

Piperazinediium tetrachloridocadmate monohydrate

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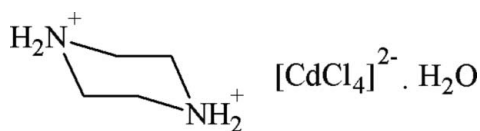
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.033; wR factor = 0.081; data-to-parameter ratio = 27.5.

In the title compound, $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{CdCl}_4]\cdot\text{H}_2\text{O}$, the $[\text{CdCl}_4]^{2-}$ anions adopt a slightly distorted tetrahedral configuration. In the crystal, $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds link the anions and water molecules into corrugated inorganic chains along the b axis which are interconnected *via* piperazinediium $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{Cl}$ interactions into a three-dimensional framework structure.

Related literature

For common applications of organic–inorganic hybrid materials, see: Kobel & Hanack (1986); Pierpont & Jung (1994). For a related structure and discussion of geometrical features, see: Sutherland & Harrison (2009). For the coordination around the Cd^{II} cation, see: El Glaoui *et al.* (2009).



Experimental

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_2)[\text{CdCl}_4]\cdot\text{H}_2\text{O}$
 $M_r = 360.38$
Monoclinic, $P2_1/c$
 $a = 6.6204$ (2) Å
 $b = 12.8772$ (3) Å
 $c = 14.0961$ (4) Å
 $\beta = 92.1710$ (12)°

$V = 1200.86$ (6) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 2.67$ mm⁻¹
 $T = 295$ K
 $0.52 \times 0.48 \times 0.30$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995)
 $T_{\text{min}} = 0.374$, $T_{\text{max}} = 0.444$
8531 measured reflections
3461 independent reflections
2903 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.081$
 $S = 1.09$
3461 reflections
126 parameters
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.78$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.75$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{Cl1}^{\text{i}}$	0.93 (3)	2.35 (3)	3.254 (2)	164 (3)
$\text{N1}-\text{H2}\cdots\text{Cl3}$	0.89 (3)	2.41 (4)	3.155 (2)	141 (3)
$\text{N2}-\text{H3}\cdots\text{O1W}$	0.89 (3)	1.93 (3)	2.808 (3)	167 (3)
$\text{N2}-\text{H4}\cdots\text{Cl4}^{\text{ii}}$	0.81 (3)	2.46 (3)	3.190 (2)	151 (3)
$\text{O1W}-\text{H1W}\cdots\text{Cl2}^{\text{iii}}$	0.84	2.44	3.267 (3)	168
$\text{O1W}-\text{H2W}\cdots\text{Cl4}^{\text{iv}}$	0.85	2.54	3.304 (2)	150

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

Data collection: *Kappa-CCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2095).

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supporting information

Acta Cryst. (2011). E67, m340 [doi:10.1107/S1600536811005095]

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S1. Comment

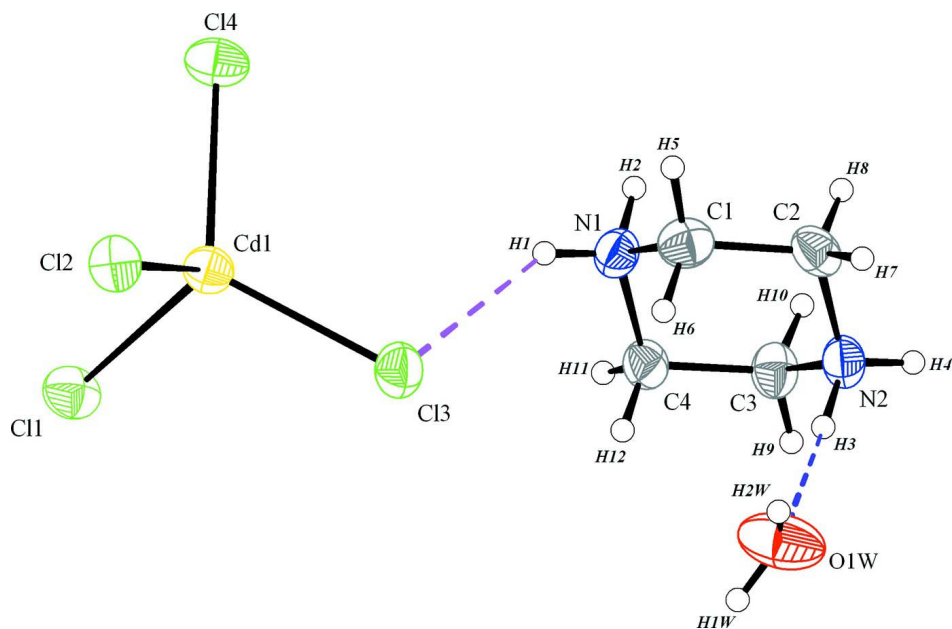
Organic-inorganic hybrid materials continue to attract much attention due to their potential applications in various field (Kobel & Hanack, 1986; Pierpont & Jung, 1994). In this work, we report the crystal structure of one such compound, $C_4H_{12}N_2 [CdCl_4] \cdot H_2O$ (I), formed from the reaction of piperazine with cadmium chloride. In (I) the asymmetric unit comprises a piperazine-1,4-diiium dication, a $[CdCl_4]^{2-}$ anion and a water molecule of solvation (Fig. 1). The atomic arrangement of (I) can be described as built up of corrugated inorganic chains of $[CdCl_4]^{2-}$ tetrahedra and water molecules held together by $O-H\cdots Cl$ hydrogen bonds and extending along the *b* direction of the unit cell. These chains are interconnected by a set of piperazinium $N-H\cdots Cl$ hydrogen bonds to form layers extending along the (1 1 0) planes (Fig. 2, Table 1). Fig 3 shows that two such layers cross the unit cell at $z = 1/4$ and $z = 3/4$ and the bodies of the organic groups are located between these layers and connect them by weak $C-H\cdots Cl$ hydrogen bonds [$C\cdots Cl$, 3.535 (3) Å], giving a three-dimensional framework structure. In the organic entity, the piperazium ring adopts a typical chair conformation and all the geometrical features agree with those found in piperazindiiium tetrachlorozincate(II) (Sutherland & Harrison, 2009). It is worth noting that in the anion of (I), the $Cd-Cl$ bond lengths and $Cl-Cd-Cl$ bond angles are not equal, but vary with the environment around the Cl atom. The $Cd-Cl$ bond lengths vary between 2.4418 (6) and 2.4892 (7) Å and the $Cl-Cd-Cl$ angles range from 103.07 (2) to 115.19 (2)°. These values are in good agreement with those reported previously, clearly indicating that the $[CdCl_4]^{2-}$ anion has a slightly distorted tetrahedral stereochemistry (El Glaoui *et al.* (2009).

S2. Experimental

An aqueous solution of piperazine (4 mmol, 0.344 g), cadmium chloride (4 mmol, 0.732 g) and HCl (10 ml, 0.8 M) in a Petri dish was slowly evaporated at room temperature. Single crystals of the title compound, suitable for X-ray diffraction analysis, were obtained after several days (yield 68%).

S3. Refinement

All $N-H$ hydrogen atoms were found in the difference Fourier map and refined isotropically. The water hydrogen atoms were also found in the difference Fourier but their positions were kept fixed during the refinement and their U_{iso} values were given a value equal to 1.2 times U_{eq} of the parent oxygen. All $C-H$ atoms were allowed to ride with $C-H = 0.97$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

**Figure 1**

A view of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme. Dashed lines indicate N—H \cdots O and N—H \cdots Cl hydrogen bonds.

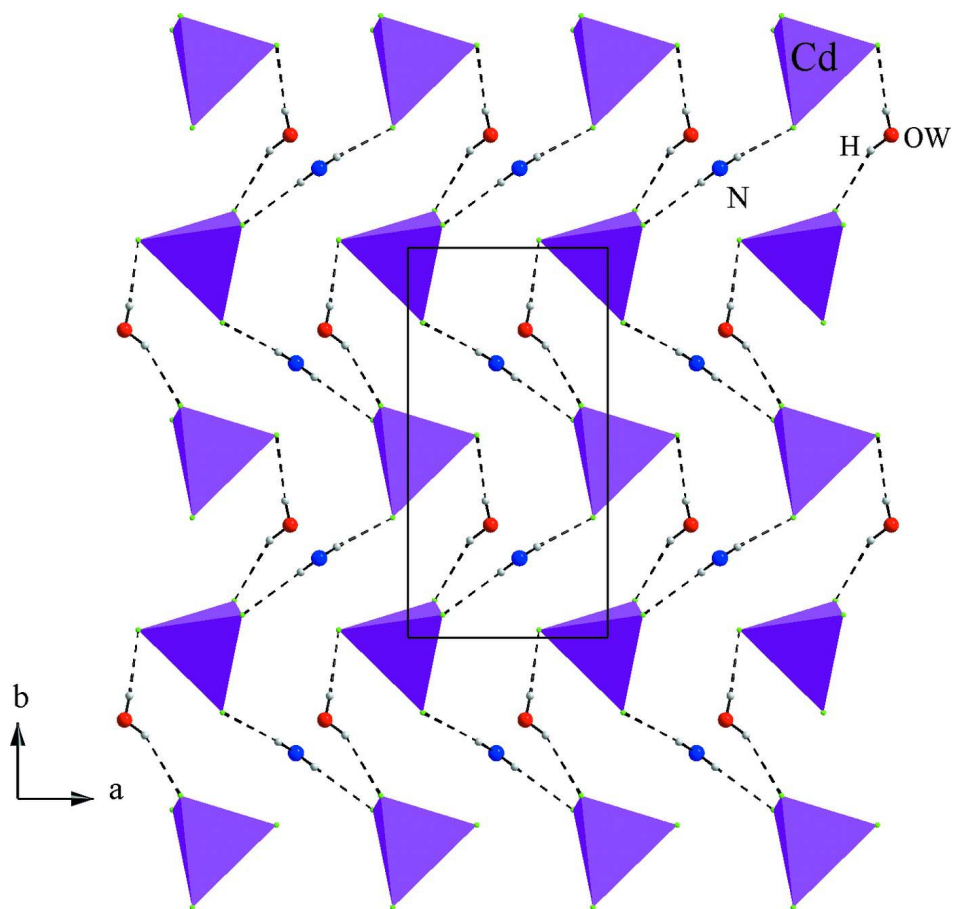
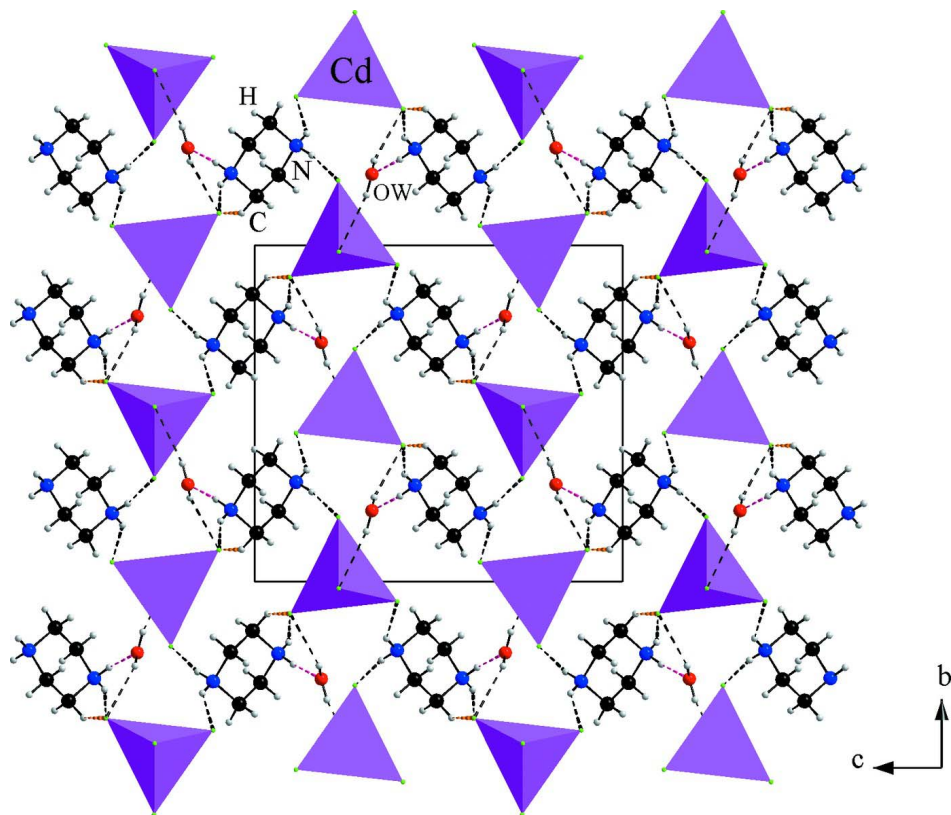


Figure 2

A projection along the c axis of the inorganic layer structure at $z = 1/4$.

**Figure 3**

The packing of the title compound viewed down the *a* axis. Hydrogen bonds are shown as dotted lines.

Piperazinedium tetrachloridocadmamate monohydrate

Crystal data

(C₄H₁₂N₂)[CdCl₄]·H₂O

M_r = 360.38

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 6.6204 (2) Å

b = 12.8772 (3) Å

c = 14.0961 (4) Å

β = 92.1710 (12)°

V = 1200.86 (6) Å³

Z = 4

F(000) = 704

D_x = 1.993 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 8531 reflections

θ = 2.0–30.0°

μ = 2.67 mm⁻¹

T = 295 K

Prismatic, colourless

0.52 × 0.48 × 0.30 mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ scans and ω scans

Absorption correction: multi-scan

(*SORTAV*; Blessing, 1995)

T_{min} = 0.374, *T_{max}* = 0.444

8531 measured reflections

3461 independent reflections

2903 reflections with *I* > 2σ(*I*)

R_{int} = 0.037

θ_{\max} = 30.0°, θ_{\min} = 3.1°

h = -9→9

k = -17→17

l = -19→19

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.033$ $wR(F^2) = 0.081$ $S = 1.09$

3461 reflections

126 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.4362P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.78 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -1.75 \text{ e } \text{Å}^{-3}$ Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0778 (19)

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 $F^2 > \sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.02921 (3)	-0.001890 (11)	0.235463 (13)	0.03178 (9)
Cl1	0.07520 (10)	-0.19208 (5)	0.22725 (4)	0.03972 (16)
Cl2	-0.34472 (9)	0.01950 (5)	0.22883 (5)	0.03628 (15)
Cl3	0.17473 (9)	0.05843 (5)	0.38740 (5)	0.03822 (15)
Cl4	0.13421 (9)	0.09489 (5)	0.09660 (5)	0.03906 (16)
N1	0.5582 (3)	0.20385 (16)	0.38723 (15)	0.0312 (4)
N2	0.7142 (3)	0.28658 (16)	0.56419 (15)	0.0321 (4)
C1	0.4546 (4)	0.29108 (19)	0.43473 (18)	0.0358 (5)
H5	0.3509	0.2636	0.4746	0.043*
H6	0.3897	0.3355	0.3871	0.043*
C2	0.6036 (4)	0.35402 (17)	0.49466 (17)	0.0343 (5)
H7	0.6991	0.3875	0.4540	0.041*
H8	0.5322	0.4077	0.5281	0.041*
C3	0.8195 (4)	0.20021 (19)	0.51588 (18)	0.0345 (5)
H9	0.8879	0.1564	0.5629	0.041*
H10	0.9203	0.2285	0.4749	0.041*
C4	0.6703 (4)	0.13687 (17)	0.45821 (17)	0.0318 (5)
H11	0.5752	0.1046	0.4998	0.038*
H12	0.7406	0.0822	0.4255	0.038*
O1W	0.4133 (3)	0.2110 (2)	0.68116 (18)	0.0644 (7)
H1	0.646 (5)	0.232 (2)	0.344 (2)	0.038 (8)*
H2	0.461 (5)	0.168 (3)	0.357 (2)	0.053 (9)*
H3	0.632 (5)	0.255 (2)	0.604 (2)	0.040 (8)*

H4	0.803 (5)	0.319 (2)	0.592 (2)	0.041 (8)*
H1W	0.3888	0.1492	0.6962	0.080*
H2W	0.3114	0.2506	0.6752	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.03183 (12)	0.03025 (13)	0.03330 (13)	0.00147 (6)	0.00181 (8)	0.00206 (6)
C11	0.0483 (4)	0.0303 (3)	0.0411 (3)	0.0064 (2)	0.0091 (3)	-0.0011 (2)
C12	0.0298 (3)	0.0379 (3)	0.0412 (3)	0.0020 (2)	0.0026 (2)	-0.0031 (2)
C13	0.0358 (3)	0.0386 (3)	0.0400 (3)	-0.0045 (2)	-0.0036 (2)	-0.0027 (2)
C14	0.0327 (3)	0.0419 (3)	0.0433 (3)	0.0050 (2)	0.0105 (2)	0.0109 (3)
N1	0.0336 (11)	0.0330 (10)	0.0270 (10)	-0.0009 (8)	0.0001 (8)	-0.0034 (8)
N2	0.0328 (11)	0.0316 (10)	0.0320 (10)	-0.0065 (8)	0.0030 (8)	-0.0065 (8)
C1	0.0362 (13)	0.0354 (12)	0.0361 (13)	0.0073 (10)	0.0022 (10)	0.0015 (10)
C2	0.0417 (14)	0.0238 (10)	0.0381 (13)	-0.0017 (9)	0.0097 (10)	-0.0025 (9)
C3	0.0304 (12)	0.0330 (11)	0.0397 (13)	0.0019 (9)	-0.0031 (10)	-0.0061 (10)
C4	0.0366 (12)	0.0252 (10)	0.0333 (12)	0.0016 (9)	-0.0009 (9)	-0.0026 (9)
O1W	0.0435 (13)	0.0692 (14)	0.0818 (18)	0.0050 (11)	0.0183 (12)	0.0334 (13)

Geometric parameters (Å, °)

Cd1—C13	2.4418 (6)	C1—C2	1.510 (4)
Cd1—C14	2.4435 (6)	C1—H5	0.9700
Cd1—C11	2.4712 (6)	C1—H6	0.9700
Cd1—C12	2.4891 (7)	C2—H7	0.9700
N1—C1	1.488 (3)	C2—H8	0.9700
N1—C4	1.497 (3)	C3—C4	1.497 (3)
N1—H1	0.93 (3)	C3—H9	0.9700
N1—H2	0.89 (3)	C3—H10	0.9700
N2—C2	1.482 (3)	C4—H11	0.9700
N2—C3	1.491 (3)	C4—H12	0.9700
N2—H3	0.89 (3)	O1W—H1W	0.84
N2—H4	0.81 (3)	O1W—H2W	0.85
C13—Cd1—C14	115.19 (2)	C2—C1—H6	109.5
C13—Cd1—C11	108.13 (2)	H5—C1—H6	108.1
C14—Cd1—C11	115.38 (2)	N2—C2—C1	110.57 (19)
C13—Cd1—C12	110.89 (2)	N2—C2—H7	109.5
C14—Cd1—C12	103.07 (2)	C1—C2—H7	109.5
C11—Cd1—C12	103.42 (2)	N2—C2—H8	109.5
C1—N1—C4	111.06 (18)	C1—C2—H8	109.5
C1—N1—H2	106 (2)	H7—C2—H8	108.1
C4—N1—H2	111 (2)	N2—C3—C4	110.14 (19)
C1—N1—H1	107.8 (18)	N2—C3—H9	109.6
C4—N1—H1	111.2 (19)	C4—C3—H9	109.6
H1—N1—H2	110 (3)	N2—C3—H10	109.6
C2—N2—C3	111.28 (19)	C4—C3—H10	109.6

C2—N2—H3	113 (2)	H9—C3—H10	108.1
C3—N2—H3	104.5 (18)	C3—C4—N1	110.45 (19)
C2—N2—H4	110 (2)	C3—C4—H11	109.6
C3—N2—H4	106 (2)	N1—C4—H11	109.6
H3—N2—H4	112 (3)	C3—C4—H12	109.6
N1—C1—C2	110.8 (2)	N1—C4—H12	109.6
N1—C1—H5	109.5	H11—C4—H12	108.1
C2—C1—H5	109.5	H1W—O1W—H2W	116
N1—C1—H6	109.5		

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

<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—H1 \cdots C11 ⁱ	0.93 (3)	2.35 (3)	3.254 (2)	164 (3)
N1—H2 \cdots C13	0.89 (3)	2.41 (4)	3.155 (2)	141 (3)
N2—H3 \cdots O1W	0.89 (3)	1.93 (3)	2.808 (3)	167 (3)
N2—H4 \cdots C14 ⁱⁱ	0.81 (3)	2.46 (3)	3.190 (2)	151 (3)
O1W—H1W \cdots C12 ⁱⁱⁱ	0.84	2.44	3.267 (3)	168
O1W—H2W \cdots C14 ^{iv}	0.85	2.54	3.304 (2)	150

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