metal-organic compounds

Poly[[bis(μ_2-6-methylpyrazin-2-carboxyl-ato-$\kappa^3N^1,O:N^4$)copper(II)] dihydrate]

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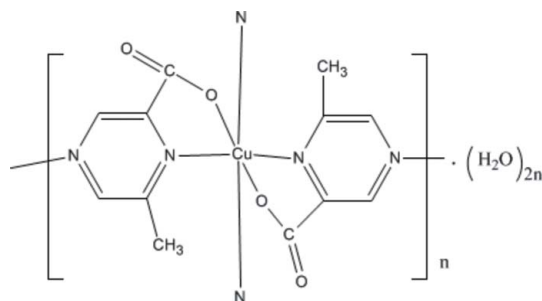Correspondence e-mail: xintingwei@cn.yahoo.com

In the title compound, $\{[Cu(C_6H_5N_2O_2)_2]\cdot 2H_2O\}_n$, the Cu^{II} ion (site symmetry $\overline{1}$) is coordinated by two N,O-bidentate ligands and two N-monodentate ligands in a distorted CuO_2N_4 octahedral geometry. Each anion acts as a bridge between two cations, thus forming a two-dimensional polymeric network parallel to the ab plane. The packing is consolidated by O—H···O hydrogen bonds. One of the O atoms of the ligand and both water molecules are disordered.

Related literature

For a related structure, see: Yigit *et al.* (2006). For background to coordination networks, see: Kesanli & Lin (2003); Barnett & Champness (2003).

Experimental

Crystal data

$[Cu(C_6H_5N_2O_2)_2]\cdot 2H_2O$	a = 8.371 (1) Å
M_r = 373.81	b = 9.7901 (11) Å
Monoclinic, $P2_1/c$	c = 10.3849 (13) Å
β = 112.277 (1)°	μ = 1.42 mm^{-1}
V = 787.55 (16) Å^3	T = 298 K
Z = 2	$0.34 \times 0.32 \times 0.30$ mm
Mo $K\alpha$ radiation	

Data collection

Bruker SMART CCD diffractometer	3821 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	1388 independent reflections
T_{min} = 0.644, T_{max} = 0.675	1094 reflections with $I > 2\sigma(I)$
	R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049	126 parameters
$wR(F^2)$ = 0.160	H-atom parameters constrained
S = 1.06	$\Delta\rho_{max}$ = 1.23 e Å^{-3}
1388 reflections	$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O1	1.949 (3)	Cu1—N1	2.354 (4)
Cu1—N2^i	2.064 (4)		

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
O3—H3C···O2^{ii}	0.85	1.78	2.624 (3)	175
O3—H3C···O2'^{ii}	0.85	2.36	3.181 (3)	163
O3—H3D···O2'^{i}	0.85	2.23	3.074 (2)	175
O4—H4D···O3^{iii}	0.85	1.97	2.73 (3)	147
O4—H4E···O3^{iv}	0.85	2.01	2.77 (2)	150

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

Barnett, S. A. & Champness, N. R. (2003). *Coord. Chem. Rev.* **246**, 145–168.
Bruker (2003). *SMART, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Kesanli, B. & Lin, W. B. (2003). *Coord. Chem. Rev.* **246**, 305–326.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yigit, M. V., Wang, Y., Moulton, B. & MacDonald, J. C. (2006). *Cryst. Growth Des.* **6**, 829–832.

supporting information

Poly[[bis(μ_2-6-methylpyrazin-2-carboxylato-$\kappa^3N^1,O:N^4$)copper(II)] dihydrate]

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S1. Comment

In recent years,the construction of metal-organic coordination polymers (MOCPs) by metal-directed self- assembly is of great interest not only for their potential applications as functional materials in ion exchange, catalysis, hydrogen storage, and magnetic devices, but also for their aesthetic structural and host–guest chemistry associated with large central cavities. (Kesanli *et al.*, 2003; Barnett *et al.*, 2003). As an extension of this work,the 6-methyl-2- pyrazinecarboxylic acid was chosen due to its chelating coordinated effect leading to a linear metal center.

As shown in Fig.1. X-ray structural analyses of complex (1) reveal the core structure of (1) is the symmetric dinuclear unit of [Cu(L)2(H$_2$O)$_2$] (L = anion of 6-methyl-2- pyrazinecarboxylic acid). Each Cu^{II} atom is coordinated to two ligands as well as to the two N atoms of the other two ligands, forming a octahedral coordination conformation.

The ligand forms a coordination polymer with tridentate and monodentate binding of Cu^{II} ions at opposite ends of the ligand bridge neighboring units and yield a two-dimensional arrangement running in the *ab* plane (Fig. 2). Yigit *et al.* (2006) recently reported a coordination polymer featuring a similar head-to-tail arrangement of pyrazine-2,3,5,6-tetra-carboxylic acid. There is intermolecular H-bonds (O3—H3···O4) showed as strong H bond, which link the molecular and water to form host–guest model.

### S2. Experimental

4.00 g Potassium permanganate was to be dissolved in 30 ml pure water in a beaker and 1.0 ml 98% H$_2$SO$_4$ was added to the solution. After stiring 10 min, and then added 2,6-dimethylpyrazine to the mixture.The recation was keeping at room temperature for 24 h. The resulting solution was filtered, and the filtrate was left in a beaker, then 2.00 g copper(II) sulfate pentahydrate was added to the filtrate. After stirrng for 20 min s, the copper(II) sulfate pentahydrate was solved completely. The blue solution was kept at the room temperature for two weeks and blue blocks of (I) were obtained. Yield: 86percent, m.p. 551 K. Anal. Calc. for C$_{12}$H$_{14}$CuN$_4$O$_6$: C: 38.5567; H:3.7750; N:14.9881; Found:*C*: 37.67; H: 3.86; N: 14.32%. Selected IR (KBr, cm-1) 3439(w), 2889 (w), 1638(*s*), 1596 (*s*), 1536(w), 1409(*s*), 1364(*m*), 1275(*m*), 1149(*s*), 1151(*s*), 1034(*s*), 941(*s*), 820(*m*), 800(*s*), 712(w), 531(*m*), 471(w).

S3. Refinement

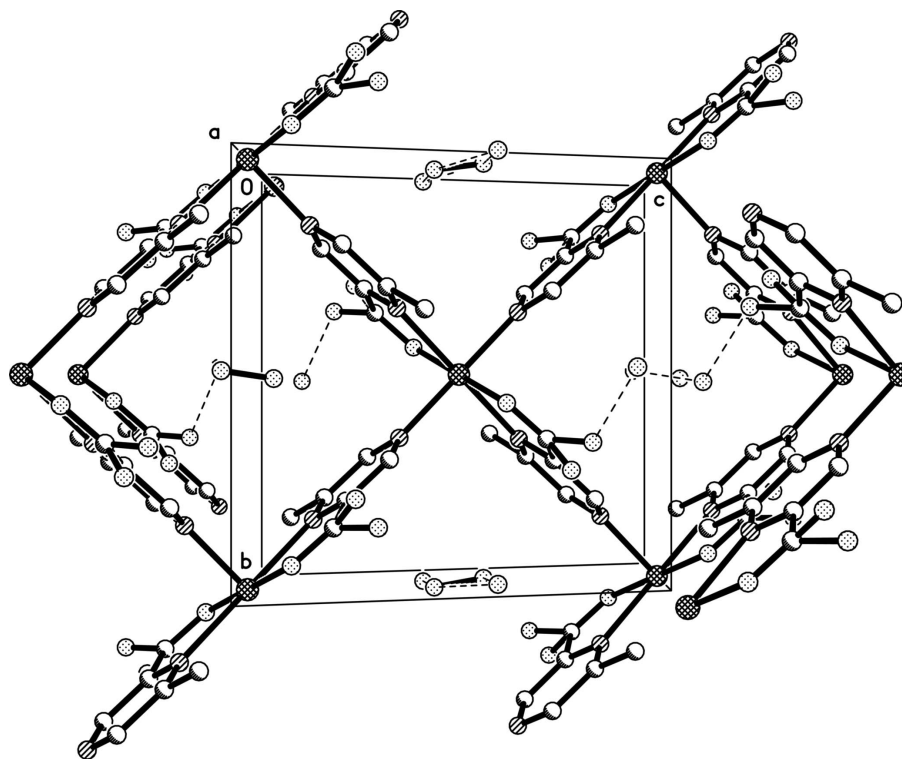All H atoms were placed geometrically and treated as riding on their parent atoms with C—H 0.93(pyrazine), C—H 0.97 (methylene) Å [U_{iso}(H) = 1.2U_{eq}(C)] and O—H 0.82 Å (hydroxyl) [U_{iso}(H) = 1.5U_{eq}(O)].
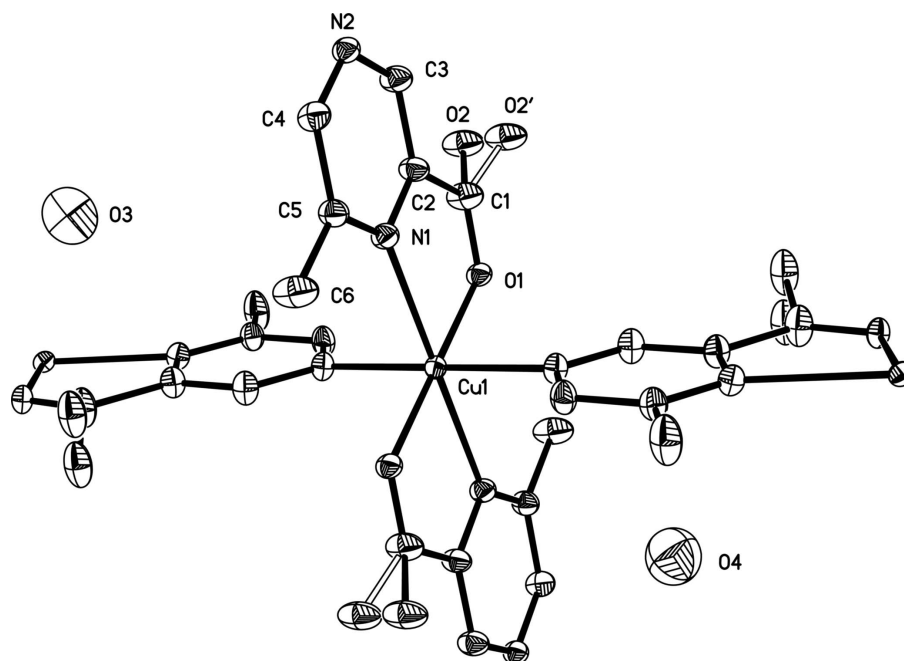
Figure 1

The molecular structure of (I) showing 30% probability displacement ellipsoids.

Figure 2

The crystal packing of (I), viewed approximately along the *c* axis.

Poly[[bis(μ₂-6-methylpyrazin-2-carboxylato- $\kappa^3N^1,O:N^4$ **)copper(II)] dihydrate]**

Crystal data

[Cu(C₆H₅N₂O₂)₂]·2H₂O	$F(000) = 382$
$M_r = 373.81$	$D_x = 1.576$ Mg m⁻³
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1598 reflections
$a = 8.371 (1)$ Å	$\theta = 2.6–26.2°$
$b = 9.7901 (11)$ Å	$\mu = 1.42$ mm⁻¹
$c = 10.3849 (13)$ Å	$T = 298$ K
$\beta = 112.277 (1)°$	Block, blue
$V = 787.55 (16)$ Å³	$0.34 \times 0.32 \times 0.30$ mm
$Z = 2$	

Data collection

Bruker SMART CCD diffractometer	3821 measured reflections
Radiation source: fine-focus sealed tube	1388 independent reflections
Graphite monochromator	1094 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	$\theta_{max} = 25.0°$, $\theta_{min} = 2.6°$
$T_{min} = 0.644$, $T_{max} = 0.675$	$h = -9\rightarrow9$
	$k = -11\rightarrow11$
	$l = -12\rightarrow9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H-atom parameters constrained
$wR(F^2) = 0.160$	$w = 1/[\sigma^2(F_o^2) + (0.0987P)^2 + 1.8186P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
1388 reflections	$(\Delta/\sigma)_{max} = 0.001$
126 parameters	$\Delta\rho_{max} = 1.23$ e Å⁻³
0 restraints	$\Delta\rho_{min} = -0.47$ e Å⁻³
Primary atom site location: structure-invariant direct methods	

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	$U_{iso}*/U_{eq}$	Occ. (<1)
Cu1	0.5000	0.5000	0.5000	0.0210 (3)	
N1	0.5565 (5)	0.3429 (4)	0.3509 (4)	0.0273 (9)	
N2	0.5246 (5)	0.1511 (4)	0.1450 (4)	0.0270 (9)	
O1	0.2704 (4)	0.4333 (3)	0.3861 (3)	0.0259 (7)	

O2	0.1014 (18)	0.343 (6)	0.184 (5)	0.049 (10)	0.46 (9)
O2′	0.1110 (16)	0.279 (5)	0.235 (4)	0.049 (9)	0.54 (9)
O3	0.8445 (18)	0.5171 (12)	0.0914 (16)	0.097 (4)	0.50
H3C	0.9307	0.4639	0.1248	0.116*	0.50
H3D	0.8631	0.5877	0.1426	0.116*	0.50
O4	0.499 (3)	0.4908 (16)	0.9398 (18)	0.126 (6)	0.50
H4D	0.5904	0.5025	1.0121	0.152*	0.50
H4E	0.4122	0.4929	0.9628	0.152*	0.50
C1	0.2469 (6)	0.3484 (6)	0.2899 (6)	0.0411 (14)	
C2	0.4033 (6)	0.2942 (5)	0.2678 (5)	0.0302 (11)	
C3	0.3863 (6)	0.1987 (6)	0.1653 (5)	0.0337 (12)	
H3	0.2771	0.1672	0.1096	0.040*	
C4	0.6768 (6)	0.1996 (5)	0.2266 (5)	0.0319 (11)	
H4A	0.7750	0.1682	0.2146	0.038*	
C5	0.6955 (6)	0.2969 (5)	0.3308 (5)	0.0301 (11)	
C6	0.8676 (7)	0.3506 (7)	0.4211 (6)	0.0496 (16)	
H6A	0.8532	0.4283	0.4721	0.074*	
H6B	0.9300	0.3775	0.3644	0.074*	
H6C	0.9309	0.2809	0.4850	0.074*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0214 (5)	0.0226 (5)	0.0193 (5)	−0.0019 (3)	0.0079 (3)	0.0006 (3)
N1	0.023 (2)	0.033 (2)	0.026 (2)	−0.0023 (17)	0.0093 (16)	−0.0047 (17)
N2	0.025 (2)	0.031 (2)	0.027 (2)	−0.0020 (18)	0.0120 (16)	−0.0056 (17)
O1	0.0234 (16)	0.0301 (18)	0.0267 (17)	−0.0018 (14)	0.0124 (13)	−0.0062 (15)
O2	0.025 (5)	0.065 (19)	0.054 (13)	−0.004 (6)	0.012 (5)	−0.030 (15)
O2′	0.025 (4)	0.065 (17)	0.054 (11)	−0.004 (5)	0.012 (5)	−0.030 (12)
O3	0.074 (8)	0.092 (10)	0.115 (11)	0.018 (6)	0.026 (8)	0.013 (7)
O4	0.120 (14)	0.133 (15)	0.129 (17)	−0.002 (9)	0.050 (14)	0.000 (11)
C1	0.019 (3)	0.058 (4)	0.045 (3)	−0.004 (2)	0.010 (2)	−0.019 (3)
C2	0.025 (3)	0.033 (3)	0.032 (3)	−0.004 (2)	0.010 (2)	−0.010 (2)
C3	0.025 (3)	0.041 (3)	0.035 (3)	−0.004 (2)	0.011 (2)	−0.012 (2)
C4	0.023 (3)	0.040 (3)	0.034 (3)	0.002 (2)	0.012 (2)	−0.007 (2)
C5	0.026 (3)	0.032 (3)	0.033 (3)	−0.002 (2)	0.012 (2)	−0.006 (2)
C6	0.024 (3)	0.068 (4)	0.054 (4)	−0.001 (3)	0.011 (3)	−0.027 (3)

Geometric parameters (Å, º)

Cu1—O1[i]	1.949 (3)	O3—H3C	0.8500
Cu1—O1	1.949 (3)	O3—H3D	0.8500
Cu1—N2[ii]	2.064 (4)	O4—O4[v]	1.26 (3)
Cu1—N2[iii]	2.064 (4)	O4—H4D	0.8500
Cu1—N1[i]	2.354 (4)	O4—H4E	0.8500
Cu1—N1	2.354 (4)	C1—C2	1.509 (7)
N1—C2	1.333 (6)	C2—C3	1.383 (7)
N1—C5	1.336 (6)	C3—H3	0.9300

N2—C4	1.322 (6)	C4—C5	1.405 (7)
N2—C3	1.337 (6)	C4—H4A	0.9300
N2—Cu1ⁱᵛ	2.065 (4)	C5—C6	1.486 (7)
O1—C1	1.256 (6)	C6—H6A	0.9600
O2—C1	1.30 (3)	C6—H6B	0.9600
O2′—C1	1.26 (2)	C6—H6C	0.9600
O1ⁱ—Cu1—O1	180.0	H4D—O4—H4E	109.0
O1ⁱ—Cu1—N2ⁱⁱ	89.70 (14)	O1—C1—O2′	124.0 (8)
O1—Cu1—N2ⁱⁱ	90.30 (14)	O1—C1—O2	121.0 (11)
O1ⁱ—Cu1—N2ⁱⁱⁱ	90.30 (14)	O2′—C1—O2	36.7 (6)
O1—Cu1—N2ⁱⁱⁱ	89.70 (14)	O1—C1—C2	118.1 (4)
N2ⁱⁱ—Cu1—N2ⁱⁱⁱ	180.0	O2′—C1—C2	115.3 (8)
O1ⁱ—Cu1—N1ⁱ	77.27 (13)	O2—C1—C2	116.5 (8)
O1—Cu1—N1ⁱ	102.73 (13)	N1—C2—C3	122.2 (5)
N2ⁱⁱ—Cu1—N1ⁱ	88.74 (15)	N1—C2—C1	116.9 (4)
N2ⁱⁱⁱ—Cu1—N1ⁱ	91.26 (15)	C3—C2—C1	120.9 (4)
O1ⁱ—Cu1—N1	102.73 (13)	N2—C3—C2	121.0 (4)
O1—Cu1—N1	77.27 (13)	N2—C3—H3	119.5
N2ⁱⁱ—Cu1—N1	91.26 (15)	C2—C3—H3	119.5
N2ⁱⁱⁱ—Cu1—N1	88.74 (15)	N2—C4—C5	122.4 (4)
N1ⁱ—Cu1—N1	180.0	N2—C4—H4A	118.8
C2—N1—C5	117.4 (4)	C5—C4—H4A	118.8
C2—N1—Cu1	106.0 (3)	N1—C5—C4	120.0 (4)
C5—N1—Cu1	136.6 (3)	N1—C5—C6	118.4 (4)
C4—N2—C3	117.1 (4)	C4—C5—C6	121.6 (4)
C4—N2—Cu1ⁱᵛ	122.0 (3)	C5—C6—H6A	109.5
C3—N2—Cu1ⁱᵛ	120.8 (3)	C5—C6—H6B	109.5
C1—O1—Cu1	121.7 (3)	H6A—C6—H6B	109.5
H3C—O3—H3D	108.5	C5—C6—H6C	109.5
O4ᵛ—O4—H4D	55.8	H6A—C6—H6C	109.5
O4ᵛ—O4—H4E	53.3	H6B—C6—H6C	109.5
O1ⁱ—Cu1—N1—C2	−179.1 (3)	C5—N1—C2—C1	−179.1 (5)
O1—Cu1—N1—C2	0.9 (3)	Cu1—N1—C2—C1	0.0 (5)
N2ⁱⁱ—Cu1—N1—C2	90.9 (3)	O1—C1—C2—N1	−1.4 (8)
N2ⁱⁱⁱ—Cu1—N1—C2	−89.1 (3)	O2′—C1—C2—N1	−164 (3)
N1ⁱ—Cu1—N1—C2	168 (100)	O2—C1—C2—N1	155 (4)
O1ⁱ—Cu1—N1—C5	−0.4 (5)	O1—C1—C2—C3	178.9 (5)
O1—Cu1—N1—C5	179.6 (5)	O2′—C1—C2—C3	17 (3)
N2ⁱⁱ—Cu1—N1—C5	−90.4 (5)	O2—C1—C2—C3	−24 (4)
N2ⁱⁱⁱ—Cu1—N1—C5	89.6 (5)	C4—N2—C3—C2	−0.2 (8)
N1ⁱ—Cu1—N1—C5	−13 (100)	Cu1ⁱᵛ—N2—C3—C2	176.2 (4)
O1ⁱ—Cu1—O1—C1	5 (100)	N1—C2—C3—N2	−0.1 (8)
N2ⁱⁱ—Cu1—O1—C1	−93.0 (4)	C1—C2—C3—N2	179.6 (5)
N2ⁱⁱⁱ—Cu1—O1—C1	87.0 (4)	C3—N2—C4—C5	0.0 (8)
N1ⁱ—Cu1—O1—C1	178.2 (4)	Cu1ⁱᵛ—N2—C4—C5	−176.3 (4)
N1—Cu1—O1—C1	−1.8 (4)	C2—N1—C5—C4	−0.8 (7)

Cu1—O1—C1—O2′	163 (3)	Cu1—N1—C5—C4	−179.5 (4)
Cu1—O1—C1—O2	−153 (4)	C2—N1—C5—C6	179.4 (5)
Cu1—O1—C1—C2	2.4 (7)	Cu1—N1—C5—C6	0.7 (8)
C5—N1—C2—C3	0.6 (7)	N2—C4—C5—N1	0.5 (8)
Cu1—N1—C2—C3	179.7 (4)	N2—C4—C5—C6	−179.7 (5)

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

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
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O4—H4D⋯O3[vii]	0.85	1.97	2.73 (3)	147
O4—H4E⋯O3[i]	0.85	2.01	2.77 (2)	150

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