Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Aminoanilinium 6-carboxypicolinate monohydrate

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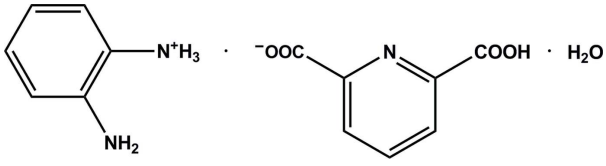
Received 25 June 2011; accepted 25 June 2011

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.040; wR factor = 0.117; data-to-parameter ratio = 8.1.

In the title compound, $C_6H_9N_2^+\cdot C_7H_4NO_4^-\cdot H_2O$, one amino group of diaminobenzene is protonated while one carboxy group of pyridine-2,6-dicarboxylic acid is deprotonated. In the anion, the CO_2 and CO_2H groups make dihedral angles of 4.0 (5) and 8.7 (4)° with the pyridine ring. In the crystal, extensive N—H···O, N—H···N and O—H···O hydrogen bonds occur between anions, cations and water molecules.

Related literature

For related compounds, see: Andre *et al.* (2011); Blagden *et al.* (2008); Smith *et al.* (2000); Kapildev *et al.* (2011).



Experimental

Crystal data

$C_6H_9N_2^+\cdot C_7H_4NO_4^-\cdot H_2O$
M_r = 293.28
Monoclinic, Cc
a = 12.408 (3) Å
b = 13.932 (3) Å
c = 8.0951 (16) Å
β = 102.41 (3)°
V = 1366.6 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 298 K
0.30 × 0.25 × 0.15 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.910, T_{max} = 1.000
7343 measured reflections
1555 independent reflections
1393 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.117
S = 1.12
1555 reflections
191 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1W^{i}	0.89	2.13	3.004 (4)	166
N1—H1B···O3^{ii}	0.89	1.98	2.862 (3)	170
N1—H1C···N3	0.89	2.12	3.003 (4)	171
N2—H2A···O1W^{iii}	0.90	2.41	3.303 (4)	172
N2—H2B···O1	0.90	2.14	3.029 (4)	168
O1W—H1WA···O2^{iv}	0.82	2.27	3.034 (3)	155
O1W—H1WB···O2	0.82	2.04	2.831 (3)	161
O4—H4···O1^{i}	0.82	1.71	2.532 (3)	179

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* data reduction: *CrystalClear*; 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*.

This work was supported by the start-up fund of Northwest A & F University, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5250).

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supporting information

Acta Cryst. (2011). E**67**, o1893 [doi:10.1107/S1600536811025050]

2-Aminoanilinium 6-carboxypicolinate monohydrate

Yu-Tang Wang and De-Jiang Gao

S1. Comment

Cocrystals are most commonly thought of as structural homogeneous crystalline materials that contain two or more organic building blocks that are present in definite stoichiometric amounts. Within the development of pharmaceutical industry, molecular cocrystals are becoming increasingly important as a new drug with higher biomedical activity than the initial components. (Kapildev *et al.* 2011). Physicochemical properties such as the melting point, stability and solubility of an active pharmaceutical ingredient can be tuned through cocrystal formulation (Andre, *et al.* 2011; Blagden, *et al.* 2008; Smith, *et al.* 2000). These cocrystal forms often relie on the acid-amide H-bonds interactions. Herein, we report the crystal structure of the title compound, 2-aminoanilinium 6-carboxypicolinate monohydrate.

The asymmetric unit is composed of one 6-carboxypicolinate anion one 2-aminoanilinium cation and one water molecule (Fig.1). The amine N1 atom was protonated. And one of the carboxyl groups was deprotonated. The interplanar angle between the benzene and the pyridine rings equals to 88.89 (10)°. The geometric parameters of the title compound are in the normal range.

The molecular packing is stabilized by strong intermolecular N—H···O, N—H···N and O—H···O hydrogen bonds. The H-bonds link the molecules into a three-dimensional network (Fig. 2 and Tab. 1).

S2. Experimental

A mixture of pyridine-2,6-dicarboxylic acid (2.0 mmol), benzene-1,2-diamine (2.0 mmol) and 40 ml water were added into a 100 ml flask and refluxed for 5 h, then cooled and filtrated. The solution was evaporated slowly in the air. Colorless block crystals suitable for X-ray analysis were obtained after one week.

S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C-H = 0.93 Å (aromatic) with U_{iso}(H) = 1.2U_{eq}(C). The H atoms bonded to N1, N2, O1W and O4 were located in a difference Fourier map, in the last stage of the refinement they were restrained with the H—N2 = 0.90, H—N1 = 0.89 and H—O = 0.82 Å. U_{iso}(H)=1.5U_{eq}(N1,O1W,O4) and U_{iso}(H) = 1.2U_{eq}(N2). As no significant anomalous scatterings, Friedel pairs were merged.

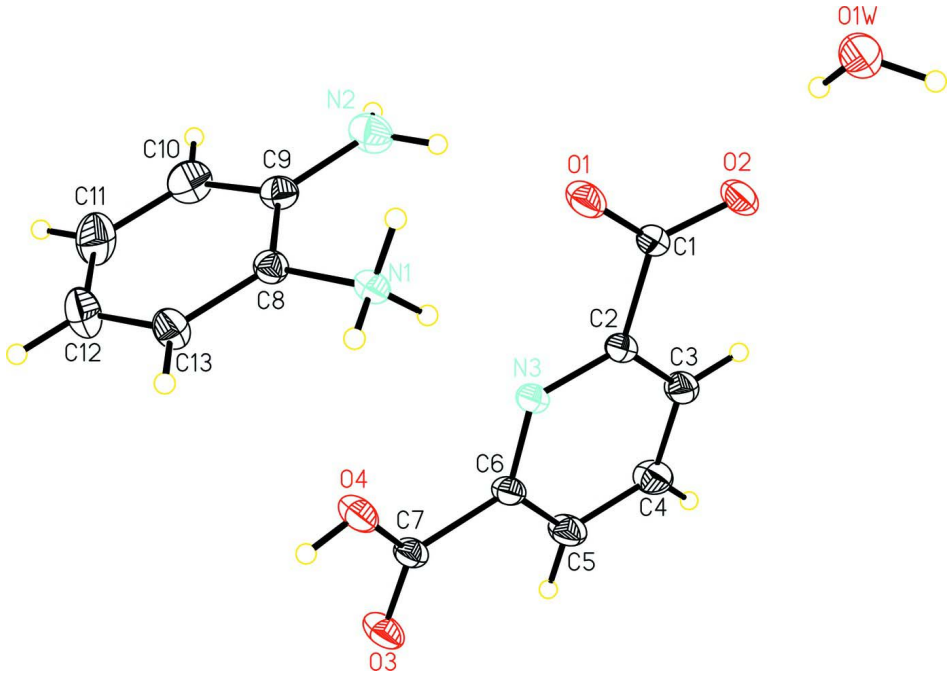

Figure 1

Molecular view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

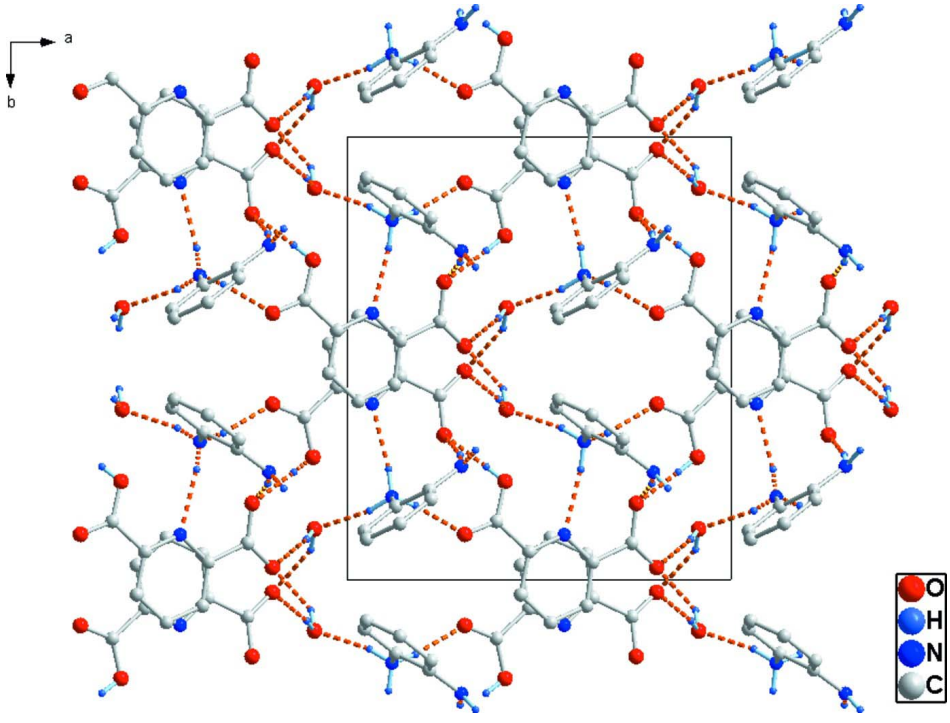

Figure 2

The crystal packing of the title compound viewed along the *c* axis showing the three-dimensionnal hydrogen bondings network (dashed line). Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

2-Aminoanilinium 6-carboxypicolinate monohydrate

Crystal data

$C_6H_9N_2^+·C_7H_4NO_4^-·H_2O$
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Monoclinic, *Cc*
Hall symbol: C -2yc
a = 12.408 (3) Å
b = 13.932 (3) Å
c = 8.0951 (16) Å
β = 102.41 (3)°
V = 1366.6 (5) Å^3
Z = 4
F(000) = 616
D_x = 1.425 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1555 reflections
θ = 2.2–27.4°
μ = 0.11 mm^{-1}
T = 298 K
Block, colorless
0.30 × 0.25 × 0.15 mm

Data collection

Rigaku Mercury2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
CCD profile fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.910, T_{max} = 1.000
7343 measured reflections
1555 independent reflections
1393 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.4°, θ_{min} = 2.2°
h = −16→15
k = −18→18
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.117
S = 1.12
1555 reflections
191 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 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.

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}
O1W	0.9144 (2)	0.11509 (17)	0.8457 (3)	0.0468 (6)
H1WA	0.9052	0.0737	0.9133	0.070*
H1WB	0.8972	0.0905	0.7516	0.070*
O1	0.75215 (19)	0.17288 (15)	0.4341 (3)	0.0456 (6)

O2	0.80493 (18)	0.02830 (16)	0.5392 (3)	0.0412 (5)
N3	0.56474 (19)	0.10218 (18)	0.2422 (3)	0.0286 (5)
O3	0.30560 (19)	0.10298 (17)	−0.0480 (3)	0.0436 (6)
O4	0.41055 (17)	0.22264 (15)	0.0827 (3)	0.0397 (5)
H4	0.3599	0.2569	0.0337	0.060*
N1	0.61623 (19)	0.31257 (19)	0.2363 (3)	0.0296 (5)
H1A	0.5582	0.3434	0.2587	0.044*
H1B	0.6772	0.3318	0.3080	0.044*
H1C	0.6076	0.2497	0.2476	0.044*
C8	0.6256 (2)	0.33386 (19)	0.0621 (3)	0.0290 (6)
N2	0.7964 (2)	0.2434 (2)	0.1010 (4)	0.0452 (7)
H2A	0.8342	0.2069	0.0413	0.054*
H2B	0.7933	0.2178	0.2020	0.054*
C1	0.7403 (2)	0.0831 (2)	0.4445 (4)	0.0304 (6)
C6	0.4728 (2)	0.0640 (2)	0.1448 (4)	0.0293 (6)
C7	0.3880 (2)	0.1321 (2)	0.0494 (3)	0.0296 (6)
C3	0.6225 (3)	−0.0586 (2)	0.3262 (4)	0.0371 (7)
H3A	0.6748	−0.0990	0.3909	0.044*
C9	0.7137 (2)	0.2968 (2)	0.0015 (4)	0.0336 (6)
C5	0.4515 (3)	−0.0335 (2)	0.1314 (4)	0.0392 (7)
H5A	0.3870	−0.0566	0.0623	0.047*
C13	0.5445 (3)	0.3890 (2)	−0.0392 (4)	0.0378 (7)
H13A	0.4864	0.4131	0.0041	0.045*
C4	0.5287 (3)	−0.0961 (2)	0.2238 (5)	0.0427 (8)
H4A	0.5173	−0.1621	0.2167	0.051*
C10	0.7174 (3)	0.3179 (3)	−0.1655 (5)	0.0471 (8)
H10A	0.7756	0.2946	−0.2097	0.057*
C2	0.6380 (2)	0.0403 (2)	0.3314 (4)	0.0289 (6)
C12	0.5500 (3)	0.4080 (3)	−0.2044 (5)	0.0503 (9)
H12A	0.4953	0.4444	−0.2731	0.060*
C11	0.6366 (4)	0.3728 (3)	−0.2669 (5)	0.0549 (10)
H11A	0.6409	0.3859	−0.3779	0.066*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1W	0.0461 (14)	0.0470 (14)	0.0444 (13)	−0.0005 (11)	0.0035 (10)	0.0032 (10)
O1	0.0368 (12)	0.0319 (12)	0.0563 (14)	−0.0070 (10)	−0.0164 (10)	0.0073 (11)
O2	0.0311 (11)	0.0399 (12)	0.0452 (12)	0.0016 (9)	−0.0085 (9)	0.0071 (10)
N3	0.0222 (10)	0.0302 (13)	0.0312 (11)	−0.0011 (9)	0.0014 (9)	0.0013 (10)
O3	0.0307 (12)	0.0408 (13)	0.0504 (14)	0.0011 (9)	−0.0108 (10)	−0.0029 (10)
O4	0.0296 (11)	0.0318 (10)	0.0500 (13)	0.0023 (8)	−0.0086 (9)	0.0000 (10)
N1	0.0244 (11)	0.0326 (12)	0.0292 (12)	0.0008 (9)	−0.0003 (9)	−0.0013 (10)
C8	0.0278 (14)	0.0293 (13)	0.0286 (14)	−0.0010 (11)	0.0035 (10)	−0.0011 (11)
N2	0.0343 (14)	0.0463 (16)	0.0553 (18)	0.0115 (12)	0.0103 (13)	−0.0012 (14)
C1	0.0246 (13)	0.0325 (14)	0.0321 (14)	−0.0003 (11)	0.0015 (10)	0.0035 (12)
C6	0.0217 (12)	0.0314 (14)	0.0331 (14)	−0.0010 (11)	0.0020 (10)	−0.0005 (12)
C7	0.0228 (13)	0.0366 (14)	0.0272 (13)	−0.0010 (11)	0.0008 (10)	−0.0015 (12)

C3	0.0298 (16)	0.0312 (15)	0.0480 (18)	0.0007 (12)	0.0033 (13)	0.0080 (13)
C9	0.0298 (14)	0.0314 (15)	0.0395 (16)	−0.0014 (12)	0.0072 (12)	−0.0035 (12)
C5	0.0291 (16)	0.0372 (15)	0.0461 (18)	−0.0059 (13)	−0.0032 (13)	−0.0018 (14)
C13	0.0357 (15)	0.0397 (16)	0.0369 (17)	0.0079 (13)	0.0054 (12)	0.0033 (13)
C4	0.0363 (16)	0.0275 (15)	0.060 (2)	−0.0048 (13)	0.0016 (15)	0.0003 (14)
C10	0.049 (2)	0.053 (2)	0.045 (2)	0.0026 (16)	0.0206 (16)	−0.0055 (16)
C2	0.0228 (13)	0.0303 (14)	0.0320 (13)	−0.0012 (11)	0.0026 (11)	0.0021 (12)
C12	0.057 (2)	0.053 (2)	0.0387 (18)	0.0148 (18)	0.0064 (15)	0.0112 (16)
C11	0.072 (3)	0.061 (2)	0.0357 (19)	0.008 (2)	0.0202 (17)	0.0082 (17)

Geometric parameters (Å, º)

O1W—H1WA	0.8201	C1—C2	1.518 (4)
O1W—H1WB	0.8201	C6—C5	1.384 (4)
O1—C1	1.264 (4)	C6—C7	1.502 (4)
O2—C1	1.245 (4)	C3—C4	1.378 (5)
N3—C2	1.345 (4)	C3—C2	1.391 (4)
N3—C6	1.349 (4)	C3—H3A	0.9300
O3—C7	1.219 (3)	C9—C10	1.394 (5)
O4—C7	1.307 (4)	C5—C4	1.390 (5)
O4—H4	0.8201	C5—H5A	0.9300
N1—C8	1.470 (4)	C13—C12	1.379 (5)
N1—H1A	0.8900	C13—H13A	0.9300
N1—H1B	0.8900	C4—H4A	0.9300
N1—H1C	0.8900	C10—C11	1.382 (6)
C8—C13	1.386 (4)	C10—H10A	0.9300
C8—C9	1.390 (4)	C12—C11	1.373 (6)
N2—C9	1.378 (4)	C12—H12A	0.9300
N2—H2A	0.9002	C11—H11A	0.9300
N2—H2B	0.8998		
H1WA—O1W—H1WB	106.3	C2—C3—H3A	120.4
C2—N3—C6	116.7 (2)	N2—C9—C8	122.5 (3)
C7—O4—H4	110.7	N2—C9—C10	120.3 (3)
C8—N1—H1A	109.5	C8—C9—C10	117.1 (3)
C8—N1—H1B	109.5	C6—C5—C4	118.4 (3)
H1A—N1—H1B	109.5	C6—C5—H5A	120.8
C8—N1—H1C	109.5	C4—C5—H5A	120.8
H1A—N1—H1C	109.5	C12—C13—C8	119.9 (3)
H1B—N1—H1C	109.5	C12—C13—H13A	120.0
C13—C8—C9	121.6 (3)	C8—C13—H13A	120.0
C13—C8—N1	118.8 (3)	C3—C4—C5	118.8 (3)
C9—C8—N1	119.6 (2)	C3—C4—H4A	120.6
C9—N2—H2A	113.6	C5—C4—H4A	120.6
C9—N2—H2B	125.0	C11—C10—C9	121.4 (3)
H2A—N2—H2B	113.1	C11—C10—H10A	119.3
O2—C1—O1	125.4 (3)	C9—C10—H10A	119.3
O2—C1—C2	118.4 (3)	N3—C2—C3	123.1 (3)

O1—C1—C2	116.3 (2)	N3—C2—C1	116.9 (2)
N3—C6—C5	123.8 (3)	C3—C2—C1	120.0 (3)
N3—C6—C7	117.6 (2)	C11—C12—C13	119.6 (3)
C5—C6—C7	118.6 (3)	C11—C12—H12A	120.2
O3—C7—O4	124.6 (3)	C13—C12—H12A	120.2
O3—C7—C6	121.3 (3)	C12—C11—C10	120.3 (3)
O4—C7—C6	114.1 (2)	C12—C11—H11A	119.8
C4—C3—C2	119.1 (3)	C10—C11—H11A	119.8
C4—C3—H3A	120.4		

C2—N3—C6—C5	−0.6 (4)	C6—C5—C4—C3	0.7 (5)
C2—N3—C6—C7	177.7 (3)	N2—C9—C10—C11	−178.8 (4)
N3—C6—C7—O3	176.1 (3)	C8—C9—C10—C11	−0.5 (5)
C5—C6—C7—O3	−5.4 (4)	C6—N3—C2—C3	0.1 (4)
N3—C6—C7—O4	−4.8 (4)	C6—N3—C2—C1	−178.6 (3)
C5—C6—C7—O4	173.7 (3)	C4—C3—C2—N3	0.8 (5)
C13—C8—C9—N2	178.7 (3)	C4—C3—C2—C1	179.4 (3)
N1—C8—C9—N2	−2.8 (4)	O2—C1—C2—N3	174.0 (3)
C13—C8—C9—C10	0.4 (4)	O1—C1—C2—N3	−5.8 (4)
N1—C8—C9—C10	178.9 (3)	O2—C1—C2—C3	−4.7 (4)
N3—C6—C5—C4	0.2 (5)	O1—C1—C2—C3	175.5 (3)
C7—C6—C5—C4	−178.1 (3)	C8—C13—C12—C11	−0.6 (6)
C9—C8—C13—C12	0.2 (5)	C13—C12—C11—C10	0.6 (6)
N1—C8—C13—C12	−178.4 (3)	C9—C10—C11—C12	0.0 (7)
C2—C3—C4—C5	−1.2 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1*W*^{i}	0.89	2.13	3.004 (4)	166
N1—H1*B*···O3^{ii}	0.89	1.98	2.862 (3)	170
N1—H1*C*···N3	0.89	2.12	3.003 (4)	171
N2—H2*A*···O1*W*^{iii}	0.90	2.41	3.303 (4)	172
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O1*W*—H1*WA*···O2^{iv}	0.82	2.27	3.034 (3)	155
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O4—H4···O1^{i}	0.82	1.71	2.532 (3)	179

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