

Di- μ -chlorido-bis[chlorido(dimethylformamide- κ N)(3,5-diphenyl-1H-pyrazole- κ N²)copper(II)]

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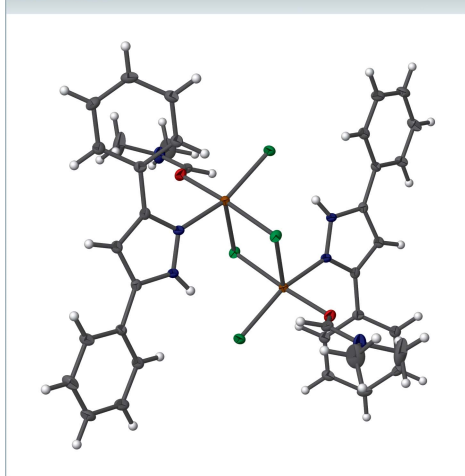
Keywords: crystal structure; copper complex; 3,5-diphenyl-1H-pyrazole.

CCDC reference: 1863262

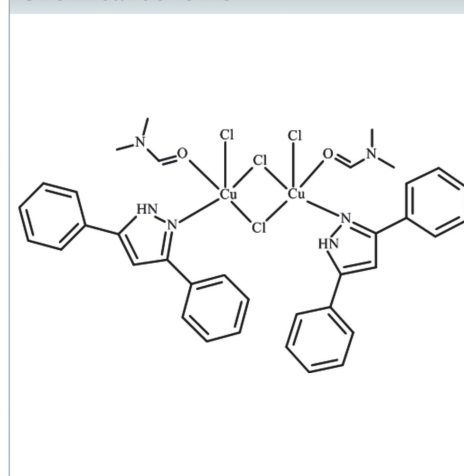
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[\text{Cu}_2\text{Cl}_4(\text{C}_{15}\text{H}_{12}\text{N}_2)_2(\text{C}_3\text{H}_7\text{NO})_2]$, $\text{Cu}_2(\mu\text{-Cl})_2\text{Cl}_2(3,5\text{-diphenyl-1H-pyrazole})_2(\text{DMF})_2$, where DMF is *N,N*-dimethylformamide, crystallizes in the monoclinic space group $P2_1/n$. The five-coordinate Cu^{II} ions have a distorted square-pyramidal geometry and are joined *via* two $\mu\text{-Cl}$ anions. The coordination environment of each Cu^{II} ion is completed by a terminal chloride anion, a nitrogen-coordinated 3,5-diphenyl-1H-pyrazole molecule, and a DMF molecule. Two intramolecular hydrogen bonds exist in the molecule as the H atom of the protonated N atom of the 3,5-diphenyl-1H-pyrazole bonds to a terminal chloride anion of the adjacent Cu^{II} cation. In addition, molecules are linked into a two-dimensional sheet *via* weak $\text{C-H}\cdots\text{Cl}$ intermolecular hydrogen bonds. Each dimer hydrogen bonds to four neighboring molecules as the H atom of the C atom in the fourth position of the pyrazole ring bonds to a $\mu\text{-Cl}$ on a neighboring molecule.

3D view



Chemical scheme



Structure description

Pyrazole-based ligands are ubiquitous in the literature for their ability to build mono-metal complexes and molecules containing multiple metal centers (Mukherjee, 2000; Viciano-Chumillas *et al.*, 2010; Doidge *et al.*, 2015; Castro *et al.*, 2016). In particular, 3,5-diphenylpyrazole and its derivatives have been used to form numerous copper complexes with the metal in either the 1+ or 2+ oxidation states (Raptis & Fackler Jr, 1988; Mezei *et al.*, 2007; Tardito *et al.*, 2011; Ahmed *et al.*, 2016; Zhang *et al.*, 2017). The title compound $\text{Cu}_2(\mu\text{-Cl})_2\text{Cl}_2(3,5\text{-diphenyl-1H-pyrazole})_2(\text{DMF})_2$ (**1**), where DMF is *N,N*-dimethylformamide, reported within relates a dicopper(II) compound with two neutral 3,5-diphenyl-1H-pyrazole ligands, two bridging chloride anions, and two terminal chloride anions. In addition, compound (**1**) has similar structural features to a number of

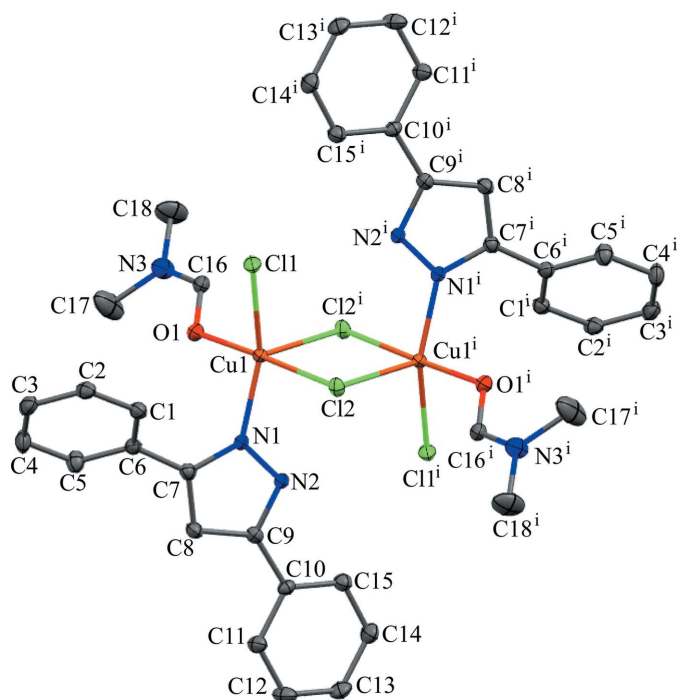


Figure 1
The molecular structure of **(1)** with displacement ellipsoids at the 50% probability level [symmetry code: (i) $-x + 1, -y + 1, -z$]. For clarity, H atoms have been omitted. Color scheme: orange – Cu^{II}, green – Cl, red – oxygen, blue – nitrogen, and gray – carbon. All figures were generated with the program *Mercury* (Macrae *et al.*, 2006).

copper(II)–chloride–pyrazole-based molecules and one copper(II)–chloride–triazole-based molecule: Cu₂(μ-Cl₂)-Cl₂(1*H*-3,5-diethyl-4-methylpyrazole)₄ (Agre *et al.*, 1977; Agre *et al.*, 1979), Cu₂(μ-Cl₂)Cl₂(3,4-dimethyl-5-phenylpyrazole)₂-(4,5-dimethyl-3-phenylpyrazole)₂ (Keij *et al.*, 1991), Cu₂(μ-Cl₂)Cl₂(3,5-diphenylpyrazole)₄ (Matecka *et al.*, 1998; Mezei & Raptis, 2004; Zhu *et al.*, 2011), Cu₂(μ-Cl₂)Cl₂(3,5-dimethyl-1*H*-pyrazole)₄ (Chandrasekhar *et al.*, 2000; Giles *et al.*, 2015), Cu₂(μ-Cl₂)Cl₂(3-methyl-5-phenyl-1*H*-pyrazole)₄ (Soltani *et al.*, 2012), Cu₂(μ-Cl₂)Cl₂(5-methyl-1*H*-pyrazole)₄ (Giles *et al.*, 2015; Feng *et al.*, 2016), Cu₂(μ-Cl₂)Cl₂(3,4,5-trimethyl-1*H*-pyrazole)₄ (Vincent *et al.*, 2018), and Cu₂(μ-Cl₂)Cl₂(3,5-diphenyl-4-amino-1,2,4-triazole)₂(H₂O)₂ (Bushuev *et al.*, 2006).

Compound **(1)** consists of two Cu^{II} ions bridged by two μ-Cl anions (Fig. 1). An inversion center exists in the molecule, resulting in identical coordination environments about the copper centers. Thus, only the coordination environment of Cu1 will be discussed. The copper ions are assigned as a 2+ oxidation state based on a bond-valence-sum value of 2.03 (Bresle & O’Keeffe, 1991; Liu & Thorp, 1993) and overall molecular charge considerations. The 3,5-diphenyl-1*H*-pyrazole ligand is not deprotonated (H atoms are well resolved in difference electron density maps); thus, the ligands have a neutral charge. The four chloride ions necessitate that each identical copper ion has a 2+ charge. Each Cu^{II} ion is five-coordinate with a distorted square-pyramidal geometry (Fig. 2). This geometry is supported by the calculated τ value of 0.28, where an ideal square-pyramidal geometry is given by

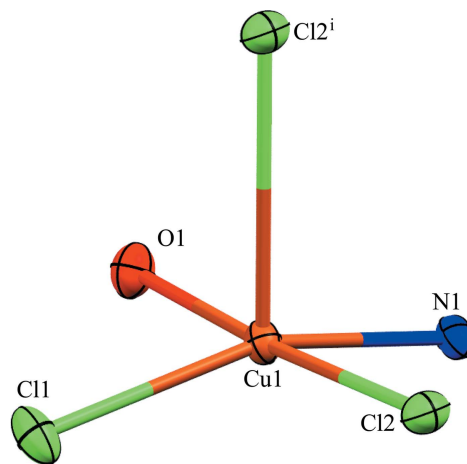


Figure 2
The distorted square-pyramidal geometry about Cu1 [symmetry code: (i) $-x + 1, -y + 1, -z$]. See Fig. 1 for display details.

$\tau = 0$ and an ideal trigonal-bipyramidal geometry is specified as $\tau = 1$ (Addison *et al.*, 1984). The basal atoms of the geometry are comprised of the non-protonated nitrogen atom (N1) of the 3,5-diphenyl-1*H*-pyrazole ligand, a terminal chloride anion (Cl1), a μ-chloride anion (Cl2), and an oxygen atom (O1) from a DMF molecule. The average bond distance between Cu1 and the basal atoms is 2.133 Å. The coordination is completed by a second μ-chloride anion (Cl2ⁱ) in the apical position [symmetry operator (i): $-x + 1, -y + 1, -z$]. The bond distance of Cu1 to the apical μ-Cl2ⁱ is elongated with a distance of 2.6693 (6) Å. For comparison, the bond distance of Cu1 to the basal μ-Cl2 is 2.2851 (5) Å. In addition, an intra-

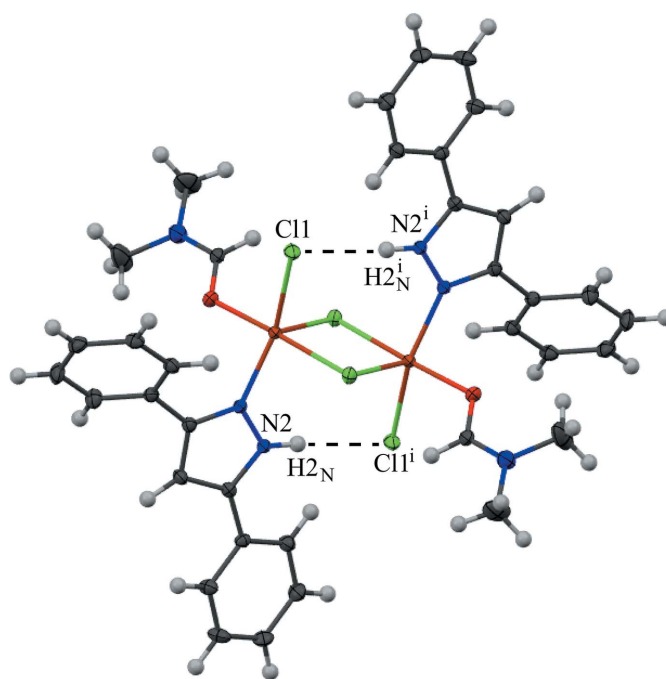


Figure 3
The intramolecular hydrogen bonds present in each molecule of **(1)** [symmetry code: (i) $-x + 1, -y + 1, -z$]. Hydrogen atoms are displayed in white. See Fig. 1 for additional display details.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots Cl1^i$	0.88	2.40	3.2766 (19)	175
$C8-H8\cdots Cl2^{ii}$	0.95	2.79	3.722 (2)	169

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

molecular hydrogen bond exists between the terminal Cl1 anion of Cu1 and the hydrogen atom of N2ⁱ of the 3,5-diphenylpyrazole attached to Cu1ⁱ (Fig. 3 and Table 1). The equivalent intramolecular hydrogen bond exists between Cl1ⁱ and the hydrogen atom of N2. Thus, two intramolecular hydrogen bonds exist in each molecule. Lastly, weak intermolecular hydrogen bonds ($C8-H8\cdots Cl2^{ii}$) connect the molecules into a two-dimensional sheet [Fig. 4; symmetry operator (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$]. The hydrogen atom of the carbon atom in the fourth position of the pyrazole ring bonds to a μ -Cl on an adjacent molecule. Since there are two 3,5-diphenyl-1*H*-pyrazole ligands and two μ -Cl anions per molecule, each individual molecule is hydrogen bonded to four neighboring molecules through this connectivity and a two-dimensional sheet is generated.

Synthesis and crystallization

Copper(II) chloride dihydrate was purchased from J. T. Baker Chemical Company, 3,5-diphenyl-1*H*-pyrazole (>98.0%) was purchased from TCI America, and *N,N*-dimethylformamide (DMF, ACS grade) was purchased Pharmco-Aaper. All reagents were used as received and without further purification.

Copper(II) chloride dihydrate (1 mmol) and 3,5-diphenyl-1*H*-pyrazole (1 mmol) were dissolved in 20 ml of DMF

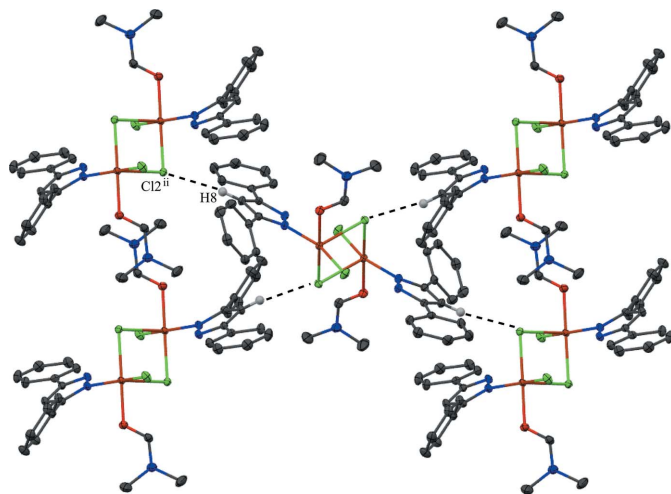


Figure 4
The intermolecular hydrogen bonds present between neighboring molecules of (**1**) that result in a two-dimensional sheet [symmetry code: (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$]. For clarity only the H atoms (white) involved in the hydrogen bonding are displayed. See Fig. 1 for additional display details.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu_2Cl_4(C_3H_7NO)_2(C_{15}H_{12}N_2)_2]$
M_r	855.60
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	12.004 (1), 9.7942 (4), 17.4116 (8)
β (°)	107.633 (3)
V (Å ³)	1950.9 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.40
Crystal size (mm)	0.31 × 0.29 × 0.22
Data collection	
Diffractometer	Nonius Kappa CCD
Absorption correction	Multi-scan (<i>SCALEPACK</i> ; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.612, 0.748
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12667, 4445, 3976
R_{int} ($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.080 0.655
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.107, 1.04
No. of reflections	4445
No. of parameters	229
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.49, -0.45

Computer programs: *COLLECT* (Nonius, 1998), *HKL-3000* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *shelXle* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

resulting in a clear yellow–green solution. The solution was allowed to stir overnight and was then gravity filtered. No precipitate was recovered, and the filtrate had a clear yellow–green color. Slow evaporation of the solvent yielded X-ray quality green plate-like crystals after 30 days. The percent yield of the reaction was 30% based on copper(II) chloride dihydrate.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2018). 3, x181186 [https://doi.org/10.1107/S2414314618011860]

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Crystal data

[Cu₂Cl₄(C₃H₇NO)₂(C₁₅H₁₂N₂)₂]

$M_r = 855.60$

Monoclinic, $P2_1/n$

$a = 12.004$ (1) Å

$b = 9.7942$ (4) Å

$c = 17.4116$ (8) Å

$\beta = 107.633$ (3)°

$V = 1950.9$ (2) Å³

$Z = 2$

$F(000) = 876$

$D_x = 1.457$ Mg m⁻³

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

Cell parameters from 12667 reflections

$\theta = 1.8$ – 27.8 °

$\mu = 1.40$ mm⁻¹

$T = 100$ K

Plate, green

$0.31 \times 0.29 \times 0.22$ mm

Data collection

Nonius Kappa CCD
diffractometer

Radiation source: fine focus X-ray tube

Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan

(SCALEPACK; Otwinowski & Minor, 1997)

$T_{\min} = 0.612$, $T_{\max} = 0.748$

12667 measured reflections

4445 independent reflections

3976 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.080$

$\theta_{\max} = 27.8$ °, $\theta_{\min} = 1.8$ °

$h = -13 \rightarrow 15$

$k = -12 \rightarrow 10$

$l = -22 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.107$

$S = 1.04$

4445 reflections

229 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

$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 1.0669P]$

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

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

$\Delta\rho_{\max} = 0.49$ e Å⁻³

$\Delta\rho_{\min} = -0.45$ e Å⁻³

Extinction correction: SHELXL2014
(Sheldrick, 2015),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0119 (13)

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. Hydrogen atoms were placed in calculated positions and refined as riding on their carrier atoms with C—H distances of 0.95 Å for sp² carbon atoms, 0.98 Å for methyl carbon atoms, and 0.88 Å for the sp² nitrogen atom. The $\langle U_{\text{iso}} \rangle$ values for hydrogen atoms were set to a multiple of the value of the carrying carbon atom (1.2 times for sp²-hybridized carbon atoms or 1.5 times for methyl carbon atoms).

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.63919 (2)	0.57447 (2)	0.01853 (2)	0.01123 (12)
Cl2	0.58568 (4)	0.36146 (5)	0.04774 (3)	0.01454 (14)
Cl1	0.68474 (5)	0.49827 (5)	−0.09070 (3)	0.01877 (15)
O1	0.67895 (14)	0.76438 (15)	−0.00269 (9)	0.0167 (3)
N1	0.66061 (15)	0.63626 (17)	0.13178 (10)	0.0128 (3)
N2	0.57490 (16)	0.63696 (18)	0.16782 (10)	0.0130 (3)
H2N	0.5038	0.6053	0.1456	0.016*
N3	0.6447 (2)	0.9468 (2)	−0.08618 (12)	0.0243 (4)
C1	0.9082 (2)	0.6007 (2)	0.12880 (12)	0.0161 (4)
H1	0.8590	0.5251	0.1072	0.019*
C2	1.0193 (2)	0.6081 (2)	0.12018 (12)	0.0179 (4)
H2	1.0460	0.5376	0.0926	0.021*
C3	1.0916 (2)	0.7185 (3)	0.15171 (13)	0.0214 (5)
H3	1.1676	0.7232	0.1457	0.026*
C4	1.0528 (2)	0.8216 (3)	0.19191 (14)	0.0238 (5)
H4	1.1022	0.8971	0.2134	0.029*
C5	0.9413 (2)	0.8147 (2)	0.20085 (14)	0.0205 (5)
H5	0.9150	0.8853	0.2285	0.025*
C6	0.86844 (19)	0.7044 (2)	0.16931 (12)	0.0149 (4)
C7	0.75421 (19)	0.6933 (2)	0.18394 (12)	0.0140 (4)
C8	0.72765 (19)	0.7317 (2)	0.25414 (12)	0.0158 (4)
H8	0.7782	0.7755	0.3003	0.019*
C9	0.61330 (18)	0.6929 (2)	0.24252 (11)	0.0130 (4)
C10	0.54215 (19)	0.7055 (2)	0.29796 (12)	0.0134 (4)
C11	0.6005 (2)	0.7341 (2)	0.37895 (12)	0.0177 (4)
H11	0.6832	0.7431	0.3967	0.021*
C12	0.5374 (2)	0.7494 (2)	0.43331 (13)	0.0220 (5)
H12	0.5775	0.7690	0.4882	0.026*
C13	0.4177 (2)	0.7367 (2)	0.40908 (13)	0.0211 (5)
H13	0.3754	0.7468	0.4469	0.025*
C14	0.3592 (2)	0.7088 (2)	0.32849 (13)	0.0208 (5)
H14	0.2765	0.7004	0.3112	0.025*
C15	0.42102 (19)	0.6930 (2)	0.27315 (12)	0.0171 (4)
H15	0.3804	0.6737	0.2183	0.021*
C16	0.62989 (19)	0.8181 (2)	−0.06975 (12)	0.0165 (4)

H16	0.5795	0.7632	-0.1107	0.020*
C17	0.7246 (3)	1.0358 (3)	-0.02662 (17)	0.0460 (8)
H17A	0.7893	1.0635	-0.0465	0.069*
H17B	0.7554	0.9863	0.0243	0.069*
H17C	0.6822	1.1170	-0.0179	0.069*
C18	0.5865 (3)	1.0043 (3)	-0.16520 (15)	0.0372 (7)
H18A	0.6450	1.0411	-0.1885	0.056*
H18B	0.5338	1.0777	-0.1599	0.056*
H18C	0.5413	0.9328	-0.2005	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01127 (17)	0.01268 (17)	0.00998 (15)	-0.00203 (9)	0.00358 (10)	-0.00140 (8)
Cl2	0.0123 (3)	0.0129 (3)	0.0168 (2)	-0.00006 (18)	0.00204 (18)	0.00201 (17)
Cl1	0.0170 (3)	0.0250 (3)	0.0169 (2)	-0.0054 (2)	0.0089 (2)	-0.00756 (19)
O1	0.0191 (8)	0.0159 (7)	0.0153 (7)	-0.0037 (6)	0.0054 (6)	0.0009 (6)
N1	0.0108 (9)	0.0162 (8)	0.0120 (7)	-0.0017 (7)	0.0044 (6)	-0.0010 (6)
N2	0.0108 (9)	0.0166 (9)	0.0125 (7)	-0.0025 (7)	0.0047 (6)	-0.0021 (7)
N3	0.0344 (12)	0.0161 (9)	0.0199 (9)	-0.0020 (8)	0.0047 (9)	0.0007 (8)
C1	0.0149 (11)	0.0185 (10)	0.0140 (9)	-0.0001 (8)	0.0029 (8)	-0.0008 (8)
C2	0.0157 (11)	0.0231 (11)	0.0156 (9)	0.0029 (9)	0.0057 (8)	-0.0007 (8)
C3	0.0148 (11)	0.0307 (13)	0.0199 (10)	-0.0010 (9)	0.0073 (9)	0.0039 (9)
C4	0.0170 (12)	0.0251 (12)	0.0298 (11)	-0.0084 (9)	0.0078 (9)	-0.0037 (10)
C5	0.0177 (11)	0.0198 (11)	0.0252 (10)	-0.0015 (9)	0.0085 (9)	-0.0047 (9)
C6	0.0141 (10)	0.0177 (10)	0.0131 (8)	0.0001 (8)	0.0043 (8)	0.0013 (8)
C7	0.0152 (10)	0.0129 (9)	0.0135 (8)	-0.0010 (8)	0.0037 (8)	-0.0006 (7)
C8	0.0149 (11)	0.0185 (10)	0.0132 (9)	-0.0014 (8)	0.0030 (8)	-0.0032 (8)
C9	0.0132 (10)	0.0123 (9)	0.0128 (8)	0.0010 (8)	0.0028 (7)	-0.0003 (7)
C10	0.0155 (11)	0.0124 (9)	0.0139 (9)	0.0011 (8)	0.0066 (8)	0.0003 (7)
C11	0.0143 (11)	0.0245 (11)	0.0144 (9)	0.0029 (9)	0.0044 (8)	0.0000 (8)
C12	0.0241 (12)	0.0304 (12)	0.0123 (9)	0.0065 (10)	0.0065 (9)	-0.0003 (9)
C13	0.0221 (12)	0.0254 (11)	0.0201 (10)	0.0019 (9)	0.0129 (9)	-0.0012 (9)
C14	0.0155 (11)	0.0261 (12)	0.0226 (10)	-0.0007 (9)	0.0083 (9)	-0.0017 (9)
C15	0.0170 (11)	0.0193 (11)	0.0151 (9)	-0.0005 (8)	0.0048 (8)	-0.0022 (8)
C16	0.0149 (11)	0.0195 (10)	0.0162 (9)	-0.0038 (8)	0.0063 (8)	-0.0015 (8)
C17	0.071 (2)	0.0207 (13)	0.0338 (14)	-0.0132 (14)	-0.0030 (14)	-0.0007 (12)
C18	0.055 (2)	0.0254 (13)	0.0255 (12)	0.0064 (12)	0.0044 (12)	0.0106 (10)

Geometric parameters (Å, °)

Cu1—O1	1.9826 (15)	C5—H5	0.9500
Cu1—N1	2.0034 (16)	C6—C7	1.473 (3)
Cu1—Cl1	2.2590 (5)	C7—C8	1.405 (3)
Cu1—Cl2	2.2851 (5)	C8—C9	1.379 (3)
Cu1—Cl2 ⁱ	2.6693 (6)	C8—H8	0.9500
Cl2—Cu1 ⁱ	2.6693 (6)	C9—C10	1.475 (3)
O1—C16	1.253 (3)	C10—C15	1.391 (3)

N1—C7	1.335 (3)	C10—C11	1.400 (3)
N1—N2	1.358 (2)	C11—C12	1.388 (3)
N2—C9	1.357 (3)	C11—H11	0.9500
N2—H2N	0.8800	C12—C13	1.375 (4)
N3—C16	1.317 (3)	C12—H12	0.9500
N3—C18	1.455 (3)	C13—C14	1.393 (3)
N3—C17	1.467 (3)	C13—H13	0.9500
C1—C2	1.388 (3)	C14—C15	1.391 (3)
C1—C6	1.400 (3)	C14—H14	0.9500
C1—H1	0.9500	C15—H15	0.9500
C2—C3	1.391 (3)	C16—H16	0.9500
C2—H2	0.9500	C17—H17A	0.9800
C3—C4	1.387 (3)	C17—H17B	0.9800
C3—H3	0.9500	C17—H17C	0.9800
C4—C5	1.395 (3)	C18—H18A	0.9800
C4—H4	0.9500	C18—H18B	0.9800
C5—C6	1.393 (3)	C18—H18C	0.9800
O1—Cu1—N1	86.20 (6)	C8—C7—C6	126.82 (19)
O1—Cu1—C11	91.13 (4)	C9—C8—C7	106.06 (18)
N1—Cu1—C11	159.53 (5)	C9—C8—H8	127.0
O1—Cu1—C12	176.18 (5)	C7—C8—H8	127.0
N1—Cu1—C12	91.01 (5)	N2—C9—C8	106.62 (17)
C11—Cu1—C12	92.39 (2)	N2—C9—C10	124.41 (19)
O1—Cu1—C12 ⁱ	88.16 (5)	C8—C9—C10	128.97 (18)
N1—Cu1—C12 ⁱ	99.55 (5)	C15—C10—C11	119.17 (19)
C11—Cu1—C12 ⁱ	100.643 (19)	C15—C10—C9	123.19 (18)
C12—Cu1—C12 ⁱ	89.727 (18)	C11—C10—C9	117.63 (19)
Cu1—C12—Cu1 ⁱ	90.273 (18)	C12—C11—C10	119.9 (2)
C16—O1—Cu1	119.72 (14)	C12—C11—H11	120.0
C7—N1—N2	106.44 (16)	C10—C11—H11	120.0
C7—N1—Cu1	128.82 (14)	C13—C12—C11	121.1 (2)
N2—N1—Cu1	124.55 (13)	C13—C12—H12	119.5
C9—N2—N1	111.11 (17)	C11—C12—H12	119.5
C9—N2—H2N	124.4	C12—C13—C14	119.2 (2)
N1—N2—H2N	124.4	C12—C13—H13	120.4
C16—N3—C18	121.2 (2)	C14—C13—H13	120.4
C16—N3—C17	121.2 (2)	C15—C14—C13	120.5 (2)
C18—N3—C17	117.6 (2)	C15—C14—H14	119.7
C2—C1—C6	120.1 (2)	C13—C14—H14	119.7
C2—C1—H1	120.0	C10—C15—C14	120.1 (2)
C6—C1—H1	120.0	C10—C15—H15	119.9
C1—C2—C3	120.2 (2)	C14—C15—H15	119.9
C1—C2—H2	119.9	O1—C16—N3	123.2 (2)
C3—C2—H2	119.9	O1—C16—H16	118.4
C4—C3—C2	120.0 (2)	N3—C16—H16	118.4
C4—C3—H3	120.0	N3—C17—H17A	109.5
C2—C3—H3	120.0	N3—C17—H17B	109.5

C3—C4—C5	120.0 (2)	H17A—C17—H17B	109.5
C3—C4—H4	120.0	N3—C17—H17C	109.5
C5—C4—H4	120.0	H17A—C17—H17C	109.5
C6—C5—C4	120.2 (2)	H17B—C17—H17C	109.5
C6—C5—H5	119.9	N3—C18—H18A	109.5
C4—C5—H5	119.9	N3—C18—H18B	109.5
C5—C6—C1	119.5 (2)	H18A—C18—H18B	109.5
C5—C6—C7	119.69 (19)	N3—C18—H18C	109.5
C1—C6—C7	120.70 (19)	H18A—C18—H18C	109.5
N1—C7—C8	109.76 (18)	H18B—C18—H18C	109.5
N1—C7—C6	123.32 (18)		
C7—N1—N2—C9	-0.4 (2)	N1—N2—C9—C8	1.0 (2)
Cu1—N1—N2—C9	-175.77 (13)	N1—N2—C9—C10	-178.41 (18)
C6—C1—C2—C3	0.0 (3)	C7—C8—C9—N2	-1.2 (2)
C1—C2—C3—C4	0.0 (3)	C7—C8—C9—C10	178.2 (2)
C2—C3—C4—C5	0.1 (4)	N2—C9—C10—C15	-16.5 (3)
C3—C4—C5—C6	-0.2 (4)	C8—C9—C10—C15	164.2 (2)
C4—C5—C6—C1	0.2 (3)	N2—C9—C10—C11	164.8 (2)
C4—C5—C6—C7	175.8 (2)	C8—C9—C10—C11	-14.5 (3)
C2—C1—C6—C5	-0.1 (3)	C15—C10—C11—C12	0.1 (3)
C2—C1—C6—C7	-175.67 (19)	C9—C10—C11—C12	178.8 (2)
N2—N1—C7—C8	-0.3 (2)	C10—C11—C12—C13	0.1 (4)
Cu1—N1—C7—C8	174.72 (14)	C11—C12—C13—C14	-0.4 (4)
N2—N1—C7—C6	176.29 (18)	C12—C13—C14—C15	0.4 (4)
Cu1—N1—C7—C6	-8.6 (3)	C11—C10—C15—C14	-0.1 (3)
C5—C6—C7—N1	148.5 (2)	C9—C10—C15—C14	-178.7 (2)
C1—C6—C7—N1	-35.9 (3)	C13—C14—C15—C10	-0.2 (3)
C5—C6—C7—C8	-35.4 (3)	Cu1—O1—C16—N3	174.50 (17)
C1—C6—C7—C8	140.1 (2)	C18—N3—C16—O1	179.6 (2)
N1—C7—C8—C9	1.0 (2)	C17—N3—C16—O1	2.2 (4)
C6—C7—C8—C9	-175.5 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N \cdots C11 ⁱ	0.88	2.40	3.2766 (19)	175
C8—H8 \cdots Cl2 ⁱⁱ	0.95	2.79	3.722 (2)	169

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