

Synthesis and crystal structure of *trans*-diaqua-(1,4,8,11-tetraazaundecane)copper(II) isophthalate monohydrate

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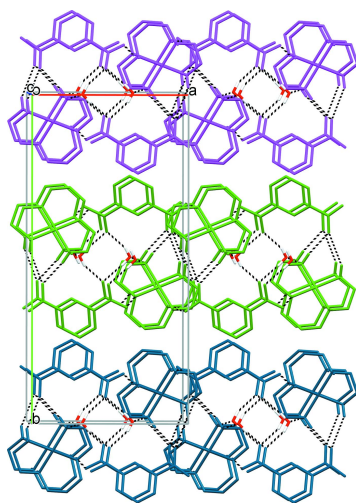
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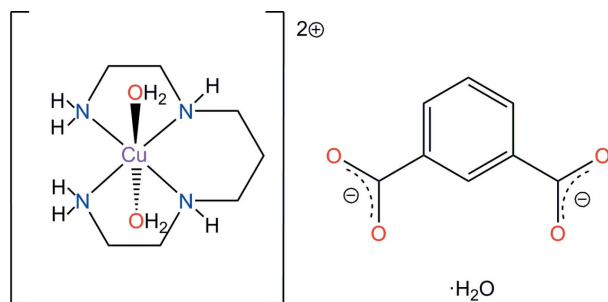
Keywords: crystal structure; tetraamine ligand; copper; isophthalic acid; hydrogen bonds.**CCDC reference:** 2190232**Supporting information:** this article has supporting information at journals.iucr.org/e

In the title hydrated molecular salt, $[\text{Cu}(\text{C}_7\text{H}_{20}\text{N}_4)(\text{H}_2\text{O})_2](\text{C}_8\text{H}_4\text{O}_4)\cdot\text{H}_2\text{O}$, the metal ion is coordinated by the two primary and two secondary N atoms of the amine ligand and the mutually *trans* O atoms of the water molecules in a tetragonally distorted octahedral geometry. The average equatorial Cu–N bond lengths (2.013 and 2.026 Å for Cu–N_{prim} and Cu–N_{sec}, respectively) are substantially shorter than the average axial Cu–O bond length (2.518 Å). The tetraamine ligand adopts its energetically favored conformation with its five- and six-membered chelate rings in *gauche* and chair conformations, respectively. In the crystal, the N–H donor groups of the tetraamine, the acceptor carboxylate groups of the isophthalate dianion and both the coordinated water molecules and the water molecule of crystallization are involved in numerous N–H···O and O–H···O hydrogen bonds, resulting in the formation of electroneutral layers oriented parallel to the *ac* plane.

1. Chemical context

The copper(II) and nickel(II) complexes of tetradentate azamacrocyclic ligands, in particular, cyclam and its structural analogues (cyclam = 1,4,8,11-tetraazacyclotetradecane, $\text{C}_{10}\text{H}_{24}\text{N}_4$), are widely used for the construction of metal–organic frameworks (MOFs) based on oligocarboxylate linkers, which possess many promising applications (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh *et al.*, 2012; Stackhouse & Ma, 2018; Lee & Moon, 2018). At the same time, open-chain aliphatic tetraamines like *L* (*L* = 1,4,8,11-tetraazaundecane, $\text{C}_7\text{H}_{20}\text{N}_4$), which is the closest structural and electronic analogue of cyclam, are practically unexploited in this respect and only one work dealing with the crystal structures of MOFs formed by the $[\text{Ni}(\text{L})]^{2+}$ cation with tris(4-carboxylatobenzyl)amine has been reported to date (Jiang *et al.*, 2012). Besides, the $[\text{M}(\text{L})]$ synthons ($\text{M} = \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}$) are convenient precursors for the one-pot template preparation of corresponding metal complexes of 14-membered azacyclam macrocycles (azacyclam = 1,4,8,11,13-pentaazacyclotetradecane) (Rosokha *et al.*, 1993; Gerbeleu *et al.*, 1999) and some complexes of this type functionalized at the N¹³ position of the macrocyclic backbone have been structurally characterized by our group (Andriichuk *et al.*, 2019; Tsymbal *et al.*, 2010, 2021). Herein, we report the syntheses and crystal structure of the product of the reaction of CuCl_2 , *L* and the isophthalate anion (ip^{2-}) as its sodium salt, namely, *trans*-diaqua(1,4,8,11-tetraazaundecane-*k*⁴N¹,N⁴,N⁸,N¹¹)-copper(II) isophthalate monohydrate, $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2](\text{ip})\cdot\text{H}_2\text{O}$, **I**.





2. Structural commentary

The asymmetric unit of the title hydrated molecular salt **I** consists of a complex di-cation $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]^{2+}$, a non-coordinated isophthalate di-anion ip^{2-} and one water molecule of crystallization (Fig. 1). The Cu^{II} ion is coordinated in the equatorial plane by the two primary and two secondary N atoms of the amine ligand in a nearly square-planar fashion (the deviations of the N atoms from the mean N_4 plane are $\pm 0.006 \text{ \AA}$), and by the two O atoms from the water molecules in the axial positions.

The average equatorial $\text{Cu}-\text{N}_{\text{prim}}$ bond length for N1 and N4 (2.013 \AA) is slightly shorter than $\text{Cu}-\text{N}_{\text{sec}}$ one for N2 and N3 (2.025 \AA), probably reflecting the stronger donating ability of the N atoms of primary *versus* secondary amine groups (Table 1). The average axial $\text{Cu}-\text{O}$ bond length (2.518 \AA) is substantially longer than the equatorial $\text{Cu}-\text{N}$ bonds, which is likely due to a large Jahn–Teller distortion inherent in metal ions with a d^9 electronic configuration. It is noteworthy that the $\text{Cu}-\text{O}$ distances in **I** differ considerably (Table 1) and the Cu^{II} ion is displaced from the mean N_4 plane of the ligand by 0.082 \AA towards the O1W water molecule.

The ligand *L* in **I** adopts its energetically favored conformation with the five-membered chelate rings in *gauche* [average bite angle 85.74°] and six-membered chelate ring in *chair* conformations, which resemble the *trans*-III conformation usually observed in cyclam complexes (Barefield *et al.*,

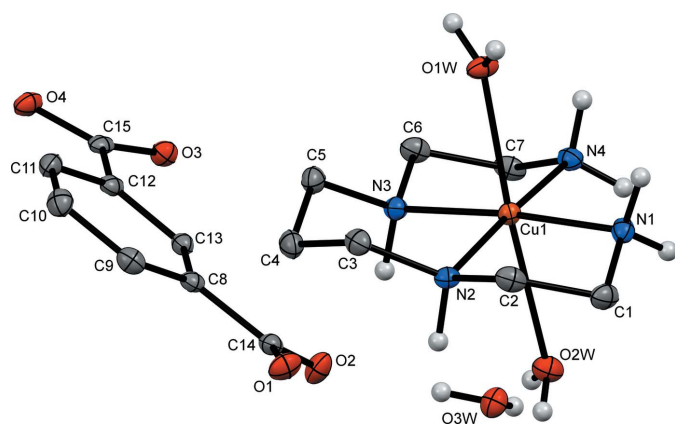


Figure 1

View of the asymmetric unit of **I**, showing the atom-labelling scheme, with displacement ellipsoids drawn at the 40% probability level. H atoms attached to carbon atoms have been omitted for clarity.

Table 1

Selected geometric parameters (\AA , $^\circ$).

$\text{Cu1}-\text{N1}$	2.0203 (18)	$\text{Cu1}-\text{O2W}$	2.6562 (16)
$\text{Cu1}-\text{N2}$	2.0218 (18)	$\text{C14}-\text{O1}$	1.256 (3)
$\text{Cu1}-\text{N3}$	2.0279 (18)	$\text{C14}-\text{O2}$	1.261 (3)
$\text{Cu1}-\text{N4}$	2.0064 (19)	$\text{C15}-\text{O3}$	1.258 (3)
$\text{Cu1}-\text{O1W}$	2.3800 (16)	$\text{C15}-\text{O4}$	1.271 (3)
$\text{N1}-\text{Cu1}-\text{N2}$	85.64 (8)	$\text{N4}-\text{Cu1}-\text{N1}$	95.19 (8)
$\text{N2}-\text{Cu1}-\text{N3}$	92.97 (7)	$\text{N4}-\text{Cu1}-\text{N3}$	85.83 (8)

1986; Bosnich *et al.*, 1965). The pseudo ‘bite’ angle formed by the primary amine donors $\text{N1}-\text{Cu1}-\text{N4}$ is slightly larger than that for $\text{N2}-\text{Cu1}-\text{N3}$ (Table 1).

The isophthalate di-anion in the title compound counterbalances the charge of the complex cation. The mean planes of the pendant carboxylate groups are slightly tilted relative to the mean plane of the aromatic ring [average angle = 9.8°]. The C–O bond lengths in the carboxylate groups are nearly equal (Table 1), thus indicating essentially complete electron delocalization.

3. Supramolecular features

In the crystal of **I**, the complex cation $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]^{2+}$, isophthalate anion ip^{2-} and both coordinated water molecules and water molecule of crystallization are linked by numerous hydrogen bonds (Table 2), resulting in its distinct lamellar structure. In particular, hydrogen-bonding interactions between the N1, N2 and N3 amine groups and O1W and O2W water molecules as the donors and carboxylate atoms O1, O3 and O4 as the acceptors result in the formation of electro-neutral sheets (Fig. 2). Additionally, due to hydrogen bonds $\text{N4}-\text{H4B}\cdots\text{O3}$ ($-x+1, -y+1, -z+1$) and $\text{N1}-\text{H1A}\cdots\text{O2W}$ ($-x, -y+1, -z+1$) and four bonds formed by the water molecule O3W these sheets double into bilayers oriented parallel to the *ac* plane (Fig. 3). It is noteworthy that all the polar groups in **I** are saturated from the point of view of the number of possible hydrogen bonds, which equal to 2, 1, 2, 4 and 2 for the primary, secondary amine groups, coordinated water molecule, water molecule of crystallization and carboxylate O atoms, respectively.

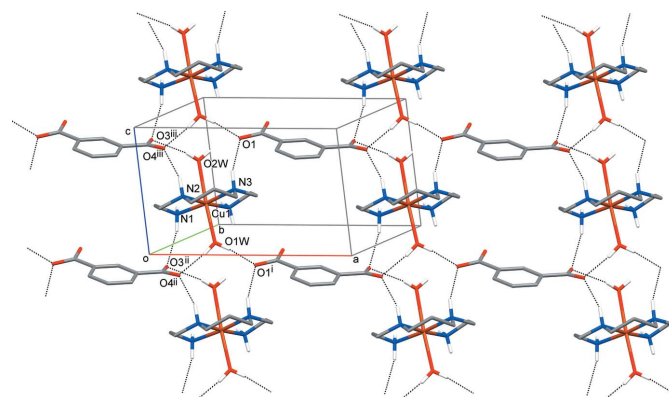


Figure 2

The hydrogen-bonded (dashed lines) sheets in **I**. C-bound H atoms and water molecule of crystallization have been omitted.

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N1—H1A···O2W ⁱ	0.97	2.30	3.143 (2)	145
N1—H1B···O3 ⁱⁱⁱ	0.97	2.07	3.007 (2)	161
N2—H2···O4 ⁱⁱⁱ	0.98	1.95	2.907 (2)	163
N3—H3···O1	0.98	2.19	3.063 (3)	148
N4—H4A···O3W ^{iv}	0.97	2.10	3.042 (2)	163
N4—H4B···O3 ^v	0.97	2.17	3.054 (2)	151
O1W—H1WA···O1 ^{iv}	0.87	1.89	2.747 (2)	169
O1W—H1WB···O4 ⁱⁱ	0.87	1.89	2.760 (2)	174
O2W—H2WA···O3 ⁱⁱⁱ	0.87	2.09	2.930 (2)	161
O2W—H2WB···O3W	0.87	2.00	2.872 (2)	175
O3W—H3WA···O2 ⁱⁱ	0.87	2.00	2.823 (2)	157
O3W—H3WB···O2	0.87	1.85	2.712 (2)	174

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

There are no hydrogen-bonding contacts between the layers in **I** (Fig. 3). The three-dimensional coherence of the crystal is provided by van der Waals interactions between the methine and methylene fragments of the constituents.

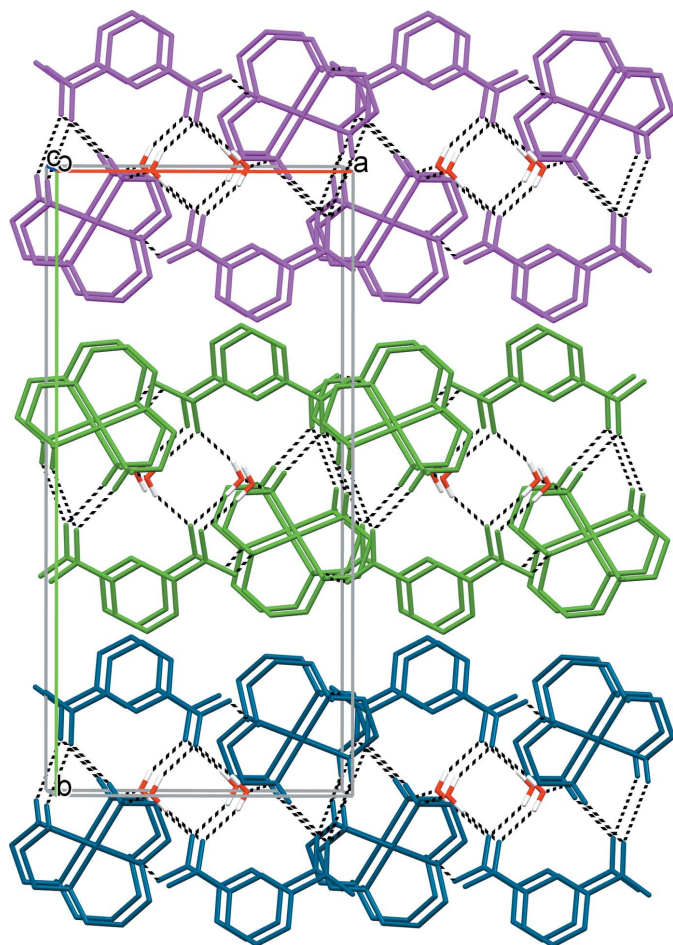


Figure 3
Side view of the bilayers in **I** along the *c* axis. C-bound H atoms and coordinated water molecules have been omitted, hydrogen bonds are shown as dashed lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Cu(C ₇ H ₂₀ N ₄)(H ₂ O) ₂](C ₈ H ₄ O ₄)·H ₂ O
<i>M_r</i>	441.97
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.4727 (8), 24.1694 (18), 7.1591 (5)
β (°)	96.679 (4)
<i>V</i> (Å ³)	1971.7 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.15
Crystal size (mm)	0.15 × 0.15 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.846, 0.934
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	53784, 3698, 3232
<i>R_{int}</i>	0.050
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.608
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.079, 1.11
No. of reflections	3698
No. of parameters	248
No. of restraints	11
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.50, -0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.43, last update March 2022; Groom *et al.*, 2016) gave nine hits related to the compounds formed by the [Cu(L)]²⁺ core. Among them, the *trans*-CuN₄O₂ chromophores are characteristic of three complexes [CSD refcodes DAFYOA (Heeg *et al.*, 2010), FICDEA (Lawrance *et al.*, 1987) and TECCUA (Fawcett *et al.*, 1980)] all of which contain coordinated perchlorate anions. Thus, the present work is the first structural characterization of a Cu^{II} diaqua complex of this open-chain tetraamine.

In general, conformations of the amine ligand and geometrical parameters of coordination polyhedra in both types of cations are similar, even though the axial Cu—O bond lengths in the perchlorate complexes are longer. This can be explained by poorer donating ability of this anion as compared to aqua ligand. As in **I**, the Cu—O distances in previously mentioned compounds are non-equivalent even though the differences between them are smaller than in **I** and do not exceed 0.14 Å.

5. Synthesis and crystallization

All chemicals and solvents used in this work were purchased from Sigma–Aldrich and used without further purification.

The title compound **I** was prepared as follows. A solution of Na₂zip (105 mg, 0.5 mmol) in water (5 ml) was added to a solution of CuCl₂·2H₂O (85 mg, 0.5 mmol) and *L* (80 mg (0.5 mmol) in water (5 ml). The blue precipitate, which formed in several days, was filtered off, washed with methanol (2 ml) and diethyl ether and dried in air. Yield: 106 mg (48%). Analysis calculated for C₁₅H₃₀CuN₄O₇: C 40.76, H 6.84, N 12.67%. Found: C 40.56, H 6.96, N 12.42%. Single crystals of **I** of X-ray diffraction quality were selected from the sample resulting from the synthesis.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms in **I** were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.95 (ring H atoms) or 0.99 Å (aliphatic H atoms), N–H distances of 0.97 (primary amine groups) or 0.98 Å (secondary amine groups) with *U*_{iso}(H) values of 1.2*U*_{eq} of the parent atoms. Water H atoms were positioned geometrically (O–H distances of 0.87 Å) and refined as riding with *U*_{iso}(H) = 1.5*U*_{eq}(O).

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supporting information

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Synthesis and crystal structure of *trans*-diaqua(1,4,8,11-tetraazaundecane)-copper(II) isophthalate monohydrate

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

trans-Diaqua(1,4,8,11-tetraazaundecane- $\kappa^4N^1, N^4, N^8, N^{11}$)copper(II) benzene-1,3-dicarboxylate monohydrate

Crystal data

[Cu(C₇H₂₀N₄)(H₂O)₂](C₈H₄O₄)·H₂O

$M_r = 441.97$

Monoclinic, $P2_1/c$

$a = 11.4727$ (8) Å

$b = 24.1694$ (18) Å

$c = 7.1591$ (5) Å

$\beta = 96.679$ (4)°

$V = 1971.7$ (2) Å³

$Z = 4$

$F(000) = 932$

$D_x = 1.489$ Mg m⁻³

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

Cell parameters from 2350 reflections

$\theta = 2.0$ – 25.0 °

$\mu = 1.15$ mm⁻¹

$T = 100$ K

Prism, light blue

$0.15 \times 0.15 \times 0.06$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.846$, $T_{\max} = 0.934$

53784 measured reflections

3698 independent reflections

3232 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 25.6$ °, $\theta_{\min} = 2.0$ °

$h = -13 \rightarrow 13$

$k = -29 \rightarrow 29$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.079$

$S = 1.11$

3698 reflections

248 parameters

11 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2 + 1.9773P]$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.50$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.16222 (2)	0.41162 (2)	0.30691 (4)	0.01549 (9)
O1W	0.19539 (13)	0.37755 (7)	0.0057 (2)	0.0222 (4)
H1WB	0.140042	0.364422	−0.075635	0.033*
H1WA	0.262802	0.372482	−0.036104	0.033*
N1	0.00154 (16)	0.44151 (8)	0.2133 (3)	0.0187 (4)
H1B	−0.009406	0.441387	0.076913	0.022*
H1A	−0.008806	0.479637	0.250343	0.022*
N2	0.07640 (16)	0.34306 (8)	0.3776 (3)	0.0162 (4)
H2	0.070058	0.343234	0.512940	0.019*
N3	0.31993 (16)	0.38284 (8)	0.4245 (3)	0.0173 (4)
H3	0.320619	0.384199	0.561434	0.021*
N4	0.24838 (16)	0.48139 (8)	0.2576 (3)	0.0185 (4)
H4B	0.207629	0.515358	0.281406	0.022*
H4A	0.264879	0.480508	0.127836	0.022*
C1	−0.0875 (2)	0.40536 (10)	0.2874 (3)	0.0225 (5)
H1C	−0.164157	0.409352	0.209563	0.027*
H1D	−0.097246	0.415929	0.418270	0.027*
C2	−0.04516 (19)	0.34645 (10)	0.2813 (3)	0.0210 (5)
H2A	−0.097361	0.321866	0.344534	0.025*
H2B	−0.046743	0.334230	0.148997	0.025*
C3	0.1331 (2)	0.28961 (10)	0.3430 (3)	0.0208 (5)
H3A	0.138014	0.285553	0.206536	0.025*
H3B	0.084020	0.259027	0.382426	0.025*
C4	0.2563 (2)	0.28505 (10)	0.4492 (3)	0.0223 (5)
H4C	0.251528	0.292366	0.584128	0.027*
H4D	0.284504	0.246613	0.438010	0.027*
C5	0.3461 (2)	0.32440 (10)	0.3804 (3)	0.0213 (5)
H5A	0.425481	0.314656	0.440994	0.026*
H5B	0.345745	0.320183	0.242808	0.026*
C6	0.4108 (2)	0.42145 (10)	0.3695 (3)	0.0214 (5)
H6A	0.429531	0.412384	0.241485	0.026*
H6B	0.483487	0.417883	0.457819	0.026*
C7	0.3643 (2)	0.48003 (10)	0.3738 (3)	0.0216 (5)
H7A	0.355909	0.491074	0.504759	0.026*
H7B	0.419204	0.506014	0.322469	0.026*
O1	0.39258 (13)	0.35317 (7)	0.8377 (2)	0.0242 (4)
O2	0.50998 (14)	0.42314 (7)	0.9402 (2)	0.0241 (4)
O3	0.92569 (13)	0.42289 (7)	0.8018 (2)	0.0199 (4)
O4	1.00945 (13)	0.34100 (7)	0.7569 (2)	0.0215 (4)

C8	0.59710 (19)	0.34397 (9)	0.8164 (3)	0.0159 (5)
C9	0.5866 (2)	0.28909 (10)	0.7585 (3)	0.0197 (5)
H9	0.512981	0.270876	0.754070	0.024*
C10	0.6837 (2)	0.26072 (10)	0.7071 (3)	0.0220 (5)
H10	0.676259	0.223180	0.668228	0.026*
C11	0.7912 (2)	0.28737 (10)	0.7129 (3)	0.0202 (5)
H11	0.857145	0.267874	0.677579	0.024*
C12	0.80347 (19)	0.34233 (9)	0.7697 (3)	0.0167 (5)
C13	0.70586 (19)	0.37043 (9)	0.8219 (3)	0.0158 (4)
H13	0.713443	0.407907	0.861456	0.019*
C14	0.49156 (19)	0.37561 (9)	0.8704 (3)	0.0171 (5)
C15	0.92127 (19)	0.37139 (10)	0.7764 (3)	0.0172 (5)
O2W	0.13469 (14)	0.45839 (7)	0.6347 (2)	0.0227 (4)
H2WA	0.083740	0.442503	0.698016	0.039 (9)*
H2WB	0.194230	0.469203	0.712486	0.040 (9)*
O3W	0.33455 (14)	0.49839 (7)	0.8756 (2)	0.0224 (4)
H3WA	0.369284	0.528915	0.915066	0.029 (7)*
H3WB	0.387514	0.472565	0.893226	0.044 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01437 (15)	0.01537 (15)	0.01669 (15)	-0.00035 (10)	0.00163 (10)	0.00072 (11)
O1W	0.0143 (8)	0.0350 (10)	0.0176 (8)	-0.0001 (7)	0.0028 (6)	-0.0051 (7)
N1	0.0202 (10)	0.0174 (10)	0.0180 (10)	0.0036 (8)	-0.0001 (8)	-0.0015 (8)
N2	0.0166 (9)	0.0184 (10)	0.0138 (9)	-0.0012 (7)	0.0025 (7)	-0.0009 (7)
N3	0.0173 (9)	0.0188 (10)	0.0158 (10)	0.0003 (8)	0.0025 (7)	0.0005 (8)
N4	0.0231 (10)	0.0155 (10)	0.0173 (10)	-0.0019 (8)	0.0039 (8)	-0.0003 (8)
C1	0.0154 (11)	0.0325 (14)	0.0197 (12)	0.0018 (10)	0.0024 (9)	0.0009 (10)
C2	0.0166 (11)	0.0283 (13)	0.0177 (12)	-0.0059 (9)	0.0005 (9)	0.0007 (10)
C3	0.0266 (12)	0.0168 (12)	0.0188 (12)	-0.0022 (9)	0.0024 (9)	-0.0011 (9)
C4	0.0277 (13)	0.0170 (12)	0.0217 (13)	0.0032 (10)	0.0010 (10)	0.0013 (9)
C5	0.0200 (12)	0.0231 (13)	0.0204 (12)	0.0055 (9)	0.0002 (9)	0.0006 (10)
C6	0.0160 (11)	0.0284 (14)	0.0196 (12)	-0.0039 (9)	0.0012 (9)	0.0019 (10)
C7	0.0220 (12)	0.0247 (13)	0.0180 (12)	-0.0079 (10)	0.0019 (9)	0.0005 (10)
O1	0.0139 (8)	0.0326 (10)	0.0264 (9)	-0.0032 (7)	0.0042 (7)	-0.0062 (8)
O2	0.0180 (8)	0.0205 (9)	0.0344 (10)	0.0007 (7)	0.0064 (7)	-0.0047 (7)
O3	0.0163 (8)	0.0221 (9)	0.0213 (9)	-0.0015 (6)	0.0027 (6)	0.0006 (7)
O4	0.0141 (8)	0.0318 (10)	0.0189 (8)	0.0030 (7)	0.0029 (6)	-0.0025 (7)
C8	0.0160 (11)	0.0201 (12)	0.0115 (11)	-0.0006 (9)	0.0004 (8)	0.0027 (9)
C9	0.0196 (12)	0.0212 (12)	0.0177 (12)	-0.0045 (9)	-0.0005 (9)	0.0014 (9)
C10	0.0253 (12)	0.0192 (12)	0.0210 (12)	0.0013 (10)	-0.0002 (9)	-0.0023 (10)
C11	0.0202 (11)	0.0234 (13)	0.0170 (12)	0.0062 (9)	0.0021 (9)	-0.0006 (9)
C12	0.0153 (11)	0.0240 (12)	0.0103 (10)	0.0017 (9)	0.0000 (8)	0.0026 (9)
C13	0.0189 (11)	0.0151 (11)	0.0132 (11)	0.0006 (9)	0.0013 (8)	0.0009 (9)
C14	0.0180 (11)	0.0201 (12)	0.0134 (11)	0.0002 (9)	0.0031 (8)	0.0024 (9)
C15	0.0162 (11)	0.0267 (13)	0.0085 (10)	0.0019 (9)	0.0010 (8)	0.0007 (9)
O2W	0.0220 (9)	0.0260 (9)	0.0201 (9)	-0.0036 (7)	0.0021 (7)	0.0005 (7)

O3W 0.0202 (8) 0.0216 (9) 0.0249 (9) 0.0006 (7) 0.0005 (7) -0.0031 (7)

Geometric parameters (Å, °)

Cu1—N1	2.0203 (18)	C4—H4D	0.9900
Cu1—N2	2.0218 (18)	C4—C5	1.526 (3)
Cu1—N3	2.0279 (18)	C5—H5A	0.9900
Cu1—N4	2.0064 (19)	C5—H5B	0.9900
Cu1—O1W	2.3800 (16)	C6—H6A	0.9900
Cu1—O2W	2.6562 (16)	C6—H6B	0.9900
O1W—H1WB	0.8700	C6—C7	1.514 (3)
O1W—H1WA	0.8698	C7—H7A	0.9900
N1—H1B	0.9699	C7—H7B	0.9900
N1—H1A	0.9701	C14—O1	1.256 (3)
N1—C1	1.488 (3)	C14—O2	1.261 (3)
N2—H2	0.9798	C15—O3	1.258 (3)
N2—C2	1.485 (3)	C15—O4	1.271 (3)
N2—C3	1.480 (3)	C8—C9	1.390 (3)
N3—H3	0.9799	C8—C13	1.399 (3)
N3—C5	1.486 (3)	C8—C14	1.520 (3)
N3—C6	1.486 (3)	C9—H9	0.9500
N4—H4B	0.9696	C9—C10	1.393 (3)
N4—H4A	0.9699	C10—H10	0.9500
N4—C7	1.485 (3)	C10—C11	1.388 (3)
C1—H1C	0.9900	C11—H11	0.9500
C1—H1D	0.9900	C11—C12	1.392 (3)
C1—C2	1.506 (3)	C12—C13	1.397 (3)
C2—H2A	0.9900	C12—C15	1.519 (3)
C2—H2B	0.9900	C13—H13	0.9500
C3—H3A	0.9900	O2W—H2WA	0.8698
C3—H3B	0.9900	O2W—H2WB	0.8699
C3—C4	1.529 (3)	O3W—H3WA	0.8699
C4—H4C	0.9900	O3W—H3WB	0.8699
O1W—Cu1—O2W	174.64 (6)	N2—C3—C4	112.24 (19)
N1—Cu1—O1W	93.38 (7)	H3A—C3—H3B	107.9
N1—Cu1—N2	85.64 (8)	C4—C3—H3A	109.2
N1—Cu1—N3	174.88 (8)	C4—C3—H3B	109.2
N1—Cu1—O2W	86.75 (6)	C3—C4—H4C	108.6
N2—Cu1—O1W	94.42 (7)	C3—C4—H4D	108.6
N2—Cu1—N3	92.97 (7)	H4C—C4—H4D	107.6
N2—Cu1—O2W	90.93 (6)	C5—C4—C3	114.52 (19)
N3—Cu1—O1W	91.63 (7)	C5—C4—H4C	108.6
N3—Cu1—O2W	88.35 (6)	C5—C4—H4D	108.6
N4—Cu1—O1W	89.86 (7)	N3—C5—C4	111.29 (19)
N4—Cu1—N1	95.19 (8)	N3—C5—H5A	109.4
N4—Cu1—N2	175.59 (7)	N3—C5—H5B	109.4
N4—Cu1—N3	85.83 (8)	C4—C5—H5A	109.4

N4—Cu1—O2W	84.80 (6)	C4—C5—H5B	109.4
Cu1—O1W—H1WB	123.5	H5A—C5—H5B	108.0
Cu1—O1W—H1WA	127.1	N3—C6—H6A	109.9
H1WB—O1W—H1WA	109.1	N3—C6—H6B	109.9
Cu1—N1—H1B	109.8	N3—C6—C7	108.80 (18)
Cu1—N1—H1A	112.6	H6A—C6—H6B	108.3
H1B—N1—H1A	105.8	C7—C6—H6A	109.9
C1—N1—Cu1	108.02 (14)	C7—C6—H6B	109.9
C1—N1—H1B	110.1	N4—C7—C6	107.68 (18)
C1—N1—H1A	110.5	N4—C7—H7A	110.2
Cu1—N2—H2	109.8	N4—C7—H7B	110.2
C2—N2—Cu1	107.27 (14)	C6—C7—H7A	110.2
C2—N2—H2	106.6	C6—C7—H7B	110.2
C3—N2—Cu1	115.92 (14)	H7A—C7—H7B	108.5
C3—N2—H2	104.7	C9—C8—C13	119.4 (2)
C3—N2—C2	112.19 (18)	C9—C8—C14	120.8 (2)
Cu1—N3—H3	107.9	C13—C8—C14	119.8 (2)
C5—N3—Cu1	115.52 (14)	C8—C9—H9	119.9
C5—N3—H3	105.4	C8—C9—C10	120.3 (2)
C5—N3—C6	112.04 (18)	C10—C9—H9	119.9
C6—N3—Cu1	107.10 (14)	C9—C10—H10	120.0
C6—N3—H3	108.6	C11—C10—C9	119.9 (2)
Cu1—N4—H4B	115.0	C11—C10—H10	120.0
Cu1—N4—H4A	107.8	C10—C11—H11	119.6
H4B—N4—H4A	109.8	C10—C11—C12	120.7 (2)
C7—N4—Cu1	108.08 (14)	C12—C11—H11	119.6
C7—N4—H4B	109.8	C11—C12—C13	119.0 (2)
C7—N4—H4A	105.9	C11—C12—C15	120.7 (2)
N1—C1—H1C	110.1	C13—C12—C15	120.3 (2)
N1—C1—H1D	110.1	C8—C13—H13	119.7
N1—C1—C2	107.93 (18)	C12—C13—C8	120.7 (2)
H1C—C1—H1D	108.4	C12—C13—H13	119.7
C2—C1—H1C	110.1	O1—C14—O2	125.0 (2)
C2—C1—H1D	110.1	O1—C14—C8	117.7 (2)
N2—C2—C1	109.08 (18)	O2—C14—C8	117.24 (19)
N2—C2—H2A	109.9	O3—C15—O4	124.6 (2)
N2—C2—H2B	109.9	O3—C15—C12	118.88 (19)
C1—C2—H2A	109.9	O4—C15—C12	116.5 (2)
C1—C2—H2B	109.9	Cu1—O2W—H2WA	115.4
H2A—C2—H2B	108.3	Cu1—O2W—H2WB	121.9
N2—C3—H3A	109.2	H2WA—O2W—H2WB	108.9
N2—C3—H3B	109.2	H3WA—O3W—H3WB	106.0
Cu1—N1—C1—C2	−38.5 (2)	C9—C8—C14—O1	−9.2 (3)
Cu1—N2—C2—C1	−39.5 (2)	C9—C8—C14—O2	172.7 (2)
Cu1—N2—C3—C4	58.8 (2)	C9—C10—C11—C12	0.1 (3)
Cu1—N3—C5—C4	−60.6 (2)	C10—C11—C12—C13	0.2 (3)
Cu1—N3—C6—C7	38.7 (2)	C10—C11—C12—C15	179.8 (2)

Cu1—N4—C7—C6	39.9 (2)	C11—C12—C13—C8	-0.3 (3)
N1—C1—C2—N2	52.4 (2)	C11—C12—C15—O3	169.8 (2)
N2—C3—C4—C5	-67.6 (3)	C11—C12—C15—O4	-10.7 (3)
N3—C6—C7—N4	-52.8 (2)	C13—C8—C9—C10	0.2 (3)
C2—N2—C3—C4	-177.47 (18)	C13—C8—C14—O1	169.8 (2)
C3—N2—C2—C1	-167.89 (18)	C13—C8—C14—O2	-8.3 (3)
C3—C4—C5—N3	68.4 (3)	C13—C12—C15—O3	-10.6 (3)
C5—N3—C6—C7	166.35 (18)	C13—C12—C15—O4	168.89 (19)
C6—N3—C5—C4	176.36 (18)	C14—C8—C9—C10	179.2 (2)
C8—C9—C10—C11	-0.3 (3)	C14—C8—C13—C12	-178.94 (19)
C9—C8—C13—C12	0.1 (3)	C15—C12—C13—C8	-179.90 (19)

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>
N1—H1 <i>A</i> ...O2 <i>W</i> ⁱ	0.97	2.30	3.143 (2)	145
N1—H1 <i>B</i> ...O3 ⁱⁱ	0.97	2.07	3.007 (2)	161
N2—H2...O4 ⁱⁱⁱ	0.98	1.95	2.907 (2)	163
N3—H3...O1	0.98	2.19	3.063 (3)	148
N4—H4 <i>A</i> ...O3 <i>W</i> ^{iv}	0.97	2.10	3.042 (2)	163
N4—H4 <i>B</i> ...O3 ^v	0.97	2.17	3.054 (2)	151
O1 <i>W</i> —H1 <i>WA</i> ...O1 ^{iv}	0.87	1.89	2.747 (2)	169
O1 <i>W</i> —H1 <i>WB</i> ...O4 ⁱⁱ	0.87	1.89	2.760 (2)	174
O2 <i>W</i> —H2 <i>WA</i> ...O3 ⁱⁱⁱ	0.87	2.09	2.930 (2)	161
O2 <i>W</i> —H2 <i>WB</i> ...O3 <i>W</i>	0.87	2.00	2.872 (2)	175
O3 <i>W</i> —H3 <i>WA</i> ...O2 ^{vi}	0.87	2.00	2.823 (2)	157
O3 <i>W</i> —H3 <i>WB</i> ...O2	0.87	1.85	2.712 (2)	174

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