

Crystal structure of diaqua(3,14-diethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane)copper(II) dichloride tetrahydrate

Dohyun Moon^a and Jong-Ha Choi^{b*}

^aBeamline Department, Pohang Accelerator Laboratory, POSTECH, Pohang 37673, Republic of Korea, and ^bDepartment of Chemistry, Andong National University, Andong 36729, Republic of Korea. *Correspondence e-mail: jhchoi@anu.ac.kr

Received 13 April 2021

Accepted 24 April 2021

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; macrocycle; diaquacopper(II) complex; hydrogen bonding; synchrotron radiation.

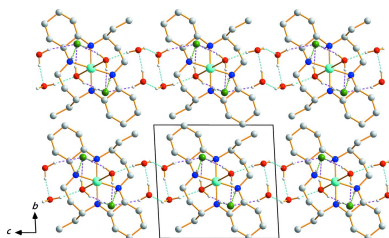
CCDC reference: 2079818

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

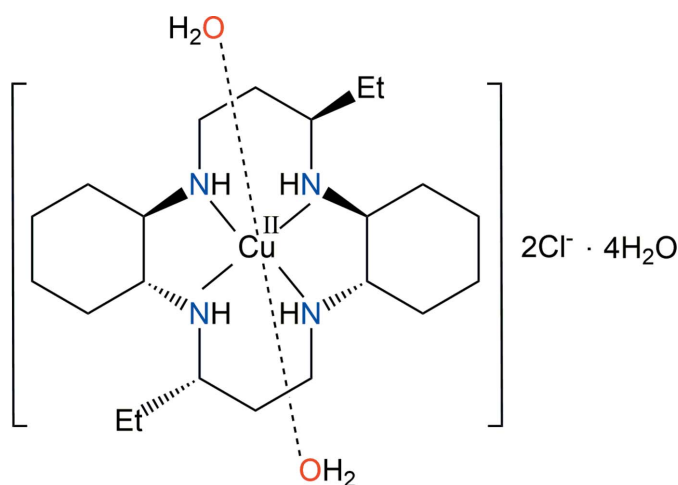
The crystal structure of the novel hydrated Cu^{II} salt, [Cu(L)(H₂O)₂]Cl₂·4H₂O (*L* = 3,14-diethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane, C₂₂H₄₄N₄) has been determined using synchrotron radiation. The asymmetric unit contains one half of the [Cu(L)(H₂O)₂]²⁺ cation (completed by crystallographic inversion symmetry), one chloride anion and two lattice water molecules. The copper(II) atom exists in a tetragonally distorted octahedral environment with the four N atoms of the macrocyclic ligand in equatorial and two O atoms from water molecules in axial positions. The latter exhibit a long axial Cu—O bond length of 2.7866 (16) Å due to the Jahn–Teller distortion. The macrocyclic ring adopts a stable *trans*-III conformation with typical Cu—N bond lengths of 2.0240 (11) and 2.0441 (3) Å. The complex is stabilized by hydrogen bonds formed between the O atoms of coordinated water molecules and the NH groups as donors, and chloride anions as acceptors. The chloride anions are further connected to the lattice water solvent molecules through O—H···Cl hydrogen bonds, giving rise to a three-dimensional network structure.

1. Chemical context

The macrocycle 3,14-diethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane (C₂₂H₄₄N₄, *L*) contains a cyclam backbone with two cyclohexane subunits and two ethyl groups attached to carbon atoms of the propyl chains that bridge opposite pairs of N atoms. The syntheses, crystal structures and spectroscopic properties of numerous metal complexes with this ligand have previously been reported, *viz.* [Ni(L)(NO₃)₂] (Subhan & Choi, 2014), [Ni(L)(N₃)₂] (Lim *et al.*, 2015), [Ni(L)(NCS)₂] (Lim & Choi, 2017), [Cu(L)(ClO₄)₂] (Lim *et al.*, 2006), [Cu(L)(NO₃)₂] and [Cu(L)(H₂O)₂](SCN)₂ (Choi *et al.*, 2012). In these complexes, Cu^{II} or Ni^{II} cations have a tetragonally distorted octahedral coordination environment with the four N atoms of the macrocyclic ligand in the equatorial position and O/N atoms of anions or water molecules in the axial position. In contrast, [Ni(L)](ClO₄)₂·2H₂O (Subhan & Choi, 2014) and [Ni_x(H₂(1-x)L)]Cl₂·2H₂O (*x* = 0.34) (Moon *et al.*, 2020) have a square-planar coordination environment around each Ni^{II} ion that binds to the four nitrogen atoms of the macrocyclic ligand. The macrocyclic ligands in these Cu^{II} and Ni^{II} complexes adopt the most stable *trans*-III conformation. The crystal structures of (*L*)·NaClO₄ (Aree *et al.*, 2018), [H₂L](ClO₄)₂ (Aree *et al.*, 2018), [H₂L]Cl₂·4H₂O (Moon *et al.*, 2013), [H₂L](NO₃)₂·2H₂O (Moon *et al.*, 2019) and [H₄L]Cl₄·4H₂O (Moon & Choi, 2021) have also been determined.



OPEN ACCESS



We report here synthesis and structural characterization of the novel complex $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, (I), in order to obtain detailed information on the conformation of the macrocyclic ligand, and the bonding mode of water molecules and chloride anions in the crystal.

2. Structural commentary

The molecular structure of (I) is shown in Fig. 1. The Cu^{II} complex cation lies across a crystallographic inversion center, and hence the asymmetric unit consists of one half of the $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]^{2+}$ cation, one chloride anion and two lattice water solvents. The macrocyclic skeleton adopts the most stable *trans*-III conformation. The Cu–N bond lengths

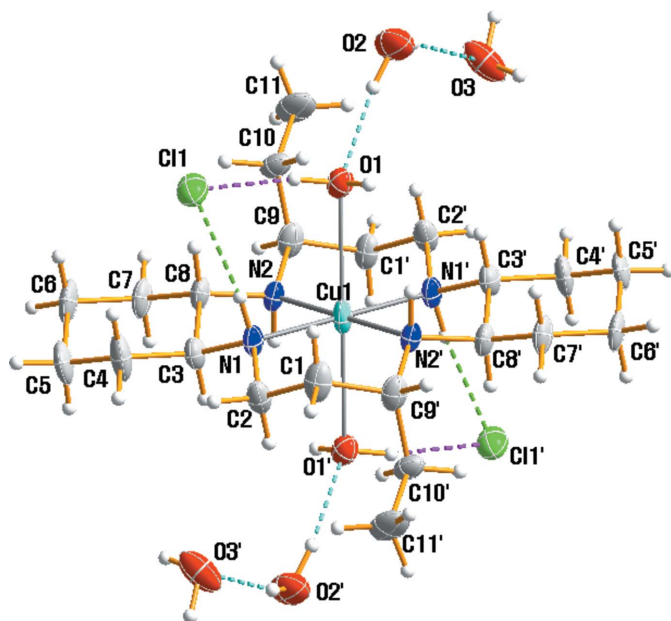


Figure 1
Molecular structure of (I), drawn with displacement ellipsoids at the 50% probability level. Dashed lines represent hydrogen-bonding interactions; primed atoms are related by the symmetry operation $(-x + 1, -y + 1, -z + 1)$.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1} \cdots \text{Cl1}^{\text{i}}$	0.99	2.45	3.4383 (14)	173
$\text{N2}-\text{H2} \cdots \text{Cl1}^{\text{i}}$	0.99	2.54	3.4962 (14)	163
$\text{O1}-\text{H1O1} \cdots \text{Cl1}^{\text{iii}}$	0.92 (1)	2.26 (1)	3.1799 (19)	173 (2)
$\text{O1}-\text{H2O1} \cdots \text{Cl1}$	0.93 (1)	2.21 (1)	3.1153 (15)	166 (2)
$\text{O2}-\text{H1O2} \cdots \text{O1}$	0.93 (1)	1.98 (1)	2.902 (2)	172 (3)
$\text{O2}-\text{H2O2} \cdots \text{O3}$	0.93 (1)	1.94 (2)	2.794 (3)	152 (3)
$\text{O3}-\text{H1O3} \cdots \text{Cl1}^{\text{iii}}$	0.93 (1)	2.39 (2)	3.266 (2)	157 (3)
$\text{O3}-\text{H2O3} \cdots \text{O2}^{\text{iv}}$	0.93 (1)	1.87 (1)	2.796 (4)	170 (3)

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

[2.0240 (11)–2.0441 (3) \AA] are within the typical range, and are comparable to those observed in related complexes, *e.g.* in $[\text{Cu}(\text{L})(\text{ClO}_4)_2]$ [2.01064 (18)–2.0403 (18) \AA] (Lim *et al.*, 2006), $[\text{Cu}(\text{L})(\text{NO}_3)_2]$ [2.021 (2)–2.046 (2) \AA] and $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2](\text{SCN})_2$ [2.014 (2)–2.047 (2) \AA] (Choi *et al.*, 2012). The coordination environment of the copper(II) atom may be considered as square-planar or octahedral with a tetragonal distortion, depending upon whether or not the remote oxygen atoms of the water molecules are considered to be bonded to the copper(II) atom. The concept of a semi-coordinating atom was introduced to describe a situation where a polyatomic anion or ligand occupies the long axial position in an otherwise square-planar copper(II) complex with an atom in the distance range of 2.5–3.0 \AA (Murphy & Hathaway, 2003). The axial Cu1–O1 distance of 2.7866 (16) \AA is longer than corresponding distances in $[\text{Cu}(\text{L})(\text{ClO}_4)_2]$ [2.762 (2) \AA] (Lim *et al.*, 2006), $[\text{Cu}(\text{L})(\text{NO}_3)_2]$ [2.506 (2) \AA] and $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2](\text{SCN})_2$ [2.569 (2) \AA] (Choi *et al.*, 2012). The tetragonally elongated octahedron is a common polyhedron around six-coordinate Cu^{II} atoms in complexes (involving also non-equivalent ligands), and the distortion arises from the Jahn–Teller effect operative on the metal cation with its d^9 electronic configuration (Murphy & Hathaway, 2003).

The two ethyl groups on the six-membered chelate rings and the two $-(\text{CH}_2)_4-$ parts of the cyclohexane backbones are *anti* with respect to the macrocyclic plane. As usually observed, the five-membered chelate rings adopt a *gauche* conformation whereas the six-membered rings are in chair conformations. The ethyl groups are attached axially as substituents to the six-membered rings, while the methylene C substituents at the five-membered rings are equatorial. The cyclohexane rings are also in a chair conformation, with the N substituents in equatorial positions.

3. Supramolecular features

Numerical details of the hydrogen bonding are given in Table 1. The supramolecular structure involves interactions between the NH groups of the macrocycle and OH groups of the semi-coordinated water molecules as donors, and the chloride anions and the O atoms of the lattice water molecules

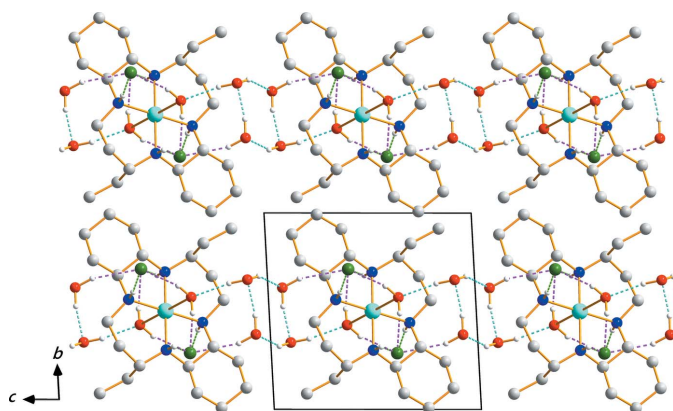


Figure 2
Crystal packing of (I), viewed perpendicular to the *bc* plane. Dashed lines represent O—H...Cl (purple), O—H...O (cyan), and N—H...Cl (green) hydrogen-bonding interactions, respectively. H atoms bound to C atoms have been omitted for clarity.

as acceptors, resulting in a three-dimensional network structure. The chloride anions remain outside the coordination sphere [Cu...Cl (4.523 Å)] and are connected both to the semi-coordinated and to the lattice water solvents through O—H...Cl hydrogen bonds. The lattice water solvents are additionally linked to the semi-coordinated water molecules and other lattice water solvents *via* O—H...O hydrogen bonds. The crystal packing of (I) in a view perpendicular to the *bc* plane is shown in Fig. 2.

4. Database survey

A search of the Cambridge Structural (Version 5.42, update February 2021; Groom *et al.*, 2016) indicated 21 hits for organic and transition-metal compounds containing the macrocycle (*L*, C₂₂H₄₄N₄). The hits include (*L*)·NaClO₄ (Aree *et al.*, 2018), [H₂L](ClO₄)₂ (Aree *et al.*, 2018), [H₂L]Cl₂·4H₂O (Moon *et al.*, 2013), [H₂L](NO₃)₂·2H₂O (Moon *et al.*, 2019), [H₄L]Cl₄·4H₂O (Moon & Choi, 2021), [Cu(*L*)(ClO₄)₂] (Lim *et al.*, 2006), [Cu(*L*)(NO₃)₂] and [Cu(*L*)(H₂O)₂](SCN)₂ (Choi *et al.*, 2012). Until now, no crystal structure of the [Cu(*L*)(H₂O)₂]²⁺ cation with chloride counter-anions and four lattice water molecules has been deposited.

5. Synthesis and crystallization

Ethyl vinyl ketone (97%), *trans*-1,2-cyclohexanediamine (99%) and copper(II) chloride dihydrate (99%) were purchased from Sigma-Aldrich and were used as received. All other chemicals were analytical reagent grade. 3,14-Diethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane (*L*) was prepared according to a published procedure (Lim *et al.*, 2006). A solution of the macrocycle *L* (0.091 g, 0.25 mmol) in water (10 mL) was added dropwise to a stirred solution of CuCl₂·2H₂O (0.085 g, 0.5 mmol) in water (20 mL). After

Table 2
Experimental details.

Crystal data	[Cu(C ₂₂ H ₄₄ N ₄)(H ₂ O) ₂]Cl ₂ ·4H ₂ O
Chemical formula	607.14
<i>M_r</i>	Triclinic, <i>P</i> $\bar{1}$
Crystal system, space group	220
Temperature (K)	8.0220 (16), 10.020 (2), 10.354 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	81.36 (3), 72.84 (3), 69.71 (3)
α , β , γ (°)	744.8 (3)
<i>V</i> (Å ³)	1
<i>Z</i>	Synchrotron, λ = 0.610 Å
Radiation type	0.63
μ (mm ⁻¹)	0.12 × 0.12 × 0.04
Crystal size (mm)	
Data collection	
Diffractometer	Rayonix MX225HS CCD area detector
Absorption correction	Empirical (using intensity measurements) (<i>HKL3000sm SCALEPACK</i> ; Otwinowski <i>et al.</i> , 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.597, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	8262, 4141, 4013
<i>R_{int}</i>	0.019
(sin θ/λ) _{max} (Å ⁻¹)	0.693
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.109, 1.10
No. of reflections	4141
No. of parameters	179
No. of restraints	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.86, -0.88

Computer programs: *PAL BL2D-SMDC* (Shin *et al.*, 2016), *HKL3000sm* (Otwinowski *et al.*, 2003), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *DIAMOND* (Putz & Brandenburg, 2014) and *pubCIF* (Westrip, 2010).

cooling to 298 K, the pH was adjusted to 3.0 by the addition of 1.0 M HCl. A mixture of colorless and violet crystals had formed from the solution over the next few days. To the mixture were added 30 mL of MeOH under stirring, and the stirring was continued for 30 min. The colourless crystals of [H₄L]Cl₄·4H₂O (Moon & Choi, 2021) were removed by filtration. The filtrate was left at 298 K. After few days, plate-like violet single crystals of (I) suitable for X-ray analysis were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C- and N-bound H atoms in the complex were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.97–0.99 Å, and with an N—H distance of 0.99 Å with *U*_{iso}(H) values of 1.2 and 1.5 *U*_{eq} of the parent atoms, respectively. The hydrogen atoms of the water molecules were found in difference-Fourier maps, and were restrained using DFIX and DANG commands during the least-squares refinement with *U*_{iso}(H) values of 1.2 *U*_{eq} of the oxygen atom.

Acknowledgements

The X-ray crystallography experiment at the PLS-II BL2D-SMC beamline was supported in part by MSIT and POSTECH.

Funding information

This work was supported by a Research Grant from Andong National University.

References

- Aree, T., Hong, Y. P. & Choi, J.-H. (2018). *J. Mol. Struct.* **1163**, 86–93.
- Choi, J.-H., Subhan, M. A. & Ng, S. W. (2012). *J. Coord. Chem.* **65**, 3481–3491.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Lim, I.-T. & Choi, K.-Y. (2017). *Polyhedron*, **127**, 361–368.
- Lim, I.-T., Kim, C.-H. & Choi, K.-Y. (2015). *Polyhedron*, **100**, 43–48.
- Lim, J. H., Kang, J. S., Kim, H. C., Koh, E. K. & Hong, C. S. (2006). *Inorg. Chem.* **45**, 7821–7827.
- Moon, D. & Choi, J.-H. (2021). *Acta Cryst.* **E77**, 213–216.
- Moon, D., Jeon, J. & Choi, J.-H. (2020). *J. Coord. Chem.* **73**, 2029–2041.
- Moon, D., Jeon, S., Ryoo, K. S. & Choi, J.-H. (2019). *Acta Cryst.* **E75**, 921–924.
- Moon, D., Subhan, M. A. & Choi, J.-H. (2013). *Acta Cryst.* **E69**, o1620.
- Murphy, B. & Hathaway, B. J. (2003). *Coord. Chem. Rev.* **243**, 237–262.
- Otwinowski, Z., Borek, D., Majewski, W. & Minor, W. (2003). *Acta Cryst.* **A59**, 228–234.
- Putz, H. & Brandenburg, K. (2014). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shin, J. W., Eom, K. & Moon, D. (2016). *J. Synchrotron Rad.* **23**, 369–373.
- Subhan, M. A. & Choi, J.-H. (2014). *Spectrochim. Acta Part A*, **123**, 410–415.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2021). E77, 569-572 [https://doi.org/10.1107/S2056989021004382]

Crystal structure of diaqua(3,14-diethyl-2,6,13,17-tetraazatricyclo-[16.4.0.0^{7,12}]docosane)copper(II) dichloride tetrahydrate

Dohyun Moon and Jong-Ha Choi

Computing details

Data collection: *PAL BL2D-SMDC* (Shin *et al.*, 2016); cell refinement: *HKL3000sm* (Otwinowski *et al.*, 2003); data reduction: *HKL3000sm* (Otwinowski *et al.*, 2003); program(s) used to solve structure: *SHELXT2018* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Diaqua(3,14-diethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane)copper(II) dichloride tetrahydrate

Crystal data

[Cu(C₂₂H₄₄N₄)(H₂O)₂]Cl₂·4H₂O

M_r = 607.14

Triclinic, *P* $\bar{1}$

a = 8.0220 (16) Å

b = 10.020 (2) Å

c = 10.354 (2) Å

α = 81.36 (3)°

β = 72.84 (3)°

γ = 69.71 (3)°

V = 744.8 (3) Å³

Z = 1

F(000) = 327

D_x = 1.354 Mg m⁻³

Synchrotron radiation, λ = 0.610 Å

Cell parameters from 49370 reflections

θ = 0.4–33.7°

μ = 0.63 mm⁻¹

T = 220 K

Plate, violet

0.12 × 0.12 × 0.04 mm

Data collection

Rayonix MX225HS CCD area detector
diffractometer

Radiation source: PLSII 2D bending magnet
 ω scan

Absorption correction: empirical (using
intensity measurements)

(*HKL3000sm Scalepack*; Otwinowski *et al.*,
2003)

T_{min} = 0.597, *T_{max}* = 1.000

8262 measured reflections

4141 independent reflections

4013 reflections with *I* > 2 σ (*I*)

R_{int} = 0.019

θ_{\max} = 25.0°, θ_{\min} = 1.8°

h = -11→11

k = -13→13

l = -14→14

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.039

wR(*F*²) = 0.109

S = 1.10

4141 reflections

179 parameters

9 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[$\sigma^2(F_o^2) + (0.074P)^2 + 0.2905P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

$\Delta\rho_{\max}$ = 0.86 e Å⁻³

$\Delta\rho_{\min}$ = -0.88 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	0.500000	0.500000	0.500000	0.01142 (9)
N1	0.51043 (14)	0.55835 (11)	0.67558 (11)	0.01005 (19)
H1	0.615585	0.595592	0.652199	0.012*
N2	0.31184 (14)	0.69854 (11)	0.49340 (11)	0.00997 (19)
H2	0.191904	0.681599	0.531917	0.012*
C1	0.71839 (18)	0.32162 (13)	0.73164 (14)	0.0148 (2)
H1A	0.755423	0.264611	0.810137	0.018*
H1B	0.816429	0.361734	0.682545	0.018*
C2	0.5438 (2)	0.44417 (14)	0.78296 (13)	0.0167 (2)
H2A	0.438576	0.408346	0.814450	0.020*
H2B	0.554800	0.483575	0.860014	0.020*
C3	0.34162 (16)	0.68194 (12)	0.72187 (12)	0.0110 (2)
H3	0.233945	0.647336	0.753181	0.013*
C4	0.3491 (2)	0.75727 (15)	0.83728 (14)	0.0188 (3)
H4A	0.352331	0.692132	0.917871	0.023*
H4B	0.461760	0.783661	0.810983	0.023*
C5	0.1815 (2)	0.89088 (16)	0.87053 (16)	0.0224 (3)
H5A	0.069628	0.863517	0.904981	0.027*
H5B	0.191875	0.939817	0.941531	0.027*
C6	0.1665 (2)	0.99167 (15)	0.74592 (16)	0.0209 (3)
H6A	0.273938	1.024974	0.715722	0.025*
H6B	0.056173	1.074922	0.769256	0.025*
C7	0.15596 (18)	0.91777 (14)	0.63083 (15)	0.0166 (3)
H7A	0.042053	0.893014	0.657577	0.020*
H7B	0.153337	0.983052	0.550302	0.020*
C8	0.32144 (16)	0.78275 (12)	0.59713 (12)	0.0103 (2)
H8	0.434051	0.810898	0.561857	0.012*
C9	0.29426 (17)	0.77801 (12)	0.36087 (13)	0.0123 (2)
H9	0.175786	0.856733	0.379043	0.015*
C10	0.4461 (2)	0.84486 (16)	0.29985 (15)	0.0206 (3)
H10A	0.565865	0.770339	0.290927	0.025*
H10B	0.436977	0.913687	0.361642	0.025*
C11	0.4366 (3)	0.9202 (2)	0.16157 (18)	0.0339 (4)
H11A	0.471172	0.849892	0.095303	0.051*
H11B	0.520561	0.975525	0.135068	0.051*
H11C	0.312058	0.982978	0.166352	0.051*
Cl1	0.85009 (5)	0.71364 (5)	0.60787 (4)	0.02792 (11)
O1	0.81875 (19)	0.57072 (14)	0.37263 (14)	0.0307 (3)
H1O1	0.919 (2)	0.4892 (16)	0.370 (3)	0.037*

H2O1	0.823 (3)	0.628 (2)	0.433 (2)	0.037*
O2	0.9753 (3)	0.6599 (2)	0.09693 (19)	0.0573 (5)
H1O2	0.919 (4)	0.641 (4)	0.1865 (13)	0.069*
H2O2	0.897 (4)	0.678 (4)	0.041 (2)	0.069*
O3	0.7816 (3)	0.6189 (3)	-0.06985 (19)	0.0642 (6)
H1O3	0.813 (5)	0.665 (3)	-0.154 (2)	0.077*
H2O3	0.855 (4)	0.5235 (15)	-0.068 (3)	0.077*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01753 (13)	0.00598 (12)	0.00936 (12)	0.00037 (8)	-0.00540 (8)	-0.00249 (7)
N1	0.0121 (4)	0.0065 (4)	0.0101 (4)	0.0000 (3)	-0.0032 (3)	-0.0025 (3)
N2	0.0125 (4)	0.0069 (4)	0.0112 (5)	-0.0020 (3)	-0.0045 (4)	-0.0025 (3)
C1	0.0184 (6)	0.0116 (5)	0.0161 (6)	-0.0007 (4)	-0.0110 (5)	-0.0022 (4)
C2	0.0239 (6)	0.0112 (5)	0.0110 (5)	0.0002 (5)	-0.0055 (5)	-0.0009 (4)
C3	0.0113 (5)	0.0086 (5)	0.0113 (5)	-0.0002 (4)	-0.0021 (4)	-0.0038 (4)
C4	0.0223 (6)	0.0163 (6)	0.0152 (6)	0.0024 (5)	-0.0066 (5)	-0.0101 (5)
C5	0.0214 (6)	0.0199 (6)	0.0207 (7)	0.0029 (5)	-0.0029 (5)	-0.0139 (5)
C6	0.0216 (6)	0.0119 (6)	0.0291 (7)	0.0025 (5)	-0.0105 (5)	-0.0120 (5)
C7	0.0156 (6)	0.0098 (5)	0.0232 (6)	0.0033 (4)	-0.0087 (5)	-0.0079 (5)
C8	0.0114 (5)	0.0068 (5)	0.0128 (5)	-0.0005 (4)	-0.0043 (4)	-0.0038 (4)
C9	0.0155 (5)	0.0078 (5)	0.0135 (5)	-0.0003 (4)	-0.0077 (4)	-0.0004 (4)
C10	0.0295 (7)	0.0207 (6)	0.0173 (6)	-0.0149 (6)	-0.0095 (5)	0.0054 (5)
C11	0.0573 (11)	0.0326 (9)	0.0209 (7)	-0.0262 (8)	-0.0163 (7)	0.0126 (6)
Cl1	0.02403 (19)	0.0315 (2)	0.0321 (2)	-0.01328 (15)	-0.00442 (15)	-0.00825 (16)
O1	0.0371 (7)	0.0302 (6)	0.0299 (6)	-0.0124 (5)	-0.0141 (5)	-0.0017 (5)
O2	0.0797 (13)	0.0716 (12)	0.0341 (8)	-0.0444 (11)	-0.0144 (8)	0.0048 (8)
O3	0.0475 (10)	0.1017 (17)	0.0319 (8)	-0.0083 (10)	-0.0118 (7)	-0.0040 (9)

Geometric parameters (Å, °)

Cu1—N1 ⁱ	2.0240 (11)	C5—C6	1.521 (2)
Cu1—N1	2.0240 (11)	C5—H5A	0.9800
Cu1—N2	2.0441 (13)	C5—H5B	0.9800
Cu1—N2 ⁱ	2.0441 (13)	C6—C7	1.5310 (19)
Cu1—O1 ⁱ	2.7866 (16)	C6—H6A	0.9800
Cu1—O1	2.7866 (16)	C6—H6B	0.9800
N1—C2	1.4826 (17)	C7—C8	1.5288 (18)
N1—C3	1.4932 (16)	C7—H7A	0.9800
N1—H1	0.9900	C7—H7B	0.9800
N2—C8	1.4958 (15)	C8—H8	0.9900
N2—C9	1.4983 (16)	C9—C10	1.5216 (19)
N2—H2	0.9900	C9—H9	0.9900
C1—C2	1.5217 (19)	C10—C11	1.525 (2)
C1—C9 ⁱ	1.5295 (17)	C10—H10A	0.9800
C1—H1A	0.9800	C10—H10B	0.9800
C1—H1B	0.9800	C11—H11A	0.9700

C2—H2A	0.9800	C11—H11B	0.9700
C2—H2B	0.9800	C11—H11C	0.9700
C3—C8	1.5272 (18)	O1—H1O1	0.924 (9)
C3—C4	1.5315 (18)	O1—H2O1	0.928 (9)
C3—H3	0.9900	O2—H1O2	0.927 (10)
C4—C5	1.528 (2)	O2—H2O2	0.931 (10)
C4—H4A	0.9800	O3—H1O3	0.931 (10)
C4—H4B	0.9800	O3—H2O3	0.934 (10)
N1 ⁱ —Cu1—N1	180.0	C3—C4—H4B	109.5
N1 ⁱ —Cu1—N2	95.42 (5)	H4A—C4—H4B	108.1
N1—Cu1—N2	84.58 (5)	C6—C5—C4	111.05 (12)
N1 ⁱ —Cu1—N2 ⁱ	84.58 (5)	C6—C5—H5A	109.4
N1—Cu1—N2 ⁱ	95.42 (5)	C4—C5—H5A	109.4
N2—Cu1—N2 ⁱ	180.0	C6—C5—H5B	109.4
N1 ⁱ —Cu1—O1 ⁱ	88.11 (5)	C4—C5—H5B	109.4
N1—Cu1—O1 ⁱ	91.89 (5)	H5A—C5—H5B	108.0
N2—Cu1—O1 ⁱ	81.60 (5)	C5—C6—C7	111.09 (12)
N2 ⁱ —Cu1—O1 ⁱ	98.40 (5)	C5—C6—H6A	109.4
N1 ⁱ —Cu1—O1	91.89 (5)	C7—C6—H6A	109.4
N1—Cu1—O1	88.11 (5)	C5—C6—H6B	109.4
N2—Cu1—O1	98.40 (5)	C7—C6—H6B	109.4
N2 ⁱ —Cu1—O1	81.60 (5)	H6A—C6—H6B	108.0
O1 ⁱ —Cu1—O1	180.00 (5)	C8—C7—C6	110.69 (11)
C2—N1—C3	113.32 (10)	C8—C7—H7A	109.5
C2—N1—Cu1	116.78 (8)	C6—C7—H7A	109.5
C3—N1—Cu1	107.51 (8)	C8—C7—H7B	109.5
C2—N1—H1	106.2	C6—C7—H7B	109.5
C3—N1—H1	106.2	H7A—C7—H7B	108.1
Cu1—N1—H1	106.2	N2—C8—C3	106.51 (9)
C8—N2—C9	115.20 (9)	N2—C8—C7	113.49 (10)
C8—N2—Cu1	107.77 (8)	C3—C8—C7	111.87 (11)
C9—N2—Cu1	120.89 (8)	N2—C8—H8	108.3
C8—N2—H2	103.6	C3—C8—H8	108.3
C9—N2—H2	103.6	C7—C8—H8	108.3
Cu1—N2—H2	103.6	N2—C9—C10	111.93 (10)
C2—C1—C9 ⁱ	116.20 (11)	N2—C9—C1 ⁱ	108.49 (10)
C2—C1—H1A	108.2	C10—C9—C1 ⁱ	114.34 (11)
C9 ⁱ —C1—H1A	108.2	N2—C9—H9	107.2
C2—C1—H1B	108.2	C10—C9—H9	107.2
C9 ⁱ —C1—H1B	108.2	C1 ⁱ —C9—H9	107.2
H1A—C1—H1B	107.4	C9—C10—C11	112.89 (13)
N1—C2—C1	111.40 (11)	C9—C10—H10A	109.0
N1—C2—H2A	109.3	C11—C10—H10A	109.0
C1—C2—H2A	109.3	C9—C10—H10B	109.0
N1—C2—H2B	109.3	C11—C10—H10B	109.0
C1—C2—H2B	109.3	H10A—C10—H10B	107.8
H2A—C2—H2B	108.0	C10—C11—H11A	109.5

N1—C3—C8	106.11 (10)	C10—C11—H11B	109.5
N1—C3—C4	113.33 (10)	H11A—C11—H11B	109.5
C8—C3—C4	111.49 (10)	C10—C11—H11C	109.5
N1—C3—H3	108.6	H11A—C11—H11C	109.5
C8—C3—H3	108.6	H11B—C11—H11C	109.5
C4—C3—H3	108.6	Cu1—O1—H1O1	108.4 (16)
C5—C4—C3	110.76 (12)	Cu1—O1—H2O1	103.4 (16)
C5—C4—H4A	109.5	H1O1—O1—H2O1	106.2 (16)
C3—C4—H4A	109.5	H1O2—O2—H2O2	113 (2)
C5—C4—H4B	109.5	H1O3—O3—H2O3	111 (2)
C3—N1—C2—C1	-179.24 (10)	C9—N2—C8—C7	57.28 (14)
Cu1—N1—C2—C1	54.98 (13)	Cu1—N2—C8—C7	-164.43 (9)
C9 ⁱ —C1—C2—N1	-75.35 (15)	N1—C3—C8—N2	57.32 (12)
C2—N1—C3—C8	-175.98 (10)	C4—C3—C8—N2	-178.85 (10)
Cu1—N1—C3—C8	-45.40 (10)	N1—C3—C8—C7	-178.14 (10)
C2—N1—C3—C4	61.34 (14)	C4—C3—C8—C7	-54.31 (14)
Cu1—N1—C3—C4	-168.07 (9)	C6—C7—C8—N2	175.13 (11)
N1—C3—C4—C5	174.44 (11)	C6—C7—C8—C3	54.58 (15)
C8—C3—C4—C5	54.79 (16)	C8—N2—C9—C10	54.25 (14)
C3—C4—C5—C6	-56.45 (16)	Cu1—N2—C9—C10	-78.16 (12)
C4—C5—C6—C7	57.37 (16)	C8—N2—C9—C1 ⁱ	-178.65 (10)
C5—C6—C7—C8	-56.05 (16)	Cu1—N2—C9—C1 ⁱ	48.93 (12)
C9—N2—C8—C3	-179.19 (9)	N2—C9—C10—C11	177.17 (13)
Cu1—N2—C8—C3	-40.90 (10)	C1 ⁱ —C9—C10—C11	53.30 (17)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots C11	0.99	2.45	3.4383 (14)	173
N2—H2 \cdots C11 ⁱⁱ	0.99	2.54	3.4962 (14)	163
O1—H1O1 \cdots C11 ⁱⁱⁱ	0.92 (1)	2.26 (1)	3.1799 (19)	173 (2)
O1—H2O1 \cdots C11	0.93 (1)	2.21 (1)	3.1153 (15)	166 (2)
O2—H1O2 \cdots O1	0.93 (1)	1.98 (1)	2.902 (2)	172 (3)
O2—H2O2 \cdots O3	0.93 (1)	1.94 (2)	2.794 (3)	152 (3)
O3—H1O3 \cdots C11 ^{iv}	0.93 (1)	2.39 (2)	3.266 (2)	157 (3)
O3—H2O3 \cdots O2 ^v	0.93 (1)	1.87 (1)	2.796 (4)	170 (3)

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