

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

catena-Poly[[bis(nitrato- κ O)copper(II)]-bis[μ -1,4-bis(pyridin-3-ylmethoxy)-benzene- κ^2 N:N']]

Ping Zou,^a Ying Liu,^{b,c} Guang-Feng Hou^b and Jin-Sheng Gao^{b*}

^aCollege of Life Science, Sichuan Agriculture University, Ya'an 625014, People's Republic of China, ^bCollege of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and ^cDepartment of Materials and Chemistry Engineering, Heilongjiang Institute of Technology, Harbin 150050, People's Republic of China

Correspondence e-mail: hg1000@163.com

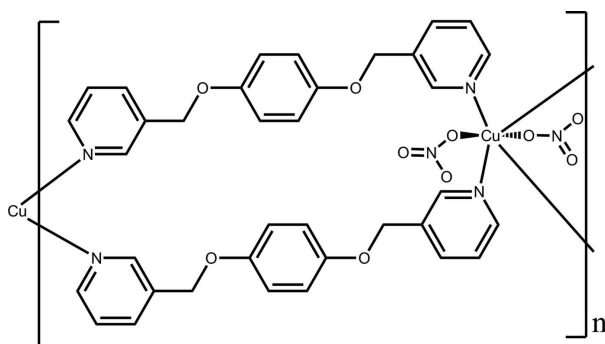
Received 15 April 2011; accepted 28 April 2011

Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.037; wR factor = 0.097; data-to-parameter ratio = 15.3.

In the title compound, $[\text{Cu}(\text{NO}_3)_2(\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2)_2]_n$, the Cu^{II} ion lies on an inversion center and is six-coordinated in a Jahn–Teller-distorted octahedral geometry defined by four N atoms of the pyridine derivative forming a square plane, above and below which are the O atoms of the nitrate anion. The ligand links the metal atoms into a linear chain running along the a axis. One of the nitrate O atoms is equally disordered over two sets of sites.

Related literature

For the synthesis and background to network structures built up from flexible pyridyl-based aromatic ligands and transition metals, see Liu *et al.* (2010*a,b*).



Experimental

Crystal data

$[\text{Cu}(\text{NO}_3)_2(\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2)_2]$
 $M_r = 772.22$

Monoclinic, $P2_1/c$

$a = 8.4859$ (17) Å

$b = 17.030$ (3) Å

$c = 12.986$ (4) Å

$\beta = 116.22$ (2)°

$V = 1683.6$ (7) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.72$ mm⁻¹

$T = 291$ K

$0.20 \times 0.18 \times 0.17$ mm

Data collection

Rigaku R-Axis RAPID
diffractometer

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\text{min}} = 0.867$, $T_{\text{max}} = 0.889$

16256 measured reflections

3831 independent reflections

3067 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.097$

$S = 1.07$

3831 reflections

251 parameters

12 restraints

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.45$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalClear* (Rigaku/MSK, 2002); 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: *SHELXL97*.

The authors thank the Youth Fundation of the Education Department of Sichuan Province, China (No. 08ZB031), Sichuan Agriculture University, Heilongjiang University and Heilongjiang Institute of Technology for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5152).

References

- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Liu, Y., Yan, P.-F., Yu, Y.-H., Hou, G.-F. & Gao, J.-S. (2010*a*). *Cryst. Growth Des.* **10**, 1559–1568.
Liu, Y., Yan, P.-F., Yu, Y.-H., Hou, G.-F. & Gao, J.-S. (2010*b*). *Inorg. Chem. Commun.* **13**, 630–632.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSK (2002). *CrystalStructure*. Rigaku/MSK Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2011). E67, m692 [doi:10.1107/S1600536811016096]

catena-Poly[[bis(nitrato- κ O)copper(II)]-bis[μ -1,4-bis(pyridin-3-ylmethoxy)-benzene- κ^2 N:N']]

Ping Zou, Ying Liu, Guang-Feng Hou and Jin-Sheng Gao

S1. Comment

The bridging pyridyl ligands can be used to construct interesting 0D to three-dimensional supramolecular architectures. Our group has reported some isolated molecule, chain, plane and three-dimensional network structures built up by flexible pyridyl-based aromatic ligands and transition metals. (Liu *et al.*, 2010a; Liu *et al.*, 2010b). As our continuing work for pyridyl ligands, we report here the synthesis and crystal structure of the title compound.

An asymmetric unit of the title compound consists of a 1,4-bis(pyridin-3-ylmethoxy)benzene molecule, a nitrate anion and a Cu^{II} cation (Figure 1). The Cu^{II} cations lie on the inversion centers and are six-coordinated in the Jahn-Teller distorted octahedral geometry environments defined by four N atoms forming the square planes and two O atoms locating the polar axis.

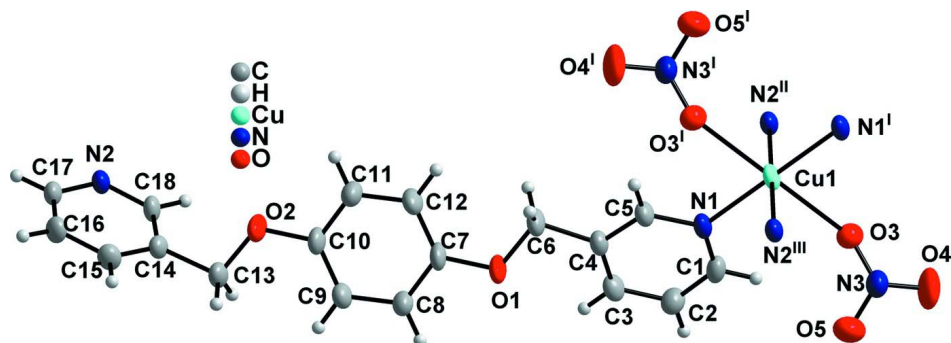
In the crystal, ribbon structures along [2 0 1] direction are built up by heterocyclic ligands bridging Cu^{II} cations (Figure 2, Table 1).

S2. Experimental

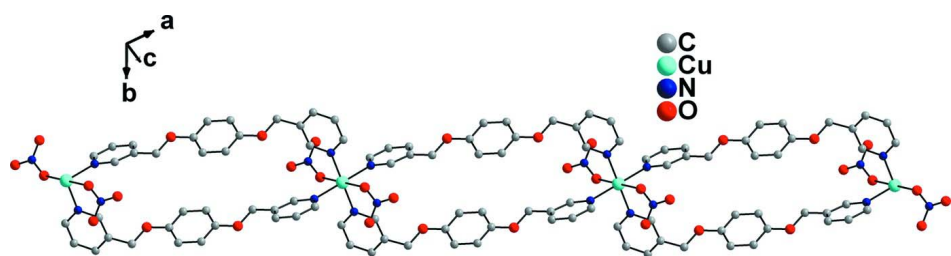
The 1,4-bis(pyridin-3-ylmethoxy)benzene ligand was synthesized as the reference method (Liu *et al.*, 2010a): A mixture of 1,4-dihydroxybenzene (1.1 g, 10 mmol), 3-chloromethylpyridine hydrochloride (3.28 g, 20 mmol) and NaOH (1.6 g, 40 mmol) in acetonitrile (50 ml) was refluxed under nitrogen with stirring for 24 h. After cooling to room temperature, the solution was filtered and the residue was washed with acetonitrile for several times. The mixed filtrate was dropped into 300 ml water solution to get the powder crude product. A total of 2.51 g (yield 86%) pure product was obtained by recrystallizing from the mixed solution of 10 ml water and 10 ml methanol. The title compound was synthesized by reaction of 1,4-bis(pyridin-3-ylmethoxy)benzene ligand (0.29 g, 1.0 mmol) and Cu(NO₃)₂·3H₂O (0.22 g, 1.0 mmol) in 5 ml water and 5 ml methanol mixed solution. After filtration, blue block crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature for several days in 46% yield.

S3. Refinement

O4 atom of nitrate was disordered over two positions with site occupancy factors of *ca* 0.51 and 0.49, and then, the two positions were restraint refined with command 'Iosr 0.01 O4 O4''. H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.93 Å (aromatic); C—H = 0.97 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.


Figure 1

The molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level for non-H atoms, disordered O4' atom has been omitted for clarity.


Figure 2

A partial packing view, showing the ribbon structure along [2 0 1] direction. Disordered O4' atoms and no involving H atoms have been omitted for clarity.

catena-Poly[[bis(nitrato- κ O)copper(II)]-bis[μ -1,4-bis(pyridin-3-ylmethoxy)benzene- κ^2 N:N']]

Crystal data

[Cu(NO₃)₂(C₁₈H₁₆N₂O₂)₂]

$M_r = 772.22$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 8.4859$ (17) Å

$b = 17.030$ (3) Å

$c = 12.986$ (4) Å

$\beta = 116.22$ (2)°

$V = 1683.6$ (7) Å³

$Z = 2$

$F(000) = 798$

$D_x = 1.523$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 13022 reflections

$\theta = 3.4$ – 27.4 °

$\mu = 0.72$ mm⁻¹

$T = 291$ K

Block, blue

$0.20 \times 0.18 \times 0.17$ mm

Data collection

Rigaku R-AXIS RAPID
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.867$, $T_{\max} = 0.889$

16256 measured reflections

3831 independent reflections

3067 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.4$ °

$h = -11 \rightarrow 10$

$k = -22 \rightarrow 22$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.097$
 $S = 1.07$
 3831 reflections
 251 parameters
 12 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.4137P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	-0.3511 (2)	0.87028 (12)	0.16557 (18)	0.0353 (4)	
H1	-0.4698	0.8612	0.1432	0.042*	
C2	-0.2290 (3)	0.82377 (13)	0.25037 (19)	0.0383 (5)	
H2	-0.2657	0.7837	0.2833	0.046*	
C3	-0.0520 (3)	0.83705 (12)	0.28601 (18)	0.0351 (4)	
H3	0.0317	0.8065	0.3435	0.042*	
C4	-0.0017 (2)	0.89662 (11)	0.23463 (17)	0.0303 (4)	
C5	-0.1310 (2)	0.93984 (12)	0.14835 (18)	0.0325 (4)	
H5	-0.0970	0.9788	0.1120	0.039*	
C6	0.1879 (2)	0.91934 (13)	0.27306 (19)	0.0385 (5)	
H6A	0.2070	0.9342	0.2073	0.046*	
H6B	0.2181	0.9637	0.3252	0.046*	
C7	0.4713 (2)	0.86583 (12)	0.39043 (19)	0.0372 (5)	
C8	0.5671 (2)	0.80017 (12)	0.44675 (18)	0.0350 (4)	
H8	0.5101	0.7526	0.4415	0.042*	
C9	0.7480 (2)	0.80513 (12)	0.51103 (18)	0.0349 (4)	
H9	0.8124	0.7609	0.5482	0.042*	
C10	0.8320 (2)	0.87615 (12)	0.51957 (18)	0.0360 (5)	
C11	0.7367 (3)	0.94163 (13)	0.4634 (2)	0.0419 (5)	
H11	0.7937	0.9892	0.4690	0.050*	
C12	0.5558 (3)	0.93666 (13)	0.3987 (2)	0.0425 (5)	
H12	0.4917	0.9808	0.3611	0.051*	
C13	1.1170 (2)	0.82248 (12)	0.63460 (19)	0.0381 (5)	
H13A	1.1171	0.7852	0.5781	0.046*	
H13B	1.0739	0.7963	0.6835	0.046*	

C14	1.2990 (2)	0.85426 (11)	0.70499 (17)	0.0305 (4)	
C15	1.4412 (3)	0.83865 (12)	0.68279 (19)	0.0375 (5)	
H15	1.4282	0.8078	0.6205	0.045*	
C16	1.6027 (3)	0.86992 (12)	0.75514 (19)	0.0377 (5)	
H16	1.6998	0.8600	0.7418	0.045*	
C17	1.6204 (2)	0.91564 (11)	0.84668 (18)	0.0319 (4)	
H17	1.7306	0.9354	0.8955	0.038*	
C18	1.3260 (2)	0.90220 (11)	0.79731 (16)	0.0300 (4)	
H18	1.2301	0.9139	0.8113	0.036*	
Cu1	-0.5000	1.0000	0.0000	0.03106 (12)	
N1	-0.30485 (19)	0.92812 (9)	0.11430 (14)	0.0304 (3)	
N2	1.48165 (18)	0.93268 (9)	0.86752 (13)	0.0279 (3)	
N3	-0.8293 (2)	0.86505 (11)	-0.01848 (17)	0.0411 (4)	
O1	0.29285 (18)	0.85382 (9)	0.32890 (17)	0.0579 (5)	
O2	1.01067 (18)	0.88797 (9)	0.57993 (16)	0.0536 (5)	
O3	-0.74035 (19)	0.92569 (8)	0.02595 (14)	0.0421 (4)	
O4	-0.9828 (11)	0.8623 (6)	-0.035 (2)	0.085 (4)	0.49 (4)
O5	-0.7554 (2)	0.80297 (10)	-0.01836 (19)	0.0654 (5)	
O4'	-0.9848 (9)	0.8748 (6)	-0.0923 (18)	0.080 (4)	0.51 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0205 (9)	0.0423 (11)	0.0386 (11)	-0.0021 (8)	0.0088 (8)	-0.0068 (9)
C2	0.0323 (10)	0.0405 (11)	0.0392 (12)	-0.0036 (9)	0.0132 (9)	0.0031 (9)
C3	0.0270 (9)	0.0401 (11)	0.0304 (10)	0.0059 (8)	0.0056 (8)	0.0042 (8)
C4	0.0195 (8)	0.0351 (10)	0.0305 (10)	0.0041 (7)	0.0058 (7)	-0.0003 (8)
C5	0.0216 (9)	0.0352 (10)	0.0343 (10)	0.0040 (7)	0.0065 (8)	0.0048 (8)
C6	0.0194 (9)	0.0427 (11)	0.0436 (12)	0.0033 (8)	0.0049 (9)	0.0093 (9)
C7	0.0152 (8)	0.0442 (11)	0.0429 (12)	0.0024 (8)	0.0044 (8)	0.0069 (9)
C8	0.0236 (9)	0.0351 (10)	0.0415 (12)	-0.0008 (8)	0.0100 (9)	0.0045 (9)
C9	0.0233 (9)	0.0365 (10)	0.0360 (11)	0.0040 (8)	0.0050 (8)	0.0043 (8)
C10	0.0179 (8)	0.0424 (11)	0.0355 (11)	-0.0001 (8)	0.0008 (8)	0.0011 (9)
C11	0.0252 (10)	0.0369 (11)	0.0524 (14)	-0.0033 (8)	0.0069 (9)	0.0042 (10)
C12	0.0247 (10)	0.0383 (11)	0.0518 (13)	0.0057 (8)	0.0054 (9)	0.0119 (10)
C13	0.0216 (9)	0.0371 (10)	0.0417 (12)	0.0011 (8)	0.0012 (8)	-0.0056 (9)
C14	0.0206 (8)	0.0306 (9)	0.0308 (10)	0.0011 (7)	0.0028 (8)	-0.0006 (8)
C15	0.0323 (10)	0.0383 (11)	0.0383 (11)	0.0028 (8)	0.0123 (9)	-0.0087 (9)
C16	0.0251 (9)	0.0400 (11)	0.0489 (13)	0.0013 (8)	0.0172 (9)	-0.0063 (9)
C17	0.0184 (8)	0.0316 (9)	0.0385 (11)	0.0010 (7)	0.0059 (8)	-0.0019 (8)
C18	0.0164 (8)	0.0376 (10)	0.0299 (10)	0.0025 (7)	0.0046 (7)	-0.0007 (8)
Cu1	0.01777 (16)	0.03750 (19)	0.02666 (18)	0.00767 (13)	-0.00042 (12)	-0.00511 (14)
N1	0.0193 (7)	0.0353 (8)	0.0292 (8)	0.0048 (6)	0.0041 (6)	-0.0024 (7)
N2	0.0186 (7)	0.0312 (8)	0.0289 (8)	0.0032 (6)	0.0059 (6)	-0.0011 (6)
N3	0.0276 (9)	0.0427 (10)	0.0492 (11)	-0.0003 (7)	0.0136 (8)	0.0019 (8)
O1	0.0167 (7)	0.0448 (9)	0.0878 (14)	0.0030 (6)	0.0009 (8)	0.0187 (9)
O2	0.0205 (7)	0.0427 (9)	0.0697 (12)	-0.0023 (6)	-0.0055 (7)	0.0095 (8)
O3	0.0392 (8)	0.0356 (7)	0.0475 (9)	-0.0028 (6)	0.0154 (7)	-0.0007 (7)

O4	0.028 (2)	0.096 (4)	0.124 (9)	0.000 (2)	0.027 (4)	0.004 (5)
O5	0.0593 (11)	0.0374 (9)	0.0899 (15)	0.0023 (8)	0.0243 (11)	-0.0022 (9)
O4'	0.022 (2)	0.086 (4)	0.102 (8)	-0.005 (2)	0.001 (3)	-0.006 (4)

Geometric parameters (Å, °)

C1—N1	1.341 (3)	C13—O2	1.413 (2)
C1—C2	1.380 (3)	C13—C14	1.505 (3)
C1—H1	0.9300	C13—H13A	0.9700
C2—C3	1.381 (3)	C13—H13B	0.9700
C2—H2	0.9300	C14—C18	1.383 (3)
C3—C4	1.381 (3)	C14—C15	1.385 (3)
C3—H3	0.9300	C15—C16	1.381 (3)
C4—C5	1.384 (3)	C15—H15	0.9300
C4—C6	1.509 (3)	C16—C17	1.373 (3)
C5—N1	1.354 (2)	C16—H16	0.9300
C5—H5	0.9300	C17—N2	1.351 (2)
C6—O1	1.412 (2)	C17—H17	0.9300
C6—H6A	0.9700	C18—N2	1.334 (2)
C6—H6B	0.9700	C18—H18	0.9300
C7—O1	1.380 (2)	Cu1—N2 ⁱ	2.0153 (16)
C7—C12	1.383 (3)	Cu1—N2 ⁱⁱ	2.0153 (16)
C7—C8	1.386 (3)	Cu1—N1	2.0669 (16)
C8—C9	1.389 (3)	Cu1—N1 ⁱⁱⁱ	2.0669 (16)
C8—H8	0.9300	Cu1—O3	2.5460 (15)
C9—C10	1.383 (3)	N2—Cu1 ^{iv}	2.0153 (16)
C9—H9	0.9300	N3—O4	1.226 (7)
C10—O2	1.380 (2)	N3—O5	1.229 (2)
C10—C11	1.382 (3)	N3—O4'	1.253 (8)
C11—C12	1.389 (3)	N3—O3	1.259 (2)
C11—H11	0.9300	O4—O4'	0.773 (8)
C12—H12	0.9300		
N1—C1—C2	122.43 (18)	H13A—C13—H13B	108.7
N1—C1—H1	118.8	C18—C14—C15	117.88 (17)
C2—C1—H1	118.8	C18—C14—C13	118.12 (17)
C1—C2—C3	119.7 (2)	C15—C14—C13	124.00 (18)
C1—C2—H2	120.1	C16—C15—C14	118.58 (19)
C3—C2—H2	120.1	C16—C15—H15	120.7
C2—C3—C4	118.72 (18)	C14—C15—H15	120.7
C2—C3—H3	120.6	C17—C16—C15	120.29 (18)
C4—C3—H3	120.6	C17—C16—H16	119.9
C3—C4—C5	118.58 (17)	C15—C16—H16	119.9
C3—C4—C6	122.69 (17)	N2—C17—C16	121.55 (17)
C5—C4—C6	118.65 (18)	N2—C17—H17	119.2
N1—C5—C4	123.05 (19)	C16—C17—H17	119.2
N1—C5—H5	118.5	N2—C18—C14	123.85 (17)
C4—C5—H5	118.5	N2—C18—H18	118.1

O1—C6—C4	107.81 (17)	C14—C18—H18	118.1
O1—C6—H6A	110.1	N2 ⁱ —Cu1—N2 ⁱⁱ	180.000 (1)
C4—C6—H6A	110.1	N2 ⁱ —Cu1—N1	89.35 (6)
O1—C6—H6B	110.1	N2 ⁱⁱ —Cu1—N1	90.65 (6)
C4—C6—H6B	110.1	N2 ⁱ —Cu1—N1 ⁱⁱⁱ	90.65 (6)
H6A—C6—H6B	108.5	N2 ⁱⁱ —Cu1—N1 ⁱⁱⁱ	89.35 (6)
O1—C7—C12	124.94 (18)	N1—Cu1—N1 ⁱⁱⁱ	180.000 (1)
O1—C7—C8	115.08 (18)	N2 ⁱ —Cu1—O3	86.22 (6)
C12—C7—C8	119.98 (17)	N2 ⁱⁱ —Cu1—O3	93.78 (6)
C7—C8—C9	120.21 (19)	N1—Cu1—O3	92.59 (6)
C7—C8—H8	119.9	N1 ⁱⁱⁱ —Cu1—O3	87.41 (6)
C9—C8—H8	119.9	C1—N1—C5	117.48 (16)
C10—C9—C8	119.67 (18)	C1—N1—Cu1	118.31 (12)
C10—C9—H9	120.2	C5—N1—Cu1	123.96 (13)
C8—C9—H9	120.2	C18—N2—C17	117.81 (16)
O2—C10—C11	114.98 (18)	C18—N2—Cu1 ^{iv}	118.98 (12)
O2—C10—C9	124.83 (18)	C17—N2—Cu1 ^{iv}	123.21 (13)
C11—C10—C9	120.18 (17)	O4—N3—O5	118.1 (5)
C10—C11—C12	120.20 (19)	O4—N3—O4'	36.3 (4)
C10—C11—H11	119.9	O5—N3—O4'	118.6 (4)
C12—C11—H11	119.9	O4—N3—O3	119.1 (5)
C7—C12—C11	119.76 (19)	O5—N3—O3	120.22 (18)
C7—C12—H12	120.1	O4'—N3—O3	117.2 (5)
C11—C12—H12	120.1	C7—O1—C6	117.53 (16)
O2—C13—C14	106.10 (16)	C10—O2—C13	117.89 (16)
O2—C13—H13A	110.5	N3—O3—Cu1	134.44 (13)
C14—C13—H13A	110.5	O4'—O4—N3	73.8 (10)
O2—C13—H13B	110.5	O4—O4'—N3	69.9 (10)
C14—C13—H13B	110.5		

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