



Crystal structure of *N,N'*-bis(pyridin-4-ylmethyl)-cyclohexane-1,4-diammonium dichloride dihydrate

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Received 14 September 2016

Accepted 15 September 2016

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; diprotonated structure; dipyridyl salt; hydrogen bonding; condensation reaction.

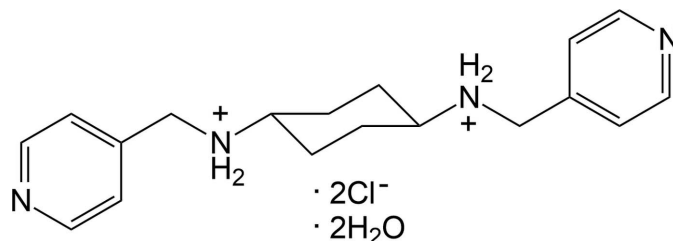
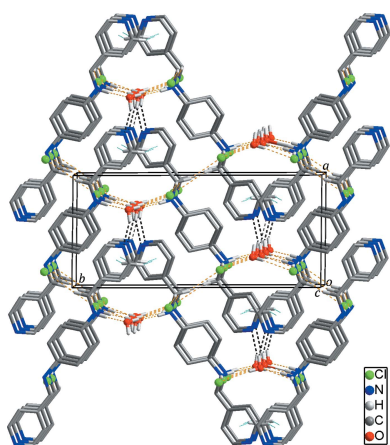
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Treatment of *N,N*-bis(pyridin-4-ylmethyl)cyclohexane-1,4-diamine with hydrochloric acid in ethanol led to the formation of the title salt, $C_{18}H_{26}N_4^{2+} \cdot 2Cl^- \cdot 2H_2O$, which lies about a crystallographic inversion center at the center of the cyclohexyl ring. The asymmetric unit therefore comprises one half of the *N,N*-bis(pyridin-4-ylmethyl)cyclohexane-1,4-diammonium dication, a chloride anion, and a solvent water molecule. In the dication, the two *trans*-(4-pyridine)- CH_2-NH_2- moieties occupy equatorial sites at the 1- and 4-positions of the central cyclohexyl ring, which is in a chair conformation. The terminal pyridine ring is tilted by 27.98 (5)° with respect to the mean plane of the central cyclohexyl moiety (r.m.s. deviation = 0.2379 Å). In the crystal, dications, anions, and solvent water molecules are connected *via* $N/C/O-H \cdots Cl$ and $N-H \cdots O$ hydrogen bonds together with $C-H \cdots \pi$ interactions, forming a three-dimensional network.

1. Chemical context

An enormous number of metal–organic frameworks (MOFs) have been developed over the last two decades because of their attractive topologies and their desirable applications in a wide range of fields (Silva *et al.*, 2015; Furukawa *et al.*, 2014). For the development of these MOFs, many chemists have designed and prepared various dipyridyl-type ligands (Robin & Fromm, 2006; Robson, 2008; Leong & Vittal, 2011). Our group has also focused on the search for extended dipyridyl-type ligands with a bulky central section for the development of MOFs with intriguing topologies or useful properties. As a part of our ongoing efforts, we prepared just such a dipyridyl-type ligand with a central cyclohexyl moiety, namely *N,N*-bis(pyridin-4-ylmethyl)cyclohexane-1,4-diamine, synthesized by a condensation reaction between 1,4-cyclohexanediamine and 4-pyridinecarboxaldehyde according to a literature procedure (Huh & Lee, 2007). Herein we report on the crystal structure of the title salt obtained by the protonation of both amine groups in this molecule.



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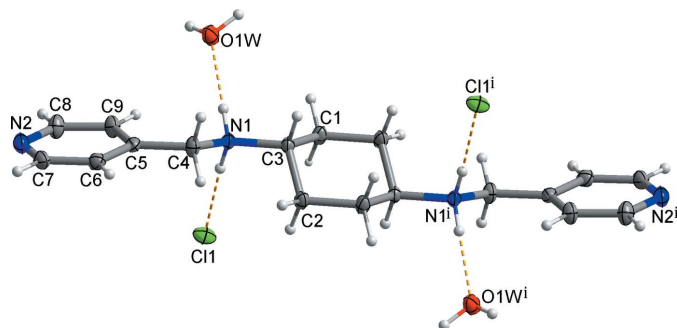


Figure 1
A view of the molecular structure of the title salt with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and yellow dashed lines represent the intermolecular N—H...O and N—H...Cl hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]

2. Structural commentary

The asymmetric unit of the centrosymmetric title salt, $C_{18}H_{26}N_4^{2+} \cdot 2Cl^- \cdot 2H_2O$, comprises one half of *N,N*-bis(pyridin-4-ylmethyl)cyclohexane-1,4-diammonium dication, a chloride anion and a solvent water molecule (Fig. 1) due to the crystallographic inversion center located at the center of the cyclohexyl ring. The central cyclohexyl moiety of the dication adopts a chair conformation. The two *trans*-(4-pyridine)—CH₂—NH₂— moieties at the 1- and 4-positions of the central cyclohexyl ring occupy equatorial positions. The terminal pyridine ring is tilted by 27.98 (5)° with respect to the mean plane through the central cyclohexyl moiety (r.m.s. deviation = 0.2379 Å). The distance between the two terminal pyridine nitrogen atoms in the dication is 15.864 (2) Å. This is slightly shorter than the N...N separation [15.970 (3) Å] in the dication ligand of a one-dimensional zigzag-like Co^{II} coordination

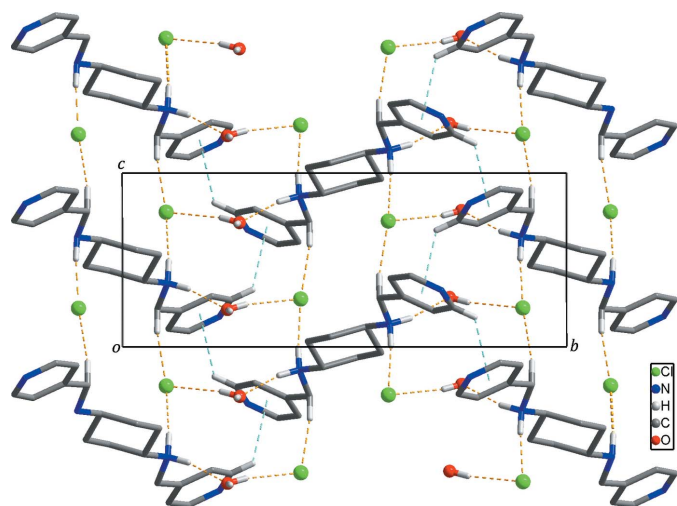


Figure 2
The two-dimensional undulating layer formed through intermolecular C—H... π interactions (light-blue dashed lines) and N—H...O/Cl and C—H...Cl hydrogen bonds (yellow dashed lines). H atoms not involved in intermolecular interactions have been omitted for clarity.

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

Cg1 is the centroid of the N2/C5—C9 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1 <i>NA</i> ...O1 <i>W</i>	0.878 (18)	1.881 (18)	2.7456 (15)	168.1 (16)
N1—H1 <i>NB</i> ...Cl1	0.952 (17)	2.167 (18)	3.1166 (11)	174.8 (13)
C4—H4 <i>A</i> ...Cl1 ⁱ	0.99	2.64	3.6133 (13)	168
C4—H4 <i>B</i> ...Cl1 ⁱⁱ	0.99	2.64	3.5788 (13)	158
O1 <i>W</i> —H1 <i>WA</i> ...Cl1 ⁱⁱⁱ	0.78 (2)	2.37 (2)	3.1444 (11)	170.8 (18)
O1 <i>W</i> —H1 <i>WB</i> ...N2 ^{iv}	0.86 (2)	1.99 (2)	2.8242 (15)	161 (2)
C8—H8...Cg1 ^v	0.95	2.74	3.3882 (15)	126

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

polymer built up from alternate Co^{II} ions and the dication of the title salt (Lee & Lee, 2010).

3. Supramolecular features

In the crystal, adjacent dications are linked by weak C—H... π interactions, Table 1 (light-blue dashed lines in Figs. 2 and 3), resulting in the formation of a two-dimensional undulating layer-like structure extending parallel to the *bc* plane. The undulating layer is further stabilized by N—H...O/Cl and C—

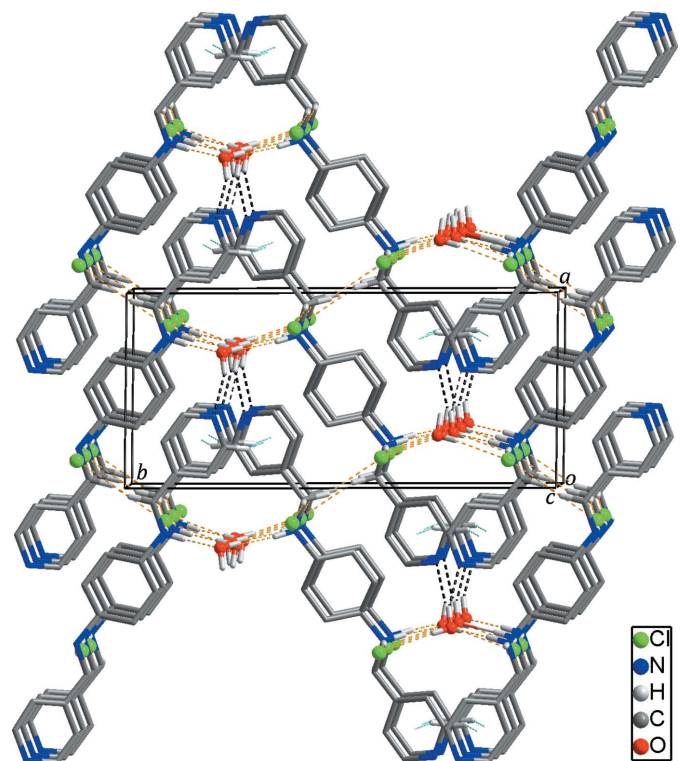


Figure 3
The three-dimensional supramolecular network formed through intermolecular N—H...O hydrogen bonds (black dashed lines). Intermolecular C—H... π interactions, and N—H...O/Cl and C—H...Cl hydrogen bonds within the two-dimensional undulating layer are shown as light-blue and yellow dashed lines, respectively. H atoms not involved in intermolecular interactions have been omitted for clarity.

H···Cl hydrogen bonds (yellow dashed lines in Fig. 2) between the dications and the solvent water molecules/chloride anions, respectively. Furthermore, neighboring undulating layers are connected through O—H···N hydrogen bonds (black dashed lines in Fig. 3) between the solvent water molecules and the pyridine nitrogen atoms, forming a three-dimensional supramolecular network. In addition, O—H···Cl hydrogen bonds (Fig. 1 and Table 1) between the solvent water molecules and the chloride anions are also found in the crystal.

4. Synthesis and crystallization

2 M hydrochloric acid in ethanol was added to an ethanol solution of *N,N*-bis(pyridin-4-ylmethylene)cyclohexane-1,4-diamine, synthesized according to a literature method (Huh & Lee, 2007), until pH = 4–5. The resulting mixture was left to evaporate slowly over several days, resulting in the formation of X-ray quality single crystals of the title salt.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound H atoms were positioned geometrically with $d(\text{C—H}) = 0.95 \text{ \AA}$ for $\text{Csp}^2\text{—H}$, 0.99 \AA for methylene, 1.00 \AA for methine H atoms, and were refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The N- and O-bound H atoms involved in hydrogen bonding were located in difference Fourier maps and refined freely [$\text{N—H} = 0.878 (18)$ and $0.952 (17) \text{ \AA}$; $\text{O—H} = 0.78 (2)$ and $0.86 (2) \text{ \AA}$].

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) project (2015R1D1A3A01020410).

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Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{18}\text{H}_{26}\text{N}_4^{2+}\cdot 2\text{Cl}^- \cdot 2\text{H}_2\text{O}$
M_r	405.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	8.2739 (2), 17.4955 (5), 7.2365 (2)
β (°)	108.756 (1)
V (Å ³)	991.90 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.35
Crystal size (mm)	0.45 × 0.38 × 0.28
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker 2013)
T_{min} , T_{max}	0.663, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9616, 2475, 2199
R_{int}	0.026
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.088, 1.04
No. of reflections	2475
No. of parameters	134
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.33, -0.28

Computer programs: *APEX2* and *SAINTE* (Bruker, 2013), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 2010).

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supporting information

Acta Cryst. (2016). E72, 1453-1455 [https://doi.org/10.1107/S2056989016014626]

Crystal structure of *N,N'*-bis(pyridin-4-ylmethyl)cyclohexane-1,4-diammonium dichloride dihydrate

Suk-Hee Moon, Donghyun Kang and Ki-Min Park

Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

N,N'-Bis(pyridin-4-ylmethyl)cyclohexane-1,4-diammonium dichloride dihydrate

Crystal data

$C_{18}H_{26}N_4^{2+} \cdot 2(Cl^-) \cdot 2H_2O$

$M_r = 405.36$

Monoclinic, $P2_1/c$

$a = 8.2739$ (2) Å

$b = 17.4955$ (5) Å

$c = 7.2365$ (2) Å

$\beta = 108.756$ (1)°

$V = 991.90$ (5) Å³

$Z = 2$

$F(000) = 432$

$D_x = 1.357$ Mg m⁻³

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

Cell parameters from 4837 reflections

$\theta = 2.6$ – 28.3 °

$\mu = 0.35$ mm⁻¹

$T = 173$ K

Block, colourless

$0.45 \times 0.38 \times 0.28$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker 2013)

$T_{\min} = 0.663$, $T_{\max} = 0.746$

9616 measured reflections

2475 independent reflections

2199 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 2.6$ °

$h = -10 \rightarrow 11$

$k = -23 \rightarrow 18$

$l = -7 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.088$

$S = 1.04$

2475 reflections

134 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.3432P]$

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

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

$\Delta\rho_{\max} = 0.33$ e Å⁻³

$\Delta\rho_{\min} = -0.28$ 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.16235 (4)	0.40135 (2)	1.27614 (5)	0.02515 (11)
N1	0.21335 (12)	0.39798 (6)	0.86785 (16)	0.0163 (2)
H1NA	0.243 (2)	0.3529 (10)	0.836 (2)	0.029 (4)*
H1NB	0.198 (2)	0.3956 (9)	0.993 (3)	0.027 (4)*
N2	-0.38725 (13)	0.28164 (7)	0.67407 (17)	0.0249 (3)
C1	0.48104 (14)	0.58254 (7)	0.96734 (19)	0.0195 (3)
H1A	0.5016	0.5882	0.8406	0.023*
H1B	0.4582	0.6339	1.0105	0.023*
C2	0.32520 (14)	0.53131 (7)	0.94108 (19)	0.0193 (3)
H2A	0.2981	0.5292	1.0647	0.023*
H2B	0.2254	0.5530	0.8390	0.023*
C3	0.36023 (14)	0.45089 (7)	0.88272 (17)	0.0162 (2)
H3	0.3791	0.4532	0.7531	0.019*
C4	0.05169 (14)	0.42138 (7)	0.71776 (18)	0.0195 (3)
H4A	0.0688	0.4217	0.5885	0.023*
H4B	0.0233	0.4741	0.7460	0.023*
C5	-0.09626 (14)	0.36983 (7)	0.70865 (17)	0.0172 (2)
C6	-0.25944 (15)	0.39624 (7)	0.60508 (18)	0.0202 (3)
H6	-0.2743	0.4451	0.5446	0.024*
C7	-0.39921 (15)	0.35070 (8)	0.59139 (19)	0.0228 (3)
H7	-0.5094	0.3694	0.5196	0.027*
C8	-0.23028 (16)	0.25662 (8)	0.7712 (2)	0.0259 (3)
H8	-0.2191	0.2073	0.8291	0.031*
C9	-0.08246 (15)	0.29821 (8)	0.79263 (19)	0.0221 (3)
H9	0.0261	0.2778	0.8638	0.027*
O1W	0.28682 (13)	0.26372 (6)	0.71524 (16)	0.0265 (2)
H1WA	0.263 (2)	0.2234 (13)	0.743 (3)	0.043 (6)*
H1WB	0.388 (3)	0.2576 (12)	0.707 (3)	0.056 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.02915 (18)	0.02300 (19)	0.02559 (18)	0.00706 (12)	0.01200 (13)	0.00199 (12)
N1	0.0129 (4)	0.0159 (5)	0.0193 (5)	-0.0018 (4)	0.0040 (4)	-0.0008 (4)
N2	0.0176 (5)	0.0311 (6)	0.0261 (6)	-0.0060 (4)	0.0073 (4)	-0.0029 (5)
C1	0.0153 (5)	0.0144 (6)	0.0260 (6)	-0.0004 (4)	0.0027 (5)	-0.0002 (5)
C2	0.0131 (5)	0.0156 (6)	0.0275 (6)	0.0000 (4)	0.0042 (4)	-0.0017 (5)
C3	0.0129 (5)	0.0158 (6)	0.0197 (6)	-0.0025 (4)	0.0049 (4)	-0.0009 (4)
C4	0.0137 (5)	0.0208 (6)	0.0214 (6)	-0.0016 (4)	0.0021 (4)	0.0027 (5)

C5	0.0154 (5)	0.0204 (6)	0.0161 (5)	-0.0022 (4)	0.0052 (4)	-0.0044 (5)
C6	0.0186 (6)	0.0201 (6)	0.0202 (6)	0.0007 (5)	0.0040 (4)	-0.0024 (5)
C7	0.0147 (5)	0.0288 (7)	0.0237 (6)	0.0005 (5)	0.0044 (4)	-0.0051 (5)
C8	0.0226 (6)	0.0269 (7)	0.0272 (7)	-0.0053 (5)	0.0068 (5)	0.0041 (5)
C9	0.0158 (5)	0.0251 (7)	0.0234 (6)	-0.0015 (5)	0.0034 (5)	0.0030 (5)
O1W	0.0232 (5)	0.0182 (5)	0.0418 (6)	-0.0017 (4)	0.0155 (4)	0.0001 (4)

Geometric parameters (Å, °)

N1—C4	1.4839 (15)	C3—H3	1.0000
N1—C3	1.5037 (14)	C4—C5	1.5047 (16)
N1—H1NA	0.878 (18)	C4—H4A	0.9900
N1—H1NB	0.952 (17)	C4—H4B	0.9900
N2—C8	1.3361 (17)	C5—C9	1.3812 (18)
N2—C7	1.3378 (18)	C5—C6	1.3955 (16)
C1—C3 ⁱ	1.5257 (16)	C6—C7	1.3814 (17)
C1—C2	1.5311 (16)	C6—H6	0.9500
C1—H1A	0.9900	C7—H7	0.9500
C1—H1B	0.9900	C8—C9	1.3883 (17)
C2—C3	1.5234 (17)	C8—H8	0.9500
C2—H2A	0.9900	C9—H9	0.9500
C2—H2B	0.9900	O1W—H1WA	0.78 (2)
C3—C1 ⁱ	1.5257 (16)	O1W—H1WB	0.86 (2)
C4—N1—C3	113.58 (9)	C1 ⁱ —C3—H3	108.9
C4—N1—H1NA	108.5 (11)	N1—C4—C5	113.32 (10)
C3—N1—H1NA	106.7 (11)	N1—C4—H4A	108.9
C4—N1—H1NB	110.1 (10)	C5—C4—H4A	108.9
C3—N1—H1NB	108.0 (10)	N1—C4—H4B	108.9
H1NA—N1—H1NB	109.9 (14)	C5—C4—H4B	108.9
C8—N2—C7	116.79 (11)	H4A—C4—H4B	107.7
C3 ⁱ —C1—C2	111.21 (10)	C9—C5—C6	117.74 (11)
C3 ⁱ —C1—H1A	109.4	C9—C5—C4	124.99 (11)
C2—C1—H1A	109.4	C6—C5—C4	117.26 (11)
C3 ⁱ —C1—H1B	109.4	C7—C6—C5	119.38 (12)
C2—C1—H1B	109.4	C7—C6—H6	120.3
H1A—C1—H1B	108.0	C5—C6—H6	120.3
C3—C2—C1	110.33 (9)	N2—C7—C6	123.30 (12)
C3—C2—H2A	109.6	N2—C7—H7	118.3
C1—C2—H2A	109.6	C6—C7—H7	118.3
C3—C2—H2B	109.6	N2—C8—C9	124.02 (13)
C1—C2—H2B	109.6	N2—C8—H8	118.0
H2A—C2—H2B	108.1	C9—C8—H8	118.0
N1—C3—C2	111.53 (9)	C5—C9—C8	118.76 (12)
N1—C3—C1 ⁱ	107.82 (9)	C5—C9—H9	120.6
C2—C3—C1 ⁱ	110.72 (10)	C8—C9—H9	120.6
N1—C3—H3	108.9	H1WA—O1W—H1WB	104 (2)
C2—C3—H3	108.9		

C3 ⁱ —C1—C2—C3	-56.73 (15)	C9—C5—C6—C7	0.35 (18)
C4—N1—C3—C2	61.58 (13)	C4—C5—C6—C7	179.52 (12)
C4—N1—C3—C1 ⁱ	-176.66 (10)	C8—N2—C7—C6	-1.06 (19)
C1—C2—C3—N1	176.51 (10)	C5—C6—C7—N2	0.4 (2)
C1—C2—C3—C1 ⁱ	56.44 (15)	C7—N2—C8—C9	1.0 (2)
C3—N1—C4—C5	-177.89 (10)	C6—C5—C9—C8	-0.41 (19)
N1—C4—C5—C9	-14.96 (18)	C4—C5—C9—C8	-179.51 (12)
N1—C4—C5—C6	165.94 (11)	N2—C8—C9—C5	-0.3 (2)

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

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

Cg1 is the centroid of the N2/C5—C9 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1NA \cdots O1W	0.878 (18)	1.881 (18)	2.7456 (15)	168.1 (16)
N1—H1NB \cdots C11	0.952 (17)	2.167 (18)	3.1166 (11)	174.8 (13)
C4—H4A \cdots C11 ⁱⁱ	0.99	2.64	3.6133 (13)	168
C4—H4B \cdots C11 ⁱⁱⁱ	0.99	2.64	3.5788 (13)	158
O1W—H1WA \cdots C11 ^{iv}	0.78 (2)	2.37 (2)	3.1444 (11)	170.8 (18)
O1W—H1WB \cdots N2 ^v	0.86 (2)	1.99 (2)	2.8242 (15)	161 (2)
C8—H8 \cdots Cg1 ^{vi}	0.95	2.74	3.3882 (15)	126

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