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Bis(4-aminopyridinium) tetraiodidocadmate monohydrate

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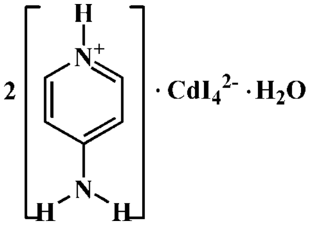
Key indicators: single-crystal X-ray study; *T* = 293 K; mean σ(C–C) = 0.007 Å; *R* factor = 0.025; *wR* factor = 0.064; data-to-parameter ratio = 18.2.

The title compound, $(C_5H_7N_2)_2[CdI_4]\cdot H_2O$, contains one $[CdI_4]^{2-}$ anion, two prontonated 4-aminopyridine molecules and one water molecule in the asymmetric unit. In the anion, the Cd^{II} atom is coordinated by four I atoms in a slightly distorted tetrahedral geometry. The $[CdI_4]^{2-}$ anion and the water molecule are bisected by a crystallographic mirror plane perpendicular to the *c*-axis direction, with the Cd^{II} atom, two of the I atoms and the atoms of the water molecule located on this plane. The crystal packing is stabilized by intermolecular N—H⋯I, N—H⋯O and O—H⋯I hydrogen bonds and by π–π stacking interactions [centroid–centroid distance = 3.798 (3) Å) between pyridine rings, which build up a three-dimensional network.

Related literature

For background literature on the magnetism, antiviral activity and luminescence of organic–inorganic hybrid compounds, see: Bauer *et al.* (2003); Cavicchioli *et al.* (2010); Li *et al.* (2007). For ion channel inhibitor properties of 4-aminopyridine, see: Picolo *et al.* (2003). For metal complexes of 4-aminopyridine, see: Das *et al.* (2010); Ivanova *et al.* (2005); Jebas *et al.* (2009); Kulicka *et al.* (2006); Rademeyer *et al.* (2007); Zaouali Zgolli *et al.* (2009). For bond-length data, see: Anderson *et al.* (2005); Hines *et al.* (2006).



Experimental

Crystal data

$(C_5H_7N_2)_2[CdI_4]\cdot H_2O$
M_r = 828.27
Orthorhombic, *Pbcm*
a = 7.3987 (2) Å
b = 14.7348 (4) Å
c = 18.7286 (4) Å
V = 2041.76 (9) Å^3
Z = 4
Mo *K*α radiation
μ = 7.12 mm^{-1}
T = 293 K
0.40 × 0.24 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.145, T_{max} = 0.340
11964 measured reflections
1860 independent reflections
1755 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.064
S = 1.02
1860 reflections
102 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1*B*⋯O*W*1^{i}	0.86	2.03	2.886 (5)	173
N2—H2*A*⋯I2^{ii}	0.86	3.12	3.938 (4)	161
N2—H2*B*⋯I2	0.86	3.04	3.843 (4)	157
O*W*1—H*W*1*A*⋯I2^{ii}	0.83 (2)	3.24 (1)	3.828 (4)	130 (1)
O*W*1—H*W*1*A*⋯I2^{iii}	0.83 (2)	3.24 (1)	3.828 (4)	130 (1)
O*W*1—H*W*1*A*⋯I1	0.83 (2)	3.27 (4)	3.704 (5)	116 (3)
O*W*1—H*W*1*B*⋯I3^{iv}	0.85 (2)	2.99 (2)	3.761 (5)	152 (4)
O*W*1—H*W*1*A*⋯I1	0.83 (2)	3.27 (4)	3.704 (5)	116 (3)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2495).

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Acta Cryst. (2012). E**68**, m1160–m1161 Sun *et al.* • $(C_5H_7N_2)_2[CdI_4]\cdot H_2O$ **m1161**

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Acta Cryst. (2012). E**68**, m1160–m1161   [doi:10.1107/S1600536812034447]

Bis(4-aminopyridinium) tetraiodidocadmate monohydrate

Qiaozhen Sun, Songyi Liao, Junjun Yao, Junke Wang and Qiongjiali Fang

S1. Comment

Studies of hydrogen bonds connecting organic-inorganic hybrid compounds continue to be a topic of intense research in crystal engineering because such compounds not only allow for rational bottom-up construction but hydrogen bonds also effectively regulate the molecular architecture. Hydrogen bond connected organic-inorganic hybrid compounds can exhibit novel properties related to e.g magnetism, luminescence, antiviral activity and even multifunctional properties (Bauer *et al.*, 2003; Cavicchioli *et al.*, 2010; Li *et al.*, 2007). The protonated form of 4-aminopyridine (4-AP) has hydrogen-bonding capability at both ends of the molecule, and it is also biologically active and can be used as a K^+ and Ca^{2+} channel inhibitor (Picolo *et al.*, 2003). Structures of 4-AP with the metals Mn^{II}, Co^{II}, Cu^{II}, Ni^{II}, Sn^{IV}, Sb^{V} and Pd^{II} have been reported (Das *et al.*, 2010; Ivanova *et al.*, 2005; Jebas *et al.*, 2009; Kulicka *et al.*, 2006; Rademeyer *et al.*, 2007; Zaouali Zgolli *et al.*, 2009). Here we report the crystal structure of the title compound, which is a salt that comprises two symmetry related 4-AP cations and a complex $[CdI_4]^{2-}$ anion, Fig. 1. The $[CdI_4]^{2-}$ anion and the water molecule are bisected by a crystallographic mirror plane perpendicular to the c-axis direction, with the the atoms Cd1, I1, I3 and the water molecule located on this plane at x, y, 1/4. In the anion, the Cd^{II} ion is coordinated by four I atoms, exhibiting a slightly distorted tetrahedral geometry. The mean Cd···I bond distance is 2.78 Å, which is similar to that of related compounds reported in the literature (Hines *et al.*, 2006).

In the cation, the nitrogen atom of the pyridine ring is protonated. Both of the nitrogen atoms of 4-AP are not metal coordinated, but are instead involved in an extensive hydrogen bonding network that includes the amine hydrogen atoms and the iodine atoms, the protonated pyridyl hydrogen atom, and the water molecule. The bond distances and bond angles of the 4-AP cation are comparable with values reported earlier for its uncomplexed form (Anderson *et al.*, 2005).

Packing of the title complex (Fig. 2 and Fig. 3) is facilitated through π–π interactions between pyridine rings [ring centroid distance: 3.798 (3) Å], through the N—H···I hydrogen bonds between the $[CdI_4]^{2-}$ anions and the 4-AP cations, and through O—H···I and N—H···O hydrogen bonds, which link the components of the structure into a three dimensional network.

S2. Experimental

A mixture of CdI_2 (0.36 g, 0.98 mmol), pyridine-2,3-dicarboxylic acid (0.08 g, 0.48 mmol), and 4-aminopyridine (0.06 g, 0.64 mmol) in H_2O (12.0 mL) was sealed in a 20 mL stainless-steal reactor with Teflon liner and heated at 423 K for 60 h under autogenous pressure. Colorless block crystals were collected after the reaction solution was cooled. Yield: 16%. IR: 3314(*s*), 1653(*s*), 1608(*s*), 1526(*s*), 1407(*s*), 1197(*m*), 993(*m*), 865(w), 806(*m*), 758(*m*), 715(w), 495(*m*).

S3. Refinement

All of the non-hydrogen atoms were refined with anisotropic thermal displacement parameters. The O—H distances of water molecules were restrained to 0.84 Å with a standard deviation of 0.001 Å. The other H atoms were not located in the difference map and placed in calculated positions using the riding model approximation with C—H distances of 0.93 Å and an N—H distances of 0.86 Å. U_{iso}(H) were set to 1.2U_{eq}(C, N) or 1.5U_{eq}(O).

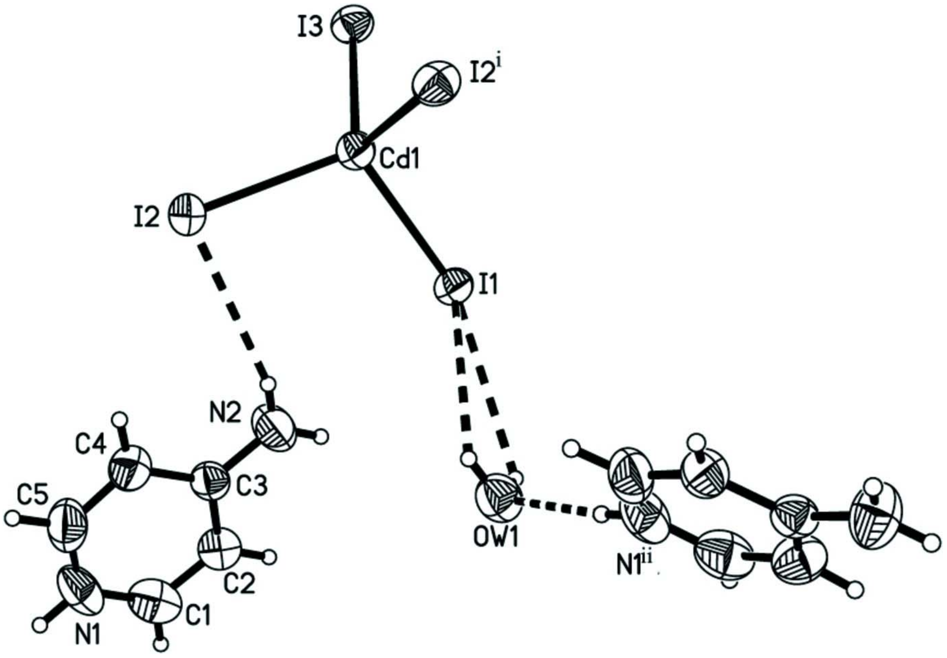

Figure 1

The title compound showing the atom-numbering scheme, with displacement ellipsoids shown at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) x, y, $-z$+0.5; (ii) $-x$+1, $-y$+1, 0.5+z]

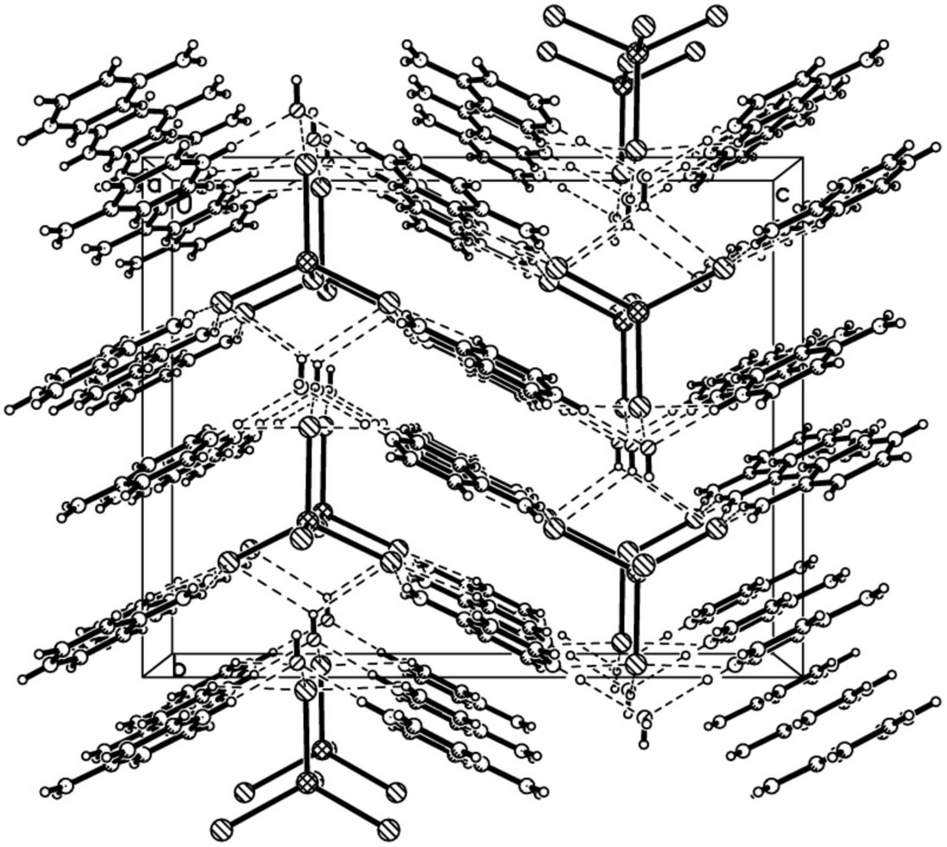

Figure 2

A packing diagram of the title compound, viewed in perspective along the *a* axis.

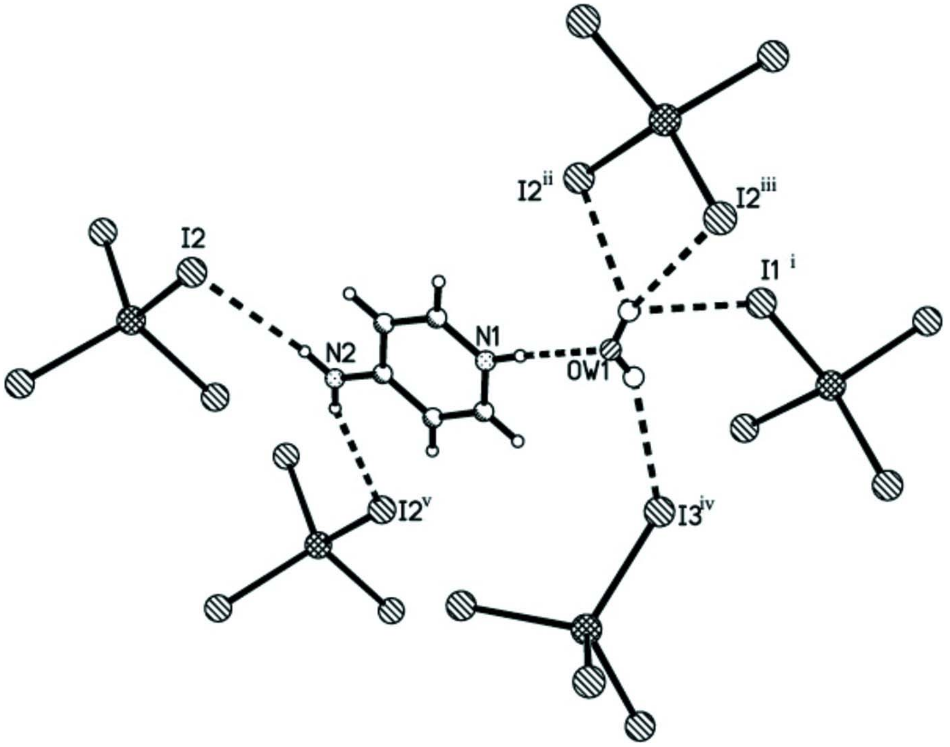

Figure 3

A view of the various N—H···I, N—H···O and O—H···I hydrogen bonds in the (1 1 2) plane, with hydrogen bonds shown as dashed lines. [Symmetry codes: (i) -*x*+1, -*y*+1, -*z*; (ii) -*x*+2, -*y*+1, -*z*; (iii) -*x*+2, -*y*+1, *z*-0.5; (iv) *x*-1, -*y*+0.5, *z*-0.5; (v) *x*-1, *y*, *z*.]

Bis(4-aminopyridinium) tetraiodidocadmate monohydrate

Crystal data

$(C_5H_7N_2)_2[CdI_4]\cdot H_2O$
$M_r = 828.27$
Orthorhombic, *Pbcm*
Hall symbol: -P2c2b
$a = 7.3987$ (2) Å
$b = 14.7348$ (4) Å
$c = 18.7286$ (4) Å
$V = 2041.76$ (9) Å^3
$Z = 4$
$F(000) = 1488$
$D_x = 2.694$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 7689 reflections
$\theta = 2.6$–28.2°
$\mu = 7.12$ mm^{-1}
$T = 293$ K
Block, colourless
0.40 × 0.24 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.145$, $T_{max} = 0.340$
11964 measured reflections
1860 independent reflections
1755 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.8°$
$h = -8\rightarrow8$
$k = -17\rightarrow14$
$l = -22\rightarrow22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.02$
1860 reflections
102 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 1.5671P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.91$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00433 (17)

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 $F^2 > 2\text{sigma}(F^2)$ 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_{iso}*/U_{eq}
Cd1	1.01826 (6)	0.20199 (3)	0.2500	0.03793 (14)
I1	0.64576 (5)	0.22518 (3)	0.2500	0.03959 (14)
I2	1.14547 (4)	0.28284 (2)	0.125323 (15)	0.04579 (13)
I3	1.11401 (5)	0.01921 (3)	0.2500	0.04403 (15)
N1	0.6396 (7)	0.4593 (3)	−0.11682 (19)	0.0606 (12)
H1B	0.6371	0.4870	−0.1572	0.073*
N2	0.6522 (6)	0.3361 (3)	0.0766 (2)	0.0617 (11)
H2A	0.5548	0.3145	0.0950	0.074*
H2B	0.7526	0.3324	0.0996	0.074*
C1	0.4861 (8)	0.4240 (3)	−0.0903 (2)	0.0588 (13)
H1A	0.3794	0.4282	−0.1163	0.071*
C2	0.4861 (6)	0.3821 (3)	−0.0254 (2)	0.0467 (10)
H2C	0.3797	0.3583	−0.0067	0.056*
C3	0.6476 (6)	0.3755 (3)	0.0125 (2)	0.0407 (9)
C4	0.8047 (7)	0.4105 (3)	−0.0187 (3)	0.0547 (11)
H4A	0.9155	0.4048	0.0043	0.066*
C5	0.7938 (8)	0.4524 (3)	−0.0821 (3)	0.0626 (13)
H5A	0.8977	0.4772	−0.1021	0.075*
OW1	0.4000 (7)	0.4442 (3)	0.2500	0.0552 (11)
HW1A	0.355 (5)	0.3924 (19)	0.2500	0.083*
HW1B	0.514 (3)	0.439 (3)	0.2500	0.083*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0368 (3)	0.0395 (3)	0.0375 (2)	0.00051 (18)	0.000	0.000
I1	0.0341 (2)	0.0429 (2)	0.0418 (2)	0.00329 (15)	0.000	0.000
I2	0.0395 (2)	0.0539 (2)	0.04392 (19)	0.00186 (12)	0.00688 (10)	0.01025 (11)
I3	0.0430 (3)	0.0383 (2)	0.0508 (2)	0.00445 (16)	0.000	0.000
N1	0.101 (4)	0.046 (2)	0.0349 (18)	−0.001 (2)	0.0029 (19)	0.0039 (16)
N2	0.059 (3)	0.072 (3)	0.054 (2)	−0.008 (2)	−0.0031 (17)	0.022 (2)
C1	0.077 (4)	0.049 (3)	0.051 (2)	0.002 (3)	−0.018 (2)	−0.009 (2)
C2	0.048 (3)	0.044 (2)	0.048 (2)	−0.002 (2)	−0.0030 (19)	−0.0044 (18)
C3	0.047 (3)	0.033 (2)	0.042 (2)	0.0019 (17)	0.0029 (16)	0.0002 (16)
C4	0.048 (3)	0.056 (3)	0.061 (3)	0.002 (2)	0.008 (2)	0.006 (2)
C5	0.071 (4)	0.061 (3)	0.056 (3)	0.000 (3)	0.023 (3)	0.001 (2)
OW1	0.067 (3)	0.051 (3)	0.047 (2)	0.001 (2)	0.000	0.000

Geometric parameters (Å, º)

Cd1—I1	2.7771 (6)	C1—C2	1.363 (6)
Cd1—I3	2.7849 (6)	C1—H1A	0.9300
Cd1—I2ⁱ	2.7852 (4)	C2—C3	1.394 (6)
Cd1—I2	2.7852 (4)	C2—H2C	0.9300
N1—C5	1.317 (7)	C3—C4	1.400 (6)
N1—C1	1.345 (7)	C4—C5	1.341 (7)
N1—H1B	0.8600	C4—H4A	0.9300
N2—C3	1.333 (5)	C5—H5A	0.9300
N2—H2A	0.8600	OW1—HW1A	0.83 (2)
N2—H2B	0.8600	OW1—HW1B	0.85 (2)
I1—Cd1—I3	111.805 (18)	C2—C1—H1A	119.8
I1—Cd1—I2ⁱ	106.423 (13)	C1—C2—C3	119.1 (5)
I3—Cd1—I2ⁱ	109.129 (13)	C1—C2—H2C	120.5
I1—Cd1—I2	106.423 (13)	C3—C2—H2C	120.5
I3—Cd1—I2	109.129 (13)	N2—C3—C2	120.8 (4)
I2ⁱ—Cd1—I2	113.94 (2)	N2—C3—C4	121.0 (4)
C5—N1—C1	121.2 (4)	C2—C3—C4	118.3 (4)
C5—N1—H1B	119.4	C5—C4—C3	119.3 (5)
C1—N1—H1B	119.4	C5—C4—H4A	120.3
C3—N2—H2A	120.0	C3—C4—H4A	120.3
C3—N2—H2B	120.0	N1—C5—C4	121.7 (5)
H2A—N2—H2B	120.0	N1—C5—H5A	119.1
N1—C1—C2	120.3 (5)	C4—C5—H5A	119.1
N1—C1—H1A	119.8	HW1A—OW1—HW1B	108 (3)

Symmetry code: (i) *x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O*W*1^{ii}	0.86	2.03	2.886 (5)	173
N2—H2*A*···I2^{iii}	0.86	3.12	3.938 (4)	161
N2—H2*B*···I2	0.86	3.04	3.843 (4)	157
O*W*1—H*W*1*A*···I2^{iii}	0.83 (2)	3.24 (1)	3.828 (4)	130 (1)
O*W*1—H*W*1*A*···I2^{iv}	0.83 (2)	3.24 (1)	3.828 (4)	130 (1)
O*W*1—H*W*1*A*···I1	0.83 (2)	3.27 (4)	3.704 (5)	116 (3)
O*W*1—H*W*1*B*···I3^{v}	0.85 (2)	2.99 (2)	3.761 (5)	152 (4)
O*W*1—H*W*1*A*···I1	0.83 (2)	3.27 (4)	3.704 (5)	116 (3)

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