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Crystal structure of {(but-3-en-1-yl)bis[(pyridin-2-yl)methyl]amine- κ^3N,N',N'' }dichlorido-copper(II) diethyl ether hemisolvate

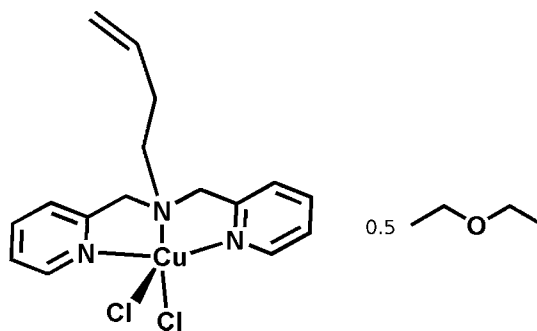
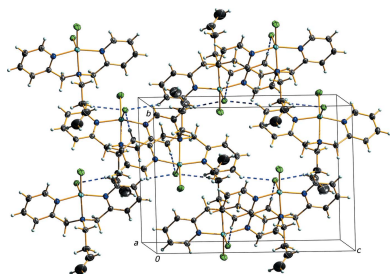
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The five-coordinate Cu^{II} atom in the title complex [CuCl₂(C₁₆H₁₉N₃)]·0.5C₄H₁₀O, adopts a near-ideal square-pyramidal geometry (τ -5 = 0.01). The apical Cu—Cl distance is 0.2626 (6) Å longer than the basal Cu—Cl distance. Weak C—H···Cl interactions between pyridine rings and the Cl atoms of adjacent complex molecules are present. The solvent molecule, located on a twofold rotation axis, is situated in the voids of this arrangement. Copper atoms coordinated by tridentate nitrogen-containing ligands have been found to be excellent promoters of Atom Transfer Radical Addition (ATRA) reactions.

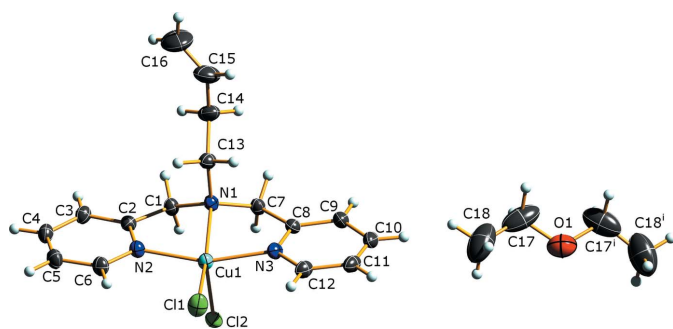
1. Chemical context

Transition-metal-catalyzed Atom Transfer Radical Addition (ATRA) reactions of haloalkanes and α -halocarbonyls to α -olefins have emerged as some of the most atom economical methods for simultaneously forming C—C and C—X bonds, leading to the production of more attractive molecules with well-defined compositions, architectures, and functionalities (Pintauer & Matyjaszewski, 2005). Copper(I) complexes with tridentate and tetradentate nitrogen-based ligands are currently some of the most active multidentate ligand structures developed for use in ATRA reactions (Matyjaszewski *et al.*, 2001). In view of the importance of these types of complexes, we report the synthesis and structural characterization of the title compound {(but-3-en-1-yl)bis[(pyridin-2-yl)methyl]amine- κ^3N,N',N'' } dichloridocopper(II) diethyl ether hemisolvate, (I).



2. Structural commentary

The title complex, (I) (Fig. 1), adopts a typical-for-this-class of compounds (*vide infra*), slightly distorted square-pyramidal geometry, as shown in the bond angles about the Cu^{II} atom. A

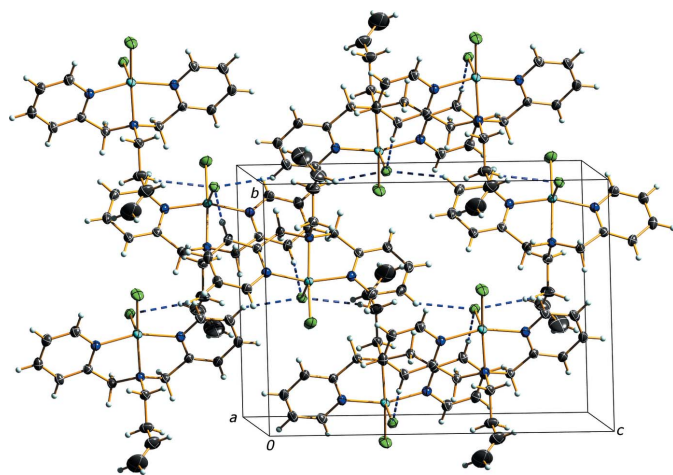

Figure 1

The molecular structure and atom-labeling scheme for (I). Displacement parameters are depicted at the 50% probability level. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$]

τ -5 analysis of the distortions about the Cu^{II} atom yields a value of 0.01, close to an ideal value of zero for a perfect square-pyramidal geometry [Addison *et al.*, 1984; τ -5 = $(\beta - \alpha)/60$ where β and α are the angles formed by atoms *trans* across the metal atom that do not include the apical atom]. In the complex, the Cu^{II} atom lies 0.2761 (5) Å out of the mean basal plane formed by the three coordinating N atoms and atom Cl1, reflecting the slight distortion from a true square plane. The Cu–N bond lengths are all similar [1.9980 (11)–2.0700 (10) Å] and the apical Cu–Cl2 distance is considerably longer [2.5134 (4) Å] than that of Cu–Cl1 [2.2508 (4) Å] in the basal plane. The diethyl ether molecule of crystallization is located in the unit cell with the O atom on the crystallographic twofold rotation axis at $[\frac{1}{2}, y, \frac{3}{4}]$.

3. Supramolecular features

Despite an open coordination site on the Cu^{II} atom, the complex does not dimerize through a chloride bridge, that is often observed in similar complexes (*vide infra*). There are weak electrostatic C–H \cdots Cl interactions between pyridine


Figure 2

Packing diagram viewed along the *a* direction demonstrating the linear C–H \cdots Cl electrostatic interactions (blue dashed lines).

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
C3–H3 \cdots Cl2 ⁱ	0.95	2.67	3.5541 (15)	156
C11–H11 \cdots Cl2 ⁱⁱ	0.95	2.74	3.4767 (15)	135
C14–H14A \cdots Cl2 ⁱⁱⁱ	0.99	2.80	3.7127 (18)	153

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

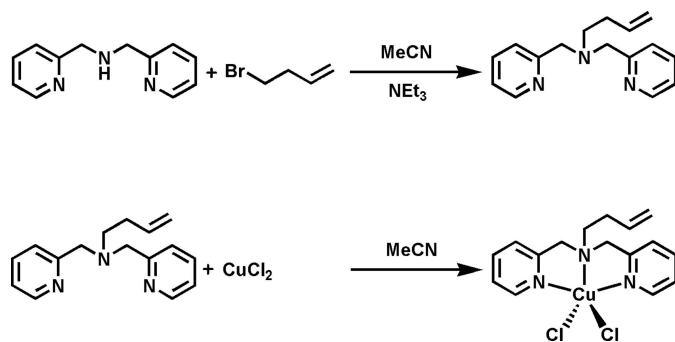
rings and the basal chlorine of adjacent molecules (Table 1 and Fig. 2). Close contacts about the butenyl chain are typical van der Waals contacts. The orientation of the butenyl chain is such that it is *anti* to the apical Cl ligand, effectively proximal to the vacant sixth coordination site of the Cu^{II} atom. Instead, the diethyl ether molecule of crystallization is located in the pocket formed by the butenyl chain and the basal coordination plane of the Cu^{II} atom. Perhaps surprisingly, the ether O atom is not oriented towards, or spatially close to, the Cu atom [Cu \cdots O1ⁱⁱ = 4.9130 (9) Å; symmetry code (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$] and merely serves to occupy a void space that would otherwise be formed by molecular packing.

4. Database survey

Although there are 80 copper chloride structures that incorporate the bis(pyridin-2-ylmethyl)amine ligand (Groom & Allen, 2014; CSD Version 5.36 plus one update), only 20 have a sole bis(pyridin-2-ylmethyl)amine ligand chelating to a CuCl_2 moiety within an overall five coordination. The remaining 60 structures either have a tethered pair or tethered triplet of ligands, or have the bridging chlorines between two complexes and are thus the more common geometry adopted by copper coordinated by a bis(pyridin-2-ylmethyl)amine based ligand. The geometry of the ligand and pendant group observed herein, is also a common feature of these structures, *vis-a-vis*, the pendant chain is oriented *anti* to the apical chlorine.

5. Synthesis and crystallization

For the preparation of (but-3-en-1-yl)bis[(pyridin-2-yl)methyl]amine (see Scheme 1 below), the bis(pyridin-2-ylmethyl)amine (BPMA) precursor was synthesized and purified following literature procedures (Carvalho *et al.*, 2006). BPMA (8.064 g, 40.5 mmol) was dissolved in acetonitrile (15 ml) followed by the addition of triethylamine (4.098 g, 40.5 mmol) and 4-bromobutene (5.468 g, 40.5 mmol). The reaction vessel was sealed and allowed to mix for 4 d to ensure complete deprotonation and coupling occurred. Generation of the triethylamine hydrogen bromide salt, $\text{Et}_3\text{NH}^+\cdot\text{Br}^-$, was observed as white crystals in the brown-colored solution. The mixture was filtered and the desired product extracted from the filtrate using a hexane/water mixture. The hexane layer was separated and solvent removed to yield the ligand as a yellow colored oil (yield 8.516 g, 83%). The ligand was stored in a septum-sealed round-bottomed flask under argon gas in a refrigerator.



For the synthesis of the title compound, (I), 1-butene-BPMA (2.000 g, 7.900 mmol) was dissolved in acetonitrile (20 ml) in a 50 ml round-bottomed flask. CuCl₂ (1.062 g, 7.900 mmol) was added to the flask to give a green-colored solution. The reaction was allowed to mix for 6 h, then pentane (20 ml) was added slowly to the solution to generate a bright-green precipitate. The solvent was removed from the round-bottomed flask by connecting it to a rotary evaporator. The precipitate obtained was washed twice by transferring two 15 ml aliquots of pentane into the flask and stirring vigorously for 30 min. The solvent was removed and the precipitate dried under vacuum for 2 h to yield a green solid (yield 2.909 g, 95%). Slow diffusion of diethyl ether into an acetonitrile solution of the complex at room temperature produced crystals of (I) suitable for X-ray analysis.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-H atoms were refined with anisotropic displacement parameters. H atoms were included in idealized positions, with C–H = 0.95 (aromatic), 0.98 (methyl), and 0.99 Å (ethylenic/methylene). Methyl H atoms were allowed to rotate to minimize their electron-density contribution. The $U_{\text{iso}}(\text{H})$ values were set at $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and at $1.2U_{\text{eq}}(\text{C})$ otherwise.

Acknowledgements

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Table 2
Experimental details.

Crystal data	[CuCl ₂ (C ₁₆ H ₁₉ N ₃)]·0.5C ₄ H ₁₀ O
Chemical formula	424.84
M_r	424.84
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	150
a, b, c (Å)	22.1614 (13), 11.5738 (5), 16.4530 (7)
β (°)	108.771 (1)
V (Å ³)	3995.6 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.37
Crystal size (mm)	0.50 × 0.28 × 0.10
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.471, 0.840
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24823, 6872, 5660
R_{int}	0.025
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.758
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.072, 1.03
No. of reflections	6872
No. of parameters	223
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.53, -0.43

Computer programs: APEX2 and SAINT (Bruker, 2010), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), DIAMOND (Brandenburg, 2006), POV-RAY (Cason, 2013) and publCIF (Westrip, 2010).

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supporting information

Acta Cryst. (2015). E71, 309-311 [doi:10.1107/S2056989015003448]

Crystal structure of {(but-3-en-1-yl)bis[(pyridin-2-yl)methyl]amine- κ^3N,N',N'' }dichloridocopper(II) diethyl ether hemisolvate

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Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINTE* (Bruker, 2010); data reduction: *SAINTE* (Bruker, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *POV-RAY* (Cason, 2013); software used to prepare material for publication: *publCIF* (Westrip, 2010).

{(But-3-en-1-yl)bis[(pyridin-2-yl)methyl]amine- κ^3N,N',N'' } dichloridocopper(II) diethyl ether hemisolvate

Crystal data

[CuCl₂(C₁₆H₁₉N₃)]·0.5C₄H₁₀O

M_r = 424.84

Monoclinic, *C2/c*

a = 22.1614 (13) Å

b = 11.5738 (5) Å

c = 16.4530 (7) Å

β = 108.771 (1)°

V = 3995.6 (3) Å³

Z = 8

F(000) = 1760

D_x = 1.412 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 8841 reflections

θ = 2.2–32.2°

μ = 1.37 mm⁻¹

T = 150 K

Rhomboïd, blue

0.50 × 0.28 × 0.10 mm

Data collection

Bruker APEXII
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

φ and ω scans

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

T_{min} = 0.471, *T_{max}* = 0.840

24823 measured reflections

6872 independent reflections

5660 reflections with *I* > 2 σ (*I*)

R_{int} = 0.025

θ_{\max} = 32.6°, θ_{\min} = 1.9°

h = -32→33

k = -17→17

l = -23→24

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.028

wR(*F*²) = 0.072

S = 1.03

6872 reflections

223 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 2.0749P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$

$$\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.15616 (2)	0.59899 (2)	0.13662 (2)	0.01989 (5)
Cl1	0.09795 (2)	0.43892 (3)	0.13435 (2)	0.03418 (8)
Cl2	0.25976 (2)	0.52731 (3)	0.12375 (2)	0.02394 (7)
N1	0.18137 (5)	0.77181 (9)	0.14348 (6)	0.01978 (19)
N2	0.11788 (5)	0.64014 (9)	0.01190 (7)	0.0215 (2)
N3	0.19179 (5)	0.61566 (9)	0.26406 (7)	0.0223 (2)
C1	0.19332 (6)	0.79568 (11)	0.06162 (8)	0.0219 (2)
H1A	0.2363	0.7679	0.0650	0.026*
H1B	0.1915	0.8800	0.0508	0.026*
C2	0.14371 (6)	0.73526 (11)	-0.01065 (8)	0.0205 (2)
C3	0.12747 (6)	0.77160 (12)	-0.09536 (8)	0.0240 (2)
H3	0.1460	0.8393	-0.1099	0.029*
C4	0.08364 (6)	0.70725 (13)	-0.15849 (8)	0.0275 (3)
H4	0.0728	0.7289	-0.2171	0.033*
C5	0.05600 (7)	0.61125 (13)	-0.13490 (9)	0.0287 (3)
H5	0.0251	0.5674	-0.1770	0.034*
C6	0.07399 (6)	0.57991 (12)	-0.04920 (9)	0.0263 (3)
H6	0.0549	0.5141	-0.0331	0.032*
C7	0.23897 (6)	0.78269 (11)	0.22018 (8)	0.0223 (2)
H7A	0.2440	0.8638	0.2403	0.027*
H7B	0.2773	0.7607	0.2053	0.027*
C8	0.23224 (6)	0.70480 (11)	0.29021 (8)	0.0219 (2)
C9	0.26692 (7)	0.72191 (12)	0.37617 (9)	0.0284 (3)
H9	0.2956	0.7850	0.3935	0.034*
C10	0.25854 (8)	0.64431 (13)	0.43618 (9)	0.0315 (3)
H10	0.2825	0.6525	0.4952	0.038*
C11	0.21516 (7)	0.55514 (13)	0.40935 (9)	0.0298 (3)
H11	0.2076	0.5034	0.4499	0.036*
C12	0.18308 (7)	0.54244 (12)	0.32283 (9)	0.0263 (3)
H12	0.1540	0.4802	0.3042	0.032*
C13	0.12613 (6)	0.83899 (11)	0.15197 (9)	0.0250 (2)
H13A	0.1182	0.8139	0.2052	0.030*
H13B	0.0879	0.8187	0.1031	0.030*
C14	0.13334 (8)	0.97031 (13)	0.15463 (11)	0.0370 (3)
H14A	0.1719	0.9922	0.2024	0.044*
H14B	0.1387	0.9976	0.1003	0.044*

C15	0.07651 (10)	1.02672 (16)	0.16678 (14)	0.0517 (5)
H15	0.0648	1.0031	0.2150	0.062*
C16	0.04196 (14)	1.1043 (2)	0.1180 (2)	0.0866 (9)
H16A	0.0519	1.1306	0.0691	0.104*
H16B	0.0064	1.1356	0.1308	0.104*
O1	0.5000	0.71720 (17)	0.7500	0.0552 (5)
C17	0.46509 (12)	0.7851 (2)	0.6791 (2)	0.0809 (9)
H17A	0.4948	0.8292	0.6570	0.097*
H17B	0.4381	0.8409	0.6973	0.097*
C18	0.42468 (16)	0.7095 (4)	0.6110 (2)	0.1069 (12)
H18A	0.4016	0.7564	0.5610	0.160*
H18B	0.3941	0.6687	0.6323	0.160*
H18C	0.4515	0.6531	0.5942	0.160*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02130 (8)	0.01992 (8)	0.01888 (8)	-0.00387 (5)	0.00706 (6)	0.00069 (5)
Cl1	0.03288 (17)	0.03282 (17)	0.03443 (18)	-0.01494 (14)	0.00746 (14)	0.00510 (13)
Cl2	0.02487 (14)	0.02391 (14)	0.02458 (14)	-0.00119 (11)	0.01009 (11)	-0.00181 (11)
N1	0.0212 (5)	0.0208 (5)	0.0182 (5)	-0.0017 (4)	0.0076 (4)	-0.0003 (4)
N2	0.0209 (5)	0.0229 (5)	0.0205 (5)	-0.0029 (4)	0.0064 (4)	-0.0002 (4)
N3	0.0255 (5)	0.0233 (5)	0.0203 (5)	0.0010 (4)	0.0106 (4)	0.0013 (4)
C1	0.0241 (6)	0.0234 (6)	0.0193 (5)	-0.0051 (4)	0.0083 (5)	-0.0001 (4)
C2	0.0202 (5)	0.0217 (6)	0.0207 (5)	-0.0004 (4)	0.0081 (4)	-0.0004 (4)
C3	0.0223 (6)	0.0292 (6)	0.0214 (6)	0.0015 (5)	0.0082 (5)	0.0034 (5)
C4	0.0254 (6)	0.0367 (7)	0.0195 (6)	0.0040 (5)	0.0058 (5)	0.0017 (5)
C5	0.0243 (6)	0.0344 (7)	0.0237 (6)	-0.0024 (5)	0.0024 (5)	-0.0041 (5)
C6	0.0228 (6)	0.0290 (7)	0.0250 (6)	-0.0049 (5)	0.0048 (5)	-0.0016 (5)
C7	0.0247 (6)	0.0214 (6)	0.0199 (5)	-0.0034 (4)	0.0061 (5)	-0.0011 (4)
C8	0.0251 (6)	0.0212 (6)	0.0202 (5)	0.0029 (4)	0.0081 (5)	-0.0011 (4)
C9	0.0364 (7)	0.0254 (6)	0.0211 (6)	0.0046 (5)	0.0060 (5)	-0.0027 (5)
C10	0.0433 (8)	0.0305 (7)	0.0196 (6)	0.0122 (6)	0.0089 (6)	0.0005 (5)
C11	0.0383 (7)	0.0302 (7)	0.0251 (6)	0.0110 (6)	0.0161 (6)	0.0078 (5)
C12	0.0303 (6)	0.0267 (6)	0.0257 (6)	0.0031 (5)	0.0142 (5)	0.0056 (5)
C13	0.0271 (6)	0.0240 (6)	0.0255 (6)	0.0033 (5)	0.0107 (5)	0.0002 (5)
C14	0.0349 (8)	0.0245 (7)	0.0458 (9)	0.0048 (6)	0.0048 (7)	-0.0025 (6)
C15	0.0609 (12)	0.0382 (9)	0.0612 (12)	0.0139 (8)	0.0269 (10)	-0.0075 (8)
C16	0.0783 (18)	0.0776 (18)	0.095 (2)	0.0474 (15)	0.0156 (16)	-0.0047 (15)
O1	0.0521 (11)	0.0461 (11)	0.0708 (13)	0.000	0.0244 (10)	0.000
C17	0.0600 (14)	0.0728 (17)	0.124 (2)	0.0280 (13)	0.0496 (16)	0.0421 (16)
C18	0.0760 (19)	0.158 (4)	0.078 (2)	0.036 (2)	0.0130 (16)	0.035 (2)

Geometric parameters (Å, °)

Cu1—N3	1.9980 (11)	C8—C9	1.3895 (18)
Cu1—N2	2.0093 (11)	C9—C10	1.391 (2)
Cu1—N1	2.0700 (10)	C9—H9	0.9500

Cu1—C11	2.2508 (4)	C10—C11	1.383 (2)
Cu1—C12	2.5134 (4)	C10—H10	0.9500
N1—C1	1.4800 (15)	C11—C12	1.379 (2)
N1—C7	1.4837 (16)	C11—H11	0.9500
N1—C13	1.4942 (16)	C12—H12	0.9500
N2—C6	1.3466 (16)	C13—C14	1.527 (2)
N2—C2	1.3469 (16)	C13—H13A	0.9900
N3—C8	1.3434 (17)	C13—H13B	0.9900
N3—C12	1.3455 (16)	C14—C15	1.488 (2)
C1—C2	1.5067 (17)	C14—H14A	0.9900
C1—H1A	0.9900	C14—H14B	0.9900
C1—H1B	0.9900	C15—C16	1.281 (3)
C2—C3	1.3878 (17)	C15—H15	0.9500
C3—C4	1.3883 (19)	C16—H16A	0.9500
C3—H3	0.9500	C16—H16B	0.9500
C4—C5	1.383 (2)	O1—C17 ⁱ	1.413 (3)
C4—H4	0.9500	O1—C17	1.413 (3)
C5—C6	1.3845 (19)	C17—C18	1.476 (4)
C5—H5	0.9500	C17—H17A	0.9900
C6—H6	0.9500	C17—H17B	0.9900
C7—C8	1.5077 (17)	C18—H18A	0.9800
C7—H7A	0.9900	C18—H18B	0.9800
C7—H7B	0.9900	C18—H18C	0.9800
N3—Cu1—N2	160.62 (5)	H7A—C7—H7B	108.3
N3—Cu1—N1	80.84 (4)	N3—C8—C9	121.93 (12)
N2—Cu1—N1	81.05 (4)	N3—C8—C7	115.75 (11)
N3—Cu1—C11	97.34 (3)	C9—C8—C7	122.30 (12)
N2—Cu1—C11	97.28 (3)	C8—C9—C10	118.31 (13)
N1—Cu1—C11	159.94 (3)	C8—C9—H9	120.8
N3—Cu1—C12	93.27 (3)	C10—C9—H9	120.8
N2—Cu1—C12	95.11 (3)	C11—C10—C9	119.57 (13)
N1—Cu1—C12	94.92 (3)	C11—C10—H10	120.2
C11—Cu1—C12	105.136 (14)	C9—C10—H10	120.2
C1—N1—C7	113.65 (9)	C12—C11—C10	118.92 (13)
C1—N1—C13	112.33 (10)	C12—C11—H11	120.5
C7—N1—C13	112.52 (10)	C10—C11—H11	120.5
C1—N1—Cu1	104.77 (7)	N3—C12—C11	121.94 (13)
C7—N1—Cu1	105.76 (7)	N3—C12—H12	119.0
C13—N1—Cu1	107.05 (8)	C11—C12—H12	119.0
C6—N2—C2	119.11 (11)	N1—C13—C14	116.05 (11)
C6—N2—Cu1	127.29 (9)	N1—C13—H13A	108.3
C2—N2—Cu1	113.44 (8)	C14—C13—H13A	108.3
C8—N3—C12	119.27 (11)	N1—C13—H13B	108.3
C8—N3—Cu1	114.07 (8)	C14—C13—H13B	108.3
C12—N3—Cu1	126.42 (9)	H13A—C13—H13B	107.4
N1—C1—C2	109.43 (10)	C15—C14—C13	110.80 (14)
N1—C1—H1A	109.8	C15—C14—H14A	109.5

C2—C1—H1A	109.8	C13—C14—H14A	109.5
N1—C1—H1B	109.8	C15—C14—H14B	109.5
C2—C1—H1B	109.8	C13—C14—H14B	109.5
H1A—C1—H1B	108.2	H14A—C14—H14B	108.1
N2—C2—C3	121.90 (12)	C16—C15—C14	125.8 (2)
N2—C2—C1	115.39 (10)	C16—C15—H15	117.1
C3—C2—C1	122.65 (11)	C14—C15—H15	117.1
C2—C3—C4	118.80 (12)	C15—C16—H16A	120.0
C2—C3—H3	120.6	C15—C16—H16B	120.0
C4—C3—H3	120.6	H16A—C16—H16B	120.0
C5—C4—C3	119.17 (12)	C17 ⁱ —O1—C17	112.4 (3)
C5—C4—H4	120.4	O1—C17—C18	109.5 (2)
C3—C4—H4	120.4	O1—C17—H17A	109.8
C4—C5—C6	119.20 (13)	C18—C17—H17A	109.8
C4—C5—H5	120.4	O1—C17—H17B	109.8
C6—C5—H5	120.4	C18—C17—H17B	109.8
N2—C6—C5	121.79 (13)	H17A—C17—H17B	108.2
N2—C6—H6	119.1	C17—C18—H18A	109.5
C5—C6—H6	119.1	C17—C18—H18B	109.5
N1—C7—C8	109.24 (10)	H18A—C18—H18B	109.5
N1—C7—H7A	109.8	C17—C18—H18C	109.5
C8—C7—H7A	109.8	H18A—C18—H18C	109.5
N1—C7—H7B	109.8	H18B—C18—H18C	109.5
C8—C7—H7B	109.8		
C7—N1—C1—C2	155.62 (10)	C12—N3—C8—C9	1.93 (19)
C13—N1—C1—C2	-75.20 (13)	Cu1—N3—C8—C9	-172.73 (10)
Cu1—N1—C1—C2	40.65 (11)	C12—N3—C8—C7	-179.82 (11)
C6—N2—C2—C3	-1.47 (18)	Cu1—N3—C8—C7	5.52 (14)
Cu1—N2—C2—C3	174.32 (10)	N1—C7—C8—N3	22.88 (15)
C6—N2—C2—C1	-178.80 (11)	N1—C7—C8—C9	-158.88 (12)
Cu1—N2—C2—C1	-3.00 (13)	N3—C8—C9—C10	-0.6 (2)
N1—C1—C2—N2	-26.50 (15)	C7—C8—C9—C10	-178.72 (12)
N1—C1—C2—C3	156.20 (11)	C8—C9—C10—C11	-1.8 (2)
N2—C2—C3—C4	-0.47 (19)	C9—C10—C11—C12	2.7 (2)
C1—C2—C3—C4	176.66 (12)	C8—N3—C12—C11	-0.91 (19)
C2—C3—C4—C5	2.0 (2)	Cu1—N3—C12—C11	173.03 (10)
C3—C4—C5—C6	-1.7 (2)	C10—C11—C12—N3	-1.4 (2)
C2—N2—C6—C5	1.8 (2)	C1—N1—C13—C14	-63.24 (15)
Cu1—N2—C6—C5	-173.32 (10)	C7—N1—C13—C14	66.53 (14)
C4—C5—C6—N2	-0.2 (2)	Cu1—N1—C13—C14	-177.71 (10)
C1—N1—C7—C8	-152.29 (10)	N1—C13—C14—C15	-177.66 (13)
C13—N1—C7—C8	78.63 (12)	C13—C14—C15—C16	-125.1 (3)
Cu1—N1—C7—C8	-37.91 (11)	C17 ⁱ —O1—C17—C18	-174.1 (3)

Symmetry code: (i) $-x+1, y, -z+3/2$.

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>
C3—H3···Cl2 ⁱⁱ	0.95	2.67	3.5541 (15)	156
C11—H11···Cl2 ⁱⁱⁱ	0.95	2.74	3.4767 (15)	135
C14—H14 <i>A</i> ···Cl2 ^{iv}	0.99	2.80	3.7127 (18)	153

Symmetry codes: (ii) $-x+1/2, -y+3/2, -z$; (iii) $x, -y+1, z+1/2$; (iv) $-x+1/2, y+1/2, -z+1/2$.