å for Cu1—O1; 2.002 (2)Å for Cu1—N1; 2.371 (2)Å for Cu1—O3. Each Cu(2) atom has a triangular geometry, coordinated to one N atom and one C atom from two bridging cyanide ligands and another N atom from $Cu(2\text{-pac})_2(H_2O)_2$, with 1.860 (3)Å for Cu2—C6; 1.885 (3)Å for Cu2—N3; 2.163 (2)Å for Cu2—N2.

Fig. 2 shows the independent cyanide ligands bridging Cu(2) to form a zigzag chain of $[Cu(CN)]_n$ units. Such chains are interconnected through two $Cu(2\text{-pac})_2(H_2O)_2$ N donor ligands giving rise to a two-dimensional sheet network. Furthermore, an extensive hydrogen bonding network is formed, which involves the coordinated, free water molecules and the 2-pac ligand substituents, affording a three-dimensional network, as shown in Fig. 3. It is noted that one proton of the free water molecule has no apparent hydrogen acceptor atom.

The present structure is quite different from the mixed-valence copper complex $[Cu^{II}Cu^{I}(2\text{-pac})_2(NO_3)(H_2O)]_n$ reported by Fan *et al.* (2006). In the latter structure the coordination number of monovalent Cu atom is 4, but for the present structure the coordination number is 3.

S2. Experimental

Red crystals from complex (I) were obtained by hydrothermal synthesis of a mixture of $Cu(NO_3)_2.3H_2O$ (0.1241 g, 0.5 mmol), 0.4 ml H_3PO_3 and 2-pac (0.0673 g, 0.5 mmol) in 6 ml H_2O, sealed in a Teflon-lined stainless container, heated at 363 K for 24 h and slowly cooled to room temperature.

S3. Refinement

All H atoms attached to C atoms from the organic ligands were generated in idealized positions and constrained to ride on their parent atoms, with d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq} (C). The water H-atoms were located in a different Fourier map, and the geometry of the two water molecules was restrained to its ideal geometry by in total six restraints on angles and bond distances.

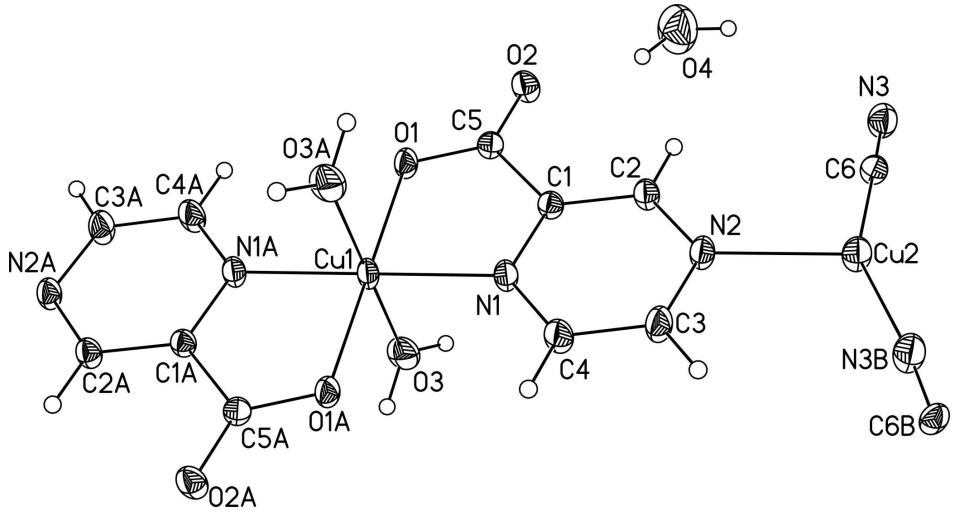

Figure 1

A view of the molecular structure of (I) with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry code for A: 1-*x*, -y, -*z*; B: –*x*, -0.5+y, 0.5-*z*.

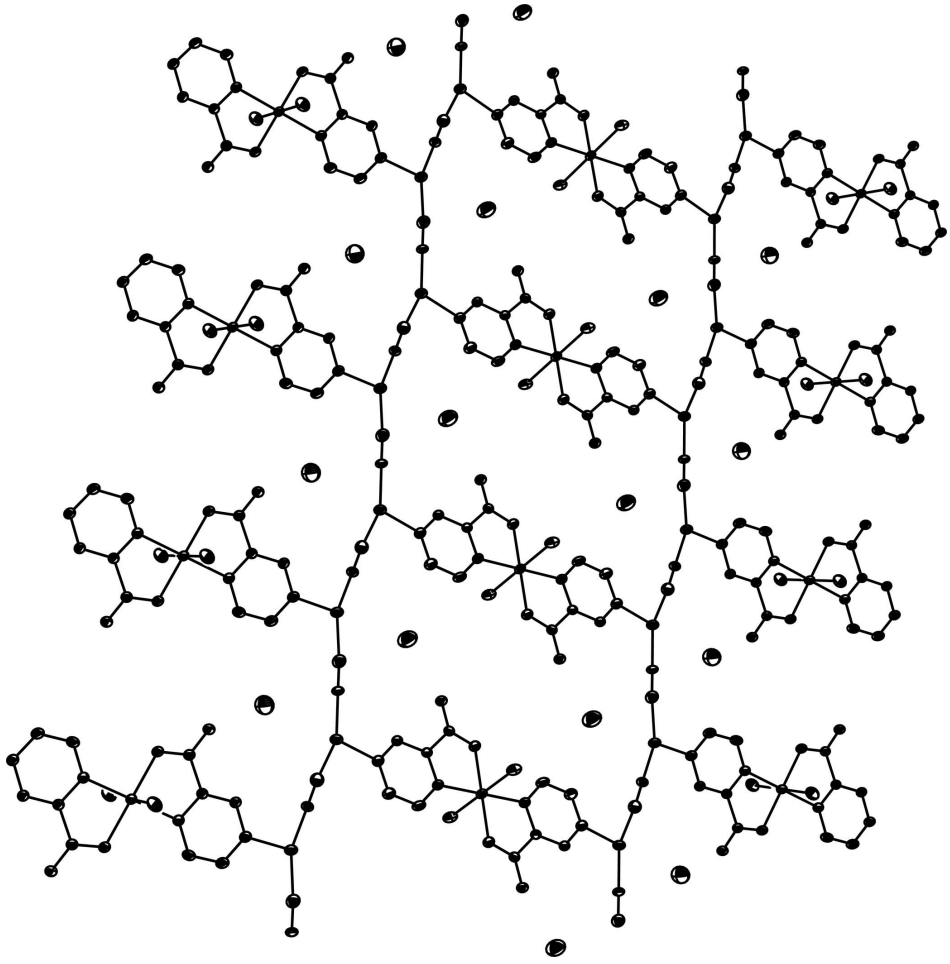

Figure 2

Two-dimensional sheet structure for complex (I). Hydrogen atoms have been omitted for clarity.

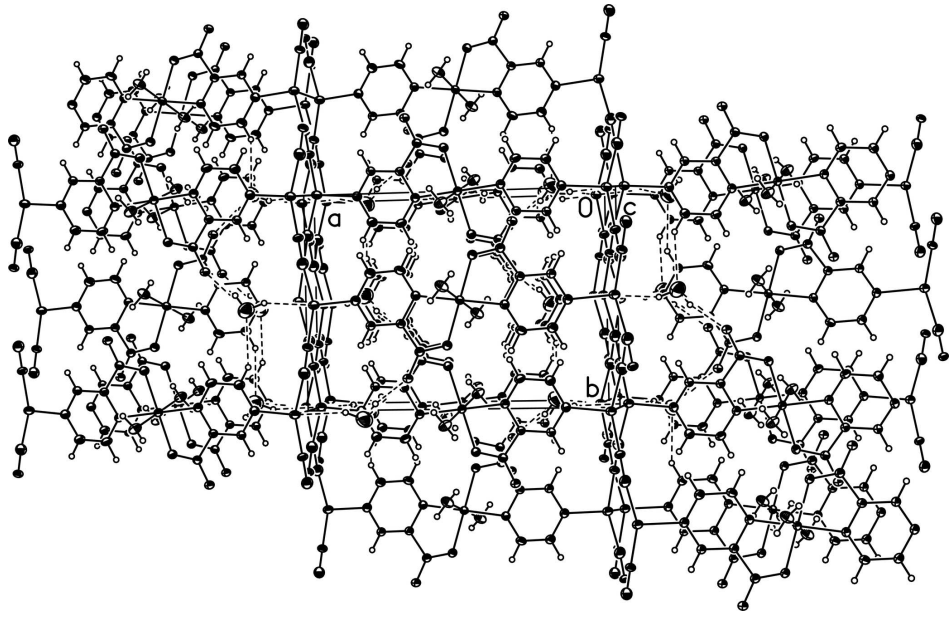

Figure 3

Three-dimensional stacking diagram for complex (I) along the *c* axis.

Poly[[diaquadi-μ_2-cyanido-bis(μ_2-pyrazine-2-carboxylato)dicopper(I)copper(II)] dihydrate]

Crystal data

$[Cu_3(C_5H_3N_2O_2)_2(CN)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 560.91$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 13.8297$ (4) Å
$b = 9.4906$ (3) Å
$c = 7.1272$ (3) Å
$\beta = 100.768$ (3)°
$V = 918.99$ (6) Å^3
$Z = 2$
$F(000) = 558$
$D_x = 2.027$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 117 reflections
$\theta = 2.5$–19.1°
$\mu = 3.50$ mm^{-1}
$T = 296$ K
Block, red
0.10 × 0.08 × 0.05 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.721$, $T_{max} = 0.845$
4141 measured reflections
1615 independent reflections
1269 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.1°$, $\theta_{min} = 3.6°$
$h = -16\rightarrow16$
$k = -11\rightarrow11$
$l = -7\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.095$
$S = 0.99$
1615 reflections
145 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 1.5206P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.5000	0.0000	0.0000	0.0296 (2)
Cu2	0.03571 (3)	0.00934 (4)	0.21527 (8)	0.0366 (2)
O1	0.45839 (17)	0.1989 (2)	−0.0394 (4)	0.0316 (6)
O2	0.33417 (17)	0.3429 (2)	−0.0167 (4)	0.0356 (6)
O3	0.5540 (2)	0.0613 (3)	0.3263 (4)	0.0433 (7)
H3A	0.588 (3)	−0.001 (4)	0.393 (6)	0.065*
H3B	0.524 (3)	0.113 (4)	0.390 (6)	0.065*
C5	0.3724 (2)	0.2253 (3)	−0.0104 (5)	0.0258 (7)
N1	0.3627 (2)	−0.0237 (3)	0.0479 (5)	0.0297 (7)
N2	0.1722 (2)	−0.0069 (3)	0.1101 (5)	0.0330 (7)
N3	−0.0012 (2)	0.3197 (4)	0.2534 (5)	0.0422 (8)
C1	0.3146 (2)	0.0996 (3)	0.0357 (5)	0.0253 (7)
C4	0.3148 (3)	−0.1381 (4)	0.0874 (6)	0.0401 (10)
H4	0.3458	−0.2254	0.0941	0.048*
C2	0.2195 (2)	0.1067 (3)	0.0676 (5)	0.0293 (8)
H2	0.1877	0.1935	0.0591	0.035*
C6	0.0122 (2)	0.2013 (3)	0.2401 (5)	0.0288 (8)
C3	0.2199 (3)	−0.1284 (4)	0.1185 (6)	0.0405 (10)
H3	0.1881	−0.2100	0.1463	0.049*
O4	0.1922 (3)	0.5271 (4)	0.1144 (8)	0.0884 (13)
H4A	0.229 (4)	0.457 (5)	0.093 (11)	0.133*
H4B	0.133 (2)	0.495 (7)	0.108 (13)	0.133*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0222 (3)	0.0210 (3)	0.0499 (4)	0.0014 (2)	0.0178 (3)	0.0025 (2)
Cu2	0.0345 (3)	0.0214 (3)	0.0572 (4)	−0.00078 (17)	0.0176 (2)	−0.0008 (2)
O1	0.0256 (12)	0.0243 (12)	0.0487 (16)	−0.0007 (10)	0.0170 (11)	0.0041 (11)
O2	0.0297 (12)	0.0217 (13)	0.0564 (18)	0.0009 (10)	0.0109 (12)	0.0014 (11)
O3	0.0502 (17)	0.0366 (16)	0.0452 (18)	0.0128 (13)	0.0138 (14)	−0.0037 (13)

C5	0.0267 (17)	0.0226 (17)	0.029 (2)	−0.0009 (13)	0.0070 (15)	−0.0010 (14)
N1	0.0240 (14)	0.0234 (15)	0.0449 (19)	0.0010 (12)	0.0147 (14)	0.0007 (13)
N2	0.0267 (15)	0.0260 (16)	0.050 (2)	−0.0008 (11)	0.0173 (15)	0.0018 (13)
N3	0.0386 (17)	0.042 (2)	0.050 (2)	0.0022 (15)	0.0172 (16)	0.0012 (16)
C1	0.0251 (16)	0.0212 (17)	0.031 (2)	0.0003 (13)	0.0079 (14)	−0.0012 (14)
C4	0.036 (2)	0.0215 (18)	0.068 (3)	0.0060 (15)	0.023 (2)	0.0058 (18)
C2	0.0248 (17)	0.0225 (18)	0.042 (2)	−0.0004 (14)	0.0106 (16)	−0.0012 (15)
C6	0.0322 (18)	0.0183 (17)	0.039 (2)	0.0033 (14)	0.0139 (16)	−0.0011 (15)
C3	0.0326 (19)	0.0267 (19)	0.068 (3)	−0.0008 (16)	0.0245 (19)	0.0055 (19)
O4	0.082 (3)	0.077 (3)	0.115 (4)	0.013 (2)	0.043 (3)	−0.001 (3)

Geometric parameters (Å, º)

Cu1—O1^{i}	1.978 (2)	C5—C1	1.507 (4)
Cu1—O1	1.978 (2)	N1—C4	1.329 (4)
Cu1—N1^{i}	2.003 (3)	N1—C1	1.340 (4)
Cu1—N1	2.003 (3)	N2—C3	1.324 (5)
Cu1—O3^{i}	2.378 (3)	N2—C2	1.326 (4)
Cu1—O3	2.378 (3)	N3—C6	1.146 (5)
Cu2—C6	1.865 (3)	N3—Cu2^{iv}	1.886 (4)
Cu2—N3^{ii}	1.886 (4)	C1—C2	1.377 (5)
Cu2—N2	2.163 (3)	C4—C3	1.375 (5)
Cu2—Cu2^{iii}	3.0481 (11)	C4—H4	0.9300
O1—C5	1.269 (4)	C2—H2	0.9300
O2—C5	1.232 (4)	C3—H3	0.9300
O3—H3A	0.844 (19)	O4—H4A	0.86 (2)
O3—H3B	0.824 (19)	O4—H4B	0.87 (2)
O1^{i}—Cu1—O1	180.00 (14)	O2—C5—O1	125.6 (3)
O1^{i}—Cu1—N1^{i}	82.62 (10)	O2—C5—C1	118.9 (3)
O1—Cu1—N1^{i}	97.38 (10)	O1—C5—C1	115.5 (3)
O1^{i}—Cu1—N1	97.38 (10)	C4—N1—C1	117.8 (3)
O1—Cu1—N1	82.62 (10)	C4—N1—Cu1	130.8 (2)
N1^{i}—Cu1—N1	180.00 (3)	C1—N1—Cu1	111.5 (2)
O1^{i}—Cu1—O3^{i}	86.28 (10)	C3—N2—C2	117.1 (3)
O1—Cu1—O3^{i}	93.72 (10)	C3—N2—Cu2	120.4 (2)
N1^{i}—Cu1—O3^{i}	89.72 (11)	C2—N2—Cu2	121.4 (2)
N1—Cu1—O3^{i}	90.28 (11)	C6—N3—Cu2^{iv}	173.8 (3)
O1^{i}—Cu1—O3	93.72 (10)	N1—C1—C2	120.7 (3)
O1—Cu1—O3	86.28 (10)	N1—C1—C5	115.4 (3)
N1^{i}—Cu1—O3	90.28 (11)	C2—C1—C5	124.0 (3)
N1—Cu1—O3	89.72 (11)	N1—C4—C3	120.6 (3)
O3^{i}—Cu1—O3	180.00 (14)	N1—C4—H4	119.7
C6—Cu2—N3^{ii}	150.28 (16)	C3—C4—H4	119.7
C6—Cu2—N2	106.34 (13)	N2—C2—C1	121.7 (3)
N3^{ii}—Cu2—N2	103.29 (12)	N2—C2—H2	119.2
C6—Cu2—Cu2^{iii}	97.07 (12)	C1—C2—H2	119.2
N3^{ii}—Cu2—Cu2^{iii}	91.27 (11)	N3—C6—Cu2	178.9 (4)

N2—Cu2—Cu2^{iii}	77.67 (9)	N2—C3—C4	122.2 (3)
C5—O1—Cu1	114.9 (2)	N2—C3—H3	118.9
Cu1—O3—H3A	115 (3)	C4—C3—H3	118.9
Cu1—O3—H3B	126 (3)	H4A—O4—H4B	107 (4)
H3A—O3—H3B	113 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O2	0.86 (2)	2.08 (3)	2.910 (5)	160 (7)
O3—H3*B*···O1^{v}	0.82 (2)	2.11 (2)	2.883 (3)	156 (4)
O3—H3*A*···O2^{vi}	0.84 (2)	1.94 (2)	2.783 (4)	172 (4)

Symmetry codes: (v) *x*, −*y*+1/2, *z*+1/2; (vi) −*x*+1, *y*−1/2, −*z*+1/2.