

[N-(1-Azanidyl-2,2,2-trichloroethylidene)-2,2,2-trichloroethanimidamide]-copper(II)

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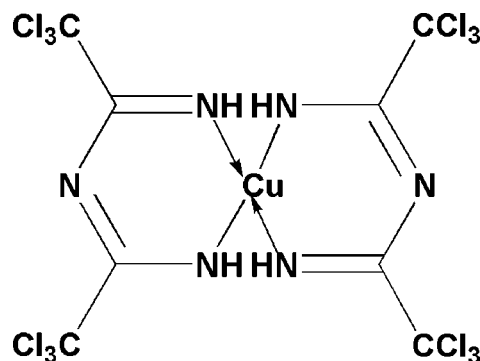
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.047; wR factor = 0.133; data-to-parameter ratio = 19.5.

The title compound, $[\text{Cu}(\text{C}_4\text{H}_2\text{Cl}_6\text{N}_3)_2]$, was obtained by the reaction of CCl_3CN with ammonia in presence of CuCl . The Cu^{II} atom is located about an inversion centre. The molecule consists of three planar units (one central square CuN_4 and two C_2N_3 fragments), adopting a staircase-like structure. The six-membered metalocycles have a sofa conformation with the Cu atom out of the plane of the 1,3,5-triazapentadienyl ligands by 0.246 (5) Å. The *ipso*-C atoms of the CCl_3 substituents are slightly out of the 1,3,5-triazapentadienyl planes by 0.149 (6) and -0.106 (6) Å. The CCl_3 groups of each 1,3,5-triazapentadienyl ligand are practically in the energetically favourable mutually eclipsed conformation. In the crystal, the molecules are packed in stacks along the a axis. The molecules in the stacks are held together by two additional axial $\text{Cu} \cdots \text{Cl}$ interactions of 3.354 (2) Å. Taking the axial $\text{Cu} \cdots \text{Cl}$ interactions into account, the Cu^{II} atom exhibits a distorted [4 + 2]-octahedral coordination environment. The stacks are bound to each other by weak intermolecular attractive $\text{Cl} \cdots \text{Cl}$ [3.505 (2)–3.592 (3) Å] interactions.

Related literature

For a catalytic olefination reaction, see: Shastin *et al.* (2001); Korotchenko *et al.* (2001); Nenajdenko *et al.* (2003, 2004*a,b,c*, 2005, 2007). For related compounds, see: Boča *et al.* (1996); Kajiwara *et al.* (2002); Zhang *et al.* (2005); Igashira-Kamiyama *et al.* (2006); Zheng *et al.* (2007); Figiel *et al.* (2010).



Experimental

Crystal data

$[\text{Cu}(\text{C}_4\text{H}_2\text{Cl}_6\text{N}_3)_2]$	$\gamma = 103.662$ (5)°
$M_r = 673.11$	$V = 552.1$ (3) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.9317$ (17) Å	Mo $K\alpha$ radiation
$b = 9.078$ (3) Å	$\mu = 2.45$ mm ⁻¹
$c = 10.831$ (3) Å	$T = 296$ K
$\alpha = 98.475$ (5)°	$0.33 \times 0.24 \times 0.06$ mm
$\beta = 97.525$ (5)°	

Data collection

Bruker APEXII CCD diffractometer	5662 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2414 independent reflections
$T_{\min} = 0.499$, $T_{\max} = 0.867$	2108 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	124 parameters
$wR(F^2) = 0.133$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 1.18$ e Å ⁻³
2414 reflections	$\Delta\rho_{\text{min}} = -0.85$ e Å ⁻³

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2001); 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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AA2069).

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supporting information

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[*N*-(1-Azanidyl)-2,2,2-trichloroethylidene)-2,2,2-trichloroethanimidamide]-copper(II)

Namig G. Shikhaliyev, Abel M. Maharramov, Vasily M. Muzalevskiy, Valentine G. Nenajdenko and Victor N. Khrustalev

S1. Comment

Recently we have discovered a new catalytic olefination reaction as a general method for the preparation of alkenes from polyhalogenated compounds and hydrazones (Fig. 1) (Shastin *et al.*, 2001; Korotchenko *et al.*, 2001; Nenajdenko *et al.*, 2003, 2004*a*, 2004*b*, 2005, 2007).

During our study of the catalytic olefination reaction we have found that the reaction with trichloroacetonitrile demand the use of ethylenediamine as a base because in the case of ammonia no target alkene is formed (Nenajdenko *et al.*, 2004*c*). We decided to study the reaction of CCl₃CN with ammonia in presence of CuCl more thoroughly and found that the formation of the title copper (II) chelate complex takes place (Fig. 2). The formation of this complex can be explained by high electrophilicity of trichloroacetonitrile (Fig. 3). At the first stage, ammonia reacts with CN bond to form amidine **A** as an intermediate. The subsequent reaction of **A** with second molecule of trichloroacetonitrile gives **B**. And finally, **B** reacts with CuCl₂ resulting in the copper(II) complex **I** in a high yield. We believe that Cu²⁺ is formed by oxidation of Cu¹⁺ with CCl₃CN as it was confirmed previously for catalytic olefination reaction.

The structure of the title compound **I**, C₈H₄N₆Cl₁₂Cu, was unambiguously established by X-ray diffraction study (Fig. 4). The compound **I** crystallizes in the triclinic space group *P*-1 and there is a crystallographically imposed inversion centre at the Cu atom of each molecule. The Cu atom has a square-planar coordination. The 1,3,5-triazapentadienyl ligands are also planar (r.m.s. deviation is 0.021 Å). However, the six-membered metalocycles deviate significantly from the planarity and have a *sofa* conformation with the Cu atom out of the plane of the 1,3,5-triazapentadienyl ligands by 0.246 (5) Å. Thus, the molecule of **I** consists of the three planar units adopting the *staircase*-like structure. The similar molecular conformation has been previously observed in the related compounds (Zhang *et al.*, 2005; Igashira-Kamiyama *et al.*, 2006; Figiel *et al.*, 2010). Nevertheless, it is important to note that the analogous complexes can adopt the planar conformation also (Boča *et al.*, 1996; Kajiwara *et al.*, 2002; Zheng *et al.*, 2007). The *ipso*-C atoms of the CCl₃-substituents are slightly out of the 1,3,5-triazapentadienyl planes by 0.149 (6) and -0.106 (6) Å. The CCl₃-groups of each 1,3,5-triazapentadienyl ligand are practically in the energetically favorable eclipsed mutual conformation.

In the crystal, the molecules are packed in stacks along the *a* axis (Fig. 5). The molecules in the stacks are held together by the two additional axial Cu⋯Cl [Cu1⋯Cl1ⁱ and Cu1⋯Cl1ⁱⁱ] interactions of 3.354 (2) Å. Taking the axial Cu⋯Cl interactions into account, the Cu atom attains the distorted [4 + 2]-octahedral coordination environment. The different stacks are bound to each other by weak intermolecular attractive interactions [Cu2⋯Cl2ⁱⁱⁱ 3.505 (2), Cu2⋯Cl2^{iv} 3.592 (3), Cu3⋯Cl4^v 3.516 (2) and Cu3⋯Cl6^{vi} 3.564 (2) Å]. Symmetry codes: (i) -*x*, -*y* + 2, -*z* + 2; (ii) *x* - 1, *y*, *z*; (iii) -*x* + 2, -*y* + 3, -*z* + 2; (iv) -*x* + 1, -*y* + 3, -*z* + 2; (v) *x* + 1, *y* + 1, *z*; (vi) -*x*, -*y* + 2, -*z* + 1.

S2. Experimental

A solution of trichloroacetonitrile (7.3 ml) in DMSO (15 ml) was dropped to a mixture of aqueous ammonia (5 ml) and freshly purified copper monochloride (0.3 g) during 3 min. upon keeping of the room temperature by the cooling on water-bath. The reaction mixture was stirred for 4 h. At the end of the reaction, the mixture was washed with water (150 ml) and filtered off. The formed product was re-crystallized from aqueous ethanol to give 1.47 g of red crystals of **I**. Yield is 73%. *M.p.* = 472–474 K.

S3. Refinement

The hydrogen atoms were placed in calculated positions with $N-H = 0.86 \text{ \AA}$ and refined in the riding model with fixed isotropic displacement parameters [$U_{iso}(H) = 1.2U_{eq}(N)$].

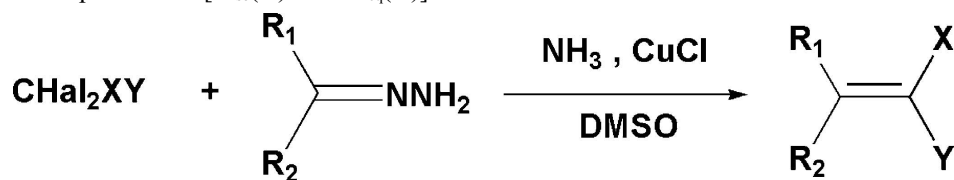


Figure 1

New catalytic olefination reaction as a general method for the preparation of alkenes; *X* and *Y* are H, Hal, CHal₃, CN.

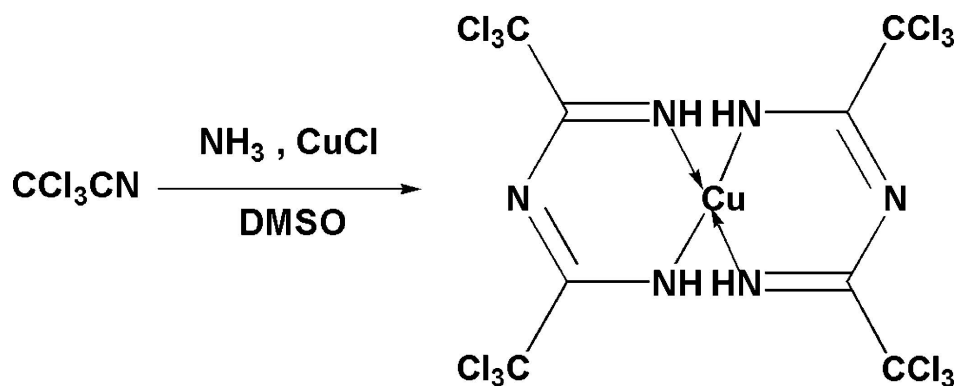


Figure 2

Reaction of CCl_3CN with ammonia in presence of $CuCl$.

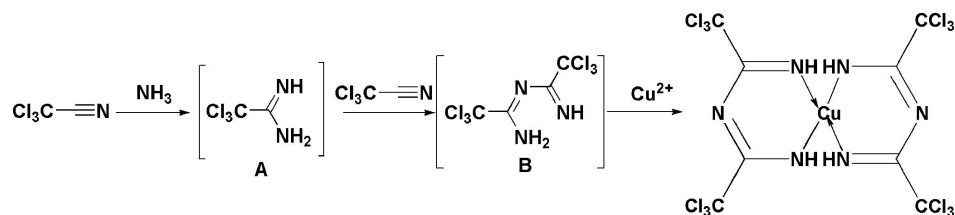
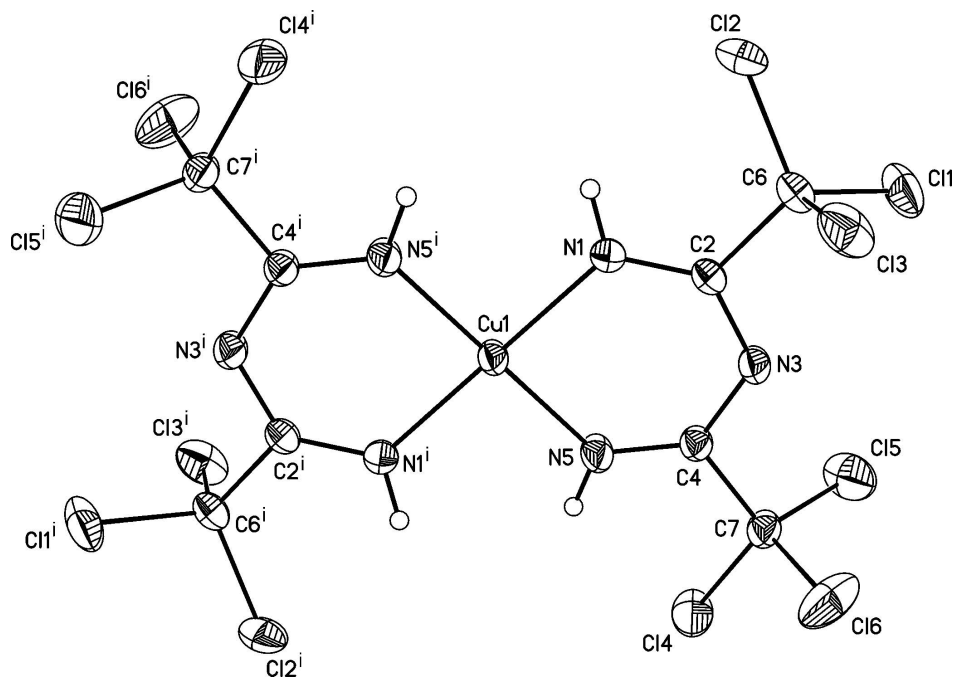
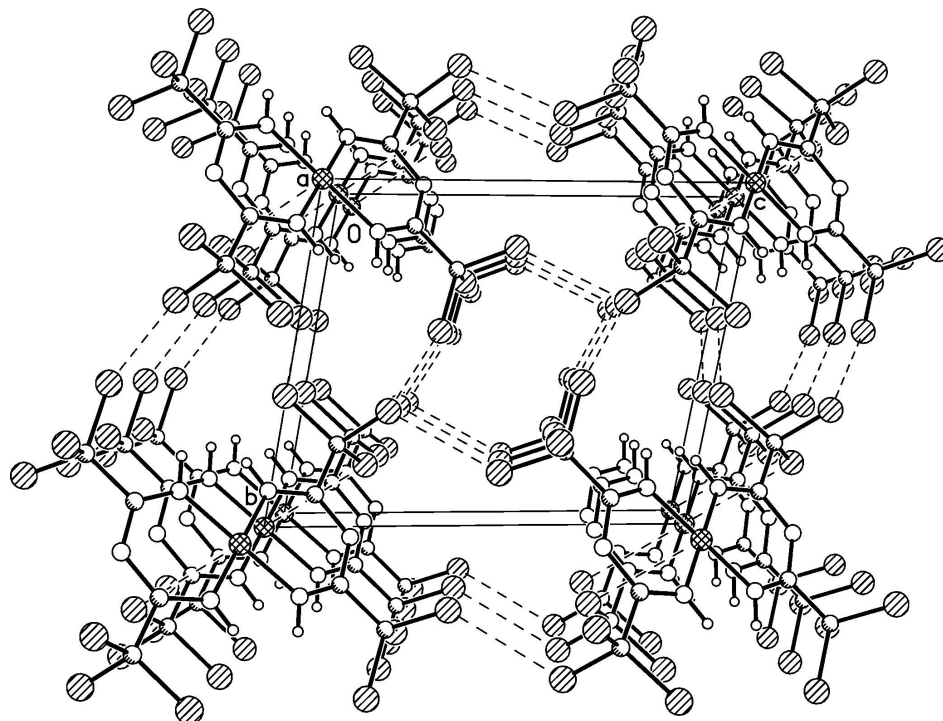


Figure 3

The stage-to-stage reaction mechanism of the formation of **I**.

**Figure 4**

Molecular structure of **I** with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. Symmetry code: (i) $-x, -y + 2, -z + 2$.

**Figure 5**

The crystal packing of **I** along the a axis. Dashed lines indicate the intermolecular axial $\text{Cu}\cdots\text{Cl}$ and attractive $\text{Cl}\cdots\text{Cl}$ interactions.

[N-(1-Azanidyl-2,2,2-trichloroethylidene)-2,2,2-trichloroethanimidamide]copper(II)*Crystal data*[Cu(C₄H₂Cl₆N₃)₂] $M_r = 673.11$ Triclinic, $P\bar{1}$

Hall symbol: -P 1

 $a = 5.9317 (17) \text{ \AA}$ $b = 9.078 (3) \text{ \AA}$ $c = 10.831 (3) \text{ \AA}$ $\alpha = 98.475 (5)^\circ$ $\beta = 97.525 (5)^\circ$ $\gamma = 103.662 (5)^\circ$ $V = 552.1 (3) \text{ \AA}^3$ $Z = 1$ $F(000) = 327$ $D_x = 2.024 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3874 reflections

 $\theta = 2.4\text{--}27.7^\circ$ $\mu = 2.45 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Plate, red

 $0.33 \times 0.24 \times 0.06 \text{ mm}$ *Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 2003)

 $T_{\min} = 0.499$, $T_{\max} = 0.867$

5662 measured reflections

2414 independent reflections

2108 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.029$ $\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 1.9^\circ$ $h = -7 \rightarrow 7$ $k = -11 \rightarrow 11$ $l = -13 \rightarrow 13$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.133$ $S = 1.00$

2414 reflections

124 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

 $w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.84P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 1.18 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$ *Special details*

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	1.0000	1.0000	0.0000	0.03611 (19)
Cl1	0.20230 (19)	0.81177 (15)	0.21612 (13)	0.0696 (3)
Cl2	0.28874 (19)	0.61212 (13)	0.01081 (11)	0.0644 (3)

Cl3	0.5633 (2)	0.65213 (14)	0.25606 (12)	0.0677 (3)
Cl4	1.0465 (2)	1.42819 (12)	0.33037 (12)	0.0730 (4)
Cl5	0.5879 (2)	1.27757 (17)	0.35949 (16)	0.0868 (5)
Cl6	0.9881 (3)	1.18805 (17)	0.47247 (11)	0.0886 (5)
N1	0.7097 (5)	0.8671 (3)	0.0275 (3)	0.0437 (7)
H1	0.6365	0.7918	-0.0331	0.052*
C2	0.6169 (5)	0.8813 (4)	0.1278 (3)	0.0358 (6)
N3	0.6704 (5)	0.9993 (3)	0.2235 (3)	0.0441 (7)
C4	0.8405 (6)	1.1234 (4)	0.2244 (3)	0.0353 (6)
N5	0.9823 (6)	1.1456 (3)	0.1452 (3)	0.0446 (7)
H5	1.0802	1.2351	0.1582	0.054*
C6	0.4243 (6)	0.7471 (4)	0.1511 (4)	0.0421 (7)
C7	0.8629 (7)	1.2489 (4)	0.3416 (3)	0.0425 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0386 (3)	0.0301 (3)	0.0377 (3)	0.0011 (2)	0.0172 (2)	0.0035 (2)
Cl1	0.0495 (6)	0.0725 (7)	0.0932 (9)	0.0109 (5)	0.0390 (6)	0.0205 (6)
Cl2	0.0505 (5)	0.0531 (6)	0.0697 (7)	-0.0144 (4)	0.0029 (5)	0.0011 (5)
Cl3	0.0586 (6)	0.0634 (7)	0.0806 (8)	0.0026 (5)	0.0025 (5)	0.0422 (6)
Cl4	0.0951 (9)	0.0370 (5)	0.0731 (7)	-0.0102 (5)	0.0382 (6)	-0.0097 (5)
Cl5	0.0568 (7)	0.0793 (8)	0.1141 (11)	0.0171 (6)	0.0303 (7)	-0.0268 (8)
Cl6	0.1405 (14)	0.0778 (9)	0.0422 (6)	0.0311 (9)	-0.0047 (7)	0.0076 (5)
N1	0.0425 (15)	0.0386 (15)	0.0407 (15)	-0.0039 (12)	0.0135 (12)	-0.0039 (12)
C2	0.0343 (15)	0.0320 (15)	0.0399 (16)	0.0027 (12)	0.0094 (12)	0.0099 (12)
N3	0.0496 (16)	0.0379 (15)	0.0401 (15)	-0.0022 (12)	0.0199 (13)	0.0035 (12)
C4	0.0397 (16)	0.0312 (15)	0.0346 (15)	0.0058 (12)	0.0109 (12)	0.0063 (12)
N5	0.0515 (17)	0.0300 (14)	0.0478 (16)	-0.0025 (12)	0.0241 (13)	0.0003 (12)
C6	0.0341 (16)	0.0409 (17)	0.0505 (19)	0.0028 (13)	0.0118 (14)	0.0136 (14)
C7	0.0497 (19)	0.0364 (17)	0.0394 (17)	0.0066 (14)	0.0158 (14)	0.0014 (13)

Geometric parameters (Å, °)

Cu1—N5	1.931 (3)	N1—C2	1.284 (4)
Cu1—N1	1.941 (3)	N1—H1	0.8600
Cl1—C6	1.749 (4)	C2—N3	1.322 (4)
Cl2—C6	1.767 (4)	C2—C6	1.537 (4)
Cl3—C6	1.759 (4)	N3—C4	1.321 (4)
Cl4—C7	1.762 (4)	C4—N5	1.282 (4)
Cl5—C7	1.742 (4)	C4—C7	1.544 (4)
Cl6—C7	1.736 (4)	N5—H5	0.8600
N5—Cu1—N1	87.83 (12)	Cu1—N5—H5	116.4
C2—N1—Cu1	126.0 (2)	C2—C6—Cl1	111.9 (2)
C2—N1—H1	117.0	C2—C6—Cl3	106.7 (2)
Cu1—N1—H1	117.0	Cl1—C6—Cl3	110.2 (2)
N1—C2—N3	128.5 (3)	C2—C6—Cl2	112.5 (2)

N1—C2—C6	120.3 (3)	C11—C6—C12	107.50 (19)
N3—C2—C6	111.2 (3)	C13—C6—C12	108.0 (2)
C4—N3—C2	120.5 (3)	C4—C7—C16	107.4 (2)
N5—C4—N3	128.3 (3)	C4—C7—C15	110.5 (2)
N5—C4—C7	120.3 (3)	C16—C7—C15	111.2 (2)
N3—C4—C7	111.4 (3)	C4—C7—C14	112.4 (2)
C4—N5—Cu1	127.1 (2)	C16—C7—C14	108.0 (2)
C4—N5—H5	116.4	C15—C7—C14	107.3 (2)
N5—Cu1—N1—C2	-14.1 (3)	N1—C2—C6—C11	-140.6 (3)
N5 ⁱ —Cu1—N1—C2	165.9 (3)	N3—C2—C6—C11	41.9 (4)
Cu1—N1—C2—N3	12.6 (6)	N1—C2—C6—C13	98.8 (3)
Cu1—N1—C2—C6	-164.4 (2)	N3—C2—C6—C13	-78.7 (3)
N1—C2—N3—C4	-0.4 (6)	N1—C2—C6—C12	-19.5 (4)
C6—C2—N3—C4	176.7 (3)	N3—C2—C6—C12	163.0 (3)
C2—N3—C4—N5	-5.2 (6)	N5—C4—C7—C16	-105.0 (3)
C2—N3—C4—C7	177.1 (3)	N3—C4—C7—C16	72.9 (3)
N3—C4—N5—Cu1	-2.2 (6)	N5—C4—C7—C15	133.5 (3)
C7—C4—N5—Cu1	175.3 (2)	N3—C4—C7—C15	-48.6 (4)
N1—Cu1—N5—C4	9.6 (3)	N5—C4—C7—C14	13.7 (4)
N1 ⁱ —Cu1—N5—C4	-170.4 (3)	N3—C4—C7—C14	-168.4 (3)

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