

# Crystal structure of poly[[*(acetato-κO)*{ $\mu_3$ -*N*-[(*pyridin-4-yl*)methyl]pyrazine-2-carboxamido- $\kappa^4$ *N:N^1,N^2:N^4*]copper(II)] dihydrate]: a metal–organic framework (MOF)

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**Keywords:** crystal structure; metal–organic framework; 10 (3) network topology; copper(II); pyrazine-2-carboxamide

**CCDC reference:** 1004264

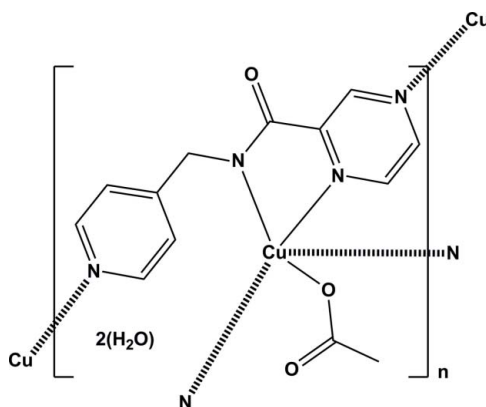
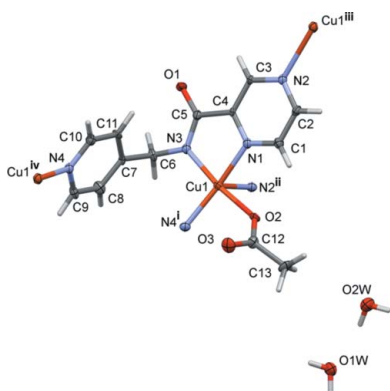
**Supporting information:** this article has supporting information at journals.iucr.org/e

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The title compound, [Cu(C<sub>11</sub>H<sub>9</sub>N<sub>4</sub>O)(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O (CuL), is a hydrated copper acetate complex of the ligand *N*-[(*pyridin-4-yl*)methyl]pyrazine-2-carboxamide (HL). Complex CuL has a metal–organic framework (MOF) structure with a 10 (3) network topology. The ligand coordinates in a bidentate and a bis-monodentate manner, bridging three equivalent Cu<sup>II</sup> atoms *via* the pyridine N atom and the second pyrazine N atom. The Cu<sup>II</sup> atom has a fivefold coordination sphere, CuN<sub>4</sub>O, being coordinated to three N atoms of the ligand and the acetate O atom in the equatorial plane and to the second pyrazine atom in the apical position. This gives rise to a fairly regular square-pyramidal geometry. In the crystal, the water molecules are linked to each other and to the three-dimensional framework *via* O–H···O hydrogen bonds. There are also a number of C–H···O hydrogen bonds present within the framework.

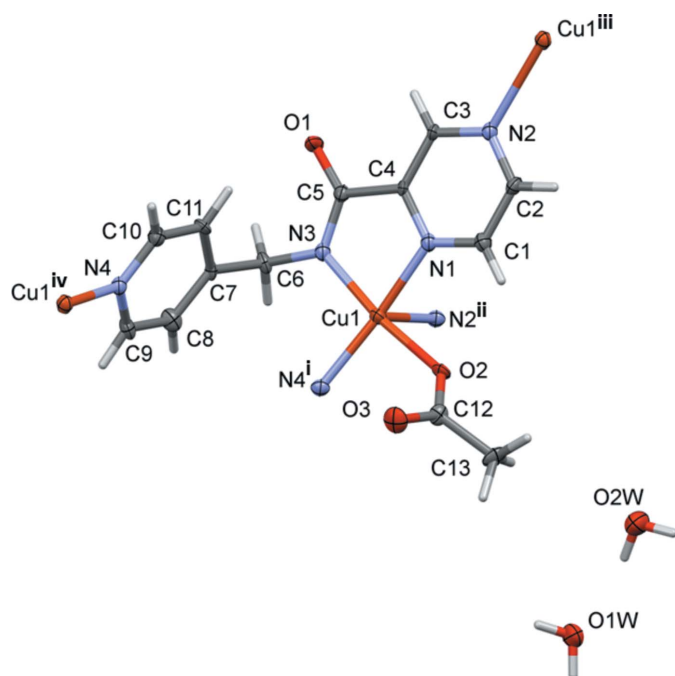
## 1. Chemical context

The ligand *N*-[(*pyridin-4-yl*)methyl]pyrazine-2-carboxamide (HL) is one of a series of ligands which were synthesized in order to study their coordination behaviour towards first-row transition metals (Cati, 2002; Cati *et al.*, 2004; Cati & Stoeckli-Evans, 2014). HL is expected to coordinate in a bidentate and possibly a monodentate manner, with eventual bridging of metal atoms to construct two- or three-dimensional networks. A excellent review on the subject of coordination polymers and network structures has been published by Batten *et al.* (2009).



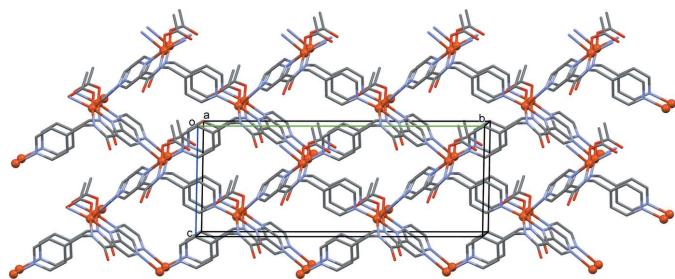
## 2. Structural commentary

The title compound, CuL, is a copper acetate complex of the ligand *N*-[(*pyridin-4-yl*)methyl]pyrazine-2-carboxamide (HL)



**Figure 1**  
A view of the asymmetric unit of complex CuL, with atom labelling [symmetry codes: (i)  $x, -y, z - \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $x, -y, z + \frac{1}{2}$ ]. Displacement ellipsoids are drawn at the 50% probability level.

[Cati & Stoeckli-Evans, 2014]. In complex CuL the ligand coordinates in a bidentate and a bis-monodentate manner, so bridging three equivalent copper atoms (Fig. 1). This gives rise to the formation of a three-dimensional coordination polymer, or MOF (metal–organic framework) structure, as shown in Fig. 2. The copper···copper distances are 7.156 (2) Å *via* the bridging pyrazine ring (Cu1···Cu1<sup>iii</sup>) and 7.420 (2) Å *via* the pyridine N atom Cu1···Cu1<sup>iv</sup>; see Fig. 1). Atom Cu1 has a fivefold coordination sphere, CuN<sub>4</sub>O, with three N atoms (N1, N3 and N4<sup>i</sup>) and the acetate O atom, O2, in the equatorial plane and the second pyrazine N atom, N2<sup>ii</sup>, in the apical position [Fig. 2; symmetry codes: (i)  $x, -y, z - \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ]. The apical Cu1–N2 bond distance of 2.393 (3) Å is considerably longer than the Cu1–N1, Cu1–N3 and Cu1–N4 bond lengths [2.003 (8), 1.964 (9) and 1.993 (7) Å, respectively], and the Cu1–O2 bond length



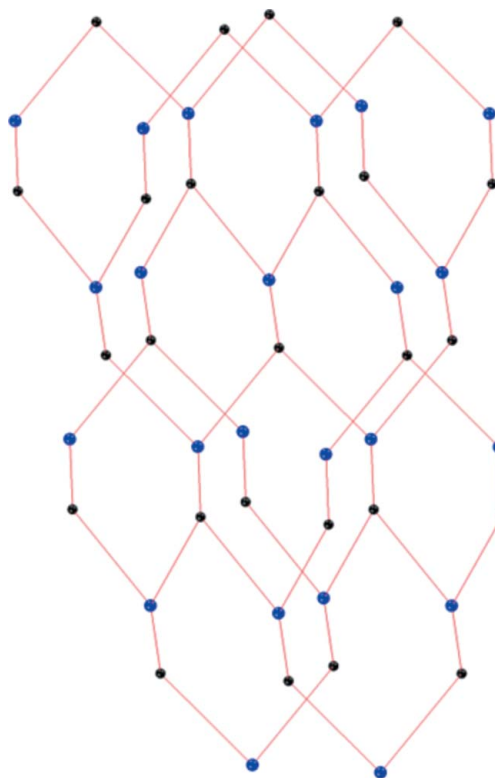
**Figure 2**  
A view along the *a* axis of the metal–organic framework (MOF) structure of complex CuL. Solvent water molecules and H atoms have been omitted for clarity.

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

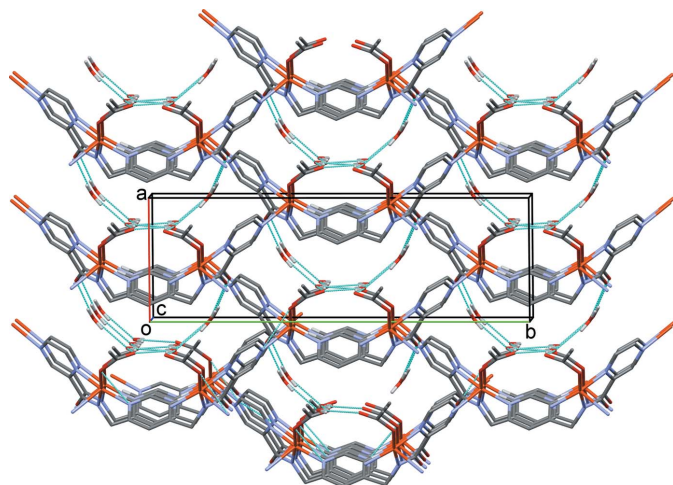
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1W–H1WA···O3 <sup>i</sup>	0.84 (3)	2.13 (5)	2.908 (9)	154 (9)
O1W–H1WB···O3 <sup>iii</sup>	0.84 (3)	2.23 (5)	2.964 (10)	146 (8)
O2W–H2WA···O1W	0.86 (3)	2.11 (4)	2.951 (10)	165 (10)
O2W–H2WB···O1 <sup>iv</sup>	0.85 (3)	2.20 (3)	3.033 (8)	169 (10)
C2–H2···O2 <sup>v</sup>	0.95	2.37	2.987 (13)	123
C8–H8···O3 <sup>vi</sup>	0.95	2.57	3.364 (11)	141
C9–H9···O2W <sup>vii</sup>	0.95	2.50	3.358 (12)	151

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

[1.947 (7) Å] in the equatorial plane. Bond angles O2–Cu1–N3 and N4–Cu1–N1 are 172.2 (3) and 170.6 (3)°, respectively, and this leads to a perfect square-pyramidal geometry with  $\tau = 0.03$  ( $\tau = 0$  square-pyramidal;  $\tau = 1$  trigonal-bipyramidal; Addison *et al.*, 1984). The pyridine ring is inclined to the pyrazine ring by 79.6 (5)° compared to 84.33 (12)° in the free ligand (Cati & Stoeckli-Evans, 2014). The bond distances and angles are normal when compared with geometrical parameters of related copper(II) complexes in the Cambridge Structural Database (Version 5.35, last update November 2013; Allen, 2002), and are similar to those observed in the mononuclear copper(II) acetate complex of the analogous ligand *N*-[(pyridin-2-yl)methyl]pyrazine-2-carboxamide (Mohamadou *et al.*, 2012). The title compound crystallizes with two solvent water molecules per asymmetric unit.



**Figure 3**  
A view of the 10(3) network topology of the title metal–organic framework (MOF) structure, illustrating the 3-connected three-dimensional nets with ten-membered rings.


**Figure 4**

A view along the *c* axis of the crystal packing of complex CuL, with the hydrogen bonds involving the water molecules shown as dashed lines (see Table 1 for details; H atoms not involved in these hydrogen bonding have been omitted for clarity).

### 3. Supramolecular features

The three-dimensional network of the title MOF structure has a 10 (3) network topology (Fig. 3). It is one of the most commonly encountered 3-connected three-dimensional nets with ten-membered rings (Wells, 1984). It is a cubic (10,3)-a net, also known as the srs (SrSi<sub>2</sub>) net, which is chiral [note that the Flack *x* parameter = −0.01 (3)]. Such structures contain fourfold helices along the three axes all of the same hand (Batten *et al.*, 2009).

In the crystal of CuL, the water molecules are located in the cavities of the MOF structure. They are hydrogen bonded to one another and to the ligand and acetate carbonyl O atoms (Table 1 and Fig. 4). There are also a number of C—H...O hydrogen bonds present within the framework (Table 1).

### 4. Database survey

A search of the Cambridge Structural Database (Version 5.35, last update November 2013; Allen, 2002) indicated that no complexes of the ligand HL have been described previously. The analogous ligand *N*-[(pyridin-2-yl)methyl]pyrazine-2-carboxamide has been described as well as a number of metal complexes. These include the mononuclear copper acetate complex (Mohamadou *et al.*, 2012). Here this ligand coordinates in a tridentate manner but in a number of other complexes it coordinates in a bis-monodentate manner *via* the pyridine N atom and a pyrazine N atom; for example, in two polymeric mercury chloride complexes (Khavasi *et al.*, 2010), and a polymeric silver tetrafluoroborate complex (Hellyer *et al.*, 2009).

### 5. Synthesis and crystallization

The synthesis of the ligand *N*-[(pyridin-4-yl)methyl]pyrazine-2-carboxamide (HL) has been described elsewhere (Cati,

**Table 2**

Experimental details.

Crystal data	
Chemical formula	[Cu(C <sub>11</sub> H <sub>9</sub> N <sub>4</sub> O)(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )]·2H <sub>2</sub> O
<i>M<sub>r</sub></i>	371.84
Crystal system, space group	Monoclinic, <i>Cc</i>
Temperature (K)	153
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.8256 (12), 22.331 (2), 8.9976 (13)
$\beta$ (°)	110.040 (16)
<i>V</i> (Å <sup>3</sup> )	1477.2 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>−1</sup> )	1.51
Crystal size (mm)	0.40 × 0.30 × 0.30
Data collection	
Diffractometer	Stoe <i>IPDS I</i>
Absorption correction	Multi-scan ( <i>MULscanABS</i> in <i>PLATON</i> ; Spek, 2009)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.979, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	5730, 2705, 1778
<i>R<sub>int</sub></i>	0.070
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>−1</sup> )	0.615
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.040, 0.072, 0.78
No. of reflections	2705
No. of parameters	203
No. of restraints	8
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>−3</sup> )	0.40, −0.59
Absolute structure	Flack <i>x</i> determined using 665 quotients [( <i>I</i> <sup>+</sup> − <i>I</i> <sup>−</sup> )/( <i>I</i> <sup>+</sup> + <i>I</i> <sup>−</sup> )] (Parsons & Flack, 2004)
Absolute structure parameter	−0.01 (3)

Computer programs: *EXPOSE* in *IPDS I*, *CELL* and *INTEGRATE* in *IPDS I* (Stoe & Cie, 2004), *SHELXS97* and *SHELXL2013* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

2002; Cati & Stoeckli-Evans, 2014). Complex CuL was prepared by adding Cu(acetate)<sub>2</sub>·H<sub>2</sub>O (64 mg, 0.318 mmol) to a hot solution (323 K) of HL (68 mg, 0.318 mmol) in dry methanol (25 ml). In 2 min a precipitate appeared and heating was stopped and the mixture stirred as the temperature decreased to room temperature. After 30 min the precipitate was filtered off and washed with dry methanol. It was then dissolved in a mixture of water (12 ml) and methanol (15 ml) and stirred with warming to between 313 to 323 K for 15 min. The resulting blue solution was allowed to stand at room temperature and yielded blue crystals in a few days [yield 72 mg, 61%]. Analysis for C<sub>13</sub>H<sub>12</sub>CuN<sub>4</sub>O<sub>3</sub>·2(H<sub>2</sub>O) (*M<sub>r</sub>* = 371.84). Calculated (%): C 41.99, H 4.34, N 15.07. Found: C 42.17, H 4.33, N 14.75.

### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The water H atoms were located in difference Fourier maps were refined with distance restraints: O—H = 0.84 (2) and H...H = 1.35 (2) Å with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O). The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 Å with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

### Acknowledgements

This work was supported by the Swiss National Science Foundation and the University of Neuchâtel.

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## supporting information

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## Crystal structure of poly[[*(acetato-κO)*{ $\mu_3$ -*N*-[(pyridin-4-yl)methyl]pyrazine-2-carboxamidato- $\kappa^4$ *N:N<sup>1</sup>,N<sup>2</sup>:N<sup>4</sup>*]copper(II)] dihydrate]: a metal–organic framework (MOF)

**Dilovan S. Cati and Helen Stoeckli-Evans**

### Computing details

Data collection: *EXPOSE* in *IPDSI* (Stoe & Cie, 2004); cell refinement: *CELL* in *IPDSI* (Stoe & Cie, 2004); data reduction: *INTEGRATE* in *IPDSI* (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

### Poly[[*(acetato-κO)*{ $\mu_3$ -*N*-[(pyridin-4-yl)methyl]pyrazine-2-carboxamidato- $\kappa^4$ *N:N<sup>1</sup>,N<sup>2</sup>:N<sup>4</sup>*]copper(II)] dihydrate]

#### Crystal data

[Cu(C<sub>11</sub>H<sub>9</sub>N<sub>4</sub>O)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)]·2H<sub>2</sub>O

*M<sub>r</sub>* = 371.84

Monoclinic, *Cc*

Hall symbol: -P 2yn

*a* = 7.8256 (12) Å

*b* = 22.331 (2) Å

*c* = 8.9976 (13) Å

$\beta$  = 110.040 (16)°

*V* = 1477.2 (4) Å<sup>3</sup>

*Z* = 4

*F*(000) = 764

*D<sub>x</sub>* = 1.672 Mg m<sup>-3</sup>

Mo *Kα* radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 2705 reflections

$\theta$  = 2.1–26.1°

$\mu$  = 1.51 mm<sup>-1</sup>

*T* = 153 K

Block, turquoise blue

0.40 × 0.30 × 0.30 mm

#### Data collection

Stoe IPDS I  
diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

$\varphi$  rotation scans

Absorption correction: multi-scan

(*MULscanABS* in *PLATON*; Spek, 2009)

*T<sub>min</sub>* = 0.979, *T<sub>max</sub>* = 1.000

5730 measured reflections

2705 independent reflections

1778 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.070

$\theta_{\max}$  = 25.9°,  $\theta_{\min}$  = 2.9°

*h* = -9→9

*k* = -27→26

*l* = -11→10

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.040

*wR*(*F*<sup>2</sup>) = 0.072

*S* = 0.78

2705 reflections

203 parameters

8 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.007P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack  $x$  determined using  
 665 quotients  $[(I^-)-(I)]/[(I^+)+(I)]$  (Parsons &  
 Flack, 2004)  
 Absolute structure parameter:  $-0.01$  (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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.44720 (19)	0.13211 (4)	0.83884 (18)	0.0155 (2)
O1	0.3072 (8)	0.1995 (2)	1.2004 (7)	0.0248 (16)
O2	0.5973 (10)	0.1326 (3)	0.7054 (9)	0.0169 (15)
O3	0.7386 (8)	0.0439 (3)	0.7464 (8)	0.0266 (15)
N1	0.5958 (11)	0.1988 (3)	0.9695 (9)	0.0155 (9)
N2	0.7658 (12)	0.2933 (3)	1.1646 (9)	0.0155 (9)
N3	0.3109 (12)	0.1421 (4)	0.9844 (11)	0.0155 (9)
N4	0.3255 (10)	-0.0570 (3)	1.2361 (9)	0.0155 (9)
C1	0.7378 (15)	0.2255 (5)	0.9510 (12)	0.018 (3)
H1	0.7839	0.2120	0.8720	0.022*
C2	0.8206 (16)	0.2742 (5)	1.0483 (12)	0.018 (3)
H2	0.9191	0.2940	1.0304	0.021*
C3	0.6208 (15)	0.2647 (4)	1.1831 (13)	0.015 (2)
H3	0.5771	0.2774	1.2644	0.018*
C4	0.5351 (15)	0.2174 (5)	1.0852 (11)	0.014 (2)
C5	0.3707 (11)	0.1848 (3)	1.0932 (10)	0.0146 (19)
C6	0.1512 (13)	0.1078 (4)	0.9801 (12)	0.015 (2)
H6A	0.0774	0.0987	0.8689	0.018*
H6B	0.0757	0.1320	1.0262	0.018*
C7	0.2058 (11)	0.0497 (3)	1.0721 (11)	0.0124 (17)
C8	0.1360 (11)	-0.0045 (4)	1.0059 (11)	0.020 (2)
H8	0.0425	-0.0061	0.9053	0.024*
C9	0.2044 (13)	-0.0571 (4)	1.0884 (13)	0.020 (2)
H9	0.1638	-0.0944	1.0381	0.024*
C10	0.3872 (11)	-0.0036 (3)	1.3001 (11)	0.019 (2)
H10	0.4747	-0.0028	1.4039	0.023*
C11	0.3310 (12)	0.0503 (4)	1.2239 (10)	0.016 (2)
H11	0.3775	0.0871	1.2748	0.019*
C12	0.6927 (13)	0.0907 (5)	0.6705 (13)	0.016 (2)
C13	0.7531 (12)	0.1058 (4)	0.5323 (10)	0.024 (2)
H13A	0.7724	0.0687	0.4820	0.035*
H13B	0.8669	0.1285	0.5701	0.035*
H13C	0.6591	0.1298	0.4552	0.035*

O1W	0.7662 (12)	0.0650 (3)	0.0791 (10)	0.0313 (19)
H1WA	0.764 (17)	0.042 (4)	0.151 (8)	0.047*
H1WB	0.752 (15)	0.044 (4)	-0.002 (7)	0.047*
O2W	0.9960 (9)	0.1546 (3)	0.2989 (8)	0.0358 (18)
H2WA	0.925 (10)	0.134 (4)	0.222 (8)	0.054*
H2WB	1.072 (10)	0.169 (4)	0.261 (10)	0.054*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0184 (5)	0.0119 (4)	0.0183 (5)	-0.0019 (8)	0.0092 (4)	-0.0025 (8)
O1	0.032 (4)	0.021 (3)	0.032 (4)	-0.011 (3)	0.025 (4)	-0.013 (3)
O2	0.023 (4)	0.008 (3)	0.023 (4)	0.000 (3)	0.012 (3)	-0.004 (3)
O3	0.025 (4)	0.019 (3)	0.037 (5)	0.009 (3)	0.013 (3)	0.005 (3)
N1	0.018 (2)	0.0133 (18)	0.018 (2)	-0.0018 (16)	0.009 (2)	0.0013 (17)
N2	0.018 (2)	0.0133 (18)	0.018 (2)	-0.0018 (16)	0.009 (2)	0.0013 (17)
N3	0.018 (2)	0.0133 (18)	0.018 (2)	-0.0018 (16)	0.009 (2)	0.0013 (17)
N4	0.018 (2)	0.0133 (18)	0.018 (2)	-0.0018 (16)	0.009 (2)	0.0013 (17)
C1	0.017 (6)	0.017 (5)	0.020 (6)	-0.004 (4)	0.007 (5)	-0.002 (5)
C2	0.019 (6)	0.022 (6)	0.016 (6)	-0.003 (5)	0.011 (5)	-0.001 (5)
C3	0.018 (6)	0.014 (5)	0.016 (6)	-0.005 (4)	0.012 (5)	-0.001 (4)
C4	0.023 (6)	0.010 (5)	0.012 (5)	-0.005 (4)	0.010 (5)	0.001 (4)
C5	0.015 (5)	0.016 (4)	0.014 (5)	-0.002 (3)	0.006 (4)	0.001 (4)
C6	0.013 (6)	0.010 (5)	0.021 (6)	-0.002 (4)	0.004 (5)	0.003 (4)
C7	0.011 (4)	0.009 (4)	0.018 (5)	0.002 (3)	0.006 (4)	0.006 (4)
C8	0.012 (5)	0.020 (4)	0.027 (6)	0.001 (4)	0.005 (4)	0.000 (4)
C9	0.020 (5)	0.012 (5)	0.028 (7)	-0.004 (4)	0.009 (5)	0.002 (4)
C10	0.024 (6)	0.017 (4)	0.017 (6)	0.000 (3)	0.009 (5)	0.002 (4)
C11	0.023 (5)	0.007 (4)	0.018 (5)	-0.003 (4)	0.008 (5)	-0.004 (4)
C12	0.007 (5)	0.022 (6)	0.019 (6)	0.001 (4)	0.004 (5)	0.001 (5)
C13	0.019 (5)	0.035 (5)	0.022 (6)	0.004 (4)	0.014 (5)	-0.003 (4)
O1W	0.047 (5)	0.019 (4)	0.033 (5)	-0.002 (4)	0.019 (5)	0.001 (3)
O2W	0.042 (5)	0.038 (4)	0.034 (5)	-0.007 (3)	0.022 (4)	-0.006 (3)

*Geometric parameters (Å, °)*

Cu1—O2	1.947 (7)	C3—H3	0.9500
Cu1—N3	1.964 (9)	C4—C5	1.500 (13)
Cu1—N4 <sup>i</sup>	1.993 (7)	C6—C7	1.520 (11)
Cu1—N1	2.003 (8)	C6—H6A	0.9900
Cu1—N2 <sup>ii</sup>	2.393 (8)	C6—H6B	0.9900
O1—C5	1.270 (9)	C7—C8	1.376 (11)
O2—C12	1.300 (12)	C7—C11	1.382 (12)
O3—C12	1.232 (11)	C8—C9	1.395 (13)
N1—C1	1.323 (13)	C8—H8	0.9500
N1—C4	1.349 (12)	C9—H9	0.9500
N2—C2	1.330 (13)	C10—C11	1.381 (11)
N2—C3	1.360 (13)	C10—H10	0.9500

N2—Cu1 <sup>iii</sup>	2.393 (8)	C11—H11	0.9500
N3—C5	1.332 (11)	C12—C13	1.512 (12)
N3—C6	1.455 (13)	C13—H13A	0.9800
N4—C10	1.341 (10)	C13—H13B	0.9800
N4—C9	1.342 (13)	C13—H13C	0.9800
N4—Cu1 <sup>iv</sup>	1.992 (7)	O1W—H1WA	0.84 (3)
C1—C2	1.405 (14)	O1W—H1WB	0.84 (3)
C1—H1	0.9500	O2W—H2WA	0.86 (3)
C2—H2	0.9500	O2W—H2WB	0.85 (3)
C3—C4	1.393 (13)		
O2—Cu1—N3	172.2 (3)	O1—C5—N3	127.8 (8)
O2—Cu1—N4 <sup>i</sup>	90.7 (3)	O1—C5—C4	118.5 (8)
N3—Cu1—N4 <sup>i</sup>	97.0 (3)	N3—C5—C4	113.7 (8)
O2—Cu1—N1	90.4 (3)	N3—C6—C7	110.9 (8)
N3—Cu1—N1	82.1 (4)	N3—C6—H6A	109.5
N4 <sup>i</sup> —Cu1—N1	170.6 (3)	C7—C6—H6A	109.5
O2—Cu1—N2 <sup>ii</sup>	86.5 (3)	N3—C6—H6B	109.5
N3—Cu1—N2 <sup>ii</sup>	91.3 (3)	C7—C6—H6B	109.5
N4 <sup>i</sup> —Cu1—N2 <sup>ii</sup>	101.5 (3)	H6A—C6—H6B	108.0
N1—Cu1—N2 <sup>ii</sup>	87.8 (2)	C8—C7—C11	118.6 (8)
C12—O2—Cu1	131.5 (6)	C8—C7—C6	121.3 (8)
C1—N1—C4	119.4 (8)	C11—C7—C6	120.1 (8)
C1—N1—Cu1	127.3 (7)	C7—C8—C9	119.2 (9)
C4—N1—Cu1	113.3 (7)	C7—C8—H8	120.4
C2—N2—C3	116.9 (9)	C9—C8—H8	120.4
C2—N2—Cu1 <sup>iii</sup>	117.4 (7)	N4—C9—C8	122.6 (9)
C3—N2—Cu1 <sup>iii</sup>	125.3 (7)	N4—C9—H9	118.7
C5—N3—C6	118.6 (9)	C8—C9—H9	118.7
C5—N3—Cu1	115.9 (6)	N4—C10—C11	123.8 (8)
C6—N3—Cu1	125.5 (7)	N4—C10—H10	118.1
C10—N4—C9	117.0 (7)	C11—C10—H10	118.1
C10—N4—Cu1 <sup>iv</sup>	120.3 (6)	C10—C11—C7	118.6 (8)
C9—N4—Cu1 <sup>iv</sup>	121.4 (6)	C10—C11—H11	120.7
N1—C1—C2	119.9 (10)	C7—C11—H11	120.7
N1—C1—H1	120.0	O3—C12—O2	124.0 (9)
C2—C1—H1	120.0	O3—C12—C13	122.0 (9)
N2—C2—C1	122.3 (10)	O2—C12—C13	113.9 (8)
N2—C2—H2	118.9	C12—C13—H13A	109.5
C1—C2—H2	118.9	C12—C13—H13B	109.5
N2—C3—C4	121.3 (10)	H13A—C13—H13B	109.5
N2—C3—H3	119.3	C12—C13—H13C	109.5
C4—C3—H3	119.3	H13A—C13—H13C	109.5
N1—C4—C3	120.1 (10)	H13B—C13—H13C	109.5
N1—C4—C5	115.0 (8)	H1WA—O1W—H1WB	107 (4)
C3—C4—C5	124.9 (9)	H2WA—O2W—H2WB	104 (4)
C4—N1—C1—C2	-2.0 (14)	N1—C4—C5—N3	0.4 (12)



Cu1—N1—C1—C2	176.4 (8)	C3—C4—C5—N3	178.4 (10)
C3—N2—C2—C1	-1.9 (15)	C5—N3—C6—C7	-95.5 (10)
Cu1 <sup>iii</sup> —N2—C2—C1	172.1 (9)	Cu1—N3—C6—C7	85.8 (10)
N1—C1—C2—N2	2.8 (17)	N3—C6—C7—C8	-128.6 (9)
C2—N2—C3—C4	0.5 (14)	N3—C6—C7—C11	49.7 (12)
Cu1 <sup>iii</sup> —N2—C3—C4	-173.0 (8)	C11—C7—C8—C9	-5.2 (12)
C1—N1—C4—C3	0.5 (14)	C6—C7—C8—C9	173.2 (8)
Cu1—N1—C4—C3	-178.0 (8)	C10—N4—C9—C8	-3.5 (12)
C1—N1—C4—C5	178.7 (9)	Cu1 <sup>iv</sup> —N4—C9—C8	-171.0 (7)
Cu1—N1—C4—C5	0.1 (11)	C7—C8—C9—N4	5.7 (13)
N2—C3—C4—N1	0.2 (16)	C9—N4—C10—C11	1.1 (11)
N2—C3—C4—C5	-177.7 (9)	Cu1 <sup>iv</sup> —N4—C10—C11	168.8 (6)
C6—N3—C5—O1	1.8 (14)	N4—C10—C11—C7	-0.9 (12)
Cu1—N3—C5—O1	-179.4 (7)	C8—C7—C11—C10	2.9 (12)
C6—N3—C5—C4	-179.5 (9)	C6—C7—C11—C10	-175.5 (8)
Cu1—N3—C5—C4	-0.7 (10)	Cu1—O2—C12—O3	-17.2 (15)
N1—C4—C5—O1	179.2 (8)	Cu1—O2—C12—C13	166.2 (7)
C3—C4—C5—O1	-2.8 (15)		

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

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA $\cdots$ O3 <sup>i</sup>	0.84 (3)	2.13 (5)	2.908 (9)	154 (9)
O1W—H1WB $\cdots$ O3 <sup>v</sup>	0.84 (3)	2.23 (5)	2.964 (10)	146 (8)
O2W—H2WA $\cdots$ O1W	0.86 (3)	2.11 (4)	2.951 (10)	165 (10)
O2W—H2WB $\cdots$ O1 <sup>vi</sup>	0.85 (3)	2.20 (3)	3.033 (8)	169 (10)
C2—H2 $\cdots$ O2 <sup>iii</sup>	0.95	2.37	2.987 (13)	123
C8—H8 $\cdots$ O3 <sup>vii</sup>	0.95	2.57	3.364 (11)	141
C9—H9 $\cdots$ O2W <sup>viii</sup>	0.95	2.50	3.358 (12)	151

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