metal-organic compounds

Bis(methanol-κO)bis(1,2-diamino-2-hydroxyiminoethanone oximato-κ²N,N′)-copper(II) bis(oxamide dioxime) methanol disolvate

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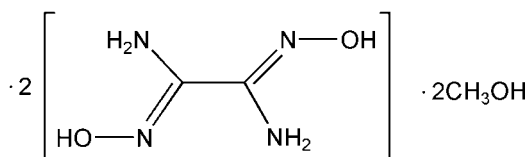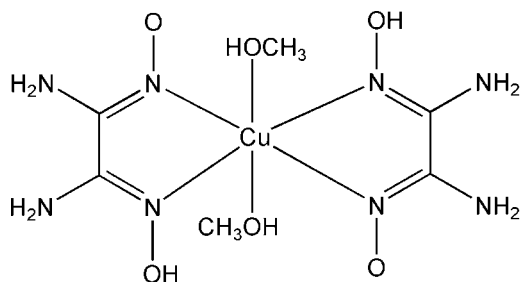
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In the title compound, $[Cu(C_2H_5N_4O_2)_2(CH_3OH)_2]\cdot2C_2H_6N_4O_2\cdot2CH_3OH$, the Cu^{II} atom, lying on an inversion center, is coordinated by four N atoms from two 1,2-diamino-2-hydroxyiminoethanone oximate anion and two O atoms from two methanol molecules in a distorted octahedral geometry. The two uncoordinating oxamide dioxime molecules, each lying on an inversion center, adopt a *trans* conformation. In the crystal, O—H⋯O, N—H⋯O and N—H⋯N hydrogen bonds link the complex molecules and the oxamide dioxime and methanol molecules.

Related literature

For related structures, see: Bélombé *et al.* (2006); Belombe *et al.* (2007); Egharevba *et al.* (1982); Endres (1980); Endres & Schlicksupp (1980); Endres *et al.* (1983); Gunasekaran *et al.* (1995).

Experimental

Crystal data

$[Cu(C_2H_5N_4O_2)_2(CH_4O)_2]\cdot$ $2C_2H_6N_4O_2\cdot2CH_4O$	$\beta = 103.327\ (9)°$
$M_r = 662.13$	$\gamma = 104.957\ (5)°$
Triclinic, $P\bar{1}$	$V = 682.5\ (5)$ Å^3
$a = 7.567\ (3)$ Å	$Z = 1$
$b = 8.874\ (4)$ Å	Mo $K\alpha$ radiation
$c = 10.867\ (5)$ Å	$\mu = 0.89$ mm^{-1}
$\alpha = 92.046\ (4)°$	$T = 113$ K
	$0.28 \times 0.24 \times 0.22$ mm

Data collection

Rigaku Saturn724 CCD diffractometer	7216 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2009) $T_{min} = 0.790$, $T_{max} = 0.829$	3212 independent reflections
	2252 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.086$	
$S = 0.99$	
3212 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
198 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O1^i	0.84	1.96	2.737 (3)	154
O3—H3⋯O5^{ii}	0.84	1.92	2.744 (3)	166
O4—H4⋯O1^{iii}	0.84	1.79	2.621 (3)	169
O5—H5⋯O1^{iv}	0.81 (2)	1.87 (3)	2.657 (3)	164 (2)
O6—H6⋯O5^v	0.79 (3)	1.94 (3)	2.721 (3)	173 (3)
N3—H3A⋯N7^{vi}	0.88	2.50	3.195 (3)	136
N3—H3B⋯O6^{vii}	0.88	2.32	3.167 (3)	162
N4—H4A⋯O4^{viii}	0.88	2.35	3.112 (3)	145
N4—H4B⋯O6^{vii}	0.88	2.00	2.878 (3)	172
N6—H6A⋯O3^{ix}	0.88	2.26	3.097 (3)	159
N6—H6B⋯N7^{vii}	0.88	2.19	3.007 (3)	155
N8—H8A⋯O4^{ix}	0.88	2.20	3.043 (3)	159
N8—H8B⋯N5^x	0.88	2.21	3.031 (3)	154

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $-x+2, -y+1, -z+1$; (iii) $x, y+1, z-1$; (iv) $x, y, z-1$; (v) $x, y, z+1$; (vi) $-x+1, -y+1, -z+2$; (vii) $x-1, y, z$; (viii) $-x, -y+1, -z+1$; (ix) $-x+1, -y+1, -z+1$; (x) $x, y-1, z$.

Data collection: *CrystalClear* (Rigaku, 2009); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2572).

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Bis(methanol-*κO*)bis(1,2-diamino-2-hydroxyiminoethanone oximato-*κ²N,N′*)copper(II) bis(oxamide dioxime) methanol disolvate

Daying Liu, Ruihong Zhang, Hui Hu, Jing Qi and Guangming Yang

S1. Comment

Owing to the variety of structures and unique properties, transition metal complexes of oxamide oxime (diaminoglyoxime, oaoH$_2$) are of great interest. So far, most of the published work concerns 4-coordinated transition metal oxamide oximate complexes (Endres, 1980; Endres & Schlicksupp, 1980; Endres *et al.*, 1983). The 6-coordinated transition metal oxamide oximate complexes have not been reported hitherto (Bélombé *et al.*, 2006; Belombe *et al.*, 2007; Egharevba *et al.*, 1982). We used oxamide oxime as ligands (Gunasekaran *et al.*, 1995) and obtained green crystals of the title compound from a methanol solution.

In the title compound, the Cu^{II} atom, lying on an inversion center, is surrounded in an octahedral environment defined by four N atoms from two oaoH ligands and two O atoms from two methanol molecules (Fig. 1). The methanol molecules are weakly coordinated to the Cu atom with a Cu—O distance of 2.797 (2) Å. In the crystal, O—H···O, N—H···O and N—H···N hydrogen bonds (Table 1) link the complex molecules and the oxamide oxime and methanol molecules.

S2. Experimental

A methanol solution (10 ml) of copper acetate (0.1 mmol) was added dropwise to a methanol solution (10 ml) of oxamide oxime (0.1 mmol). The title compound was obtained as green crystals by slow evaporation of the filtrate in air at room temperature 5 days later. Analysis, calculated for C$_{12}$H$_{38}$CuN$_{16}$O$_{12}$: C 21.77, H 5.78, N 33.85, O 29.00%; found: C 21.79, H 5.76, N 33.88, O 29.02%.

S3. Refinement

H atoms of methanol molecules were located from a difference Fourier map and refined isotropically with U_{iso}(H) = 1.5U_{eq}(O). The other H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.98, N—H = 0.88 and O—H = 0.84 Å and with U_{iso}(H) = 1.2(1.5 for methyl and hydroxyl)U_{eq}(C,N,O).
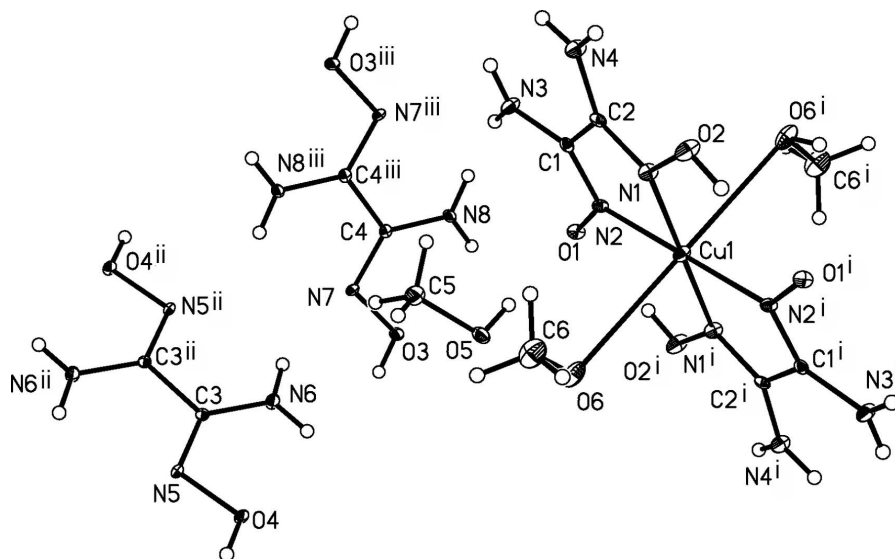
Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) 1-x, -y, 2-z; (ii) -x, 2-y, 1-z; (iii) 1-x, 1-y, 1-z.]

Bis(methanol-κO)bis(oxamide oxime oximato-κ²N,N′)copper(II) bis(oxamide dioxime) methanol disolvate

Crystal data

$[Cu(C_2H_5N_4O_2)_2(CH_4O)_2]\cdot 2C_2H_6N_4O_2\cdot 2CH_4O$	$Z = 1$
$M_r = 662.13$	$F(000) = 347$
Triclinic, $P\overline{1}$	$D_x = 1.611$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.567$ (3) Å	Cell parameters from 2266 reflections
$b = 8.874$ (4) Å	$\theta = 1.9–27.9°$
$c = 10.867$ (5) Å	$\mu = 0.89$ mm^{-1}
$\alpha = 92.046$ (4)°	$T = 113$ K
$\beta = 103.327$ (9)°	Block, green
$\gamma = 104.957$ (5)°	$0.28 \times 0.24 \times 0.22$ mm
$V = 682.5$ (5) Å^3	

Data collection

Rigaku Saturn724 CCD diffractometer	7216 measured reflections
Radiation source: rotating anode	3212 independent reflections
Multilayer monochromator	2252 reflections with $I > 2\sigma(I)$
Detector resolution: 14.22 pixels mm^{-1}	$R_{int} = 0.044$
ω scans	$\theta_{max} = 27.9°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2009)	$h = -9 \rightarrow 9$
	$k = -11 \rightarrow 11$
$T_{min} = 0.790$, $T_{max} = 0.829$	$l = -11 \rightarrow 14$

Refinement

Refinement on F^2	3212 reflections
Least-squares matrix: full	198 parameters
$R[F^2 > 2\sigma(F^2)] = 0.033$	0 restraints
$wR(F^2) = 0.086$	Primary atom site location: structure-invariant
$S = 0.99$	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

$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ 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}
C1	0.2733 (3)	0.1538 (3)	1.0896 (2)	0.0102 (5)
C2	0.2003 (3)	0.1293 (3)	0.9482 (2)	0.0102 (5)
C3	0.0546 (3)	0.9542 (3)	0.47271 (19)	0.0089 (5)
C4	0.5721 (3)	0.4615 (3)	0.53280 (19)	0.0092 (5)
C5	0.6807 (3)	0.4989 (3)	0.2349 (2)	0.0207 (6)
H5A	0.7195	0.5685	0.3141	0.031*
H5B	0.5433	0.4548	0.2126	0.031*
H5C	0.7183	0.5586	0.1666	0.031*
C6	0.7357 (4)	0.3711 (3)	0.9294 (2)	0.0317 (7)
H6C	0.7999	0.4807	0.9621	0.048*
H6D	0.5989	0.3535	0.9151	0.048*
H6E	0.7658	0.3478	0.8490	0.048*
Cu1	0.5000	0.0000	1.0000	0.01296 (13)
N1	0.3058 (2)	0.0743 (2)	0.89207 (16)	0.0131 (4)
N2	0.4170 (2)	0.0981 (2)	1.12976 (16)	0.0105 (4)
N3	0.1956 (2)	0.2296 (2)	1.16254 (18)	0.0165 (5)
H3A	0.2423	0.2452	1.2454	0.020*
H3B	0.0982	0.2636	1.1274	0.020*
N4	0.0410 (2)	0.1635 (2)	0.89006 (17)	0.0163 (5)
H4A	0.0011	0.1485	0.8067	0.020*
H4B	−0.0236	0.2010	0.9353	0.020*
N5	0.1797 (2)	1.0348 (2)	0.41876 (16)	0.0100 (4)
N6	0.0166 (3)	0.7998 (2)	0.48310 (18)	0.0168 (5)
H6A	0.0792	0.7436	0.4517	0.020*
H6B	−0.0710	0.7546	0.5214	0.020*
N7	0.7401 (2)	0.5552 (2)	0.58021 (17)	0.0118 (4)
N8	0.5201 (2)	0.3067 (2)	0.53953 (18)	0.0172 (5)
H8A	0.6030	0.2596	0.5788	0.021*
H8B	0.4030	0.2519	0.5047	0.021*

O1	0.50028 (19)	0.11732 (19)	1.25853 (13)	0.0127 (4)
O2	0.2404 (2)	0.0421 (2)	0.76012 (14)	0.0200 (4)
H2	0.3155	0.0041	0.7315	0.030*
O3	0.86131 (19)	0.46482 (19)	0.63897 (15)	0.0158 (4)
H3	0.9731	0.5217	0.6610	0.024*
O4	0.2651 (2)	0.93020 (19)	0.36628 (14)	0.0130 (4)
H4	0.3493	0.9817	0.3336	0.019*
O5	0.7699 (2)	0.3745 (2)	0.25156 (15)	0.0168 (4)
H5	0.688 (3)	0.305 (3)	0.267 (2)	0.025*
O6	0.7980 (2)	0.2702 (2)	1.02027 (16)	0.0238 (5)
H6	0.791 (4)	0.308 (3)	1.085 (3)	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0102 (11)	0.0089 (13)	0.0107 (12)	−0.0007 (10)	0.0048 (9)	0.0005 (9)
C2	0.0085 (11)	0.0089 (13)	0.0121 (12)	−0.0014 (10)	0.0041 (9)	0.0038 (9)
C3	0.0072 (11)	0.0099 (13)	0.0082 (11)	0.0025 (10)	−0.0006 (9)	0.0002 (9)
C4	0.0116 (11)	0.0100 (13)	0.0073 (11)	0.0026 (10)	0.0054 (9)	0.0003 (9)
C5	0.0196 (13)	0.0204 (16)	0.0233 (14)	0.0076 (12)	0.0047 (11)	0.0038 (11)
C6	0.0400 (17)	0.0313 (19)	0.0320 (17)	0.0188 (15)	0.0132 (13)	0.0151 (14)
Cu1	0.0131 (2)	0.0178 (3)	0.0095 (2)	0.00752 (19)	0.00211 (16)	0.00014 (17)
N1	0.0129 (10)	0.0201 (13)	0.0062 (10)	0.0060 (9)	0.0005 (8)	0.0006 (8)
N2	0.0082 (9)	0.0146 (11)	0.0079 (10)	0.0026 (8)	0.0010 (7)	0.0004 (8)
N3	0.0149 (10)	0.0232 (13)	0.0136 (11)	0.0109 (10)	0.0019 (8)	−0.0016 (9)
N4	0.0150 (10)	0.0236 (13)	0.0110 (10)	0.0086 (10)	0.0013 (8)	−0.0006 (9)
N5	0.0102 (9)	0.0090 (11)	0.0126 (10)	0.0047 (8)	0.0038 (8)	0.0002 (8)
N6	0.0185 (11)	0.0108 (12)	0.0279 (12)	0.0046 (9)	0.0177 (9)	0.0049 (9)
N7	0.0083 (9)	0.0109 (11)	0.0171 (10)	0.0055 (8)	0.0017 (8)	0.0025 (8)
N8	0.0085 (9)	0.0082 (11)	0.0307 (12)	0.0021 (9)	−0.0032 (8)	0.0016 (9)
O1	0.0122 (8)	0.0186 (10)	0.0067 (8)	0.0030 (7)	0.0025 (6)	0.0010 (7)
O2	0.0206 (9)	0.0349 (12)	0.0080 (8)	0.0158 (9)	0.0013 (7)	−0.0009 (8)
O3	0.0085 (8)	0.0121 (10)	0.0238 (9)	0.0039 (7)	−0.0030 (7)	0.0029 (7)
O4	0.0143 (8)	0.0118 (9)	0.0185 (9)	0.0053 (7)	0.0131 (7)	0.0032 (7)
O5	0.0125 (9)	0.0142 (11)	0.0210 (10)	−0.0002 (8)	0.0031 (7)	0.0030 (8)
O6	0.0330 (10)	0.0288 (12)	0.0191 (10)	0.0202 (9)	0.0114 (8)	0.0069 (8)

Geometric parameters (Å, º)

C1—N2	1.300 (3)	Cu1—N2^{iii}	1.9349 (18)
C1—N3	1.344 (3)	Cu1—N2	1.9349 (18)
C1—C2	1.496 (3)	Cu1—O6	2.797 (2)
C2—N1	1.285 (3)	N1—O2	1.397 (2)
C2—N4	1.340 (3)	N2—O1	1.380 (2)
C3—N5	1.299 (3)	N3—H3A	0.8800
C3—N6	1.340 (3)	N3—H3B	0.8800
C3—C3^{i}	1.494 (4)	N4—H4A	0.8800
C4—N7	1.302 (3)	N4—H4B	0.8800

C4—N8	1.337 (3)	N5—O4	1.430 (2)
C4—C4ⁱⁱ	1.493 (4)	N6—H6A	0.8800
C5—O5	1.431 (3)	N6—H6B	0.8800
C5—H5A	0.9800	N7—O3	1.428 (2)
C5—H5B	0.9800	N8—H8A	0.8800
C5—H5C	0.9800	N8—H8B	0.8800
C6—O6	1.437 (3)	O2—H2	0.8400
C6—H6C	0.9800	O3—H3	0.8400
C6—H6D	0.9800	O4—H4	0.8400
C6—H6E	0.9800	O5—H5	0.81 (3)
Cu1—N1ⁱⁱⁱ	1.9314 (18)	O6—H6	0.79 (2)
Cu1—N1	1.9314 (18)		
N2—C1—N3	125.9 (2)	N1—Cu1—O6	97.31 (8)
N2—C1—C2	112.90 (18)	N2ⁱⁱⁱ—Cu1—O6	90.37 (7)
N3—C1—C2	121.17 (19)	N2—Cu1—O6	89.63 (7)
N1—C2—N4	125.4 (2)	C2—N1—O2	115.67 (16)
N1—C2—C1	112.98 (18)	C2—N1—Cu1	116.25 (15)
N4—C2—C1	121.63 (19)	O2—N1—Cu1	126.33 (13)
N5—C3—N6	126.10 (19)	C1—N2—O1	118.35 (17)
N5—C3—C3ⁱ	115.4 (3)	C1—N2—Cu1	115.95 (15)
N6—C3—C3ⁱ	118.5 (3)	O1—N2—Cu1	125.67 (13)
N7—C4—N8	125.9 (2)	C1—N3—H3A	120.0
N7—C4—C4ⁱⁱ	115.2 (3)	C1—N3—H3B	120.0
N8—C4—C4ⁱⁱ	118.8 (2)	H3A—N3—H3B	120.0
O5—C5—H5A	109.5	C2—N4—H4A	120.0
O5—C5—H5B	109.5	C2—N4—H4B	120.0
H5A—C5—H5B	109.5	H4A—N4—H4B	120.0
O5—C5—H5C	109.5	C3—N5—O4	108.74 (18)
H5A—C5—H5C	109.5	C3—N6—H6A	120.0
H5B—C5—H5C	109.5	C3—N6—H6B	120.0
O6—C6—H6C	109.5	H6A—N6—H6B	120.0
O6—C6—H6D	109.5	C4—N7—O3	108.65 (19)
H6C—C6—H6D	109.5	C4—N8—H8A	120.0
O6—C6—H6E	109.5	C4—N8—H8B	120.0
H6C—C6—H6E	109.5	H8A—N8—H8B	120.0
H6D—C6—H6E	109.5	N1—O2—H2	109.5
N1ⁱⁱⁱ—Cu1—N1	179.999 (1)	N7—O3—H3	109.5
N1ⁱⁱⁱ—Cu1—N2ⁱⁱⁱ	80.90 (8)	N5—O4—H4	109.5
N1—Cu1—N2ⁱⁱⁱ	99.10 (8)	C5—O5—H5	101.6 (18)
N1ⁱⁱⁱ—Cu1—N2	99.10 (8)	C6—O6—Cu1	108.13 (15)
N1—Cu1—N2	80.90 (8)	C6—O6—H6	104 (2)
N2ⁱⁱⁱ—Cu1—N2	179.999 (1)	Cu1—O6—H6	97 (2)
N1ⁱⁱⁱ—Cu1—O6	82.69 (8)		
N2—C1—C2—N1	−7.5 (3)	N3—C1—N2—Cu1	−178.33 (18)
N3—C1—C2—N1	171.1 (2)	C2—C1—N2—Cu1	0.2 (3)
N2—C1—C2—N4	172.8 (2)	N1ⁱⁱⁱ—Cu1—N2—C1	−175.60 (18)

N3—C1—C2—N4	−8.6 (4)	N1—Cu1—N2—C1	4.40 (18)
N4—C2—N1—O2	−3.1 (4)	O6—Cu1—N2—C1	101.86 (18)
C1—C2—N1—O2	177.20 (19)	N1ⁱⁱⁱ—Cu1—N2—O1	6.43 (18)
N4—C2—N1—Cu1	−168.98 (19)	N1—Cu1—N2—O1	−173.57 (18)
C1—C2—N1—Cu1	11.3 (3)	O6—Cu1—N2—O1	−76.10 (17)
N2ⁱⁱⁱ—Cu1—N1—C2	171.00 (17)	N6—C3—N5—O4	2.8 (3)
N2—Cu1—N1—C2	−9.00 (17)	C3ⁱ—C3—N5—O4	−177.3 (2)
O6—Cu1—N1—C2	−97.45 (18)	N8—C4—N7—O3	1.0 (3)
N2ⁱⁱⁱ—Cu1—N1—O2	6.80 (19)	C4ⁱⁱ—C4—N7—O3	−179.8 (2)
N2—Cu1—N1—O2	−173.20 (19)	N1ⁱⁱⁱ—Cu1—O6—C6	169.14 (15)
O6—Cu1—N1—O2	98.35 (17)	N1—Cu1—O6—C6	−10.87 (15)
N3—C1—N2—O1	−0.2 (4)	N2ⁱⁱⁱ—Cu1—O6—C6	88.36 (15)
C2—C1—N2—O1	178.31 (17)	N2—Cu1—O6—C6	−91.64 (15)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1ⁱⁱⁱ	0.84	1.96	2.737 (3)	154
O3—H3···O5^{iv}	0.84	1.92	2.744 (3)	166
O4—H4···O1^v	0.84	1.79	2.621 (3)	169
O5—H5···O1^{vi}	0.81 (2)	1.87 (3)	2.657 (3)	164 (2)
O6—H6···O5^{vii}	0.79 (3)	1.94 (3)	2.721 (3)	173 (3)
N3—H3*A*···N7^{viii}	0.88	2.50	3.195 (3)	136
N3—H3*B*···O6^{ix}	0.88	2.32	3.167 (3)	162
N4—H4*A*···O4^x	0.88	2.35	3.112 (3)	145
N4—H4*B*···O6^{ix}	0.88	2.00	2.878 (3)	172
N6—H6*A*···O3ⁱⁱ	0.88	2.26	3.097 (3)	159
N6—H6*B*···N7^{ix}	0.88	2.19	3.007 (3)	155
N8—H8*A*···O4ⁱⁱ	0.88	2.20	3.043 (3)	159
N8—H8*B*···N5^{xi}	0.88	2.21	3.031 (3)	154

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*, −*z*+2; (iv) −*x*+2, −*y*+1, −*z*+1; (v) *x*, *y*+1, *z*−1; (vi) *x*, *y*, *z*−1; (vii) *x*, *y*, *z*+1; (viii) −*x*+1, −*y*+1, −*z*+2; (ix) *x*−1, *y*, *z*; (x) −*x*, −*y*+1, −*z*+1; (xi) *x*, *y*−1, *z*.