



Crystal structure of poly[(4-aminopyridine- κ N)-(N,N-dimethylformamide- κ O)(μ_3 -pyridine-3,5-dicarboxylato- κ^3 N:O³:O⁵)copper(II)]

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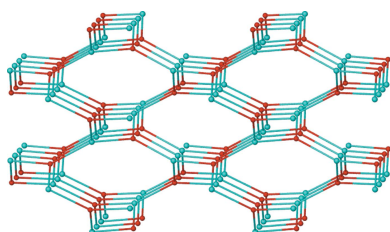
The title compound, $[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)(\text{C}_5\text{H}_6\text{N}_2)(\text{C}_3\text{H}_7\text{NO})]_n$, is an amino-functionalized chiral metal–organic framework with (10,3)-a topology. It has been constructed *via* the assembly of the achiral triconnected pyridine-3,5-dicarboxylate (3,5-PDC) building block and a triconnected Cu^{II} atom. Each Cu^{II} ion is coordinated by two O atoms and one N atom, respectively, of three crystallographically independent 3,5-PDC ligands. The square-pyramidal (CuN_2O_3) coordination geometry of the Cu^{II} ion is completed by an N atom of a terminal 4-aminopyridine (4-APY) ligand and the O atom of a terminal N,N-dimethylformamide (DMF) ligand to give a triconnected 'T'-shaped secondary building unit, which becomes trigonal in the resulting (10,3)-a topology. In the three-dimensional structure, weak N–H...O hydrogen bonds are observed in which the donor N–H groups are provided by the 4-APY ligands and the acceptor O atoms are provided by the non-coordinating carboxylate O atoms of the 3,5-PDC ligands.

1. Chemical context

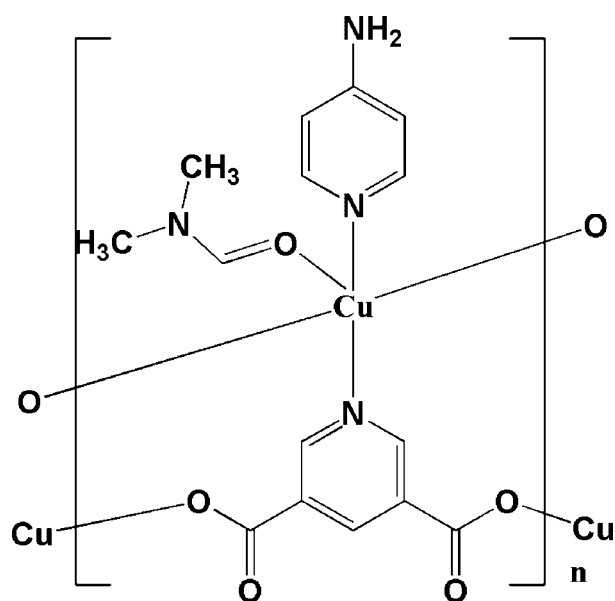
Research on metal–organic frameworks (MOFs) has attracted much attention in recent years not only for their great potential applications, such as in gas storage, separation, fluorescence and magnetism, but also for their intriguing topologies and structural diversity (Allendorf *et al.*, 2009). Of special interest is the rational design and synthesis of chiral networks, which offer great potential in non-linear optics, asymmetric catalysis, and chiral separation (Evans & Lin, 2002; Zhang & Xiong, 2012). Therefore, a logical target for synthesis would be a default structure that possesses chirality. The (10,3)-a network meets these requirements since it is mutually chiral and regarded as the default three-dimensional structure for the assembly of triconnected building blocks (Eubank *et al.*, 2005; Han *et al.*, 2013a).

On the other hand, amino-functionalized porous metal–organic frameworks have also attracted much attention. Recent research on amino-functionalized MOFs revealed that they have high CO_2 adsorption capacity at lower pressure due to the potential interaction between amino groups and CO_2 (Couck *et al.*, 2009). Amino-functionalized MOFs can also act as reaction active sites for the post-synthesis modification of metal–organic frameworks (Shultz *et al.*, 2011).

As a continuation of our group research on the assembly of amino-functionalized chiral metal–organic frameworks (Han *et al.*, 2011, 2013b; Pan *et al.*, 2014), we herein report the preparation and crystal structure of $\text{Cu}(3,5\text{-PDC})(4\text{-APY})\text{(DMF)}$, (3,5-PDC = pyridine-3,5-dicarboxylate, 4-APY =



4-aminopyridine, DMF = *N,N*-dimethylformamide), which was constructed *via* the assembly of the achiral triconnected building block pyridine-3,5-dicarboxylate (3,5- PDC) and a triconnected Cu^{II} atom, $\text{CuN}(\text{CO}_2)_2$, synthesized *in situ*. The title compound is an interesting example of an amino-functionalized chiral metal-organic framework with (10,3)-*a* topology assembled from achiral ligands. This amino-functionalized chiral framework can be used for depositing small gold nanoparticles using a solution-based adsorption/reduction preparation method, and offer myriad opportunities for chiral catalysis.



2. Structural commentary

The asymmetric unit of the title compound, $\text{Cu}(3,5\text{-PDC})(4\text{-APY})(\text{DMF})$, contains one Cu^{II} ion, one 3,5-PDC anion, one 4-apy molecule and one DMF molecule. As shown in Fig. 1, each Cu^{II} ion adopts a square-pyramidal (CuN_2O_3) coordin-

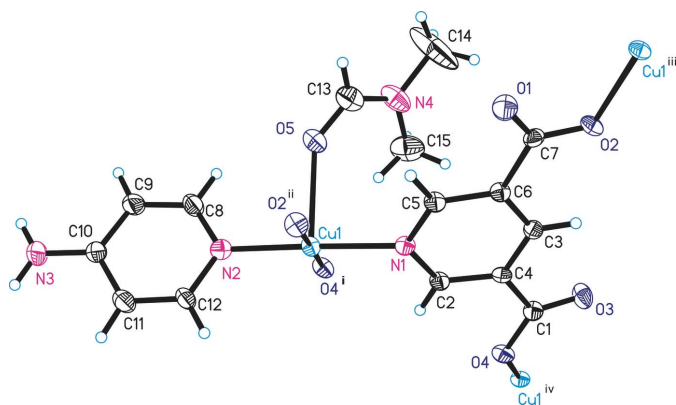


Figure 1

The asymmetric unit of title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.]

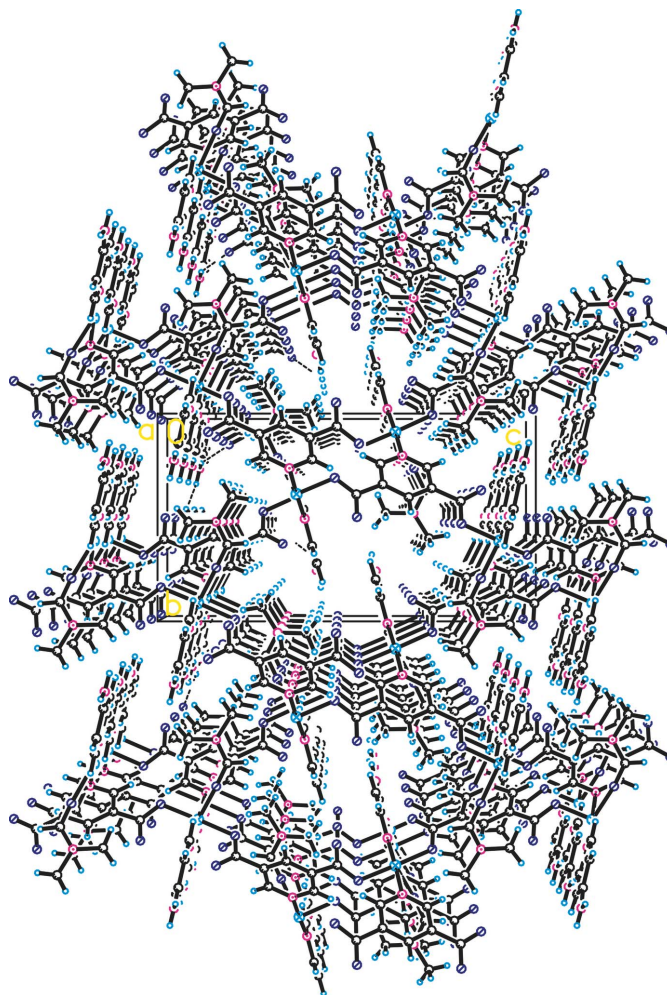


Figure 2

Crystal packing of the title compound viewed along the *a* axis, showing hydrogen bonds as dashed lines.

ation geometry. In the equatorial plane, the Cu^{II} ion is coordinated by two oxygen atoms and one nitrogen atom, respectively, of three crystallographically independent 3,5-PDC ligands, and one nitrogen atom of a terminal 4-APY ligand. The oxygen atom of a terminal DMF molecule is bonded to the Cu^{II} ion in the axial position to complete the square-pyramidal coordination geometry. The bond lengths and bond angles around the Cu^{II} ion are in good agreement with similar structures (Eubank *et al.*, 2005; Lu *et al.*, 2006). The axial $\text{Cu}-\text{O}_{\text{DMF}}$ bond length [2.396 (4) Å] is longer than the equatorial $\text{Cu}-\text{O}_{\text{carboxylate}}$ and $\text{Cu}-\text{N}_{4\text{-APY}}$ bonds due to the Jahn–Teller effect of the Cu^{2+} atom.

The three-dimensional structure of the title compound viewed along the *a* axis is shown in Fig. 2. To analyse the topology, the square-pyramidal coordination geometry of copper can act as a ‘T-shaped triconnected secondary building unit (Fig. 2), which becomes trigonal in the resulting topology. At the same time, 3,5-PDC acts as another triconnected node since it possesses two deprotonated carboxylic acid coordinating sites, and a third, neutral aromatic nitrogen coordinating site. As a result, the desired triconnected (10,3)-*a* network is obtained, as shown in Fig. 3. The terminally coor-

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-H3A\cdots O3^i$	0.86	2.28	3.101 (7)	159
$N3-H3B\cdots O1^{ii}$	0.86	2.23	2.933 (7)	139

Symmetry codes: (i) $x-1, y-1, z$; (ii) $-x-1, y-\frac{1}{2}, -z+\frac{3}{2}$.

minated 4-APY and DMF ligands are oriented to the interior of the channels and thus prevent self-interpenetration. The (10,3)-*a* topology leads to an enantiopure network of the title compound (Eubank *et al.*, 2005; Han *et al.*, 2013a), despite being formed solely from achiral molecular units.

3. Supramolecular features

By introducing 4-aminopyridine as co-ligand, the amino-functionalized chiral metal-organic framework was successfully designed and synthesized. Additionally, the $-NH_2$ group of the 4-APY ligand can act as the donor N–H groups to form hydrogen bonds (Han *et al.*, 2011). In the three-dimensional structure of the title compound, weak N–H \cdots O hydrogen bonds are observed (Table 1) in which the acceptors are provided by the non-coordinating oxygen atoms of the carboxylate groups of the 3,5-PDC ligands.

4. Synthesis and crystallization

The title compound was prepared by a solvothermal method. A mixture of pyridine-3,5-dicarboxylic acid (0.0339 g, 0.2 mmol), 4-aminopyridine (0.0098 g, 0.10 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.0484 g, 0.20 mmol) in 6 ml DMF solution was stirred at room temperature for 30 minutes, and subsequently sealed in a 25 ml Teflon-lined stainless steel reactor. The reactor was heated at 363 K for 3 d. A crop of blue, block-shaped single crystals of the title compound was obtained after cooling the solution to room temperature. The yield was approximately 70% based on Cu salt.

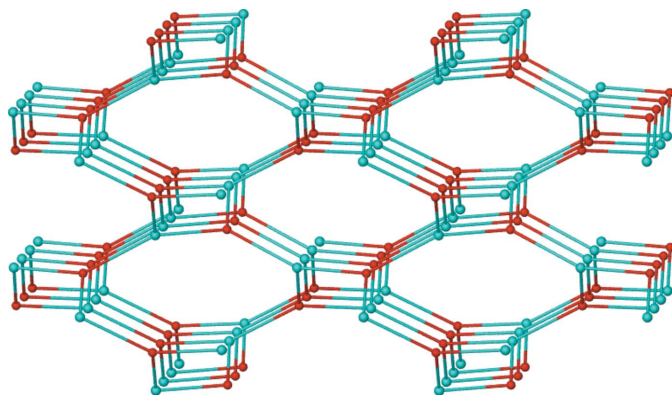


Figure 3
A representation of the (10,3)-*a* topology.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_7H_3NO_4)(C_5H_6N_2)(C_3H_7NO)]$
M_r	395.86
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	293
a, b, c (Å)	8.3365 (17), 10.453 (2), 19.030 (4)
V (Å ³)	1658.2 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.35
Crystal size (mm)	0.24 × 0.20 × 0.19
Data collection	
Diffractometer	Bruker APEXII DUO CCD
Absorption correction	Analytical [based on measured indexed crystal faces using <i>SHELXL2014</i> (Sheldrick, 2015b)]
T_{min}, T_{max}	0.716, 0.773
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16376, 3799, 2926
R_{int}	0.051
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.132, 1.15
No. of reflections	3799
No. of parameters	226
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.79, -1.17
Absolute structure	Flack (1983), 1619 Friedel pairs
Absolute structure parameter	0.00 (2)

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *XP* in *SHELXTL-Plus* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically idealized positions and refined in a riding-model approximation on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ (aromatic) and $1.5U_{eq}(C)$ (methyl) with C–H = 0.93 Å (aromatic) and 0.96 Å (methyl), and $U_{iso}(H) = 1.2U_{eq}(N)$ with N–H = 0.86 Å.

Acknowledgements

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Crystal structure of poly[(4-aminopyridine- κ N)(*N,N*-dimethylformamide- κ O)(μ_3 -pyridine-3,5-dicarboxylato- κ^3 N:O³:O⁵)copper(II)]

Cheng-Chen Shen, Xiu-Ni Hua and Lei Han

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Poly[(4-aminopyridine- κ N)(*N,N*-dimethylformamide- κ O)(μ_3 -pyridine-3,5-dicarboxylato- κ^3 N:O³:O⁵)copper(II)]

Crystal data

[Cu(C₇H₃NO₄)(C₅H₆N₂)(C₃H₇NO)]

$M_r = 395.86$

Orthorhombic, $P2_12_12_1$

$a = 8.3365$ (17) Å

$b = 10.453$ (2) Å

$c = 19.030$ (4) Å

$V = 1658.2$ (6) Å³

$Z = 4$

$F(000) = 812$

$D_x = 1.586$ Mg m⁻³

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

Cell parameters from 2974 reflections

$\theta = 3.1$ – 27.5°

$\mu = 1.35$ mm⁻¹

$T = 293$ K

Block, blue

$0.24 \times 0.20 \times 0.19$ mm

Data collection

Bruker APEXII DUO CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω -scans

Absorption correction: analytical

[based on measured indexed crystal faces using
SHELXL2014 (Sheldrick, 2015b)]

$T_{\min} = 0.716$, $T_{\max} = 0.773$

16376 measured reflections

3799 independent reflections

2926 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -10 \rightarrow 10$

$k = -13 \rightarrow 13$

$l = -24 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.132$

$S = 1.15$

3799 reflections

226 parameters

0 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

$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 1.9518P]$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.013$$

$$\Delta\rho_{\max} = 0.79 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.17 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 1619 Friedel
pairs
Absolute structure parameter: 0.00 (2)

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	-0.23946 (7)	0.10503 (5)	0.62338 (2)	0.02797 (16)
O1	0.0648 (5)	0.3766 (4)	0.83488 (17)	0.0497 (10)
O2	0.2102 (4)	0.5278 (3)	0.78331 (16)	0.0348 (8)
O3	0.3228 (5)	0.4977 (4)	0.5253 (2)	0.0498 (11)
O4	0.2342 (5)	0.3222 (3)	0.47057 (14)	0.0337 (7)
O5	-0.4048 (6)	0.2700 (4)	0.6723 (3)	0.0605 (12)
N1	-0.0413 (5)	0.2178 (4)	0.63928 (18)	0.0284 (8)
N2	-0.4300 (5)	-0.0057 (4)	0.6043 (2)	0.0347 (10)
N3	-0.8209 (6)	-0.2450 (6)	0.5764 (3)	0.0705 (18)
H3A	-0.8050	-0.3239	0.5657	0.085*
H3B	-0.9170	-0.2170	0.5822	0.085*
N4	-0.3401 (8)	0.4804 (5)	0.6705 (3)	0.0625 (17)
C1	0.2489 (6)	0.3962 (4)	0.5239 (2)	0.0315 (9)
C2	0.0476 (6)	0.2565 (4)	0.5840 (2)	0.0291 (10)
H2A	0.0301	0.2180	0.5406	0.035*
C3	0.1883 (6)	0.4086 (5)	0.6536 (2)	0.0297 (10)
H3C	0.2624	0.4745	0.6582	0.036*
C4	0.1634 (6)	0.3505 (4)	0.5889 (2)	0.0267 (9)
C5	-0.0125 (6)	0.2721 (5)	0.7013 (2)	0.0310 (10)
H5A	-0.0716	0.2450	0.7400	0.037*
C6	0.1011 (6)	0.3670 (4)	0.7112 (2)	0.0278 (10)
C7	0.1250 (6)	0.4263 (5)	0.7828 (2)	0.0316 (11)
C8	-0.5796 (7)	0.0376 (5)	0.6086 (3)	0.0448 (13)
H8A	-0.5945	0.1240	0.6183	0.054*
C9	-0.7126 (7)	-0.0366 (5)	0.5999 (3)	0.0502 (15)
H9A	-0.8141	-0.0008	0.6045	0.060*
C10	-0.6962 (7)	-0.1657 (6)	0.5839 (3)	0.0458 (14)
C11	-0.5405 (7)	-0.2092 (5)	0.5747 (3)	0.0521 (15)
H11A	-0.5225	-0.2933	0.5608	0.062*
C12	-0.4130 (7)	-0.1294 (5)	0.5860 (3)	0.0454 (13)
H12A	-0.3100	-0.1621	0.5808	0.055*
C13	-0.3972 (9)	0.3755 (6)	0.7001 (4)	0.0610 (17)

H13A	-0.4348	0.3824	0.7460	0.073*
C14	-0.330 (2)	0.5962 (7)	0.7100 (5)	0.164 (7)
H14A	-0.3715	0.5821	0.7564	0.246*
H14B	-0.3920	0.6616	0.6872	0.246*
H14C	-0.2201	0.6229	0.7130	0.246*
C15	-0.2832 (11)	0.4792 (7)	0.5991 (4)	0.076 (2)
H15A	-0.2989	0.3957	0.5793	0.114*
H15B	-0.1711	0.5001	0.5983	0.114*
H15C	-0.3418	0.5411	0.5720	0.114*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0355 (3)	0.0291 (3)	0.0193 (2)	-0.0032 (3)	-0.0035 (2)	0.0024 (2)
O1	0.054 (2)	0.074 (3)	0.0212 (16)	-0.017 (2)	0.0063 (16)	-0.0070 (18)
O2	0.044 (2)	0.0349 (16)	0.0254 (15)	-0.0002 (16)	-0.0046 (15)	-0.0092 (14)
O3	0.064 (3)	0.049 (2)	0.0366 (19)	-0.0273 (19)	0.0124 (19)	-0.0012 (17)
O4	0.051 (2)	0.0313 (15)	0.0188 (12)	0.0015 (17)	0.0056 (16)	0.0016 (12)
O5	0.058 (3)	0.047 (2)	0.077 (3)	-0.005 (2)	0.005 (2)	-0.022 (2)
N1	0.033 (2)	0.034 (2)	0.0183 (17)	-0.0005 (17)	0.0000 (15)	0.0018 (16)
N2	0.033 (2)	0.038 (2)	0.033 (2)	0.0032 (17)	-0.0033 (18)	-0.0002 (17)
N3	0.038 (3)	0.061 (3)	0.113 (5)	-0.018 (3)	0.012 (3)	-0.036 (3)
N4	0.101 (5)	0.037 (3)	0.050 (3)	0.003 (3)	-0.014 (3)	-0.001 (2)
C1	0.035 (2)	0.036 (2)	0.0233 (17)	-0.001 (3)	0.001 (2)	0.0029 (18)
C2	0.036 (3)	0.034 (2)	0.0174 (19)	-0.002 (2)	0.0006 (18)	-0.0017 (19)
C3	0.031 (2)	0.032 (2)	0.026 (2)	-0.001 (2)	0.0001 (17)	-0.002 (2)
C4	0.031 (2)	0.027 (2)	0.022 (2)	0.0041 (18)	0.0027 (18)	-0.0020 (18)
C5	0.038 (3)	0.038 (3)	0.0168 (19)	-0.002 (2)	-0.0006 (19)	0.0007 (19)
C6	0.031 (2)	0.033 (2)	0.0201 (19)	0.0017 (19)	-0.0031 (17)	0.0007 (18)
C7	0.025 (2)	0.046 (3)	0.024 (2)	0.001 (2)	0.0020 (18)	-0.006 (2)
C8	0.047 (3)	0.032 (3)	0.056 (4)	-0.002 (2)	-0.003 (3)	-0.007 (3)
C9	0.036 (3)	0.044 (3)	0.070 (4)	0.004 (3)	0.000 (3)	-0.014 (3)
C10	0.036 (3)	0.046 (3)	0.056 (3)	-0.005 (2)	0.004 (2)	-0.015 (3)
C11	0.047 (3)	0.038 (3)	0.071 (4)	-0.001 (3)	-0.003 (3)	-0.016 (3)
C12	0.038 (3)	0.033 (3)	0.065 (4)	-0.004 (2)	-0.002 (3)	-0.016 (3)
C13	0.069 (4)	0.057 (4)	0.057 (4)	0.004 (3)	-0.005 (3)	-0.011 (3)
C14	0.37 (2)	0.047 (4)	0.079 (6)	-0.036 (8)	-0.019 (9)	-0.014 (4)
C15	0.096 (7)	0.053 (4)	0.079 (5)	0.029 (4)	0.008 (4)	0.011 (3)

Geometric parameters (Å, °)

Cu1—O4 ⁱ	1.955 (3)	C2—C4	1.381 (7)
Cu1—O2 ⁱⁱ	1.966 (3)	C2—H2A	0.9300
Cu1—N2	1.999 (4)	C3—C6	1.384 (6)
Cu1—N1	2.052 (4)	C3—C4	1.388 (6)
Cu1—O5	2.396 (4)	C3—H3C	0.9300
O1—C7	1.226 (6)	C5—C6	1.384 (7)
O2—C7	1.277 (6)	C5—H5A	0.9300

O2—Cu1 ⁱⁱⁱ	1.966 (3)	C6—C7	1.511 (6)
O3—C1	1.228 (6)	C8—C9	1.362 (8)
O4—C1	1.281 (5)	C8—H8A	0.9300
O4—Cu1 ^{iv}	1.955 (3)	C9—C10	1.390 (8)
O5—C13	1.225 (7)	C9—H9A	0.9300
N1—C5	1.332 (6)	C10—C11	1.387 (8)
N1—C2	1.349 (6)	C11—C12	1.368 (8)
N2—C8	1.330 (7)	C11—H11A	0.9300
N2—C12	1.346 (6)	C12—H12A	0.9300
N3—C10	1.337 (7)	C13—H13A	0.9300
N3—H3A	0.8600	C14—H14A	0.9600
N3—H3B	0.8600	C14—H14B	0.9600
N4—C13	1.322 (8)	C14—H14C	0.9600
N4—C14	1.428 (9)	C15—H15A	0.9600
N4—C15	1.440 (9)	C15—H15B	0.9600
C1—C4	1.506 (6)	C15—H15C	0.9600
O4 ⁱ —Cu1—O2 ⁱⁱ	178.46 (14)	N1—C5—H5A	118.4
O4 ⁱ —Cu1—N2	88.29 (16)	C6—C5—H5A	118.4
O2 ⁱⁱ —Cu1—N2	91.42 (16)	C3—C6—C5	118.5 (4)
O4 ⁱ —Cu1—N1	90.10 (14)	C3—C6—C7	121.1 (4)
O2 ⁱⁱ —Cu1—N1	90.16 (14)	C5—C6—C7	120.4 (4)
N2—Cu1—N1	177.93 (16)	O1—C7—O2	125.0 (5)
O4 ⁱ —Cu1—O5	90.59 (16)	O1—C7—C6	120.1 (4)
O2 ⁱⁱ —Cu1—O5	90.93 (16)	O2—C7—C6	114.9 (4)
N2—Cu1—O5	91.74 (16)	N2—C8—C9	124.2 (5)
N1—Cu1—O5	89.57 (16)	N2—C8—H8A	117.9
C7—O2—Cu1 ⁱⁱⁱ	114.6 (3)	C9—C8—H8A	117.9
C1—O4—Cu1 ^{iv}	118.5 (3)	C8—C9—C10	119.9 (5)
C13—O5—Cu1	141.8 (5)	C8—C9—H9A	120.0
C5—N1—C2	117.7 (4)	C10—C9—H9A	120.0
C5—N1—Cu1	121.4 (3)	N3—C10—C11	120.7 (5)
C2—N1—Cu1	120.0 (3)	N3—C10—C9	123.3 (5)
C8—N2—C12	116.2 (5)	C11—C10—C9	116.0 (5)
C8—N2—Cu1	122.5 (3)	C12—C11—C10	120.5 (5)
C12—N2—Cu1	121.3 (4)	C12—C11—H11A	119.8
C10—N3—H3A	120.0	C10—C11—H11A	119.8
C10—N3—H3B	120.0	N2—C12—C11	123.0 (5)
H3A—N3—H3B	120.0	N2—C12—H12A	118.5
C13—N4—C14	120.0 (7)	C11—C12—H12A	118.5
C13—N4—C15	121.0 (6)	O5—C13—N4	125.5 (6)
C14—N4—C15	119.0 (7)	O5—C13—H13A	117.3
O3—C1—O4	126.0 (4)	N4—C13—H13A	117.3
O3—C1—C4	119.6 (4)	N4—C14—H14A	109.5
O4—C1—C4	114.4 (4)	N4—C14—H14B	109.5
N1—C2—C4	123.0 (4)	H14A—C14—H14B	109.5
N1—C2—H2A	118.5	N4—C14—H14C	109.5
C4—C2—H2A	118.5	H14A—C14—H14C	109.5

C6—C3—C4	119.1 (4)	H14B—C14—H14C	109.5
C6—C3—H3C	120.5	N4—C15—H15A	109.5
C4—C3—H3C	120.5	N4—C15—H15B	109.5
C2—C4—C3	118.4 (4)	H15A—C15—H15B	109.5
C2—C4—C1	120.1 (4)	N4—C15—H15C	109.5
C3—C4—C1	121.3 (4)	H15A—C15—H15C	109.5
N1—C5—C6	123.3 (4)	H15B—C15—H15C	109.5

Symmetry codes: (i) $x-1/2, -y+1/2, -z+1$; (ii) $-x, y-1/2, -z+3/2$; (iii) $-x, y+1/2, -z+3/2$; (iv) $x+1/2, -y+1/2, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N3—H3A \cdots O3 ^v	0.86	2.28	3.101 (7)	159
N3—H3B \cdots O1 ^{vi}	0.86	2.23	2.933 (7)	139

Symmetry codes: (v) $x-1, y-1, z$; (vi) $-x-1, y-1/2, -z+3/2$.