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Bis(2-amino-4-methylpyridinium) tetra-chloridocuprate(II)

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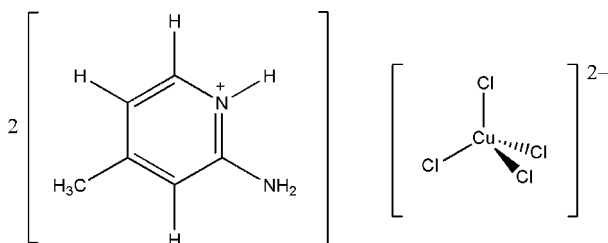
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.012$ Å; R factor = 0.059; wR factor = 0.145; data-to-parameter ratio = 16.4.

The asymmetric unit of the title compound, $(\text{C}_6\text{H}_9\text{N}_2)_2[\text{CuCl}_4]$, consists of one cation and one half-anion, bisected by a twofold rotation axis through the metal center. The anion exhibits a geometry that is intermediate between a T_d and D_{4h} arrangement about the Cu atom. The crystal structure contains chains of cations alternating with stacks of anions. The cationic groups interact *via* offset face-to-face π - π stacking, forming chains running along the c axis. The anion stacks are parallel to the cation chains, with no significant inter- nor intrastack Cl...Cl interactions. There are several anion-cation hydrogen-bonding interactions of the $(\text{N}-\text{H})_{\text{pyridine}} \cdots \text{Cl}$ and $(\text{N}-\text{H})_{\text{amino}} \cdots \text{Cl}$ types, connecting the chains of cations to the stacks of anions. Both the $\text{N}-\text{H} \cdots \text{Cl}$ and π - π stacking interactions [centroid-centroid distances 3.61 (8) and 3.92 (2) Å] contribute to the formation of a three-dimensional supramolecular architecture.

Related literature

For related literature on organic-inorganic hybrids, see: Al-Far, Ali & Haddad (2008); Ali & Al-Far (2007, 2008); Coffey *et al.* (2000). For bond-length and angle data, see: Raithby *et al.* (2000); Allen *et al.* (1987).



Experimental

Crystal data

 $(\text{C}_6\text{H}_9\text{N}_2)_2[\text{CuCl}_4]$
 $M_r = 423.65$
 Monoclinic, $C2/c$
 $a = 11.313$ (3) Å
 $b = 12.272$ (3) Å
 $c = 14.264$ (4) Å
 $\beta = 113.201$ (17)°

 $V = 1820.2$ (9) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.78$ mm⁻¹
 $T = 293$ (2) K
 $0.35 \times 0.06 \times 0.06$ mm

Data collection

 Siemens P4 diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2005)
 $T_{\text{min}} = 0.874$, $T_{\text{max}} = 0.898$
 2039 measured reflections
 1590 independent reflections

 841 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.145$
 $S = 0.99$
 1590 reflections

 97 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—Cl1	2.2614 (19)	Cu1—Cl2	2.2698 (19)
Cl1 ⁱ —Cu1—Cl1	94.33 (10)	Cl1—Cu1—Cl2	146.17 (8)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1A} \cdots \text{Cl1}$	0.86	2.65	3.407 (6)	147
$\text{N1}-\text{H1A} \cdots \text{Cl2}^i$	0.86	2.70	3.360 (6)	134
$\text{N2}-\text{H2A} \cdots \text{Cl1}$	0.86	2.50	3.294 (6)	153
$\text{N2}-\text{H2B} \cdots \text{Cl2}^{ii}$	0.86	2.53	3.359 (6)	164

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

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*; 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: BG2228).

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supporting information

Acta Cryst. (2009). E65, m73–m74 [doi:10.1107/S1600536808041652]

Bis(2-amino-4-methylpyridinium) tetrachloridocuprate(II)**Rawhi H. Al-Far and Basem Fares Ali****S1. Comment**

Hybrid organic-inorganic low dimensional magnetic lattices of the formula (cation)₂[MX₄] are of special interest (Coffey *et al.*, 2000; and references therein). A wide variety of these complexes are known. Some examples are those containing a protonated pyridine and 2-aminopyrimidine (Coffey *et al.*, 2000). The magnetic exchange in these compounds is mediated by van der Waals contacts between the halide ions of the [MX₄]²⁻ pseudo-tetrahedra and the contacts are determined by the crystal packing. In connection with ongoing studies (Al-Far *et al.*, 2008; Ali & Al-Far 2008; Ali & Al-Far 2007) of the structural aspects of organic-inorganic hybrids, here we report the crystal structure of Cu(II)-chloride complex with 2-amino-4-methylpyridinium as the organic cation.

The asymmetric unit in I contains one half anion (bisected by a two fold axis through the metal) and one cation (Fig. 1). The Cu—Cl distances and Cl—Cu—Cl, angles, Table 1, fall in the range reported previously for compounds containing Cu—Cl anions (Raithby *et al.*, 2000). The CuCl₄²⁻ anion geometry is an intermediate between regular tetrahedral (*T_d*) and square planar (*D_{4h}*); the geometry of CuX₄²⁻ anions will always distort from *T_d* due to the Jahn-Teller effect, and this generally results in a compressed tetrahedral geometry. The extent of this compression is determined principally by electrostatic interactions with the environment – in this case, the hydrogen bonding.

In the cation bond lengths and angles are in accordance with normal values (Allen *et al.*, 1987).

The crystal packing (Fig. 2) show alternating stacks of anions and chains of cations. The anion stacks are parallel to the cation chains, with no significant inter- and intra-stack Cl...Cl interactions. The cations interact *via* offset face-to-face, π - π stacking interactions leading to chains along the crystallographic *c* axis (Fig. 3), with alternating rings centroids separation distances of 3.61 (8) and 3.92 (2) Å.

There are extensive cation...anion intermolecular interactions (Table 2; Fig. 1). In these interactions H1A is involved in a bifurcated hydrogen bonding motif with Cl1 and Cl2ⁱ [N1—H1A...Cl1, Cl2ⁱ] distances are 3.407 (6) and 3.360 (6) Å, respectively, with N1—H1A...Cl1, Cl2ⁱ] angles being 147 and 134°; Symmetry codes: (i) $-x + 1, y, -z + 3/2$. The other interactions result between N2—H2A...Cl1 [N1...Cl1 distance is 3.294 (6) and N2—H2A...Cl1 angle of 153°] and N2—H2B...Cl2ⁱⁱ [with N2...Cl2ⁱⁱ distance of 3.359 (6) Å and N2—H2B...Cl2ⁱⁱ angle being 164°; Symmetry code: (ii) $-x + 3/2, y - 1/2, -z + 3/2$]. These interactions and the symmetrically related ones connect the anion to four surrounding cations.

Both N—H...Cl and π - π stacking interactions cause to the formation of a three-dimensional supramolecular architecture.

S2. Experimental

To a hot solution (100 °C) of 2-Amino-4-methylpyridine (1 mmol) in 5 ml of CH₃CN acidified with 2 ml of 3 M HCl, CuCl₂·2H₂O (1 mmol) dissolved in 10 ml CH₃CN was added. The resulting mixture was refluxed for 1.5 h. The solution was then allowed to stand undisturbed at room temperature. After 24 h yellow parallelepiped crystals were formed (yield: 0.170 g; 80.2%).

S3. Refinement

Hydrogen atoms were positioned geometrically, with N—H = 0.86 Å, C—H = 0.93 Å for aromatic H and C—H = 0.96 Å for methyl H, and constrained to ride on their parent atoms, $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{N})$, where $x = 1.5$ for methyl H, and $x = 1.2$ for all other H atoms.

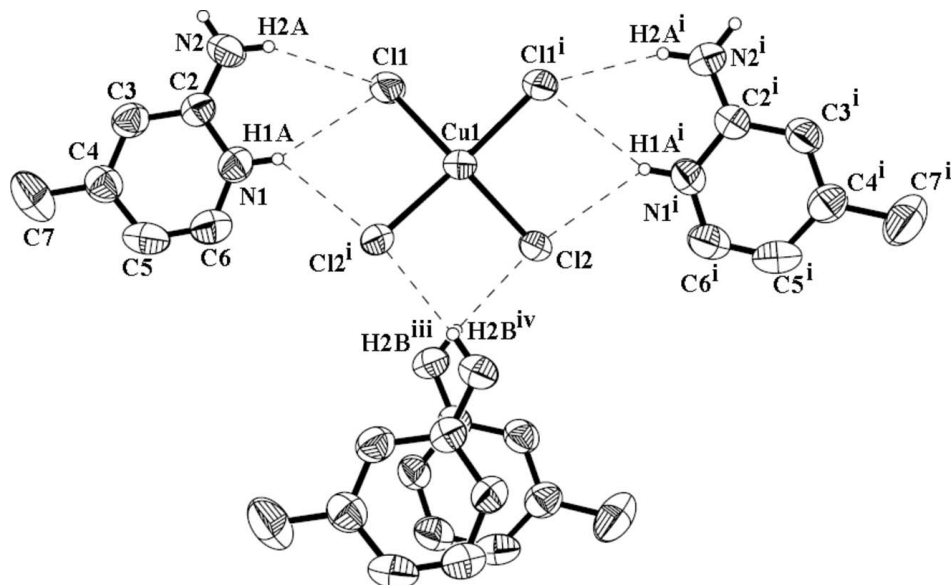


Figure 1

The structure of the title compound, viewed down c . Displacement ellipsoids are drawn at the 50% probability level. N—H \cdots Cl—Cu intermolecular interactions are shown as dashed lines. Symmetry operations: (i) $-x + 1, y, -z + 3/2$; (iii) $-1/2 + x, 1/2 + y, z$; (iv) $3/2 - x, 1/2 + y, 3/2 - z$. H atoms not involved in hydrogen bonding omitted for clarity.

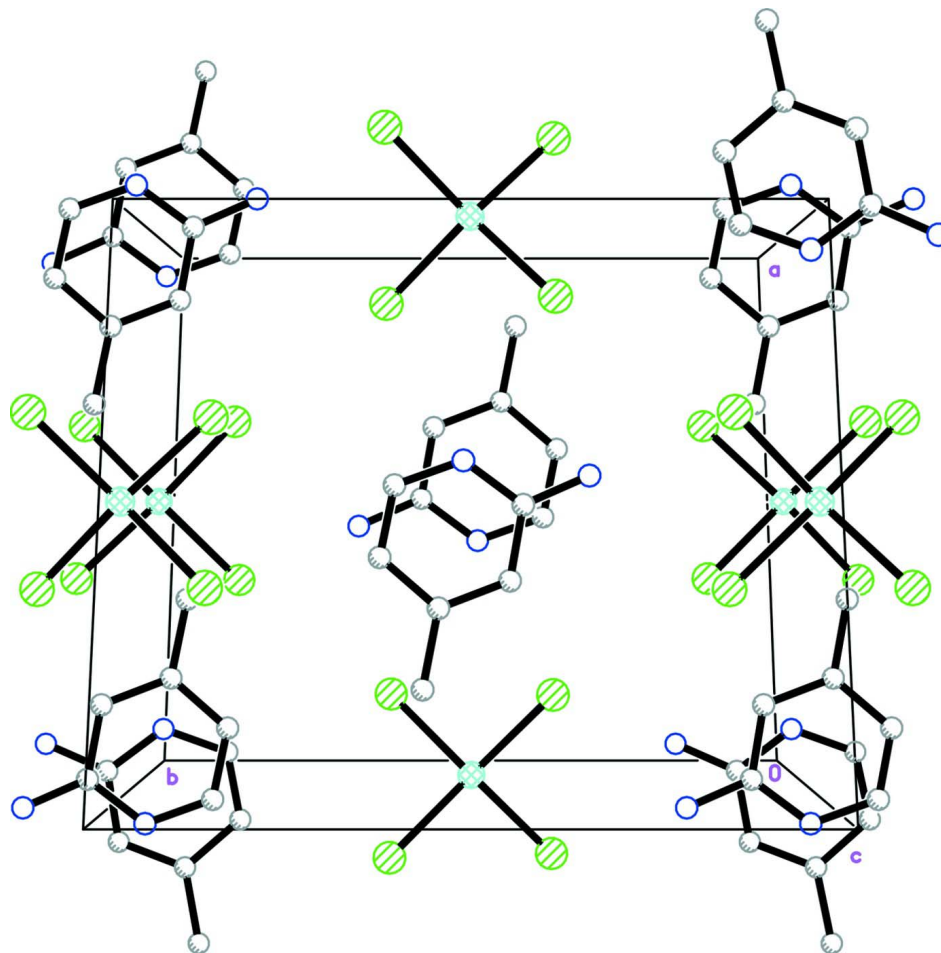


Figure 2

Crystal packing diagram showing alternating stacks of anions and chains of cations.

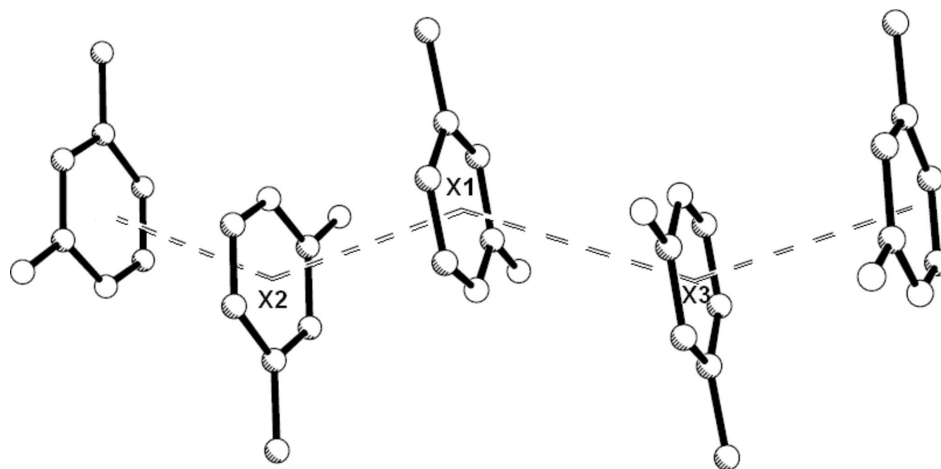


Figure 3

Cationic chains along the crystallographic c axis, assembled *via* offset face-to-face (π - π stacking; double broken lines) motifs. Centroids separation distances are $X2(2-x, y, 3/2-z) \cdots X1(x, y, z) \cdots X3(2-x, -y, 2-z)$ are 3.61 (8) and 3.92 (2) Å, respectively.

Bis(2-amino-4-methylpyridinium) tetrachloridocuprate(II)*Crystal data* $(C_6H_9N_2)_2[CuCl_4]$ $M_r = 423.65$ Monoclinic, $C2/c$ Hall symbol: $-C\ 2yc$ $a = 11.313\ (3)\ \text{\AA}$ $b = 12.272\ (3)\ \text{\AA}$ $c = 14.264\ (4)\ \text{\AA}$ $\beta = 113.201\ (17)^\circ$ $V = 1820.2\ (9)\ \text{\AA}^3$ $Z = 4$ $F(000) = 860$ $D_x = 1.546\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 290 reflections

 $\theta = 2.5\text{--}27.3^\circ$ $\mu = 1.78\ \text{mm}^{-1}$ $T = 293\ \text{K}$

Parallelepiped, yellow

 $0.35 \times 0.06 \times 0.06\ \text{mm}$ *Data collection*

Siemens P4

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.874$, $T_{\max} = 0.898$

2039 measured reflections

1590 independent reflections

841 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.058$ $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.6^\circ$ $h = -1 \rightarrow 13$ $k = -14 \rightarrow 1$ $l = -16 \rightarrow 16$

3 standard reflections every 97 reflections

intensity decay: none

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.059$ $wR(F^2) = 0.145$ $S = 0.99$

1590 reflections

97 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

 $w = 1/[\sigma^2(F_o^2) + (0.0577P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.40\ \text{e \AA}^{-3}$ $\Delta\rho_{\min} = -0.37\ \text{e \AA}^{-3}$ *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.

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	0.5000	0.00098 (10)	0.7500	0.0539 (4)
Cl1	0.64416 (17)	-0.12430 (14)	0.74530 (17)	0.0716 (7)
N1	0.9282 (5)	0.0108 (5)	0.8601 (4)	0.0552 (15)

H1A	0.8473	0.0000	0.8432	0.066*
Cl2	0.35031 (15)	0.12618 (14)	0.66064 (15)	0.0632 (6)
C2	1.0055 (6)	-0.0772 (6)	0.8719 (5)	0.0487 (18)
N2	0.9548 (6)	-0.1746 (5)	0.8554 (5)	0.0736 (19)
H2A	0.8732	-0.1825	0.8372	0.088*
H2B	1.0030	-0.2309	0.8626	0.088*
C3	1.1373 (6)	-0.0577 (6)	0.9018 (5)	0.0551 (19)
H3A	1.1933	-0.1161	0.9116	0.066*
C4	1.1850 (7)	0.0474 (7)	0.9168 (5)	0.0584 (19)
C5	1.0969 (9)	0.1339 (6)	0.9006 (6)	0.072 (2)
H5A	1.1258	0.2057	0.9089	0.087*
C6	0.9713 (9)	0.1124 (6)	0.8733 (6)	0.071 (2)
H6A	0.9138	0.1697	0.8636	0.085*
C7	1.3250 (7)	0.0704 (8)	0.9462 (7)	0.095 (3)
H7A	1.3691	0.0038	0.9454	0.143*
H7B	1.3604	0.1013	1.0134	0.143*
H7C	1.3352	0.1209	0.8985	0.143*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0460 (7)	0.0348 (6)	0.0783 (9)	0.000	0.0215 (6)	0.000
Cl1	0.0511 (11)	0.0382 (10)	0.1332 (19)	-0.0006 (8)	0.0444 (11)	-0.0103 (11)
N1	0.049 (3)	0.052 (4)	0.064 (4)	0.006 (3)	0.022 (3)	-0.005 (3)
Cl2	0.0447 (10)	0.0374 (10)	0.0867 (14)	-0.0050 (8)	0.0037 (8)	0.0074 (9)
C2	0.050 (4)	0.046 (4)	0.049 (4)	0.004 (4)	0.020 (3)	0.000 (3)
N2	0.059 (4)	0.043 (4)	0.121 (6)	-0.008 (3)	0.038 (4)	-0.007 (4)
C3	0.057 (5)	0.049 (5)	0.062 (5)	0.007 (4)	0.027 (4)	-0.002 (4)
C4	0.063 (5)	0.058 (5)	0.055 (5)	-0.007 (4)	0.023 (4)	0.002 (4)
C5	0.097 (7)	0.041 (5)	0.080 (6)	-0.006 (5)	0.035 (5)	-0.003 (4)
C6	0.073 (6)	0.049 (5)	0.085 (6)	0.008 (5)	0.026 (5)	-0.004 (5)
C7	0.078 (6)	0.104 (8)	0.109 (7)	-0.038 (6)	0.044 (6)	-0.031 (6)

Geometric parameters (Å, °)

Cu1—Cl1 ⁱ	2.2615 (19)	C3—C4	1.381 (9)
Cu1—Cl1	2.2614 (19)	C3—H3A	0.9300
Cu1—Cl2 ⁱ	2.2698 (19)	C4—C5	1.412 (10)
Cu1—Cl2	2.2698 (19)	C4—C7	1.496 (10)
N1—C6	1.326 (9)	C5—C6	1.343 (11)
N1—C2	1.358 (8)	C5—H5A	0.9300
N1—H1A	0.8600	C6—H6A	0.9300
C2—N2	1.307 (8)	C7—H7A	0.9600
C2—C3	1.400 (9)	C7—H7B	0.9600
N2—H2A	0.8600	C7—H7C	0.9600
N2—H2B	0.8600		
Cl1 ⁱ —Cu1—Cl1	94.33 (10)	C2—C3—H3A	119.6

C11 ⁱ —Cu1—C12 ⁱ	146.17 (8)	C3—C4—C5	118.0 (7)
C11—Cu1—C12 ⁱ	95.15 (7)	C3—C4—C7	121.7 (7)
C11 ⁱ —Cu1—C12	95.15 (6)	C5—C4—C7	120.3 (8)
C11—Cu1—C12	146.17 (8)	C6—C5—C4	119.8 (8)
C12 ⁱ —Cu1—C12	94.80 (10)	C6—C5—H5A	120.1
C6—N1—C2	123.2 (7)	C4—C5—H5A	120.1
C6—N1—H1A	118.4	N1—C6—C5	120.9 (8)
C2—N1—H1A	118.4	N1—C6—H6A	119.5
N2—C2—N1	119.3 (6)	C5—C6—H6A	119.5
N2—C2—C3	123.4 (7)	C4—C7—H7A	109.5
N1—C2—C3	117.3 (7)	C4—C7—H7B	109.5
C2—N2—H2A	120.0	H7A—C7—H7B	109.5
C2—N2—H2B	120.0	C4—C7—H7C	109.5
H2A—N2—H2B	120.0	H7A—C7—H7C	109.5
C4—C3—C2	120.8 (7)	H7B—C7—H7C	109.5
C4—C3—H3A	119.6		
C6—N1—C2—N2	-178.6 (7)	C2—C3—C4—C7	-178.4 (7)
C6—N1—C2—C3	1.5 (10)	C3—C4—C5—C6	1.2 (11)
N2—C2—C3—C4	179.1 (7)	C7—C4—C5—C6	179.3 (8)
N1—C2—C3—C4	-1.0 (10)	C2—N1—C6—C5	-0.6 (12)
C2—C3—C4—C5	-0.3 (11)	C4—C5—C6—N1	-0.8 (12)

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1A...C11	0.86	2.65	3.407 (6)	147
N1—H1A...C12 ⁱ	0.86	2.70	3.360 (6)	134
N2—H2A...C11	0.86	2.50	3.294 (6)	153
N2—H2B...C12 ⁱⁱ	0.86	2.53	3.359 (6)	164

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