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1,4-Diazoniabicyclo[2.2.2]octane tetra-chloridocadmate(II) monohydrate

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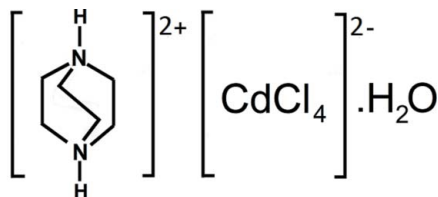
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å;
 R factor = 0.048; wR factor = 0.134; data-to-parameter ratio = 21.0.

The asymmetric unit of the title compound ($\text{C}_6\text{H}_{14}\text{N}_2$)- $[\text{CdCl}_4]\cdot\text{H}_2\text{O}$ contained one 1,4-diazabicyclo[2.2.2]octane dication, a tetrahedral CdCl_4^{2-} anion and a lattice water molecule. In the crystal, the solvate water molecule interacts with the cationic and anionic species *via* $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{Cl}$ [$\text{O}\cdots\text{Cl} = 3.289$ (7) Å] hydrogen-bond interactions, respectively, leading to a layered supramolecular structure extending parallel to (011).

Related literature

For background to this class of compounds, see: Wei & Willett (2002); Billing & Lemmerer (2009); Samet *et al.* (2010); Lemmerer & Billing (2012); Ben Rhaïem *et al.* (2013). For related structures, see: Sun & Qu (2005); Zhang & Zhu (2012).



Experimental

Crystal data

$(\text{C}_6\text{H}_{14}\text{N}_2)[\text{CdCl}_4]\cdot\text{H}_2\text{O}$
 $M_r = 386.40$

Orthorhombic, $P2_12_12_1$
 $a = 8.528$ (5) Å

$b = 11.653$ (2) Å
 $c = 13.114$ (6) Å
 $V = 1303.2$ (10) Å³
 $Z = 4$

Mo $K\alpha$ radiation $\mu = 2.47$ mm⁻¹ $T = 298$ K $0.54 \times 0.43 \times 0.29$ mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\text{min}} = 0.283$, $T_{\text{max}} = 0.536$
 5639 measured reflections

2837 independent reflections
 2632 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$
 2 standard reflections every 120 min
 intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.134$
 $S = 1.19$
 2837 reflections
 135 parameters

10 restraints
 H-atom parameters not refined
 $\Delta\rho_{\text{max}} = 1.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.44$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{O}^i$	0.84	2.01	2.783 (1)	151

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

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97*; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Supporting information for this paper is available from the IUCr electronic archives (Reference: DS2238).

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supporting information

Acta Cryst. (2014). E70, m178 [doi:10.1107/S1600536814007533]

1,4-Diazabicyclo[2.2.2]octane tetrachloridocadm(II) monohydrate

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S1. Comment

In recent years, a significant number of organic–inorganic hybrid materials based on metal halide units have been prepared and studied (Lemmerer & Billing, 2012). It has been shown that their structures can vary considerably, ranging from systems based on isolated polyhydra to ones containing extended chains and up to two- or three-dimensional networks (Ben Rhaïem *et al.*, 2013; Samet *et al.*, 2010; Billing & Lemmerer, 2009). Generally, the organic cations contain ammonium groups linked to the anionic framework by hydrogen bonds *via* halogenous tetrahedral vertices (Sun & Qu, 2005) and (Zhang & Zhu, 2012). In pseudopolymorphic cases, the water molecules can be able to coordinate the charged components strengthening the crystal cohesion as it was observed in (dabcoH₂)CuCl₄ and (dabcoH₂)CuCl₄·H₂O (Wei & Willett, 2002).

The new chloridocadm(II) compound, (C₆H₁₄N₂) [CdCl₄]·H₂O (I), is self-assembled into alternating organic and inorganic layered structure. The organic part is made up of 1,4-diazabicyclo[2.2.2]octane cations and water molecules. The inorganic component contains isolated [CdCl₄]²⁻ units. The layers are stacked along the *c* axis, as illustrated in Fig. 1.

The asymmetric unit of (I) comprises one 1,4-diazabicyclo[2.2.2]octane cation, one [CdCl₄]²⁻ anion and a lattice occluded water molecule (Fig. 2).

The [CdCl₄]²⁻ unit possesses a configuration of distorted tetrahedron, so that the central cadmium (II) ion is surrounded by four chlorine atoms. The Cd–Cl bond lengths vary from 2.430 (2) Å to 2.4864 (17) Å and the Cl–Cd–Cl angles fall in the range 101.80 (6)°–116.95 (6)°.

The protonated N2 atom of the organic cation interacts *via* a simple hydrogen bond with oxygen atom of the water molecule (Fig. 3 and Tab. 1).

S2. Experimental

The title compound (C₆H₁₄N₂) [CdCl₄]·H₂O, (I), was obtained by the reaction of cadmium iodide CdI₂ (0.19 g, 0.5 mmol) with DABCO (1,4-diazabicyclo[2.2.2]octane) (0.112 g, 1 mmol) in aqueous hydrochloric acid solution with pH ranging between 3 and 4. The mixture was stirred for several minutes. Colorless crystals suitable for X-ray diffraction analysis were obtained by slow evaporation at room temperature over 2 weeks.

S3. Refinement

Hydrogen water molecules are omitted. The C—H and N—H hydrogen atoms positions are generated geometrically by HFIX *SHELXL* command.

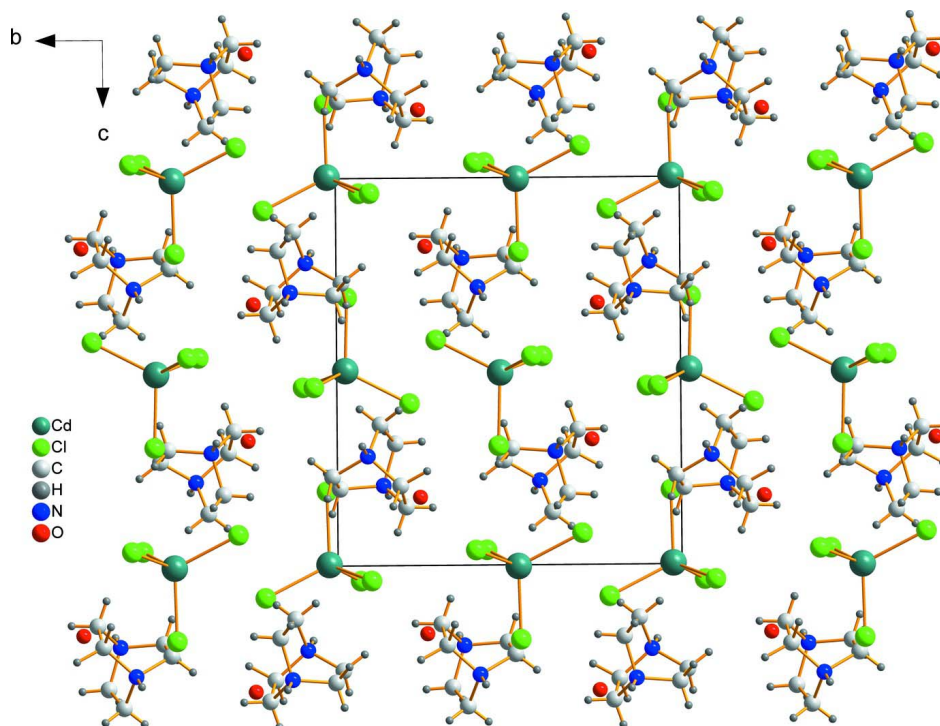


Figure 1
Packing diagram of (I), projected along the *a* axis.

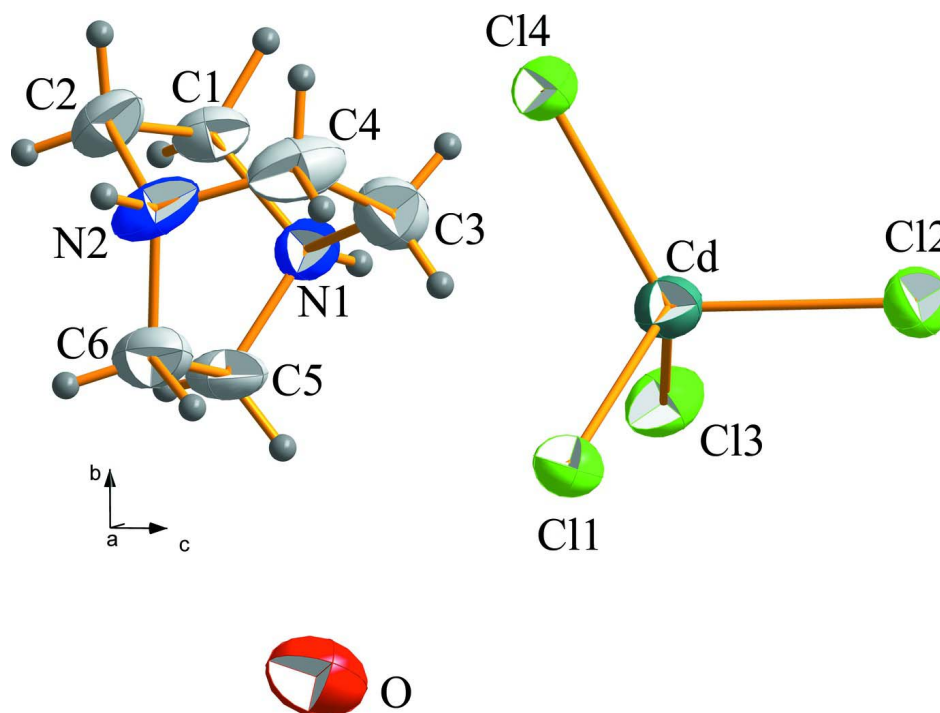


Figure 2
The asymmetric unit of (I), showing the atom numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as small spheres of arbitrary radii.

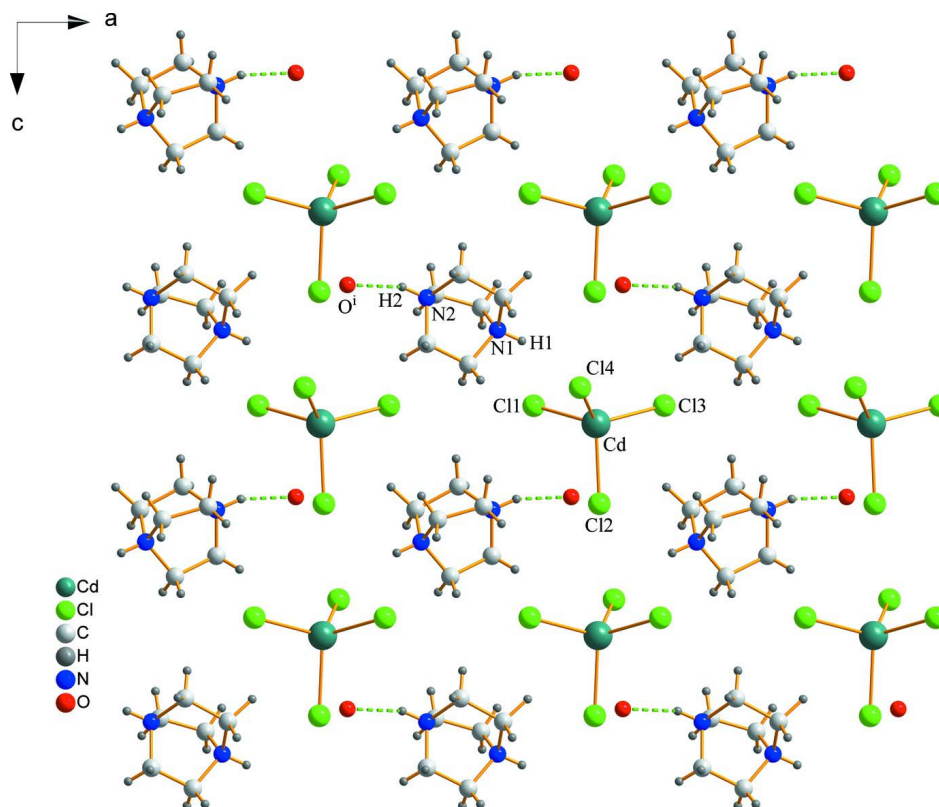


Figure 3

The arrangement of ions of (I), projected along the *b* axis. [Symmetry code: (i) $-x, y+1/2, -z+1/2$.]

1,4-Diazoniabicyclo[2.2.2]octane tetrachloridocadm(II) monohydrate

Crystal data

$(C_8H_{14}N_2)[CdCl_4] \cdot H_2O$

$M_r = 386.40$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 8.528 (5) \text{ \AA}$

$b = 11.653 (2) \text{ \AA}$

$c = 13.114 (6) \text{ \AA}$

$V = 1303.2 (10) \text{ \AA}^3$

$Z = 4$

$F(000) = 752$

$D_x = 1.959 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2837 reflections

$\theta = 2.4\text{--}27^\circ$

$\mu = 2.47 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Prism, colorless

$0.54 \times 0.43 \times 0.29 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

non-profiled $\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.* (1968))

$T_{\min} = 0.283$, $T_{\max} = 0.536$

5639 measured reflections

2837 independent reflections

2632 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.075$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -10 \rightarrow 6$

$k = -14 \rightarrow 1$

$l = -16 \rightarrow 16$

2 standard reflections every 120 min

intensity decay: 1%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.134$
 $S = 1.19$
 2837 reflections
 135 parameters
 10 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 not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 1.6133P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.58 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.44 \text{ e } \text{Å}^{-3}$

Special details

Experimental. Number of psi-scan sets used was 5 Theta correction was applied. Averaged transmission function was used. No Fourier smoothing was applied.

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd	0.74636 (5)	0.52500 (4)	0.50315 (3)	0.04606 (17)
Cl1	0.52000 (18)	0.40196 (13)	0.46103 (13)	0.0465 (3)
Cl2	0.7583 (2)	0.53068 (14)	0.69230 (11)	0.0544 (4)
Cl3	0.9940 (2)	0.43346 (15)	0.46078 (15)	0.0557 (4)
Cl4	0.6884 (2)	0.71103 (15)	0.41831 (12)	0.0542 (4)
C1	0.4091 (7)	0.6836 (5)	0.2060 (5)	0.0457 (13)
H1A	0.498 (5)	0.6620 (12)	0.153 (3)	0.055*
H1B	0.4419 (18)	0.761 (4)	0.2435 (19)	0.055*
C2	0.2540 (8)	0.6998 (6)	0.1512 (5)	0.0514 (13)
H2A	0.2282 (17)	0.776 (5)	0.1496 (5)	0.062*
H2B	0.2617 (9)	0.6741 (16)	0.086 (4)	0.062*
C3	0.2824 (8)	0.6248 (7)	0.3636 (6)	0.0583 (18)
H3A	0.3266 (11)	0.6796 (11)	0.4005 (8)	0.070*
H3B	0.2613 (9)	0.5660 (12)	0.4042 (9)	0.070*
C4	0.1319 (9)	0.6690 (6)	0.3149 (6)	0.065 (2)
H4A	0.0481 (16)	0.6394 (8)	0.3470 (8)	0.078*
H4B	0.1274 (9)	0.7458 (14)	0.3198 (7)	0.078*
C5	0.3284 (9)	0.4857 (5)	0.2294 (6)	0.0519 (16)
H5A	0.3330 (9)	0.4244 (11)	0.2713 (9)	0.062*
H5B	0.3874 (13)	0.4708 (6)	0.1738 (11)	0.062*
C6	0.1623 (9)	0.5077 (6)	0.1985 (7)	0.0586 (18)
H6A	0.0970 (14)	0.4692 (9)	0.2392 (9)	0.070*
H6B	0.1468 (9)	0.4843 (7)	0.1344 (12)	0.070*

N1	0.3888 (6)	0.5887 (5)	0.2823 (4)	0.0431 (11)
H1	0.477 (2)	0.5730 (6)	0.3082 (7)	0.052*
N2	0.1318 (6)	0.6341 (5)	0.2067 (5)	0.0554 (15)
H2	0.043 (2)	0.6488 (6)	0.1811 (8)	0.067*
O	0.1563 (8)	0.2409 (6)	0.3238 (6)	0.0861 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd	0.0463 (3)	0.0409 (2)	0.0510 (3)	0.00213 (18)	-0.0028 (2)	0.00245 (17)
Cl1	0.0486 (8)	0.0402 (7)	0.0508 (8)	-0.0018 (6)	0.0024 (6)	-0.0039 (6)
Cl2	0.0613 (8)	0.0530 (8)	0.0490 (7)	0.0058 (9)	-0.0041 (8)	-0.0042 (6)
Cl3	0.0519 (8)	0.0515 (8)	0.0635 (9)	0.0105 (7)	0.0063 (7)	0.0105 (8)
Cl4	0.0684 (9)	0.0423 (7)	0.0520 (8)	0.0014 (7)	-0.0163 (7)	0.0047 (7)
C1	0.042 (3)	0.034 (3)	0.061 (3)	-0.005 (2)	0.004 (3)	0.007 (3)
C2	0.049 (3)	0.048 (3)	0.057 (3)	-0.006 (3)	-0.001 (3)	0.020 (3)
C3	0.063 (5)	0.057 (4)	0.056 (3)	-0.006 (3)	0.006 (3)	-0.005 (3)
C4	0.062 (4)	0.046 (4)	0.087 (5)	0.012 (3)	0.032 (4)	0.012 (4)
C5	0.055 (4)	0.026 (2)	0.075 (4)	0.001 (3)	-0.008 (3)	0.002 (3)
C6	0.061 (4)	0.041 (3)	0.075 (5)	-0.008 (3)	-0.016 (4)	0.006 (3)
N1	0.042 (2)	0.040 (2)	0.047 (3)	0.002 (2)	-0.005 (2)	0.004 (2)
N2	0.038 (3)	0.044 (3)	0.084 (4)	0.004 (2)	-0.004 (3)	0.027 (3)
O	0.085 (4)	0.070 (4)	0.103 (5)	-0.014 (3)	0.008 (4)	-0.009 (4)

Geometric parameters (Å, °)

Cd—Cl3	2.430 (2)	C3—H3B	0.8860
Cd—Cl1	2.4673 (18)	C4—N2	1.476 (11)
Cd—Cl2	2.4835 (19)	C4—H4A	0.8977
Cd—Cl4	2.4864 (17)	C4—H4B	0.8977
C1—N1	1.502 (8)	C5—N1	1.479 (9)
C1—C2	1.517 (9)	C5—C6	1.496 (10)
C1—H1A	1.0614	C5—H5A	0.9026
C1—H1B	1.0614	C5—H5B	0.9026
C2—N2	1.485 (8)	C6—N2	1.499 (9)
C2—H2A	0.9127	C6—H6A	0.8931
C2—H2B	0.9127	C6—H6B	0.8931
C3—N1	1.461 (9)	N1—H1	0.8477
C3—C4	1.524 (10)	N2—H2	0.8420
C3—H3A	0.8860		
Cl3—Cd—Cl1	111.93 (7)	N2—C4—H4B	110.1
Cl3—Cd—Cl2	101.80 (6)	C3—C4—H4B	110.1
Cl1—Cd—Cl2	105.73 (6)	H4A—C4—H4B	108.4
Cl3—Cd—Cl4	116.95 (6)	N1—C5—C6	108.5 (5)
Cl1—Cd—Cl4	104.53 (6)	N1—C5—H5A	110.0
Cl2—Cd—Cl4	115.58 (6)	C6—C5—H5A	110.0
N1—C1—C2	107.9 (5)	N1—C5—H5B	110.0

N1—C1—H1A	110.1	C6—C5—H5B	110.0
C2—C1—H1A	110.1	H5A—C5—H5B	108.4
N1—C1—H1B	110.1	C5—C6—N2	108.3 (5)
C2—C1—H1B	110.1	C5—C6—H6A	110.0
H1A—C1—H1B	108.4	N2—C6—H6A	110.0
N2—C2—C1	108.4 (5)	C5—C6—H6B	110.0
N2—C2—H2A	110.0	N2—C6—H6B	110.0
C1—C2—H2A	110.0	H6A—C6—H6B	108.4
N2—C2—H2B	110.0	C3—N1—C5	111.1 (6)
C1—C2—H2B	110.0	C3—N1—C1	110.2 (5)
H2A—C2—H2B	108.4	C5—N1—C1	109.0 (5)
N1—C3—C4	108.4 (6)	C3—N1—H1	108.8
N1—C3—H3A	110.0	C5—N1—H1	108.8
C4—C3—H3A	110.0	C1—N1—H1	108.8
N1—C3—H3B	110.0	C4—N2—C2	109.2 (6)
C4—C3—H3B	110.0	C4—N2—C6	109.9 (6)
H3A—C3—H3B	108.4	C2—N2—C6	110.5 (6)
N2—C4—C3	108.0 (5)	C4—N2—H2	109.1
N2—C4—H4A	110.1	C2—N2—H2	109.1
C3—C4—H4A	110.1	C6—N2—H2	109.1

Hydrogen-bond geometry (Å, °)

<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>
N2—H2 \cdots O ⁱ	0.84	2.01	2.783 (1)	151

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