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Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane-$\kappa^4N^3,N^6,N^{10},N^{13}$)bis(perchlorato-$\kappa O$)copper(II) from synchrotron data

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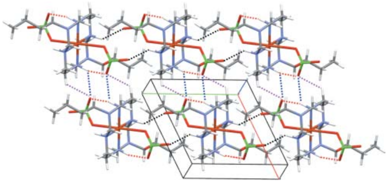
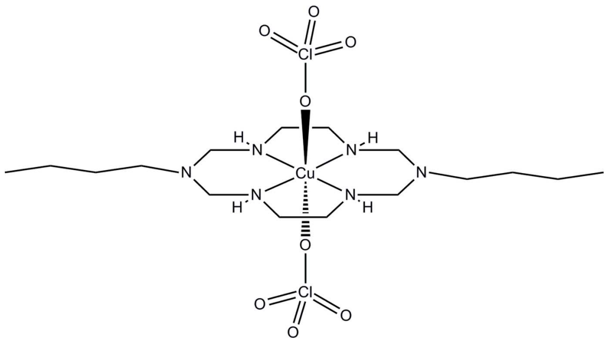
The structure of the title compound, $[Cu(ClO_4)_2(C_{16}H_{38}N_6)]$ has been determined from synchrotron data, λ = 0.62988 Å. The asymmetric unit comprises one half of the Cu^{II} complex as the Cu^{II} cation lies on an inversion center. It is coordinated by the four secondary N atoms of the macrocyclic ligand and the mutually *trans* O atoms of the two perchlorate ions in a tetragonally distorted octahedral geometry. The average equatorial Cu—N bond length is significantly shorter than the average axial Cu—O bond length [2.010 (4) and 2.569 (1) Å, respectively]. Intramolecular N—H···O hydrogen bonds between the macrocyclic ligand and uncoordinating O atoms of the perchlorate ligand stabilize the molecular structure. In the crystal structure, an extensive series of intermolecular N—H···O and C—H···O hydrogen bonds generate a three-dimensional network.



1. Chemical context

Coordination compounds with macrocyclic ligands have attracted considerable attention in chemistry, biological chemistry and materials science (Lehn, 1995). In particular, macrocyclic Cu^{II} complexes with vacant sites in the axial positions are good building blocks for assembling multi-dimensional frameworks (Ko *et al.*, 2002), with potential applications as metal extractants, radiotherapeutic materials and as medical imaging agents (Sowen *et al.*, 2013). For example, Cu^{II} complexes with tetra-azamacrocyclic ligands have been studied with various auxiliary anionic ligands such as ferricyanide and hexacyanidochromate and their biological redox-sensing and magnetic properties (Xiang *et al.*, 2009) have been investigated. Moreover, the perchlorate ion is a versatile anion which can easily bridge two transition metal complexes, allowing the assembly of multi-dimensional compounds (Kwak *et al.*, 2001).



Here, we report the synthesis and crystal structure of a Cu^{II} azamacrocyclic complex, *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexa-

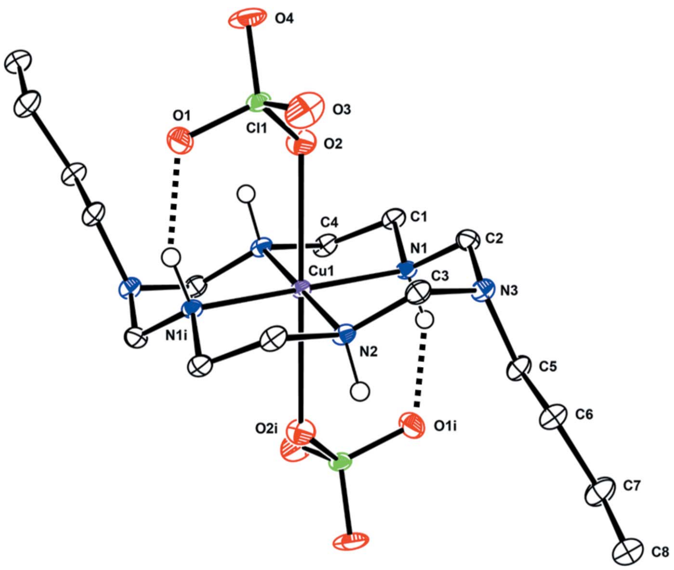


Figure 1
View of the molecular structure of the title compound, showing the atom labelling scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity. Intramolecular N—H···O hydrogen bonds are shown as black dashed lines. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

azacyclotetradecane-$\kappa^4N^3,N^6,N^{10},N^{13}$)bis(perchlorato-$\kappa O$)copper(II), which has two perchlorate ions coordinating in the axial positions of the overall six-coordinate complex.

2. Structural commentary

In the title compound, the coordination environment around the Cu^{II} ion, which lies on an inversion center, is tetragonally distorted octahedral. The copper(II) ion binds to the four secondary N atoms of the azamacrocyclic ligand in a square-planar fashion in the equatorial plane, with two O atoms from the perchlorate anions in axial positions as shown in Fig. 1. The bonds to the two axially located perchlorate anions are significantly longer than those to the donor N atoms in the equatorial plane. This can be attributed either to a rather large Jahn–Teller distortion of the Cu^{II} ion and/or to a considerable ring contraction of the azamacrocyclic ligand (Halcrow, 2013). The six-membered chelate rings adopt chair conformations and the five-membered chelate rings assume *gauche* conformations (Min & Suh, 2001). Intramolecular N—H···O hydrogen bonds between the secondary amine groups of the azamacrocyclic ligand and an O atom of each perchlorate ion contribute to the molecular conformation (Fig. 1 and Table 1).

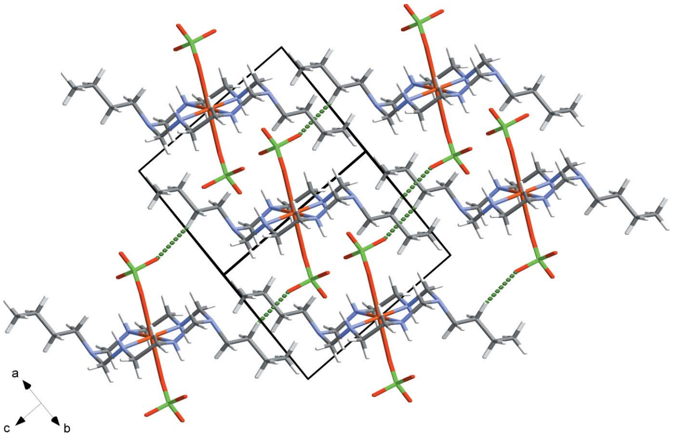


Figure 2
View of the contacts made by an individual complex molecule with hydrogen bonds drawn as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	1.00	2.50	3.136 (2)	121
N2—H2···O4^{ii}	1.00	2.17	3.000 (2)	139
C1—H1A···O1^{i}	0.99	2.46	3.160 (2)	127
N1—H1···O1^{iii}	1.00	2.08	3.018 (2)	155
C6—H6B···O3^{iv}	0.99	2.50	3.338 (3)	142

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

3. Supramolecular features

Each complex molecule forms three N—H···O and two C—H···O hydrogen bonds (Steed & Atwood, 2009), as shown in Table 1, Fig. 2. Sheets of complex molecules form in the *ab* plane, Fig. 3, and additional C6—H6B···O3 contacts link these sheets into a three-dimensional network.

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, May 2014 with three updates; Groom & Allen 2014) indicated that 51 azamacrocyclic Cu^{II} complexes with pendant alkyl groups had been reported previously. These complexes have been studied as good building blocks for supramolecular chemistry and contain a variety of pendant alkyl groups (Cho *et al.*, 2003). Their magnetic properties and guest-exchange effects with cyanido groups and carboxylic acid groups as ligands have also been investigated (Ko *et al.*, 2002; Zhou *et al.*, 2014). No corresponding azamacrocyclic Cu^{II} complex with

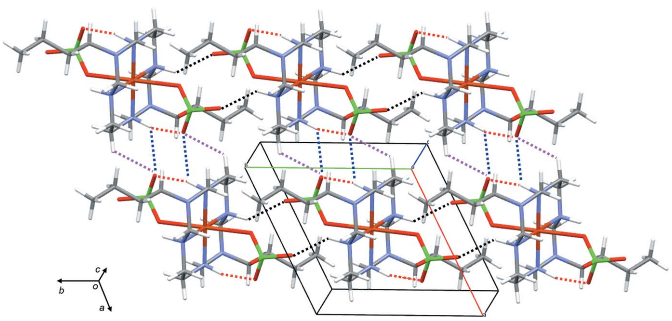


Figure 3
Sheets of complex molecules in the *ab* plane. Hydrogen-bonding interactions are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(ClO_4)_2(C_{16}H_{38}N_6)]$
M_r	576.96
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	8.2230 (16), 8.3600 (17), 10.039 (2)
α, β, γ (°)	92.87 (3), 96.12 (3), 116.60 (3)
V (Å^3)	609.8 (3)
Z	1
Radiation type	Synchrotron, λ = 0.62998 Å
μ (mm^{-1})	0.84
Crystal size (mm)	0.10 × 0.10 × 0.03
Data collection	
Diffractometer	ADSC Q210 CCD area detector
Absorption correction	Empirical (using intensity measurements) *HKL3000sm SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.921, 0.975
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6292, 3195, 2536
R_{int}	0.025
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.696
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.091, 1.02
No. of reflections	3195
No. of parameters	152
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.86

Computer programs: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2014/4* and *SHELXL2014/7* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012)and *publCIF* (Westrip, 2010).

pendant butyl groups has been reported and the title compound was newly synthesized for this research.

5. Synthesis and crystallization

The title compound was prepared as follows. Ethylenediamine (3.4 mL, 0.05 mol), paraformaldehyde (3.0 g, 0.10 mol), and butylamine (3.7 g, 0.05 mol) were slowly added to a stirred solution of $CuCl_2 \cdot 2H_2O$ (4.26 g, 0.025 mol) in MeOH (50 mL). The mixture was heated to reflux for 1 day. The solution was filtered and cooled at room temperature. $HClO_4$ (70%, 15 mL) was added to the purple solution. A bright-purple precipitate formed and was filtered off, washed with H_2O, MeOH, and diethyl ether, and dried in air. Purple crystals of the title compound were obtained by diffusion of diethyl ether into the purple solution over several days. Yield: 2.38g (17%). FT–IR (ATR, cm^{-1}): 3240, 2936, 1443, 1053, 995, 962, 746.

Safety note: Although we have experienced no problems with the compound reported in this study, perchlorate salts of metal complexes are often explosive and should be handled with great caution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.98–0.99 Å and an N—H distance of 1.0 Å with U_{iso}(H) values of 1.2 or 1.5 U_{eq} of the parent atoms.

Acknowledgements

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Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane-$\kappa^4N^3,N^6,N^{10},N^{13}$)bis(perchlorato-$\kappa O$)copper(II) from synchrotron data

Dae-Woong Kim, Jong Won Shin and Dohyun Moon

Computing details

Data collection: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

trans-(1,8-Dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane-$\kappa^4N^3,N^6,N^{10},N^{13}$)bis(perchlorato-$\kappa O$)copper(II)

Crystal data

$[Cu(ClO_4)_2(C_{16}H_{38}N_6)]$
$M_r = 576.96$
Triclinic, $P\overline{1}$
$a = 8.2230$ (16) Å
$b = 8.3600$ (17) Å
$c = 10.039$ (2) Å
$\alpha = 92.87$ (3)°
$\beta = 96.12$ (3)°
$\gamma = 116.60$ (3)°
$V = 609.8$ (3) Å^3

$Z = 1$
$F(000) = 303$
$D_x = 1.571$ Mg m^{-3}
Synchrotron radiation, $\lambda = 0.62998$ Å
Cell parameters from 16838 reflections
$\theta = 0.4$–33.6°
$\mu = 0.84$ mm^{-1}
$T = 100$ K
Plate, purple
0.10 × 0.10 × 0.03 mm

Data collection

ADSC Q210 CCD area-detector diffractometer
Radiation source: PLSII 2D bending magnet
ω scans
Absorption correction: empirical (using intensity measurements) (*HKL3000sm SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.921$, $T_{max} = 0.975$

6292 measured reflections
3195 independent reflections
2536 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.8°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.091$
$S = 1.02$
3195 reflections

152 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.5000	0.5000	0.5000	0.01063 (10)
N1	0.7678 (2)	0.6261 (2)	0.57656 (16)	0.0119 (3)
H1	0.8221	0.5443	0.5535	0.014*
N2	0.4291 (2)	0.3507 (2)	0.65492 (16)	0.0123 (3)
H2	0.4599	0.2490	0.6389	0.015*
N3	0.7247 (2)	0.5222 (2)	0.80108 (16)	0.0152 (3)
C1	0.8525 (2)	0.7860 (2)	0.5034 (2)	0.0155 (4)
H1A	0.9876	0.8328	0.5156	0.019*
H1B	0.8242	0.8821	0.5385	0.019*
C2	0.8084 (3)	0.6731 (3)	0.7267 (2)	0.0164 (4)
H2A	0.9432	0.7303	0.7541	0.020*
H2B	0.7654	0.7626	0.7508	0.020*
C3	0.5278 (3)	0.4466 (3)	0.7910 (2)	0.0158 (4)
H3A	0.4948	0.5445	0.8119	0.019*
H3B	0.4855	0.3612	0.8594	0.019*
C4	0.2256 (2)	0.2705 (3)	0.6448 (2)	0.0156 (4)
H4A	0.1894	0.3598	0.6819	0.019*
H4B	0.1786	0.1649	0.6964	0.019*
C5	0.8000 (3)	0.3919 (3)	0.7910 (2)	0.0169 (4)
H5A	0.9359	0.4586	0.8041	0.020*
H5B	0.7593	0.3265	0.6992	0.020*
C6	0.7409 (3)	0.2567 (3)	0.8931 (2)	0.0177 (4)
H6A	0.6067	0.1782	0.8721	0.021*
H6B	0.7662	0.3217	0.9840	0.021*
C7	0.8401 (3)	0.1406 (3)	0.8937 (2)	0.0221 (4)
H7A	0.9723	0.2171	0.9266	0.026*
H7B	0.8289	0.0888	0.8003	0.026*
C8	0.7636 (3)	−0.0116 (3)	0.9822 (2)	0.0215 (4)
H8A	0.7749	0.0390	1.0749	0.032*
H8B	0.8328	−0.0812	0.9806	0.032*
H8C	0.6338	−0.0904	0.9481	0.032*
Cl1	0.32457 (6)	0.78356 (6)	0.65025 (4)	0.01406 (11)
O1	0.1610 (2)	0.6610 (2)	0.56090 (18)	0.0282 (4)
O2	0.48300 (19)	0.77847 (19)	0.60352 (16)	0.0221 (3)
O3	0.3102 (3)	0.7249 (2)	0.78200 (16)	0.0319 (4)
O4	0.3413 (2)	0.96148 (19)	0.65392 (18)	0.0285 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00685 (15)	0.00798 (15)	0.01599 (17)	0.00179 (11)	0.00383 (11)	0.00327 (12)
N1	0.0092 (7)	0.0080 (6)	0.0180 (8)	0.0032 (5)	0.0030 (5)	0.0031 (6)
N2	0.0091 (6)	0.0114 (7)	0.0184 (8)	0.0053 (5)	0.0054 (6)	0.0044 (6)
N3	0.0152 (7)	0.0159 (8)	0.0170 (8)	0.0091 (6)	0.0028 (6)	0.0022 (6)
C1	0.0082 (8)	0.0091 (8)	0.0275 (10)	0.0015 (6)	0.0051 (7)	0.0069 (7)
C2	0.0143 (8)	0.0125 (8)	0.0208 (10)	0.0052 (7)	0.0009 (7)	0.0000 (7)
C3	0.0156 (9)	0.0176 (9)	0.0176 (9)	0.0100 (7)	0.0050 (7)	0.0034 (8)
C4	0.0094 (8)	0.0141 (8)	0.0253 (10)	0.0047 (7)	0.0096 (7)	0.0101 (8)
C5	0.0148 (8)	0.0199 (9)	0.0202 (9)	0.0112 (7)	0.0039 (7)	0.0046 (8)
C6	0.0197 (9)	0.0191 (9)	0.0194 (10)	0.0124 (8)	0.0057 (7)	0.0059 (8)
C7	0.0186 (9)	0.0242 (10)	0.0295 (11)	0.0133 (8)	0.0081 (8)	0.0100 (9)
C8	0.0242 (10)	0.0202 (10)	0.0244 (11)	0.0133 (8)	0.0050 (8)	0.0054 (8)
Cl1	0.0128 (2)	0.0121 (2)	0.0198 (2)	0.00762 (17)	0.00396 (16)	0.00067 (18)
O1	0.0152 (7)	0.0258 (8)	0.0420 (10)	0.0115 (6)	−0.0050 (6)	−0.0127 (7)
O2	0.0132 (6)	0.0216 (7)	0.0332 (8)	0.0088 (6)	0.0086 (6)	−0.0005 (6)
O3	0.0450 (10)	0.0412 (10)	0.0225 (8)	0.0280 (8)	0.0144 (7)	0.0124 (8)
O4	0.0297 (8)	0.0123 (7)	0.0490 (11)	0.0132 (6)	0.0101 (7)	0.0047 (7)

Geometric parameters (Å, º)

Cu1—N1	2.0073 (17)	C4—C1^{i}	1.518 (3)
Cu1—N1^{i}	2.0073 (17)	C4—H4A	0.9900
Cu1—N2^{i}	2.0131 (17)	C4—H4B	0.9900
Cu1—N2	2.0131 (17)	C5—C6	1.515 (3)
N1—C1	1.478 (2)	C5—H5A	0.9900
N1—C2	1.501 (3)	C5—H5B	0.9900
N1—H1	1.0000	C6—C7	1.522 (3)
N2—C4	1.487 (2)	C6—H6A	0.9900
N2—C3	1.496 (3)	C6—H6B	0.9900
N2—H2	1.0000	C7—C8	1.523 (3)
N3—C2	1.432 (2)	C7—H7A	0.9900
N3—C3	1.440 (2)	C7—H7B	0.9900
N3—C5	1.478 (2)	C8—H8A	0.9800
C1—C4^{i}	1.518 (3)	C8—H8B	0.9800
C1—H1A	0.9900	C8—H8C	0.9800
C1—H1B	0.9900	Cl1—O4	1.4293 (15)
C2—H2A	0.9900	Cl1—O3	1.4318 (17)
C2—H2B	0.9900	Cl1—O1	1.4420 (17)
C3—H3A	0.9900	Cl1—O2	1.4481 (14)
C3—H3B	0.9900		
N1—Cu1—N1^{i}	180.00 (9)	H3A—C3—H3B	107.7
N1—Cu1—N2^{i}	86.45 (7)	N2—C4—C1^{i}	107.28 (15)
N1^{i}—Cu1—N2^{i}	93.55 (7)	N2—C4—H4A	110.3
N1—Cu1—N2	93.55 (7)	C1^{i}—C4—H4A	110.3

N1^{i}—Cu1—N2	86.45 (7)	N2—C4—H4B	110.3
N2^{i}—Cu1—N2	180.0	C1^{i}—C4—H4B	110.3
C1—N1—C2	112.37 (15)	H4A—C4—H4B	108.5
C1—N1—Cu1	106.33 (11)	N3—C5—C6	113.14 (15)
C2—N1—Cu1	115.28 (12)	N3—C5—H5A	109.0
C1—N1—H1	107.5	C6—C5—H5A	109.0
C2—N1—H1	107.5	N3—C5—H5B	109.0
Cu1—N1—H1	107.5	C6—C5—H5B	109.0
C4—N2—C3	113.49 (15)	H5A—C5—H5B	107.8
C4—N2—Cu1	106.73 (11)	C5—C6—C7	112.19 (16)
C3—N2—Cu1	115.29 (12)	C5—C6—H6A	109.2
C4—N2—H2	107.0	C7—C6—H6A	109.2
C3—N2—H2	107.0	C5—C6—H6B	109.2
Cu1—N2—H2	107.0	C7—C6—H6B	109.2
C2—N3—C3	114.81 (15)	H6A—C6—H6B	107.9
C2—N3—C5	114.08 (15)	C6—C7—C8	112.45 (16)
C3—N3—C5	116.15 (16)	C6—C7—H7A	109.1
N1—C1—C4^{i}	107.87 (15)	C8—C7—H7A	109.1
N1—C1—H1A	110.1	C6—C7—H7B	109.1
C4^{i}—C1—H1A	110.1	C8—C7—H7B	109.1
N1—C1—H1B	110.1	H7A—C7—H7B	107.8
C4^{i}—C1—H1B	110.1	C7—C8—H8A	109.5
H1A—C1—H1B	108.4	C7—C8—H8B	109.5
N3—C2—N1	114.03 (15)	H8A—C8—H8B	109.5
N3—C2—H2A	108.7	C7—C8—H8C	109.5
N1—C2—H2A	108.7	H8A—C8—H8C	109.5
N3—C2—H2B	108.7	H8B—C8—H8C	109.5
N1—C2—H2B	108.7	O4—Cl1—O3	110.11 (11)
H2A—C2—H2B	107.6	O4—Cl1—O1	109.74 (10)
N3—C3—N2	113.39 (15)	O3—Cl1—O1	108.36 (11)
N3—C3—H3A	108.9	O4—Cl1—O2	110.65 (10)
N2—C3—H3A	108.9	O3—Cl1—O2	108.82 (10)
N3—C3—H3B	108.9	O1—Cl1—O2	109.12 (9)
N2—C3—H3B	108.9		

C2—N1—C1—C4^{i}	−169.53 (14)	C4—N2—C3—N3	179.24 (14)
Cu1—N1—C1—C4^{i}	−42.53 (15)	Cu1—N2—C3—N3	−57.23 (18)
C3—N3—C2—N1	−69.8 (2)	C3—N2—C4—C1^{i}	168.24 (15)
C5—N3—C2—N1	67.8 (2)	Cu1—N2—C4—C1^{i}	40.14 (16)
C1—N1—C2—N3	178.48 (14)	C2—N3—C5—C6	167.34 (16)
Cu1—N1—C2—N3	56.43 (18)	C3—N3—C5—C6	−55.6 (2)
C2—N3—C3—N2	70.2 (2)	N3—C5—C6—C7	−172.24 (17)
C5—N3—C3—N2	−66.5 (2)	C5—C6—C7—C8	−172.38 (18)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{ii}	1.00	2.50	3.136 (2)	121
N2—H2···O4^{iii}	1.00	2.17	3.000 (2)	139
C1—H1*A*···O1^{ii}	0.99	2.46	3.160 (2)	127
N1—H1···O1^{i}	1.00	2.08	3.018 (2)	155
C6—H6*B*···O3^{iv}	0.99	2.50	3.338 (3)	142

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