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Crystal structure of bis{μ_2-3-(pyridin-2-yl)-5-[(1,2,4-triazol-1-yl)methyl]-1,2,4-triazolato}bis[aqua-nitratocopper(II)] dihydrate

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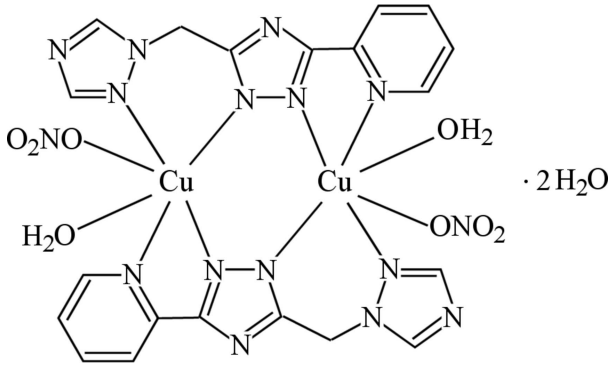
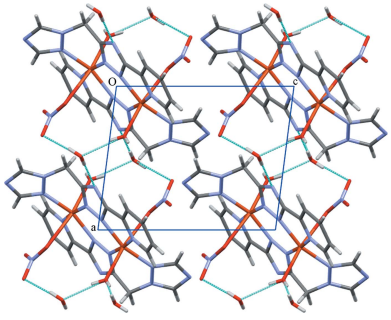
The structure of the dinuclear title complex, $[Cu_2(C_{10}H_8N_7)_2(NO_3)_2(H_2O)_2]\cdot 2H_2O$, consists of centrosymmetric dimeric units with a copper–copper separation of 4.0408 (3) Å. The Cu^{II} ions in the dimer display a distorted octahedral coordination geometry and are bridged by two triazole rings, forming an approximately planar Cu_2N_4 core (r.m.s. deviation = 0.049 Å). In the crystal, O—H···O, O—H···N and C—H···O hydrogen bonds and π–π interactions link the molecules into a three-dimensional network.

1. Chemical context

The presence in the triazole ring, three donor atoms and the possibility of introducing in the heterocycle substituents of a different nature creates the conditions for target synthesis of complexes with interesting structures and properties. The study of this type of coordination compound is promising since, as a result, a compound can be obtained with useful physical properties such as optical, magnetic or catalytic (Soghomonian *et al.*, 1993; Blake *et al.*, 1999). Another interesting aspect of these compounds is the possibility of their use as functional models of enzymes such as catechol oxidase (Moliner *et al.*, 2001; Klingele *et al.*, 2009; Selmeczi *et al.*, 2003).





2. Structural commentary

The structure of the title complex molecule (Fig. 1) has a crystallographically imposed centre of symmetry, and contains two copper(II) metal atoms doubly bridged by the triazole rings of two deprotonated ligands. Each copper(II) ion is coordinated in a distorted elongated octahedral geometry by one pyridine and three triazole nitrogen atoms forming the equatorial plane, and by the O atoms of a water molecule and

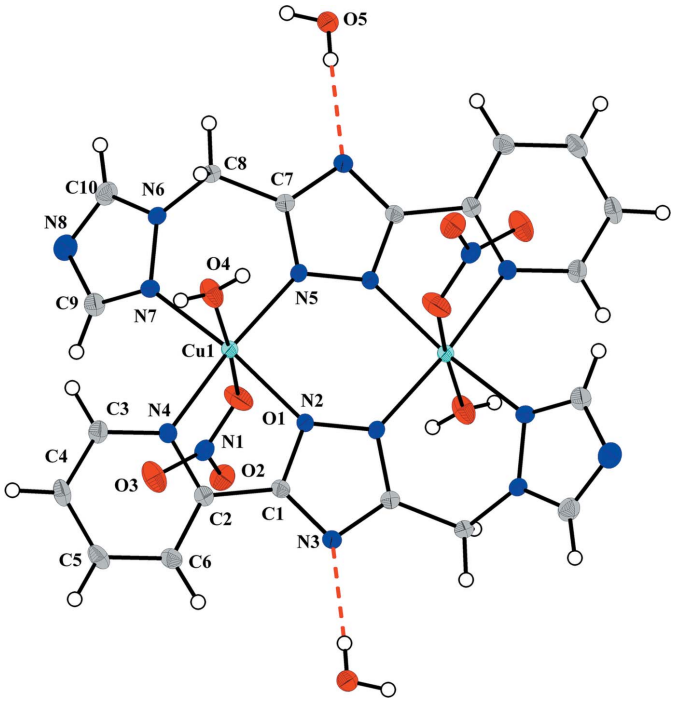


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 40% probability level. Dashed lines indicate hydrogen bonds. Unlabelled atoms are related to labelled atoms by ($-x$, $1-y$, $-z$).

a monodentate nitrate anion at the apices. The Cu—N bond lengths involving the bridging triazole ring [mean value 1.9722 (15) Å] are slightly, but significantly, shorter than those involving the pyridine and peripheral triazole rings [Cu1—N4 = 2.0386 (16) and Cu1—N7 = 2.0409 (17) Å]. The inner Cu_2N_4 core is approximately planar [r.m.s. deviation = 0.049 Å; maximum displacement 0.062 (2) Å for atom N2], with a Cu···Cu separation of 4.0408 (3) Å, in good agreement with the values usually observed in μ-triazolyl-bridged complexes (Haasnoot, 2000). The central triazole ring makes dihedral angles of 7.78 (8) and 49.30 (8)°, respectively, with the pyridine and peripheral triazole rings. The six-membered chelate ring Cu1/N5/C7/C8/N6/N7 assumes a boat conformation [puckering parameters: Q_T = 0.619 (2) Å; $\theta 2$ = 88.62 (16)°], while the five-membered Cu1/N2/C1/C2/N4 chelate ring adopts a flattened envelope conformation with the Cu atom as flap [puckering parameters: Q = 0.127 (2) Å; φ = −156.8 (8)°].

3. Supramolecular features

In the crystal, the complex molecules and water molecules of crystallization are linked through O—H···O, O—H···N and C—H···O hydrogen bonds (Table 1), forming a three-dimensional network (Fig. 2). The crystal structure is further stabilized by π–π stacking interactions with centroid–centroid separations $Cg1\cdots Cg2^{ii}$ = 3.8296 (13) Å and $Cg3\cdots Cg3^{iii}$ = 3.5372 (10), and perpendicular interplanar distances $Cg1\cdots Cg2^{ii}$ = 3.5584 (9) and $Cg3\cdots Cg3^{iii}$ = 3.3234 (10) Å

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41O···O5^{i}	0.71 (3)	2.03 (3)	2.735 (2)	172 (3)
O4—H42O···O5^{ii}	0.79 (3)	1.96 (3)	2.735 (2)	168 (3)
O5—H51O···O2^{iii}	0.78 (3)	2.02 (3)	2.773 (2)	163 (3)
O5—H52O···N3^{iv}	0.76 (3)	2.08 (3)	2.836 (2)	177 (3)
C5—H5···O1^{i}	0.95	2.43	3.360 (3)	166
C8—H8A···O4	0.99	2.56	3.160 (3)	119
C8—H8B···O2^{iii}	0.99	2.36	3.319 (3)	162
C9—H9···O3^{v}	0.95	2.44	3.205 (3)	137

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

[$Cg1$, $Cg2$ and $Cg3$ are the centroids of the N1/C2/N3/C7^{i}/N5^{i}, N4/C2–C6 and N6/N7/C9/N8/C10 rings, respectively; symmetry codes: (i) $-x$, $1-y$, $-z$; (ii) $-x$, $-y$, $-z$; (iii) $1-x$, $-y$, $1-z$].

4. Database survey

The Cambridge Structural Database (CSD Version 5.36 with three updates; Groom & Allen, 2014), returned 45 entries with the triazole bridging fragment Cu–(N–N)$_2$–Cu. The most similar are: diaquabis(μ-3,5-bis(2-pyridyl)-1,2,4-triazolato-N',N^1,N^2,N'')bis(trifluoromethanesulfonato-O)dicopper(II) (Prins *et al.*, 1985), bis[μ-5-(pyridin-2-yl)-3-(1H-1,2,4-triazol-3-yl)-1,2,4-triazolato]diaquadicopper diperchlorate (Zhou *et al.*, 2014), bis[μ_3-(pyridin-2-yl)-5-([5-(pyridin-2-yl)-1,2,4-triazol-1-id-3-yl]methyl)-1,2,4-triazol-1-ide]triaquatricopper diperchlorate dihydrate (Gusev *et al.*, 2014) and bis(μ-5-(2-ethoxy-2-oxoethyl)-3-(pyridin-2-yl)-1H-1,2,4-triazolyl)bis(acetonitrile)bis(perchlorato-O)dicopper (Khomenko *et al.*, 2012). Only 10 compounds containing a pyridyl and a methylene moiety, as substituents in the 3- and 5-positions of

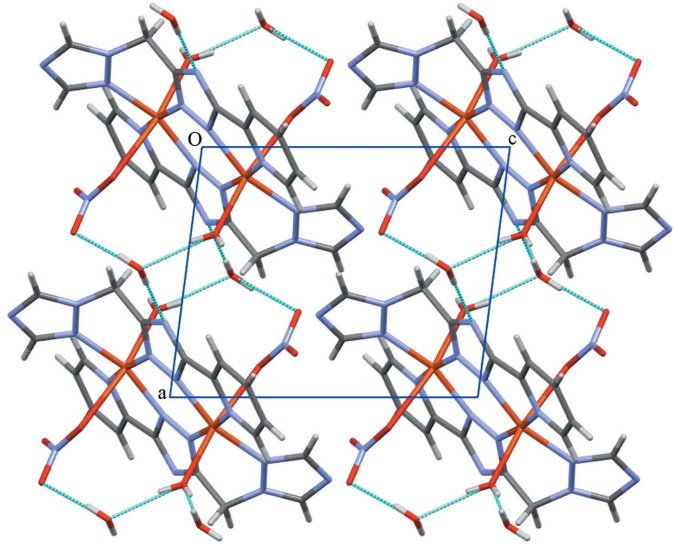


Figure 2
Packing diagram of the title compound, viewed along the b axis. Intermolecular hydrogen bonds are shown as blue dotted lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu_2(C_{10}H_8N_7)_2(NO_3)_2(H_2O)_2]\cdot 2H_2O$
M_r	775.63
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	8.8421 (2), 8.8636 (2), 10.5686 (2)
α, β, γ (°)	70.114 (1), 88.6311 (10), 66.765 (1)
V (Å^3)	709.87 (3)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.58
Crystal size (mm)	0.50 × 0.50 × 0.45
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2003)
T_{min}, T_{max}	0.505, 0.536
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8672, 2945, 2711
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.629
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.073, 1.07
No. of reflections	2945
No. of parameters	233
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.57

Computer programs: *APEX2* and *SAINT* (Bruker, 2003), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

1,2,4-triazole, were found (Lin *et al.*, 2013; Gusev *et al.*, 2014 and references therein).

5. Synthesis and crystallization

A water solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.25 mmol, 0.0605 g) was added to a hot solution of 2-[5-(1,2,4,)-triazol-1-yl-methyl-1*H*-(1,2,4)-triazol-3yl]pyridine (0.25 mmol, 0.059 g) in water (7 ml). The transparent blue solution was left to evaporate slowly in the air and after few hours, blue single crystals suitable for X-ray analysis were obtained (yield: 67%).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms of water molecules were located from a difference Fourier map and refined freely. All other H atoms were constrained to ride on their parent atoms, with C—H = 0.95–0.99 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

References

Blake, A. J., Champness, N. R., Hubberstey, P., Li, W. S., Withersby, M. A. & Schröder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.
Bruker (2003). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
Gusev, A. N., Nemec, I., Herchel, R., Bayjyyev, E., Nyshchimenko, G. A., Alexandrov, G. G., Eremenko, I. L., Trávníček, Z., Hasegawa, M. & Linert, W. (2014). *Dalton Trans.* **43**, 7153–7165.
Haasnoot, J. G. (2000). *Coord. Chem. Rev.* **200–202**, 131–185.
Khomenko, D. N., Doroshchuk, R. A., Egorov, O. A. & Lampeka, R. D. (2012). *Ukr. Khim. Zh.* **78**, 22–27.
Klingele, J., Dechert, S. & Meyer, F. (2009). *Coord. Chem. Rev.* **253**, 2698–2741.
Lin, W.-Q., Liao, X.-F., Jia, J.-H., Leng, J.-D., Liu, J.-L., Guo, F.-S. & Tong, M.-L. (2013). *Chem. Eur. J.* **19**, 12254–12258.
Moliner, N., Gaspar, A. B., Muñoz, M. C., Niel, V., Cano, J. & Real, J. A. (2001). *Inorg. Chem.* **40**, 3986–3991.
Prins, R., Birker, P. J. M. W. L., Haasnoot, J. G., Verschoor, G. C. & Reedijk, J. (1985). *Inorg. Chem.* **24**, 4128–4133.
Selmeczi, K., Réglier, M., Giorgi, M. & Speier, G. (2003). *Coord. Chem. Rev.* **245**, 191–201.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Soghomonian, V., Chen, Q., Haushalter, R. C., Zubieta, J. & O'Connor, C. J. (1993). *Science*, **259**, 1596–1599.
Zhou, Y.-H., Wan, W.-Q., Sun, D.-L., Tao, J., Zhang, L. & Wei, X. (2014). *Z. Anorg. Allg. Chem.* **640**, 249–253.

supporting information

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Crystal structure of bis{μ_2-3-(pyridin-2-yl)-5-[(1,2,4-triazol-1-yl)methyl]-1,2,4-triazolato}bis[aquanitratocopper(II)] dihydrate

Roman Doroschuk

Computing details

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Bis{μ_2-3-(pyridin-2-yl)-5-[(1,2,4-triazol-1-yl)methyl]-1,2,4-triazolato}bis[aquanitratocopper(II)] dihydrate

Crystal data

$[Cu_2(C_{10}H_8N_7)_2(NO_3)_2(H_2O)_2]\cdot 2H_2O$
M_r = 775.63
Triclinic, $P\overline{1}$
a = 8.8421 (2) Å
b = 8.8636 (2) Å
c = 10.5686 (2) Å
α = 70.114 (1)°
β = 88.6311 (10)°
γ = 66.765 (1)°
V = 709.87 (3) Å^3
Z = 1
$F(000)$ = 394
D_x = 1.814 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6116 reflections
θ = 2.5–26.5°
μ = 1.58 mm^{-1}
T = 173 K
Prism, blue
0.50 × 0.50 × 0.45 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
T_{min} = 0.505, T_{max} = 0.536
8672 measured reflections
2945 independent reflections
2711 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 26.6°, θ_{min} = 2.5°
h = −8→11
k = −11→11
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.073
S = 1.07
2945 reflections
233 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.4452P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.11824 (3)	0.26915 (3)	0.15525 (2)	0.01617 (9)
N1	−0.2107 (2)	0.3725 (2)	0.34951 (17)	0.0208 (4)
N2	−0.0714 (2)	0.3636 (2)	0.01433 (17)	0.0166 (3)
N3	−0.3010 (2)	0.3463 (2)	−0.04965 (17)	0.0185 (3)
N4	0.0614 (2)	0.0562 (2)	0.20396 (16)	0.0169 (3)
N5	0.1657 (2)	0.4800 (2)	0.08348 (17)	0.0169 (3)
N6	0.3708 (2)	0.2657 (2)	0.34195 (17)	0.0184 (3)
N7	0.2554 (2)	0.2013 (2)	0.33410 (17)	0.0185 (3)
N8	0.3280 (2)	0.1530 (3)	0.55105 (19)	0.0291 (4)
O1	−0.1224 (2)	0.4373 (2)	0.27750 (19)	0.0352 (4)
O2	−0.34096 (19)	0.4721 (2)	0.38151 (16)	0.0281 (3)
O3	−0.1751 (2)	0.2133 (2)	0.38786 (18)	0.0361 (4)
O4	0.3491 (2)	0.1266 (2)	0.07991 (19)	0.0289 (4)
H41O	0.388 (3)	0.033 (4)	0.104 (3)	0.029 (8)*
H42O	0.376 (3)	0.168 (4)	0.010 (3)	0.032 (8)*
O5	0.5124 (2)	0.7700 (2)	0.15015 (19)	0.0254 (3)
H51O	0.563 (4)	0.698 (4)	0.219 (3)	0.042 (9)*
H52O	0.458 (4)	0.736 (4)	0.125 (3)	0.041 (9)*
C1	−0.1560 (2)	0.2649 (2)	0.03218 (19)	0.0165 (4)
C2	−0.0792 (2)	0.0862 (2)	0.13281 (19)	0.0172 (4)
C3	0.1479 (3)	−0.1054 (3)	0.2939 (2)	0.0207 (4)
H3	0.2474	−0.1283	0.3438	0.025*
C4	0.0969 (3)	−0.2412 (3)	0.3170 (2)	0.0237 (4)
H4	0.1614	−0.3551	0.3810	0.028*
C5	−0.0481 (3)	−0.2088 (3)	0.2461 (2)	0.0239 (4)
H5	−0.0858	−0.2994	0.2614	0.029*
C6	−0.1384 (3)	−0.0411 (3)	0.1517 (2)	0.0221 (4)
H6	−0.2389	−0.0149	0.1013	0.027*
C7	0.3006 (2)	0.4957 (2)	0.1186 (2)	0.0173 (4)
C8	0.4370 (2)	0.3469 (3)	0.2234 (2)	0.0204 (4)
H8A	0.5019	0.2577	0.1842	0.025*
H8B	0.5126	0.3913	0.2508	0.025*
C9	0.2342 (3)	0.1361 (3)	0.4624 (2)	0.0227 (4)
H9	0.1591	0.0820	0.4898	0.027*
C10	0.4109 (3)	0.2351 (3)	0.4713 (2)	0.0249 (4)
H10	0.4888	0.2679	0.5026	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01744 (14)	0.01210 (13)	0.01794 (14)	−0.00721 (9)	−0.00253 (9)	−0.00253 (10)
N1	0.0217 (9)	0.0206 (8)	0.0188 (8)	−0.0079 (7)	−0.0028 (7)	−0.0063 (7)
N2	0.0175 (8)	0.0123 (7)	0.0186 (8)	−0.0065 (6)	−0.0017 (6)	−0.0031 (6)
N3	0.0192 (8)	0.0183 (8)	0.0192 (8)	−0.0098 (7)	0.0007 (7)	−0.0052 (7)
N4	0.0192 (8)	0.0149 (7)	0.0165 (8)	−0.0071 (6)	0.0009 (6)	−0.0054 (6)
N5	0.0165 (8)	0.0132 (7)	0.0183 (8)	−0.0058 (6)	−0.0029 (6)	−0.0027 (6)
N6	0.0178 (8)	0.0149 (7)	0.0209 (9)	−0.0071 (6)	−0.0037 (6)	−0.0038 (7)
N7	0.0168 (8)	0.0169 (8)	0.0211 (9)	−0.0079 (6)	−0.0007 (6)	−0.0047 (7)
N8	0.0331 (10)	0.0328 (10)	0.0214 (9)	−0.0139 (8)	0.0005 (8)	−0.0090 (8)
O1	0.0337 (9)	0.0291 (8)	0.0463 (11)	−0.0184 (7)	0.0147 (8)	−0.0121 (8)
O2	0.0240 (8)	0.0294 (8)	0.0283 (8)	−0.0063 (6)	0.0038 (6)	−0.0128 (7)
O3	0.0486 (11)	0.0177 (8)	0.0398 (10)	−0.0139 (7)	0.0086 (8)	−0.0074 (7)
O4	0.0316 (9)	0.0164 (8)	0.0332 (10)	−0.0058 (7)	0.0129 (7)	−0.0079 (7)
O5	0.0245 (8)	0.0180 (7)	0.0312 (9)	−0.0098 (7)	−0.0023 (7)	−0.0045 (7)
C1	0.0187 (9)	0.0154 (9)	0.0170 (9)	−0.0089 (7)	0.0013 (7)	−0.0053 (7)
C2	0.0197 (9)	0.0165 (9)	0.0164 (9)	−0.0077 (7)	0.0031 (7)	−0.0067 (8)
C3	0.0219 (10)	0.0172 (9)	0.0195 (10)	−0.0059 (8)	0.0000 (8)	−0.0049 (8)
C4	0.0341 (12)	0.0143 (9)	0.0185 (10)	−0.0087 (8)	0.0023 (8)	−0.0025 (8)
C5	0.0361 (12)	0.0179 (9)	0.0226 (11)	−0.0162 (9)	0.0069 (9)	−0.0073 (8)
C6	0.0265 (11)	0.0212 (10)	0.0221 (10)	−0.0140 (8)	0.0015 (8)	−0.0069 (8)
C7	0.0167 (9)	0.0177 (9)	0.0179 (10)	−0.0082 (7)	0.0007 (7)	−0.0056 (8)
C8	0.0168 (9)	0.0196 (9)	0.0225 (10)	−0.0090 (8)	−0.0020 (8)	−0.0027 (8)
C9	0.0244 (10)	0.0204 (10)	0.0214 (10)	−0.0087 (8)	0.0019 (8)	−0.0058 (8)
C10	0.0281 (11)	0.0234 (10)	0.0226 (11)	−0.0101 (9)	−0.0038 (8)	−0.0079 (9)

Geometric parameters (Å, º)

Cu1—N5	1.9709 (15)	N8—C9	1.349 (3)
Cu1—N2	1.9732 (16)	O4—H41O	0.71 (3)
Cu1—N4	2.0386 (16)	O4—H42O	0.79 (3)
Cu1—N7	2.0409 (17)	O5—H51O	0.78 (3)
Cu1—O4	2.2293 (16)	O5—H52O	0.76 (3)
N1—O3	1.234 (2)	C1—C2	1.463 (3)
N1—O1	1.244 (2)	C2—C6	1.376 (3)
N1—O2	1.266 (2)	C3—C4	1.391 (3)
N2—C1	1.326 (2)	C3—H3	0.9500
N2—N5^{i}	1.356 (2)	C4—C5	1.377 (3)
N3—C7^{i}	1.342 (2)	C4—H4	0.9500
N3—C1	1.346 (3)	C5—C6	1.391 (3)
N4—C3	1.335 (3)	C5—H5	0.9500
N4—C2	1.352 (3)	C6—H6	0.9500
N5—C7	1.329 (2)	C7—N3^{i}	1.342 (2)
N5—N2^{i}	1.356 (2)	C7—C8	1.496 (3)
N6—C10	1.328 (3)	C8—H8A	0.9900
N6—N7	1.368 (2)	C8—H8B	0.9900

N6—C8	1.455 (3)	C9—H9	0.9500
N7—C9	1.321 (3)	C10—H10	0.9500
N8—C10	1.323 (3)		

N5—Cu1—N2	93.75 (6)	N2—C1—N3	113.40 (17)
N5—Cu1—N4	172.58 (6)	N2—C1—C2	116.86 (17)
N2—Cu1—N4	80.29 (6)	N3—C1—C2	129.72 (17)
N5—Cu1—N7	88.59 (6)	N4—C2—C6	122.81 (18)
N2—Cu1—N7	161.96 (7)	N4—C2—C1	112.59 (16)
N4—Cu1—N7	98.45 (6)	C6—C2—C1	124.57 (18)
N5—Cu1—O4	87.79 (7)	N4—C3—C4	122.16 (19)
N2—Cu1—O4	108.72 (7)	N4—C3—H3	118.9
N4—Cu1—O4	89.95 (6)	C4—C3—H3	118.9
N7—Cu1—O4	89.23 (7)	C5—C4—C3	119.35 (19)
O3—N1—O1	120.96 (18)	C5—C4—H4	120.3
O3—N1—O2	119.57 (17)	C3—C4—H4	120.3
O1—N1—O2	119.45 (17)	C4—C5—C6	118.81 (18)
C1—N2—N5^{i}	105.92 (15)	C4—C5—H5	120.6
C1—N2—Cu1	114.60 (13)	C6—C5—H5	120.6
N5^{i}—N2—Cu1	137.73 (12)	C2—C6—C5	118.65 (19)
C7^{i}—N3—C1	101.45 (15)	C2—C6—H6	120.7
C3—N4—C2	118.20 (16)	C5—C6—H6	120.7
C3—N4—Cu1	127.56 (14)	N5—C7—N3^{i}	113.47 (17)
C2—N4—Cu1	114.23 (13)	N5—C7—C8	121.54 (17)
C7—N5—N2^{i}	105.75 (15)	N3^{i}—C7—C8	124.98 (17)
C7—N5—Cu1	126.66 (13)	N6—C8—C7	111.03 (16)
N2^{i}—N5—Cu1	127.56 (12)	N6—C8—H8A	109.4
C10—N6—N7	108.72 (16)	C7—C8—H8A	109.4
C10—N6—C8	128.56 (17)	N6—C8—H8B	109.4
N7—N6—C8	122.68 (16)	C7—C8—H8B	109.4
C9—N7—N6	102.89 (16)	H8A—C8—H8B	108.0
C9—N7—Cu1	132.81 (14)	N7—C9—N8	114.40 (19)
N6—N7—Cu1	122.03 (12)	N7—C9—H9	122.8
C10—N8—C9	102.87 (18)	N8—C9—H9	122.8
Cu1—O4—H41O	121 (2)	N8—C10—N6	111.12 (18)
Cu1—O4—H42O	123 (2)	N8—C10—H10	124.4
H41O—O4—H42O	112 (3)	N6—C10—H10	124.4
H51O—O5—H52O	107 (3)		

C10—N6—N7—C9	0.2 (2)	N4—C3—C4—C5	−0.6 (3)
C8—N6—N7—C9	178.21 (17)	C3—C4—C5—C6	0.9 (3)
C10—N6—N7—Cu1	165.14 (14)	N4—C2—C6—C5	−1.3 (3)
C8—N6—N7—Cu1	−16.9 (2)	C1—C2—C6—C5	176.53 (18)
N5^{i}—N2—C1—N3	0.8 (2)	C4—C5—C6—C2	0.0 (3)
Cu1—N2—C1—N3	168.39 (13)	N2^{i}—N5—C7—N3^{i}	0.0 (2)
N5^{i}—N2—C1—C2	179.30 (16)	Cu1—N5—C7—N3^{i}	178.11 (12)
Cu1—N2—C1—C2	−13.1 (2)	N2^{i}—N5—C7—C8	−178.85 (17)
C7^{i}—N3—C1—N2	−0.8 (2)	Cu1—N5—C7—C8	−0.8 (3)

C7^{i}—N3—C1—C2	−179.06 (19)	C10—N6—C8—C7	−127.1 (2)
C3—N4—C2—C6	1.6 (3)	N7—N6—C8—C7	55.3 (2)
Cu1—N4—C2—C6	−179.68 (15)	N5—C7—C8—N6	−46.0 (2)
C3—N4—C2—C1	−176.44 (16)	N3^{i}—C7—C8—N6	135.26 (19)
Cu1—N4—C2—C1	2.2 (2)	N6—N7—C9—N8	−0.5 (2)
N2—C1—C2—N4	7.0 (2)	Cu1—N7—C9—N8	−162.96 (15)
N3—C1—C2—N4	−174.73 (18)	C10—N8—C9—N7	0.5 (2)
N2—C1—C2—C6	−171.04 (18)	C9—N8—C10—N6	−0.3 (2)
N3—C1—C2—C6	7.2 (3)	N7—N6—C10—N8	0.1 (2)
C2—N4—C3—C4	−0.7 (3)	C8—N6—C10—N8	−177.76 (18)
Cu1—N4—C3—C4	−179.13 (14)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H41*O*···O5^{ii}	0.71 (3)	2.03 (3)	2.735 (2)	172 (3)
O4—H42*O*···O5^{iii}	0.79 (3)	1.96 (3)	2.735 (2)	168 (3)
O5—H51*O*···O2^{iv}	0.78 (3)	2.02 (3)	2.773 (2)	163 (3)
O5—H52*O*···N3^{i}	0.76 (3)	2.08 (3)	2.836 (2)	177 (3)
C5—H5···O1^{ii}	0.95	2.43	3.360 (3)	166
C8—H8*A*···O4	0.99	2.56	3.160 (3)	119
C8—H8*B*···O2^{iv}	0.99	2.36	3.319 (3)	162
C9—H9···O3^{v}	0.95	2.44	3.205 (3)	137

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