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Chloridobis(1,2,3,4-tetrahydro-1,4,6,11-tetraazanaphthacene-κN^6)copper(I)

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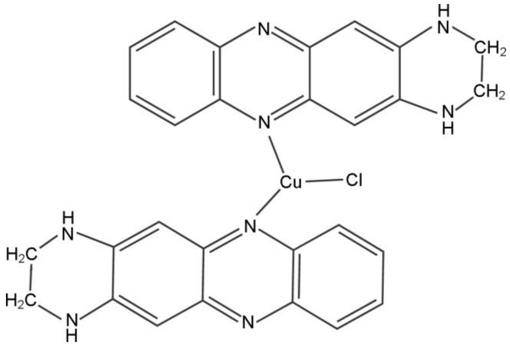
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.105; data-to-parameter ratio = 16.4.

In the title complex, [CuCl(C$_{14}$H$_{12}$N$_4$)$_2$], the Cu^{I} atom, lying on a twofold rotation axis, is coordinated by two N atoms of two 1,2,3,4-tetrahydro-1,4,6,11-tetraazanaphthacene ligands and one Cl atom, also lying on the twofold rotation axis, in a distorted trigonal-planar geometry. The complex molecules are connected into a one-dimensional structure along [001] *via* N—H$\cdots$N hydrogen bonds and further into a three-dimensional structure *via* N—H$\cdots$Cl hydrogen bonds. π–π interactions between the pyrazine and benzene rings and between the benzene rings [centroid–centroid distances = 3.5635 (15) and 3.9128 (16) Å] are present.

Related literature

For transition metal complexes with heterocyclic ligands, see: Dai *et al.* (2007); Grove *et al.* (2000, 2001); Näther & Beck (2004); Xu *et al.* (2011). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

[CuCl(C$_{14}$H$_{12}$N$_4$)$_2$]	V = 2510 (1) Å^3
M_r = 571.54	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 16.987 (4) Å	μ = 1.01 mm^{-1}
b = 11.606 (3) Å	T = 296 K
c = 14.487 (4) Å	0.29 × 0.24 × 0.06 mm
β = 118.492 (3)°	

Data collection

Bruker APEX CCD diffractometer	7571 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2839 independent reflections
$T_{\min}$ = 0.758, $T_{\max}$ = 0.942	2476 reflections with $I > 2\sigma(I)$
	R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036	173 parameters
$wR(F^2)$ = 0.105	H-atom parameters constrained
S = 1.03	$\Delta\rho_{\max}$ = 0.94 e Å^{-3}
2839 reflections	$\Delta\rho_{\min}$ = −0.34 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3N$\cdots$N2^{i}	0.86	2.22	2.986 (2)	148
N4—H4N$\cdots$Cl1^{ii}	0.86	2.76	3.4952 (18)	145

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2514).

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supplementary materials

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Chloridobis(1,2,3,4-tetrahydro-1,4,6,11-tetraazanaphthacene-κ*N*^{6})copper(I)

Xing-Shun Chen, Jing-Jing Zhang, Tai-Ke Duan, Qun Chen and Qian-Feng Zhang

Comment

The heterocyclic compounds involving aromatic system with condensed pyrazine, pyridine and piperidine rings have been shown to occur as a rigid bridge in transition metal complexes, which are expected to be good building blocks for creating coordination polymers due to the flexibility of the heterocyclic ligands (Grove *et al.*, 2000, 2001). We have recently been studying the coordination chemistry of polyamines to transition metal halides (Dai *et al.*, 2007, Xu *et al.*, 2011). In the course of this work, we have synthesized the title copper(I) complex with a new 1,2,3,4-tetrahydro-1,4,6,11-tetraazanaphthacene ligand formed from the condensing reaction of phenazine and ethane-1,2-diamine under hydrothermal conditions. Here we report the crystal structure of the mononuclear copper(I) complex.

The molecular structure of the title complex is depicted in Fig. 1. The Cu^I atom, lying on a twofold rotation axis, is coordinated by two N atoms of two organic ligands and one Cl atom. The Cu—N bond length of 1.9927 (15) Å and the Cu—Cl bond length of 2.2229 (10) Å are in the range of those found in related structures retrieved from the Cambridge Structural Database (Allen, 2002). The N—Cu—N and N—Cu—Cl angles are 123.94 (9) and 118.03 (4)°. The Cu atom shows a distorted trigonal-planar coordination geometry (Näther & Beck, 2004). In the crystal, the discrete complex molecules are connected by N—H···N and N—H···Cl hydrogen bonds (Table 1) into a three-dimensional structure (Fig. 2). π–π interactions between the pyrazine and benzene rings and between the benzene rings [centroid–centroid distances = 3.5635 (15) and 3.9128 (16) Å] are present.

Experimental

CuCl (99 mg, 1 mmol), phenazine (360 mg, 2 mmol) and ethane-1,2-diamine (300 mg, 5 mmol) were mixed in water (ca. 3 g) and placed in a 23 ml Teflon-lined stainless steel autoclave and stirred for 20 min. The vessel was sealed and heated to 140°C for 2 d and then cooled to room temperature. Yellow flake crystals were obtained and air dried (yield: 64% based on CuCl). Analysis, calculated for $C_{28}H_{24}ClCuN_8$: C 58.84, H 4.23, N 19.61%; found: C 58.76, H 4.18, N 19.55%.

Refinement

H atoms were placed in geometrically idealized positions and refined as riding atoms, with C—H = 0.93 (CH) and 0.97 (CH_2) and N—H = 0.86 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C, N).

Computing details

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

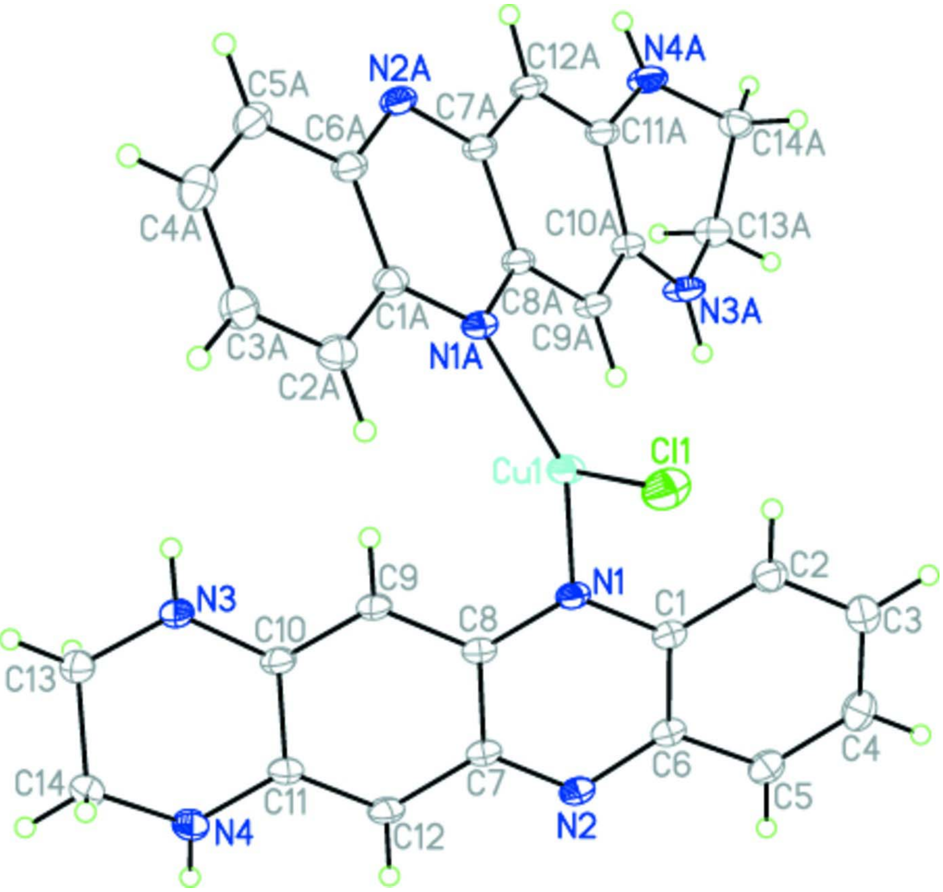

Figure 1

The molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level. [Symmetry code: (A) 1-x, y, 3/2-z.]

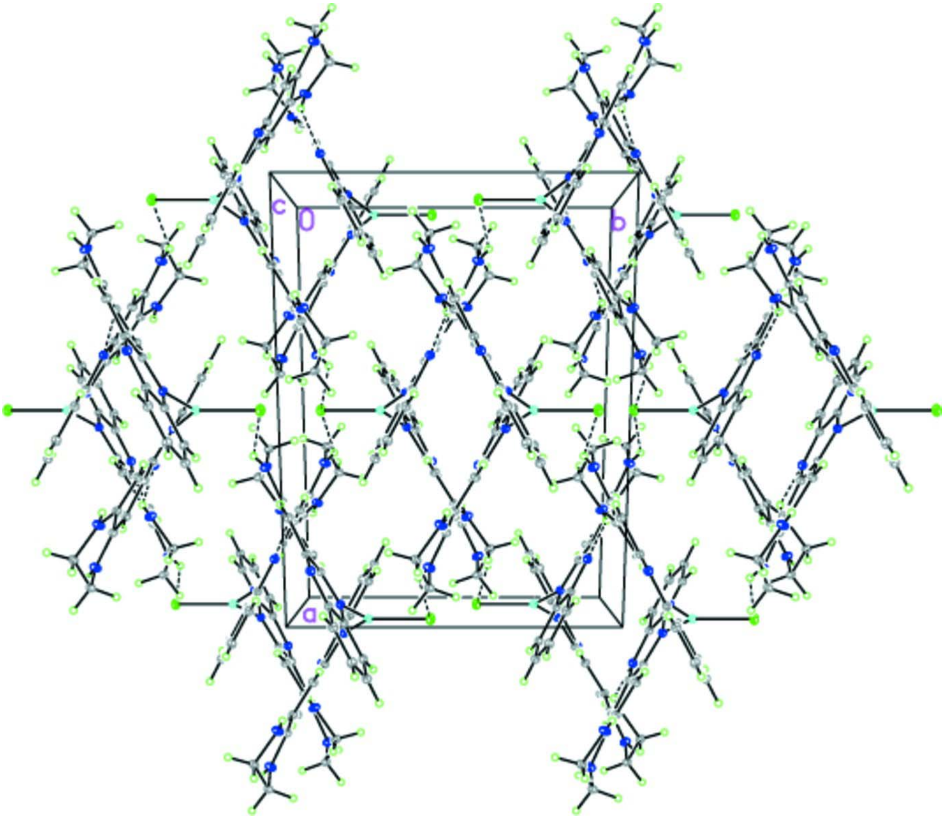

Figure 2

Packing diagram of the title compound viewed along the *c* axis. N—H···N and N—H···Cl hydrogen bonds are shown as dashed lines.

Chloridobis(1,2,3,4-tetrahydro-1,4,6,11-tetraazanaphthacene- κN^6)copper(I)

Crystal data

$[\mathrm{CuCl(C_{14}H_{12}N_4)_2}]$
$M_r = 571.54$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 16.987$ (4) Å
$b = 11.606$ (3) Å
$c = 14.487$ (4) Å
$\beta = 118.492$ (3)°
$V = 2510$ (1) Å^3
$Z = 4$

$F(000) = 1176$
$D_x = 1.512$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3886 reflections
$\theta = 2.4$–27.4°
$\mu = 1.01$ mm^{-1}
$T = 296$ K
Flake, yellow
0.29 × 0.24 × 0.06 mm

Data collection

Bruker APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.758$, $T_{\max} = 0.942$

7571 measured reflections
2839 independent reflections
2476 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.032$
$\theta_{\max} = 27.4°$, $\theta_{\min} = 2.3°$
$h = -12 \rightarrow 22$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.105$
$S = 1.03$
2839 reflections
173 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
$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 1.176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ 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. 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 > 2sigma(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*	$U_{iso}*/U_{eq}$
Cu1	0.5000	0.73465 (3)	0.7500	0.03244 (13)
Cl1	0.5000	0.92619 (6)	0.7500	0.0465 (2)
N1	0.54270 (10)	0.65395 (13)	0.66072 (12)	0.0286 (3)
N2	0.63130 (11)	0.57439 (14)	0.54935 (12)	0.0320 (3)
N3	0.75994 (11)	0.46038 (17)	0.96600 (13)	0.0410 (4)
H3N	0.7305	0.4785	0.9984	0.049*
N4	0.86565 (12)	0.42484 (17)	0.87242 (14)	0.0416 (4)
H4N	0.8924	0.3918	0.8420	0.050*
C1	0.50582 (13)	0.66976 (15)	0.55440 (14)	0.0290 (4)
C2	0.42264 (14)	0.72702 (16)	0.49896 (16)	0.0345 (4)
H2	0.3934	0.7547	0.5348	0.041*
C3	0.38508 (16)	0.74169 (17)	0.39227 (17)	0.0391 (5)
H3	0.3300	0.7785	0.3559	0.047*
C4	0.42941 (16)	0.7014 (2)	0.33765 (16)	0.0425 (5)
H4	0.4035	0.7126	0.2655	0.051*
C5	0.50959 (14)	0.64641 (18)	0.38897 (15)	0.0376 (4)
H5	0.5379	0.6205	0.3516	0.045*
C6	0.55040 (13)	0.62826 (16)	0.49911 (14)	0.0305 (4)
C7	0.66554 (13)	0.55593 (16)	0.65251 (14)	0.0301 (4)
C8	0.61892 (12)	0.59332 (15)	0.70931 (14)	0.0279 (4)
C9	0.65396 (13)	0.56262 (16)	0.81577 (14)	0.0317 (4)
H9	0.6237	0.5853	0.8519	0.038*
C10	0.73143 (12)	0.50019 (17)	0.86743 (14)	0.0309 (4)
C11	0.78465 (12)	0.47576 (16)	0.81447 (14)	0.0310 (4)
C12	0.74970 (13)	0.50098 (17)	0.70967 (15)	0.0340 (4)
H12	0.7821	0.4815	0.6753	0.041*

C13	0.83878 (14)	0.38791 (19)	1.01881 (16)	0.0398 (4)
H13A	0.8230	0.3080	0.9992	0.048*
H13B	0.8634	0.3945	1.0943	0.048*
C14	0.90674 (13)	0.42682 (19)	0.98672 (16)	0.0367 (4)
H14A	0.9268	0.5042	1.0124	0.044*
H14B	0.9583	0.3760	1.0168	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0307 (2)	0.0395 (2)	0.0346 (2)	0.000	0.02160 (15)	0.000
Cl1	0.0614 (5)	0.0364 (4)	0.0555 (4)	0.000	0.0391 (4)	0.000
N1	0.0313 (8)	0.0308 (8)	0.0322 (7)	0.0003 (6)	0.0219 (6)	0.0012 (6)
N2	0.0361 (8)	0.0371 (8)	0.0321 (8)	−0.0009 (6)	0.0238 (7)	−0.0010 (6)
N3	0.0355 (9)	0.0627 (12)	0.0353 (8)	0.0143 (8)	0.0255 (8)	0.0114 (8)
N4	0.0349 (9)	0.0594 (11)	0.0394 (9)	0.0118 (8)	0.0250 (8)	0.0033 (8)
C1	0.0332 (9)	0.0280 (9)	0.0321 (9)	−0.0029 (7)	0.0206 (8)	−0.0004 (6)
C2	0.0368 (10)	0.0321 (10)	0.0396 (10)	−0.0002 (8)	0.0221 (9)	0.0014 (7)
C3	0.0369 (11)	0.0370 (10)	0.0390 (11)	0.0012 (8)	0.0146 (9)	0.0017 (8)
C4	0.0499 (12)	0.0427 (11)	0.0311 (9)	−0.0009 (10)	0.0164 (9)	0.0004 (8)
C5	0.0453 (11)	0.0395 (10)	0.0332 (9)	−0.0018 (9)	0.0230 (9)	−0.0020 (8)
C6	0.0350 (9)	0.0313 (9)	0.0322 (9)	−0.0028 (7)	0.0218 (8)	−0.0015 (7)
C7	0.0332 (9)	0.0337 (9)	0.0325 (9)	−0.0025 (7)	0.0231 (8)	−0.0022 (7)
C8	0.0294 (9)	0.0300 (9)	0.0319 (8)	−0.0019 (7)	0.0208 (7)	−0.0022 (6)
C9	0.0335 (9)	0.0397 (10)	0.0323 (9)	0.0044 (7)	0.0241 (8)	0.0011 (7)
C10	0.0319 (9)	0.0371 (10)	0.0318 (8)	−0.0011 (7)	0.0217 (8)	−0.0011 (7)
C11	0.0305 (9)	0.0343 (9)	0.0366 (9)	0.0003 (7)	0.0229 (8)	−0.0017 (7)
C12	0.0354 (10)	0.0426 (10)	0.0362 (9)	0.0021 (8)	0.0268 (8)	−0.0019 (8)
C13	0.0374 (11)	0.0467 (12)	0.0407 (10)	0.0080 (9)	0.0229 (9)	0.0090 (9)
C14	0.0302 (10)	0.0432 (11)	0.0392 (10)	0.0051 (8)	0.0185 (8)	0.0028 (8)

Geometric parameters (Å, º)

Cu1—N1	1.9927 (15)	C4—C5	1.360 (3)
Cu1—Cl1	2.2229 (10)	C4—H4	0.9300
N1—C8	1.341 (2)	C5—C6	1.420 (2)
N1—C1	1.370 (2)	C5—H5	0.9300
N2—C7	1.337 (2)	C7—C12	1.417 (3)
N2—C6	1.362 (3)	C7—C8	1.454 (2)
N3—C10	1.352 (2)	C8—C9	1.408 (2)
N3—C13	1.452 (3)	C9—C10	1.370 (3)
N3—H3N	0.8600	C9—H9	0.9300
N4—C11	1.358 (3)	C10—C11	1.466 (2)
N4—C14	1.458 (3)	C11—C12	1.372 (3)
N4—H4N	0.8600	C12—H12	0.9300
C1—C2	1.414 (3)	C13—C14	1.505 (3)
C1—C6	1.423 (2)	C13—H13A	0.9700
C2—C3	1.373 (3)	C13—H13B	0.9700
C2—H2	0.9300	C14—H14A	0.9700
C3—C4	1.407 (3)	C14—H14B	0.9700

C3—H3	0.9300

N1^{i}—Cu1—N1	123.94 (9)	N2—C7—C12	120.33 (16)
N1^{i}—Cu1—Cl1	118.03 (4)	N2—C7—C8	121.38 (17)
N1—Cu1—Cl1	118.03 (4)	C12—C7—C8	118.28 (16)
C8—N1—C1	118.01 (15)	N1—C8—C9	120.37 (15)
C8—N1—Cu1	117.73 (12)	N1—C8—C7	120.65 (16)
C1—N1—Cu1	123.63 (12)	C9—C8—C7	118.97 (16)
C7—N2—C6	117.44 (15)	C10—C9—C8	121.74 (16)
C10—N3—C13	122.01 (16)	C10—C9—H9	119.1
C10—N3—H3N	119.0	C8—C9—H9	119.1
C13—N3—H3N	119.0	N3—C10—C9	121.64 (16)
C11—N4—C14	119.34 (16)	N3—C10—C11	119.16 (17)
C11—N4—H4N	120.3	C9—C10—C11	119.20 (16)
C14—N4—H4N	120.3	N4—C11—C12	123.55 (16)
N1—C1—C2	119.89 (16)	N4—C11—C10	117.16 (16)
N1—C1—C6	120.43 (17)	C12—C11—C10	119.24 (17)
C2—C1—C6	119.68 (17)	C11—C12—C7	121.74 (16)
C3—C2—C1	119.97 (19)	C11—C12—H12	119.1
C3—C2—H2	120.0	C7—C12—H12	119.1
C1—C2—H2	120.0	N3—C13—C14	108.31 (16)
C2—C3—C4	120.4 (2)	N3—C13—H13A	110.0
C2—C3—H3	119.8	C14—C13—H13A	110.0
C4—C3—H3	119.8	N3—C13—H13B	110.0
C5—C4—C3	120.90 (19)	C14—C13—H13B	110.0
C5—C4—H4	119.5	H13A—C13—H13B	108.4
C3—C4—H4	119.5	N4—C14—C13	108.89 (17)
C4—C5—C6	120.59 (19)	N4—C14—H14A	109.9
C4—C5—H5	119.7	C13—C14—H14A	109.9
C6—C5—H5	119.7	N4—C14—H14B	109.9
N2—C6—C5	119.74 (16)	C13—C14—H14B	109.9
N2—C6—C1	121.78 (16)	H14A—C14—H14B	108.3
C5—C6—C1	118.47 (18)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*N*···N2^{ii}	0.86	2.22	2.986 (2)	148
N4—H4*N*···Cl1^{iii}	0.86	2.76	3.4952 (18)	145

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