Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dichloridobis[3-methyl-4-phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazole-κ^2N^1,N^5]-copper(II) 3.33-hydrate

Zuoxiang Wang,* Yan Lan, Pingfeng Wu and Liaocheng Huang

Ordered Matter Science Research Center, Southeast University, Nanjing 210096, People's Republic of China
Correspondence e-mail: wangzx0908@yahoo.com.cn

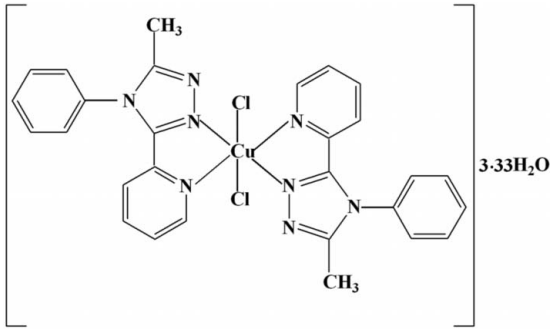
Received 19 January 2008; accepted 20 March 2008

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.057; wR factor = 0.114; data-to-parameter ratio = 15.9.

In the title compound, $[CuCl_2(C_{14}H_{12}N_4)_2]\cdot 3.33H_2O$, the Cu(II) atom is coordinated by two chelating 3-methyl-4-phenyl-5-(2-pyridyl)-1,2,4-triazole ligands and two chloride anions in a distorted octahedral geometry with a $CuN_2N'_2Cl_2$ chromophore. The Cu atom is located on an inversion center. Two uncoordinated water molecules lie on threefold rotation axes with disordered H atoms. Two hydrogen bonds are formed between the water molecules, and another between water and a chlorido ligand.

Related literature

For related literature, see: Bencini *et al.* (1987); Koningsbruggen *et al.* (1995); Moliner *et al.* (1998, 2001); Klingele & Brooker (2003); Klingele *et al.* (2005); Garcia *et al.* (1997); Lavrenova & Larionov (1998); Kahn & Martinez (1998); Koningsbruggen (2004); Matouzenko *et al.* (2004); Wang *et al.* (2005); Zhou *et al.* (2006*a*,*b*).



Experimental

Crystal data

$[CuCl_2(C_{14}H_{12}N_4)_2]\cdot 3.33H_2O$
M_r = 667.04
Rhombohedral, $R\overline{3}$
a = 21.5496 (13) Å
c = 17.619 (2) Å
V = 7086.0 (10) Å^3
Z = 9
Mo $K\alpha$ radiation
μ = 0.91 mm^{-1}
T = 293 (2) K
0.28 × 0.26 × 0.22 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.78, T_{max} = 0.82
12784 measured reflections
3091 independent reflections
2155 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.114
S = 1.06
3091 reflections
194 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	2.006 (2)	Cu1—Cl1	2.7537 (9)
Cu1—N7	2.023 (2)		
N4^i—Cu1—N7	99.70 (9)	N4—Cu1—Cl1	83.17 (8)
N4—Cu1—N7	80.30 (9)	N7—Cu1—Cl1	89.45 (7)
N4^i—Cu1—Cl1	96.83 (8)	N7—Cu1—Cl1^i	90.55 (7)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1D···Cl1	0.85	2.20	3.053 (2)	179
O1—H1A···O2	0.85	2.43	2.932 (3)	119
O2—H2B···O2^{ii}	0.85	1.88	2.505 (8)	130

Symmetry code: (ii) $-x+\frac{2}{3}, -y+\frac{4}{3}, -z+\frac{4}{3}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We are grateful to Jingye Pharmochemical Pilot Plant for financial assistance though project 8507041056.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2182).

References

Bencini, A., Gatteschi, D., Zanchini, C., Haasnoot, J. G., Prins, R. & Reedijk, J. (1987). *J. Am. Chem. Soc.* **109**, 2926–2931.
Bruker (2000). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Garcia, Y., Koningsbruggen, P. J., Codjovi, E., Lapouyade, R., Kahn, O. & Rabardel, L. (1997). *J. Mater. Chem.* **7**, 857–858.
Kahn, O. & Martinez, C. J. (1998). *Science*, **279**, 44–48.

Klingele, M. H., Boyd, P. D. W., Moubaraki, B., Murray, K. S. & Brooker, S. (2005). *Eur. J. Inorg. Chem.* pp. 910–918.
Klingele, M. H. & Brooker, S. (2003). *Coord. Chem. Rev.* **241**, 119–132.
Koningsbruggen, P. J. (2004). *Top. Curr. Chem.* **233**, 123–149.
Koningsbruggen, P. J., Gatteshi, D., Graaff, R. A. G., Hassnoot, J. G., Reedijk, J. & Zanchini, C. (1995). *Inorg. Chem.* **34**, 5175–5182.
Lavrenova, L. G. & Larionov, S. V. (1998). *Russ. J. Coord. Chem.* **24**, 379–395.
Matouzenko, G. S., Bousseksou, A., Borshch, S. A., Perrin, M., Zein, S., Salmon, L., Molnar, G. & Lecocq, S. (2004). *Inorg. Chem.* **43**, 227–236.
Moliner, N., Gaspar, A. B., Munoz, M. C., Niel, V., Cano, J. & Real, J. A. (2001). *Inorg. Chem.* **40**, 3986–3991.
Moliner, N., Munoz, M. C., Koningsbruggen, P. J. & Real, J. A. (1998). *Inorg. Chim. Acta*, **274**, 1–6.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, Z.-X., Lan, Y., Yuan, L.-T. & Liu, C.-Y. (2005). *Acta Cryst.* E**61**, o2033–o2034.
Zhou, A.-Y., Wang, Z.-X., Lan, Y., Yuan, L.-T. & Liu, C.-Y. (2006*b*). *Acta Cryst.* E**62**, m591–m592.
Zhou, B. G., Wang, Z. X., Qiao, X. Y. & Liu, C. Y. (2006*a*). *Acta Cryst.* E**62**, m3176–m3177.

supporting information

Acta Cryst. (2008). E**64**, m593–m594 [doi:10.1107/S1600536808007630]

Dichloridobis[3-methyl-4-phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazole-κ^2N^1,N^5]copper(II) 3.33-hydrate

Zuoxiang Wang, Yan Lan, Pingfeng Wu and Liaocheng Huang

S1. Comment

The coordination chemistry of 1,2,4-triazole derivatives has attracted great attention in recent years (Bencini *et al.*, 1987; Koningsbruggen *et al.*, 1995; Moliner *et al.*, 1998, 2001; Klingele & Brooker, 2003; Klingele *et al.*, 2005). Some spin-crossover complexes of 1,2,4-triazoles with iron(II) salts have been reported, which could be used as molecular-based memory devices, displays and optical switches (Garcia *et al.*, 1997; Lavrenova & Larionov, 1998; Kahn & Martinez, 1998; Koningsbruggen, 2004; Matouzenko *et al.*, 2004). We have synthesized some new 3,4-disubstituted-5-(2-pyridyl)-1,2,4-triazoles and their transition-metal complexes (Wang *et al.*, 2005; Zhou *et al.*, 2006*a*,b). We report here the crystal structure analysis of the title compound, (I).

The structure of (I) is shown in Fig.1. In the crystal structure, the Cu(II) atom is coordinated by two chelating 3-methyl-4-phenyl-5-(2-pyridyl)-1,2,4-triazole ligands and two chloride anions in a distorted octahedral geometry with a $CuN_2N'_2Cl_2$ chromophore. Two hydrogen bonds are formed between the water molecules, and another involves the chloro ligand.

S2. Experimental

To a warm solution of 0.944 g 3-methyl-4-phenyl-5-(2-pyridyl)-1,2,4-triazole (4.0 mmol) in 20 ml e thanol, 0.270 g copper(II) chloride (2.0 mmol) was added. The filtrate was left to stand at room temperature for several days, and blue single crystals suitable for X-ray diffraction were collected.

S3. Refinement

All H atoms were located in a difference Fourier map and allowed to ride on their parent atoms at distances of 0.93 Å (aromatic), 0.96 Å (methyl) and 0.85 (water), and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O). O2 and O3 lie on threefold rotation axes, and accordingly, their H atoms are disordered with a partial occupancy of 1/3 and U values in the range 0.64–0.85 Å^2.

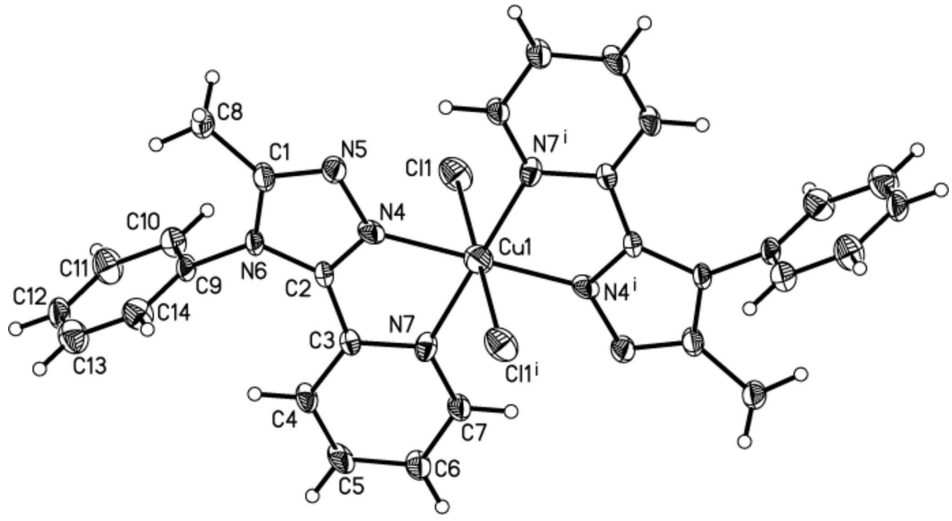


Figure 1

The molecular structure of the title compound with the atomic labelling. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code i: -*x* + 1, -*y* + 2, -*z* + 2.]

Dichloridobis[3-methyl-4-phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazole- κ^2N^1,N^5]copper(II) 3.33-hydrate

Crystal data

$[CuCl_2(C_{14}H_{12}N_4)_2]\cdot 3.33H_2O$
$M_r = 667.04$
Rhombohedral, $R\bar{3}$
Hall symbol: -R 3
$a = 21.5496\ (13)$ Å
$c = 17.619\ (2)$ Å
$\alpha = 90°$
$\gamma = 120°$
$V = 7086.0\ (10)$ Å^3
$Z = 9$
$F(000) = 3099$
$D_x = 1.407$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3501 reflections
$\theta = 2.5–23.9°$
$\mu = 0.91$ mm^{-1}
$T = 293$ K
Polyhedron, blue
0.28 × 0.26 × 0.22 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.78$, $T_{max} = 0.82$
12784 measured reflections
3091 independent reflections
2155 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.9°$
$h = -26\rightarrow26$
$k = -21\rightarrow26$
$l = -21\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.114$
$S = 1.06$
3091 reflections
194 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

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ 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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.5000	1.0000	1.0000	0.04781 (19)	
C1	0.56211 (17)	0.87212 (17)	0.88733 (16)	0.0408 (7)	
C2	0.54547 (13)	0.96307 (14)	0.86885 (15)	0.0280 (6)	
C3	0.53495 (14)	1.02034 (15)	0.84128 (15)	0.0292 (6)	
C4	0.54676 (16)	1.04762 (16)	0.76855 (16)	0.0366 (7)	
H4	0.5626	1.0287	0.7307	0.044*	
C5	0.53496 (19)	1.10252 (19)	0.75306 (16)	0.0459 (8)	
H5	0.5416	1.1206	0.7040	0.055*	
C6	0.51311 (18)	1.13172 (19)	0.80953 (16)	0.0444 (8)	
H6	0.5053	1.1696	0.7995	0.053*	
C7	0.50315 (17)	1.10251 (16)	0.88239 (17)	0.0412 (7)	
H7	0.4894	1.1222	0.9214	0.049*	
C8	0.57362 (19)	0.81162 (17)	0.87105 (17)	0.0445 (8)	
H8A	0.6136	0.8167	0.9001	0.067*	
H8B	0.5834	0.8112	0.8179	0.067*	
H8C	0.5314	0.7675	0.8845	0.067*	
C9	0.56300 (18)	0.90787 (16)	0.74991 (16)	0.0380 (7)	
C10	0.4997 (2)	0.86341 (18)	0.71288 (19)	0.0504 (8)	
H10	0.4565	0.8395	0.7389	0.061*	
C11	0.5032 (2)	0.8556 (2)	0.6345 (2)	0.0574 (9)	
H11	0.4617	0.8262	0.6072	0.069*	
C12	0.56770 (19)	0.89132 (18)	0.59789 (17)	0.0458 (8)	
H12	0.5696	0.8859	0.5457	0.055*	
C13	0.6281 (2)	0.9340 (2)	0.6358 (2)	0.0563 (9)	
H13	0.6711	0.9579	0.6093	0.068*	
C14	0.62835 (19)	0.94346 (18)	0.71455 (19)	0.0509 (8)	
H14	0.6704	0.9722	0.7413	0.061*	
N4	0.54193 (13)	0.94977 (13)	0.94163 (13)	0.0361 (6)	
N5	0.55287 (15)	0.89213 (14)	0.95473 (14)	0.0411 (6)	
N6	0.55975 (13)	0.91589 (13)	0.83203 (13)	0.0333 (5)	
N7	0.51276 (12)	1.04744 (13)	0.89762 (13)	0.0356 (6)	
Cl1	0.37209 (5)	0.88666 (5)	0.95079 (5)	0.0581 (3)	

O1	0.38596 (12)	0.77383 (11)	0.85941 (11)	0.0424 (5)	
H1D	0.3825	0.8054	0.8850	0.051*	
H1A	0.3444	0.7409	0.8465	0.051*	
O2	0.3333	0.6667	0.7377 (2)	0.0567 (11)	
H2A	0.2895	0.6359	0.7304	0.068*	0.334
H2B	0.3504	0.6925	0.6983	0.068*	0.334
O3	0.6667	0.3333	0.70495 (19)	0.0428 (9)	
H3A	0.6650	0.3103	0.6651	0.051*	0.3333
H3C	0.6474	0.3042	0.7416	0.051*	0.3333

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0484 (3)	0.0501 (4)	0.0456 (4)	0.0251 (3)	0.0044 (3)	0.0055 (3)
C1	0.0531 (19)	0.0518 (18)	0.0298 (17)	0.0356 (16)	0.0098 (14)	0.0032 (14)
C2	0.0275 (14)	0.0340 (15)	0.0229 (13)	0.0158 (12)	0.0030 (11)	−0.0039 (11)
C3	0.0295 (14)	0.0369 (15)	0.0227 (13)	0.0178 (12)	0.0003 (11)	−0.0025 (11)
C4	0.0469 (17)	0.0542 (18)	0.0184 (13)	0.0326 (15)	−0.0003 (12)	−0.0004 (13)
C5	0.062 (2)	0.068 (2)	0.0205 (14)	0.0417 (19)	0.0051 (14)	0.0132 (15)
C6	0.064 (2)	0.062 (2)	0.0292 (15)	0.0477 (18)	0.0059 (15)	0.0107 (15)
C7	0.060 (2)	0.0531 (19)	0.0302 (15)	0.0429 (16)	0.0118 (14)	0.0119 (14)
C8	0.065 (2)	0.052 (2)	0.0315 (17)	0.0406 (18)	0.0071 (15)	0.0038 (14)
C9	0.064 (2)	0.0440 (17)	0.0176 (14)	0.0356 (16)	0.0047 (14)	−0.0010 (12)
C10	0.064 (2)	0.053 (2)	0.0408 (18)	0.0341 (18)	0.0118 (17)	0.0035 (16)
C11	0.062 (2)	0.070 (2)	0.0377 (19)	0.031 (2)	−0.0055 (18)	−0.0072 (18)
C12	0.070 (2)	0.057 (2)	0.0244 (16)	0.0420 (19)	0.0051 (16)	−0.0025 (14)
C13	0.063 (2)	0.068 (2)	0.042 (2)	0.036 (2)	−0.0001 (18)	0.0004 (18)
C14	0.050 (2)	0.055 (2)	0.0416 (19)	0.0214 (17)	−0.0045 (16)	−0.0022 (16)
N4	0.0456 (14)	0.0424 (14)	0.0237 (13)	0.0245 (12)	0.0007 (10)	0.0104 (10)
N5	0.0589 (17)	0.0484 (15)	0.0291 (13)	0.0367 (14)	0.0058 (12)	0.0062 (11)
N6	0.0484 (15)	0.0400 (13)	0.0197 (11)	0.0282 (12)	0.0069 (10)	−0.0004 (10)
N7	0.0401 (13)	0.0454 (14)	0.0329 (13)	0.0303 (12)	−0.0029 (11)	−0.0059 (11)
Cl1	0.0439 (5)	0.0671 (6)	0.0520 (5)	0.0191 (4)	0.0020 (4)	0.0033 (4)
O1	0.0534 (13)	0.0488 (13)	0.0327 (11)	0.0313 (11)	0.0046 (10)	0.0029 (10)
O2	0.0633 (16)	0.0633 (16)	0.043 (3)	0.0317 (8)	0.000	0.000
O3	0.0519 (14)	0.0519 (14)	0.0245 (18)	0.0259 (7)	0.000	0.000

Geometric parameters (Å, º)

Cu1—N4^{i}	2.006 (2)	C8—H8A	0.960
Cu1—N4	2.006 (2)	C8—H8B	0.960
Cu1—N7	2.023 (2)	C8—H8C	0.960
Cu1—N7^{i}	2.023 (2)	C9—C14	1.371 (5)
Cu1—Cl1	2.7537 (9)	C9—C10	1.377 (5)
Cu1—Cl1^{i}	2.7537 (9)	C9—N6	1.463 (3)
C1—N5	1.312 (4)	C10—C11	1.398 (5)
C1—N6	1.375 (4)	C10—H10	0.930
C1—C8	1.472 (4)	C11—C12	1.368 (5)

C2—N4	1.308 (3)	C11—H11	0.930
C2—N6	1.365 (3)	C12—C13	1.338 (5)
C2—C3	1.446 (4)	C12—H12	0.930
C3—N7	1.354 (3)	C13—C14	1.402 (5)
C3—C4	1.380 (4)	C13—H13	0.930
C4—C5	1.356 (4)	C14—H14	0.930
C4—H4	0.930	N4—N5	1.395 (3)
C5—C6	1.380 (4)	O1—H1D	0.850
C5—H5	0.930	O1—H1A	0.850
C6—C7	1.398 (4)	O2—H2A	0.850
C6—H6	0.930	O2—H2B	0.8499
C7—N7	1.330 (4)	O3—H3A	0.850
C7—H7	0.930	O3—H3C	0.850

N4^{i}—Cu1—N4	180.000 (1)	C1—C8—H8B	109.5
N4^{i}—Cu1—N7	99.70 (9)	H8A—C8—H8B	109.5
N4—Cu1—N7	80.30 (9)	C1—C8—H8C	109.5
N4^{i}—Cu1—N7^{i}	80.30 (9)	H8A—C8—H8C	109.5
N4—Cu1—N7^{i}	99.70 (9)	H8B—C8—H8C	109.5
N7—Cu1—N7^{i}	180.000 (1)	C14—C9—C10	123.8 (3)
N4^{i}—Cu1—Cl1	96.83 (8)	C14—C9—N6	118.7 (3)
N4—Cu1—Cl1	83.17 (8)	C10—C9—N6	117.5 (3)
N7—Cu1—Cl1	89.45 (7)	C9—C10—C11	117.3 (3)
N4^{i}—Cu1—Cl1^{i}	83.17 (8)	C9—C10—H10	121.4
N4—Cu1—Cl1^{i}	96.83 (8)	C11—C10—H10	121.4
N7—Cu1—Cl1^{i}	90.55 (7)	C12—C11—C10	119.9 (3)
N7^{i}—Cu1—Cl1^{i}	89.45 (7)	C12—C11—H11	120.1
Cl1—Cu1—Cl1^{i}	180.00 (4)	C10—C11—H11	120.1
N5—C1—N6	110.6 (3)	C13—C12—C11	121.2 (3)
N5—C1—C8	126.0 (3)	C13—C12—H12	119.4
N6—C1—C8	123.4 (3)	C11—C12—H12	119.4
N4—C2—N6	108.2 (2)	C12—C13—C14	121.7 (3)
N4—C2—C3	120.0 (2)	C12—C13—H13	119.2
N6—C2—C3	131.8 (2)	C14—C13—H13	119.2
N7—C3—C4	121.8 (3)	C9—C14—C13	116.1 (3)
N7—C3—C2	111.2 (2)	C9—C14—H14	121.9
C4—C3—C2	127.0 (2)	C13—C14—H14	121.9
C5—C4—C3	118.9 (3)	C2—N4—N5	109.9 (2)
C5—C4—H4	120.5	C2—N4—Cu1	112.15 (18)
C3—C4—H4	120.5	N5—N4—Cu1	135.90 (18)
C4—C5—C6	120.6 (3)	C1—N5—N4	105.3 (2)
C4—C5—H5	119.7	C2—N6—C1	105.9 (2)
C6—C5—H5	119.7	C2—N6—C9	126.9 (2)
C5—C6—C7	117.9 (3)	C1—N6—C9	126.8 (2)
C5—C6—H6	121.1	C7—N7—C3	118.9 (3)
C7—C6—H6	121.1	C7—N7—Cu1	126.0 (2)
N7—C7—C6	122.0 (3)	C3—N7—Cu1	115.07 (19)
N7—C7—H7	119.0	H1D—O1—H1A	109.5

C6—C7—H7	119.0	H2A—O2—H2B	109.5
C1—C8—H8A	109.5	H3A—O3—H3C	109.5

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*D*···Cl1	0.85	2.20	3.053 (2)	179
O1—H1*A*···O2	0.85	2.43	2.932 (3)	119
O2—H2*B*···O2^{ii}	0.85	1.88	2.505 (8)	130

Symmetry code: (ii) −*x*+2/3, −*y*+4/3, −*z*+4/3.