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Synthesis and crystal structure of [2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene-κ^4N]copper(II) bis(perchlorate)

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The title copper(II) complex of a pyridine-containing macrocycle (PyMAC), $[Cu(C_{16}H_{28}N_4)](ClO_4)_2$, has been prepared. The crystal structure reveals the Cu^{II} atom to be octahedrally coordinated by a tetradentate aminopyridine macrocyclic ligand surrounding the metal cation in a square-planar geometry. Two weakly bound perchlorate counter-ions occupy the axial sites above and below the macrocyclic plane. The crystal studied was refined as a two-component pseudo-merohedral twin; the refined fractional contribution of the minor component is 38.77 (8)%

1. Chemical context

There have been several studies of the macrocycles synthesized from 2,6-diacetylpyridine and polyamines. One of the first examples, reported by Karn & Busch (1966), involved a nickel(II)-templated condensation of 2,6-diacetylpyridine and bis(3-aminopropyl)amine. Their pioneering work enabled subsequent syntheses of various pyridine-containing macrocycles (Rezaeivala & Keypour, 2014), including a family of complexes with appended arms (PyMACs) (Organo *et al.*, 2009; Herrera *et al.*, 2003) as shown in Fig. 1.

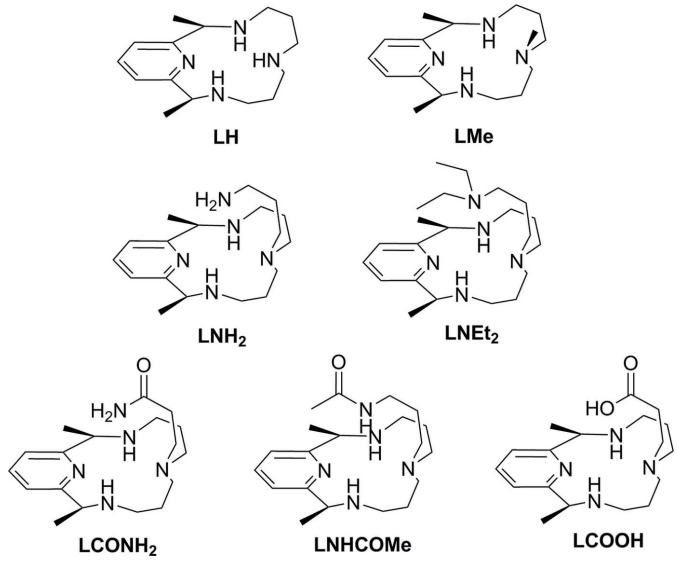
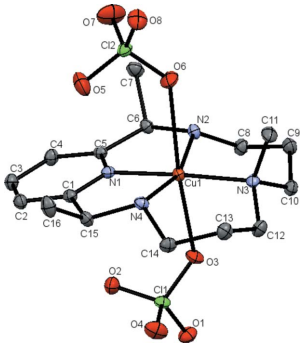


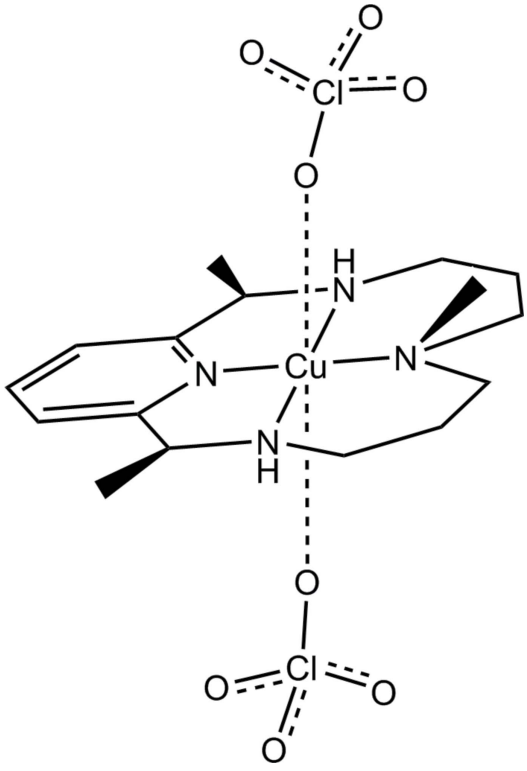
Figure 1
Pyridine-containing macrocycles (PyMACs).



Various metal ions have been incorporated into PyMAC ligands, and the resulting complexes often showed interesting catalytic properties. For example, Ni^{II}–PyMAC complexes have been found to exhibit peroxidase-like activity, with NiLCOOH (Fig. 1) being most active (Organo *et al.*, 2009). Fe^{II}–LMe (Fig. 1) was also found to have catalytic use in epoxidation reactions of cyclooctene with hydrogen peroxide (Ye *et al.*, 2012). A similar Cu^{II}–PyMAC complex but without methyl groups at the macrocyclic ring was reported by Fernandes *et al.* (2007) to scavenge superoxide.

Pyridine-containing metallomacrocycles have also found utility beyond synthetic chemistry. For example, Cu–macrocyclic complexes have become increasingly important in radiopharmaceutical applications as contrast agents in positron emission tomographic (PET) imaging (Boros *et al.*, 2014).

While there are known Cu–pyridine macrocycles, only a few have been characterized structurally (Caira *et al.*, 1975; Lindoy *et al.*, 2001; Herrera *et al.*, 2003; Autzen *et al.*, 2003). Here, we report the synthesis and crystal structure of a Cu^{II}–PyMAC perchlorate compound.



2. Structural commentary

The title compound has the Cu^{II} atom in a distorted octahedral coordination, with the tetradentate aminopyridine macrocyclic ligand surrounding the metal atom in a square-planar geometry (Fig. 2). Two perchlorate counter-ions occupy the axial sites perpendicular to the macrocyclic plane. The macrocyclic ligand incorporates a 2,6-substituted pyridine unit that is connected on both sides to an aliphatic chain of 11 atoms, including two secondary amines and a tertiary amine bearing a methyl group. When coordinated to the Cu^{II} atom,

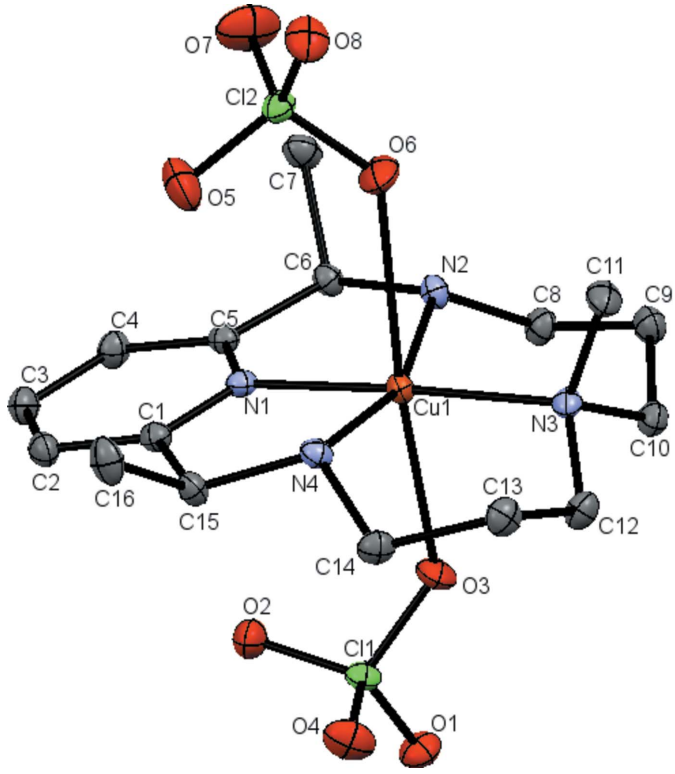


Figure 2
An *ORTEP* diagram of the molecular structure of Cu*L*Me$(ClO_4)_2$ [*L*Me = 2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, see Fig. 1], showing the atom-labeling scheme, with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

the macrocycle exhibits approximate molecular mirror symmetry with respect to the plane that bisects the pyridine and tertiary amine nitrogen atoms, and is perpendicular to the macrocyclic plane. The Cu—N distances between Cu^{II} and secondary amine nitrogen atoms [2.0417 (14) and 2.0445 (15) Å] are similar to each other; the distance between Cu^{II} and the tertiary amine N atom [2.0108 (13) Å] is slightly shorter. In contrast, the Cu—N_{py} bond length [1.9316 (13) Å] is much shorter than the Cu—N_{amine} bonds. Both perchlorate anions are only weakly bound, with Cu—O6 and Cu—O3 distances of 2.6478 (13) and 2.4736 (13) Å, respectively.

An intramolecular contact (N4—H4···O5) occurs between a perchlorate O atom and the tertiary amine NH group. The N···O distance [3.423 (2) Å] is longer than the sum of van der Waals radii of the two atoms (2.94 Å), suggesting this is a weaker interaction comparing to normal hydrogen-bonding interactions.

3. Supramolecular features

In the crystal of the complex (see Fig. 3), several N—H···O and C_{py}—H···O hydrogen bonds have longer $D\cdots A$ distances than the van der Waals radii of the corresponding pairs of atoms (3.25 Å for C···O). The resulting geometry is a chain along [010]. Numerical details are given in Table 1.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O7^{i}	0.83 (2)	2.94 (2)	3.536 (2)	130.6 (18)
N4—H4···O4^{ii}	0.86 (2)	2.45 (2)	3.1619 (19)	140.2 (18)
N4—H4···O5	0.86 (2)	2.77 (2)	3.423 (2)	134.1 (17)
C2—H2A···O5^{iii}	0.93	2.70	3.587 (2)	161
C3—H3···O1^{iv}	0.93	2.68	3.585 (2)	165
C4—H4A···O1^{v}	0.93	2.64	3.518 (2)	158

Symmetry codes: (i) $-x, -y, -z+1$; (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) $x-1, y, z$; (v) $-x, -y+1, -z+1$.

4. Synthesis and crystallization

The procedure for the synthesis of the title compound was adapted from Karn & Busch (1966) with subsequent reduction using $NaBH_4$. 10 mmol of 2,6-diacetylpyridine were dissolved in 160 ml of absolute ethanol, and the resulting solution was mixed with 10 mmol of $Cu(ClO_4)_2{\cdot}6H_2O$ in 240 ml of water. The reaction mixture was heated to 338 K and 10 mmol of *N*,*N*-bis(3-aminopropyl)methylamine were added. Subsequently, glacial acetic acid was added to the mixture until the pH was about 4. The mixture was heated to reflux of the solvent for 12 h; a color change from blue to dark blue occurred during that period. After reflux, the mixture was cooled to room temperature and 40 mmol of $NaBH_4$ were added. The mixture was left to stir for 12 h for complete reduction. Perchloric acid was added until the remaining $NaBH_4$ was consumed.

The deep-blue solution was concentrated to about a tenth of its original volume by rotary evaporation. The solution was then cooled slowly to room temperature and refrigerated. Dark-purple needle-like crystals formed upon cooling. The crystals were filtered, washed with absolute ethanol and diethyl ether, and allowed to dry. Light-purple crystals were recrystallized from hot water. Single crystals were obtained by dissolving the compound in acetonitrile followed by slow ether diffusion.

UV–Vis data: λ_{max} = 552 nm in methanol, molar extinction coefficient: 209.47 $M^{-1}{\cdot}cm^{-1}$. IR: 1619 cm^{-1} (C=N of pyridine), 1113 and 600 cm^{-1} (ClO_4^- bands) and 3400 cm^{-1} (N—H).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal structure was refined as a two-component pseudo-merohedral twin (twin operation: $\bar{1}00, 0\bar{1}0, 001$); the refined fractional contribution of the minor

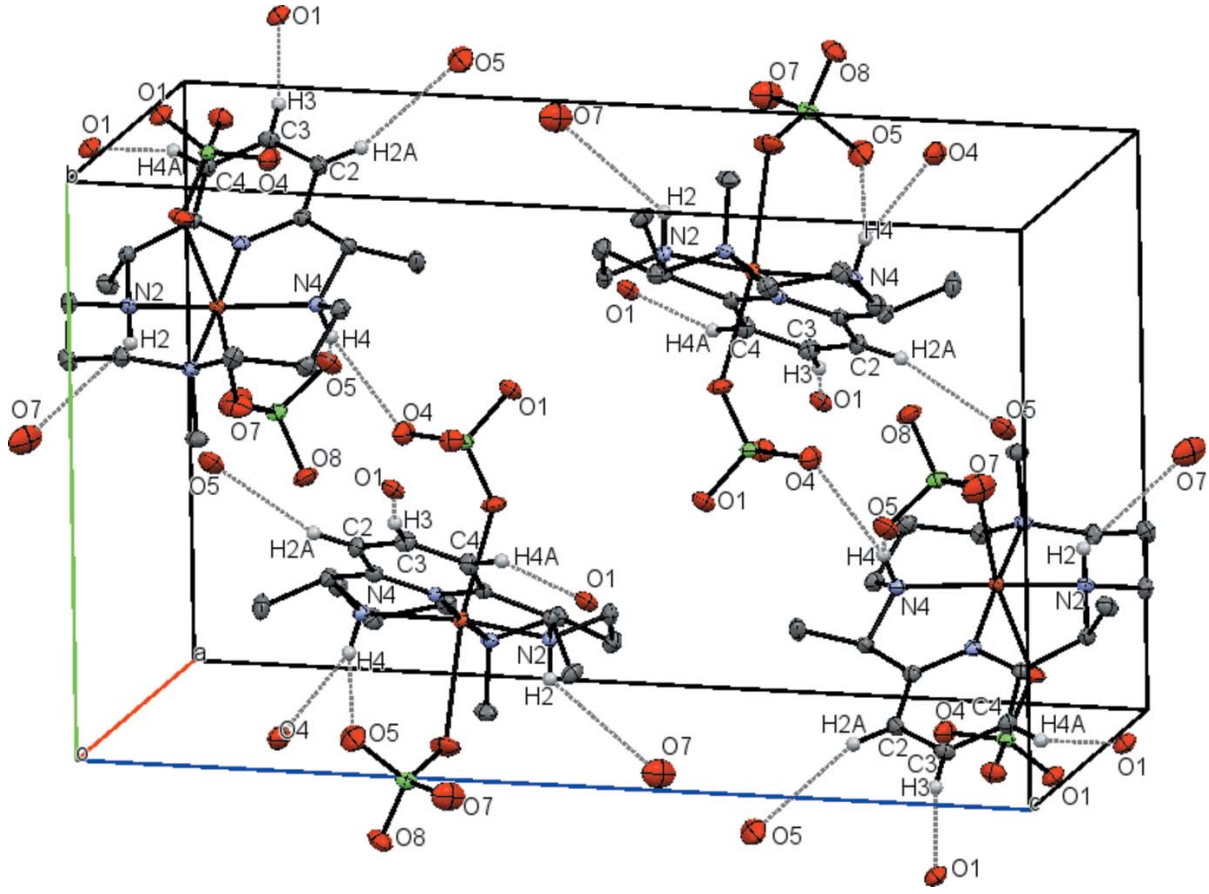


Figure 3
Crystal packing of the title complex viewed approximately down the *a* axis. Hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity.

component is 38.77 (8)%. All H atoms bonded to C atoms were placed at calculated positions using a riding model, with C—H distances of 0.98 Å for CH, 0.97 Å for CH_2, 0.96 Å for CH_3, and 0.93 Å for aromatic CH, and with U_{iso}(H) = 1.2U_{eq}(C) for all but CH_3 where U_{iso}(H) = 1.5U_{eq}(C). H2 and H4 connected to N2 and N4 were located in the difference density Fourier synthesis maps and refined freely.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_{16}H_{28}N_4)](ClO_4)_2$
M_r	538.86
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	8.6918 (12), 12.0588 (16), 20.068 (3)
β (°)	90.153 (3)
V (Å^3)	2103.4 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.35
Crystal size (mm)	0.24 × 0.21 × 0.21
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Multi-scan (Krause *et al.*, 2015)
T_{min}, T_{max}	0.414, 0.454
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	36478, 5284, 5054
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.062, 1.06
No. of reflections	5284
No. of parameters	292
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, −0.33

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2006), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

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Synthesis and crystal structure of [2,7,12-trimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene-κ^4N]copper(II) bis(perchlorate)

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Computing details

Data collection: *APEX2* and *Bruker Instrument Service* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2006) and OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

[2,7,12-Trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene-κ^4N]copper(II) bis(perchlorate)

Crystal data

$[Cu(C_{16}H_{28}N_4)](ClO_4)_2$
$M_r = 538.86$
Monoclinic, $P2_1/n$
$a = 8.6918$ (12) Å
$b = 12.0588$ (16) Å
$c = 20.068$ (3) Å
$\beta = 90.153$ (3)°
$V = 2103.4$ (5) Å^3
$Z = 4$
$F(000) = 1116$
$D_x = 1.702$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9732 reflections
$\theta = 2.9$–30.6°
$\mu = 1.35$ mm^{-1}
$T = 100$ K
Clear dark blue cube, clear dark blue
0.24 × 0.21 × 0.21 mm

Data collection

Bruker D8 QUEST diffractometer
Radiation source: sealed tube
Detector resolution: 1.024 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (Krause *et al.*, 2015)
$T_{min} = 0.414$, $T_{max} = 0.454$
36478 measured reflections
5284 independent reflections
5054 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 29.2°$, $\theta_{min} = 2.9°$
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.062$
$S = 1.06$
5284 reflections
292 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.369P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ 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.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.19755 (3)	0.24103 (2)	0.38162 (2)	0.01124 (5)
N1	0.00263 (15)	0.31793 (10)	0.38014 (7)	0.0121 (2)
N2	0.14981 (17)	0.22614 (12)	0.48078 (7)	0.0131 (3)
H2	0.131 (3)	0.1590 (18)	0.4820 (11)	0.016 (5)*
N3	0.40687 (15)	0.17015 (10)	0.38456 (7)	0.0133 (2)
N4	0.16917 (17)	0.24951 (11)	0.28059 (7)	0.0133 (3)
H4	0.126 (2)	0.1870 (18)	0.2721 (10)	0.014 (5)*
C1	−0.05040 (19)	0.35796 (13)	0.32233 (8)	0.0132 (3)
C2	−0.1787 (2)	0.42658 (14)	0.32010 (8)	0.0158 (3)
H2A	−0.2162	0.4538	0.2799	0.019*
C3	−0.24897 (18)	0.45302 (14)	0.37997 (9)	0.0169 (3)
H3	−0.3339	0.4999	0.3803	0.020*
C4	−0.1932 (2)	0.40991 (13)	0.43957 (8)	0.0160 (3)
H4A	−0.2407	0.4268	0.4798	0.019*
C5	−0.06452 (19)	0.34082 (13)	0.43793 (8)	0.0126 (3)
C6	0.00692 (19)	0.28859 (13)	0.49932 (8)	0.0135 (3)
H6	0.0363	0.3483	0.5299	0.016*
C7	−0.1071 (2)	0.21384 (15)	0.53495 (9)	0.0191 (3)
H7A	−0.1304	0.1510	0.5073	0.029*
H7B	−0.1998	0.2544	0.5438	0.029*
H7C	−0.0630	0.1888	0.5762	0.029*
C8	0.2787 (2)	0.24911 (14)	0.52748 (9)	0.0162 (4)
H8A	0.2451	0.2360	0.5728	0.019*
H8B	0.3086	0.3264	0.5238	0.019*
C9	0.4161 (2)	0.17602 (15)	0.51239 (8)	0.0186 (3)
H9A	0.3824	0.0993	0.5121	0.022*
H9B	0.4906	0.1842	0.5481	0.022*
C10	0.4954 (2)	0.20050 (14)	0.44663 (8)	0.0159 (3)
H10A	0.5183	0.2792	0.4450	0.019*
H10B	0.5927	0.1611	0.4460	0.019*
C11	0.3963 (2)	0.04734 (13)	0.38084 (10)	0.0193 (3)
H11A	0.3423	0.0199	0.4191	0.029*
H11B	0.4979	0.0162	0.3799	0.029*
H11C	0.3418	0.0265	0.3411	0.029*
C12	0.5038 (2)	0.21068 (15)	0.32814 (9)	0.0174 (3)

H12A	0.6037	0.1750	0.3311	0.021*
H12B	0.5200	0.2897	0.3337	0.021*
C13	0.4389 (2)	0.19068 (15)	0.25850 (9)	0.0177 (3)
H13A	0.5213	0.1989	0.2264	0.021*
H13B	0.4023	0.1148	0.2558	0.021*
C14	0.3084 (2)	0.26795 (13)	0.23923 (8)	0.0164 (3)
H14A	0.3422	0.3441	0.2444	0.020*
H14B	0.2825	0.2564	0.1927	0.020*
C15	0.04536 (19)	0.33025 (14)	0.26215 (8)	0.0142 (3)
H15	0.0967	0.3989	0.2484	0.017*
C16	−0.0511 (2)	0.29131 (16)	0.20309 (8)	0.0216 (4)
H16A	0.0151	0.2758	0.1660	0.032*
H16B	−0.1229	0.3483	0.1909	0.032*
H16C	−0.1061	0.2253	0.2151	0.032*
Cl1	0.31018 (5)	0.52884 (3)	0.37452 (2)	0.01419 (7)
O1	0.40486 (16)	0.60559 (10)	0.41159 (6)	0.0200 (2)
O2	0.15073 (13)	0.55835 (10)	0.38070 (7)	0.0214 (2)
O3	0.33372 (15)	0.41828 (10)	0.40105 (7)	0.0221 (3)
O4	0.35382 (17)	0.53023 (11)	0.30525 (6)	0.0254 (3)
Cl2	−0.09242 (5)	0.01135 (3)	0.35753 (2)	0.01541 (8)
O5	−0.14975 (19)	0.09033 (13)	0.30953 (8)	0.0323 (4)
O6	0.05744 (15)	0.04607 (11)	0.38012 (8)	0.0289 (3)
O7	−0.1936 (2)	0.00640 (14)	0.41356 (8)	0.0373 (4)
O8	−0.08306 (17)	−0.09626 (11)	0.32766 (7)	0.0249 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01167 (8)	0.01105 (8)	0.01101 (8)	0.00167 (6)	−0.00066 (9)	0.00045 (6)
N1	0.0128 (6)	0.0102 (5)	0.0133 (6)	−0.0014 (4)	0.0012 (5)	0.0002 (5)
N2	0.0142 (6)	0.0122 (6)	0.0130 (6)	0.0025 (5)	−0.0011 (5)	−0.0005 (5)
N3	0.0126 (6)	0.0100 (5)	0.0173 (6)	−0.0007 (5)	−0.0024 (5)	−0.0011 (5)
N4	0.0152 (8)	0.0105 (6)	0.0144 (6)	0.0008 (5)	0.0011 (5)	0.0002 (4)
C1	0.0128 (7)	0.0127 (7)	0.0141 (7)	−0.0009 (5)	−0.0001 (6)	−0.0001 (6)
C2	0.0154 (8)	0.0162 (7)	0.0156 (7)	0.0016 (6)	−0.0027 (6)	0.0016 (6)
C3	0.0140 (6)	0.0167 (7)	0.0201 (7)	0.0034 (5)	0.0009 (6)	0.0001 (7)
C4	0.0144 (7)	0.0185 (7)	0.0151 (7)	0.0023 (6)	0.0018 (6)	−0.0011 (6)
C5	0.0136 (7)	0.0123 (7)	0.0121 (7)	−0.0014 (6)	−0.0006 (5)	0.0005 (5)
C6	0.0151 (8)	0.0129 (7)	0.0124 (7)	0.0017 (6)	0.0004 (6)	0.0001 (6)
C7	0.0206 (8)	0.0182 (8)	0.0185 (8)	0.0021 (7)	0.0052 (7)	0.0038 (6)
C8	0.0149 (10)	0.0211 (8)	0.0126 (7)	−0.0006 (6)	−0.0029 (6)	0.0000 (6)
C9	0.0173 (8)	0.0214 (8)	0.0170 (8)	0.0015 (7)	−0.0028 (6)	0.0033 (6)
C10	0.0136 (7)	0.0173 (8)	0.0167 (7)	0.0000 (6)	−0.0031 (6)	0.0001 (6)
C11	0.0196 (7)	0.0119 (7)	0.0264 (8)	0.0012 (6)	−0.0035 (7)	−0.0011 (7)
C12	0.0131 (8)	0.0208 (8)	0.0182 (8)	−0.0005 (6)	0.0011 (6)	−0.0015 (6)
C13	0.0167 (8)	0.0188 (8)	0.0176 (8)	0.0026 (6)	0.0034 (6)	−0.0024 (6)
C14	0.0171 (8)	0.0175 (7)	0.0147 (7)	−0.0001 (7)	0.0037 (7)	−0.0007 (5)
C15	0.0162 (8)	0.0142 (7)	0.0122 (7)	0.0033 (6)	0.0014 (6)	0.0020 (5)

C16	0.0247 (9)	0.0277 (9)	0.0124 (7)	0.0078 (7)	−0.0030 (6)	0.0000 (7)
Cl1	0.01690 (16)	0.01039 (15)	0.01528 (15)	−0.00062 (12)	0.00114 (15)	−0.00024 (12)
O1	0.0203 (6)	0.0171 (6)	0.0225 (6)	−0.0045 (5)	−0.0008 (5)	−0.0051 (5)
O2	0.0157 (5)	0.0206 (6)	0.0280 (6)	0.0019 (4)	−0.0006 (5)	0.0012 (5)
O3	0.0252 (7)	0.0109 (5)	0.0303 (6)	−0.0007 (5)	−0.0027 (5)	0.0048 (5)
O4	0.0359 (8)	0.0230 (7)	0.0175 (6)	0.0010 (6)	0.0083 (5)	−0.0005 (5)
Cl2	0.01338 (16)	0.01372 (16)	0.01913 (17)	−0.00071 (13)	0.00050 (15)	−0.00212 (13)
O5	0.0370 (9)	0.0249 (7)	0.0349 (8)	0.0108 (6)	−0.0117 (6)	0.0023 (6)
O6	0.0200 (6)	0.0197 (6)	0.0470 (8)	−0.0074 (5)	−0.0096 (7)	0.0012 (6)
O7	0.0401 (9)	0.0351 (8)	0.0368 (8)	−0.0028 (7)	0.0230 (8)	−0.0050 (6)
O8	0.0283 (7)	0.0176 (6)	0.0287 (7)	0.0024 (5)	−0.0031 (6)	−0.0091 (5)

Geometric parameters (Å, º)

Cu1—N1	1.9316 (13)	C8—H8B	0.9700
Cu1—N2	2.0417 (14)	C8—C9	1.515 (3)
Cu1—N3	2.0108 (13)	C9—H9A	0.9700
Cu1—N4	2.0444 (15)	C9—H9B	0.9700
Cu1—O3	2.4736 (13)	C9—C10	1.519 (2)
Cu1—O6	2.6478 (13)	C10—H10A	0.9700
N1—C1	1.337 (2)	C10—H10B	0.9700
N1—C5	1.329 (2)	C11—H11A	0.9600
N2—H2	0.83 (2)	C11—H11B	0.9600
N2—C6	1.500 (2)	C11—H11C	0.9600
N2—C8	1.485 (2)	C12—H12A	0.9700
N3—C10	1.507 (2)	C12—H12B	0.9700
N3—C11	1.4857 (19)	C12—C13	1.525 (2)
N3—C12	1.496 (2)	C13—H13A	0.9700
N4—H4	0.86 (2)	C13—H13B	0.9700
N4—C14	1.486 (2)	C13—C14	1.517 (3)
N4—C15	1.497 (2)	C14—H14A	0.9700
C1—C2	1.389 (2)	C14—H14B	0.9700
C1—C15	1.506 (2)	C15—H15	0.9800
C2—H2A	0.9300	C15—C16	1.524 (2)
C2—C3	1.386 (2)	C16—H16A	0.9600
C3—H3	0.9300	C16—H16B	0.9600
C3—C4	1.390 (2)	C16—H16C	0.9600
C4—H4A	0.9300	Cl1—O1	1.4436 (13)
C4—C5	1.395 (2)	Cl1—O2	1.4365 (12)
C5—C6	1.515 (2)	Cl1—O3	1.4498 (12)
C6—H6	0.9800	Cl1—O4	1.4421 (13)
C6—C7	1.520 (2)	Cl2—O5	1.4423 (15)
C7—H7A	0.9600	Cl2—O6	1.4403 (13)
C7—H7B	0.9600	Cl2—O7	1.4308 (15)
C7—H7C	0.9600	Cl2—O8	1.4317 (13)
C8—H8A	0.9700		
N1—Cu1—N2	82.92 (6)	H8A—C8—H8B	108.0

N1—Cu1—N3	176.39 (5)	C9—C8—H8A	109.4
N1—Cu1—N4	81.79 (6)	C9—C8—H8B	109.4
N1—Cu1—O3	90.40 (5)	C8—C9—H9A	108.6
N1—Cu1—O6	91.30 (5)	C8—C9—H9B	108.6
N2—Cu1—N4	161.21 (6)	C8—C9—C10	114.84 (14)
N2—Cu1—O3	91.20 (5)	H9A—C9—H9B	107.5
N2—Cu1—O6	80.69 (6)	C10—C9—H9A	108.6
N3—Cu1—N2	96.91 (6)	C10—C9—H9B	108.6
N3—Cu1—N4	99.04 (6)	N3—C10—C9	116.03 (14)
N3—Cu1—O3	86.00 (5)	N3—C10—H10A	108.3
N3—Cu1—O6	92.23 (5)	N3—C10—H10B	108.3
N4—Cu1—O3	99.76 (5)	C9—C10—H10A	108.3
N4—Cu1—O6	88.79 (5)	C9—C10—H10B	108.3
O3—Cu1—O6	171.44 (5)	H10A—C10—H10B	107.4
C1—N1—Cu1	119.14 (11)	N3—C11—H11A	109.5
C5—N1—Cu1	118.27 (11)	N3—C11—H11B	109.5
C5—N1—C1	122.07 (14)	N3—C11—H11C	109.5
Cu1—N2—H2	99.0 (15)	H11A—C11—H11B	109.5
C6—N2—Cu1	111.60 (10)	H11A—C11—H11C	109.5
C6—N2—H2	108.8 (16)	H11B—C11—H11C	109.5
C8—N2—Cu1	116.33 (11)	N3—C12—H12A	108.3
C8—N2—H2	108.1 (15)	N3—C12—H12B	108.3
C8—N2—C6	111.95 (13)	N3—C12—C13	115.72 (14)
C10—N3—Cu1	112.38 (10)	H12A—C12—H12B	107.4
C11—N3—Cu1	111.48 (10)	C13—C12—H12A	108.3
C11—N3—C10	108.37 (13)	C13—C12—H12B	108.3
C11—N3—C12	108.83 (13)	C12—C13—H13A	108.7
C12—N3—Cu1	110.52 (10)	C12—C13—H13B	108.7
C12—N3—C10	105.00 (12)	H13A—C13—H13B	107.6
Cu1—N4—H4	101.8 (14)	C14—C13—C12	114.27 (14)
C14—N4—Cu1	117.72 (11)	C14—C13—H13A	108.7
C14—N4—H4	112.3 (14)	C14—C13—H13B	108.7
C14—N4—C15	110.53 (13)	N4—C14—C13	112.03 (13)
C15—N4—Cu1	111.25 (10)	N4—C14—H14A	109.2
C15—N4—H4	101.8 (14)	N4—C14—H14B	109.2
N1—C1—C2	121.18 (15)	C13—C14—H14A	109.2
N1—C1—C15	115.19 (14)	C13—C14—H14B	109.2
C2—C1—C15	123.48 (14)	H14A—C14—H14B	107.9
C1—C2—H2A	121.2	N4—C15—C1	110.16 (13)
C3—C2—C1	117.68 (15)	N4—C15—H15	106.9
C3—C2—H2A	121.2	N4—C15—C16	112.66 (14)
C2—C3—H3	119.8	C1—C15—H15	106.9
C2—C3—C4	120.40 (15)	C1—C15—C16	112.84 (14)
C4—C3—H3	119.8	C16—C15—H15	106.9
C3—C4—H4A	120.6	C15—C16—H16A	109.5
C3—C4—C5	118.75 (15)	C15—C16—H16B	109.5
C5—C4—H4A	120.6	C15—C16—H16C	109.5
N1—C5—C4	119.91 (14)	H16A—C16—H16B	109.5

N1—C5—C6	116.31 (14)	H16A—C16—H16C	109.5
C4—C5—C6	123.77 (15)	H16B—C16—H16C	109.5
N2—C6—C5	110.17 (13)	O1—Cl1—O3	108.70 (8)
N2—C6—H6	108.1	O2—Cl1—O1	110.21 (8)
N2—C6—C7	111.11 (13)	O2—Cl1—O3	109.36 (8)
C5—C6—H6	108.1	O2—Cl1—O4	109.67 (9)
C5—C6—C7	111.28 (14)	O4—Cl1—O1	109.77 (8)
C7—C6—H6	108.1	O4—Cl1—O3	109.11 (8)
C6—C7—H7A	109.5	Cl1—O3—Cu1	132.04 (8)
C6—C7—H7B	109.5	O6—Cl2—O5	109.19 (9)
C6—C7—H7C	109.5	O7—Cl2—O5	109.90 (10)
H7A—C7—H7B	109.5	O7—Cl2—O6	108.79 (11)
H7A—C7—H7C	109.5	O7—Cl2—O8	109.08 (9)
H7B—C7—H7C	109.5	O8—Cl2—O5	109.81 (9)
N2—C8—H8A	109.4	O8—Cl2—O6	110.05 (9)
N2—C8—H8B	109.4	Cl2—O6—Cu1	132.63 (8)
N2—C8—C9	111.04 (14)		

Cu1—N1—C1—C2	−171.12 (12)	C3—C4—C5—N1	0.4 (2)
Cu1—N1—C1—C15	4.49 (19)	C3—C4—C5—C6	−179.88 (15)
Cu1—N1—C5—C4	170.68 (12)	C4—C5—C6—N2	−175.87 (15)
Cu1—N1—C5—C6	−9.09 (18)	C4—C5—C6—C7	60.4 (2)
Cu1—N2—C6—C5	2.44 (16)	C5—N1—C1—C2	0.5 (2)
Cu1—N2—C6—C7	126.24 (12)	C5—N1—C1—C15	176.06 (14)
Cu1—N2—C8—C9	−56.21 (16)	C6—N2—C8—C9	173.83 (13)
Cu1—N3—C10—C9	55.43 (16)	C8—N2—C6—C5	134.81 (14)
Cu1—N3—C12—C13	−58.20 (16)	C8—N2—C6—C7	−101.40 (16)
Cu1—N4—C14—C13	48.28 (16)	C8—C9—C10—N3	−70.04 (19)
Cu1—N4—C15—C1	−15.39 (16)	C10—N3—C12—C13	−179.61 (15)
Cu1—N4—C15—C16	−142.35 (12)	C11—N3—C10—C9	−68.21 (18)
N1—C1—C2—C3	0.6 (2)	C11—N3—C12—C13	64.54 (18)
N1—C1—C15—N4	7.8 (2)	C12—N3—C10—C9	175.62 (15)
N1—C1—C15—C16	134.62 (15)	C12—C13—C14—N4	−66.11 (19)
N1—C5—C6—N2	3.89 (19)	C14—N4—C15—C1	−148.11 (14)
N1—C5—C6—C7	−119.80 (16)	C14—N4—C15—C16	84.93 (17)
N2—C8—C9—C10	67.86 (19)	C15—N4—C14—C13	177.62 (13)
N3—C12—C13—C14	75.39 (19)	C15—C1—C2—C3	−174.60 (15)
C1—N1—C5—C4	−1.0 (2)	O1—Cl1—O3—Cu1	169.81 (9)
C1—N1—C5—C6	179.27 (14)	O2—Cl1—O3—Cu1	49.44 (13)
C1—C2—C3—C4	−1.2 (2)	O4—Cl1—O3—Cu1	−70.51 (12)
C2—C1—C15—N4	−176.75 (15)	O5—Cl2—O6—Cu1	22.21 (15)
C2—C1—C15—C16	−49.9 (2)	O7—Cl2—O6—Cu1	−97.73 (14)
C2—C3—C4—C5	0.7 (3)	O8—Cl2—O6—Cu1	142.81 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O7^{i}	0.83 (2)	2.94 (2)	3.536 (2)	130.6 (18)

N4—H4···O4^{ii}	0.86 (2)	2.45 (2)	3.1619 (19)	140.2 (18)
N4—H4···O5	0.86 (2)	2.77 (2)	3.423 (2)	134.1 (17)
C2—H2*A*···O5^{iii}	0.93	2.70	3.587 (2)	161
C3—H3···O1^{iv}	0.93	2.68	3.585 (2)	165
C4—H4*A*···O1^{v}	0.93	2.64	3.518 (2)	158

Symmetry codes: (i) −*x*, −*y*, −*z*+1; (ii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iii) −*x*−1/2, *y*+1/2, −*z*+1/2; (iv) *x*−1, *y*, *z*; (v) −*x*, −*y*+1, −*z*+1.