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## Structure Reports

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# Hydroxonium 1-ammonioethane-1,1-diylidiphosphonate

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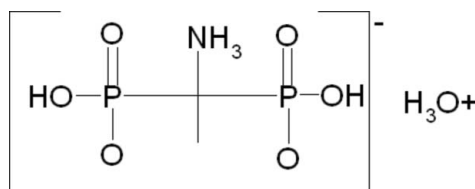
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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.032;  $wR$  factor = 0.097; data-to-parameter ratio = 14.5.

The title complex,  $\text{H}_3\text{O}^+\cdot\text{NH}_3\text{C}(\text{CH}_3)(\text{PO}_3\text{H})_2^-$ , contains a hydroxonium ion and an  $\text{NH}_3\text{C}(\text{CH}_3)(\text{PO}_3\text{H})_2^-$  anion. The three H atoms of  $\text{H}_3\text{O}^+$  form a pseudo-tetrahedron by being distributed over four positions with occupation factors of 0.75. Multiple  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds in the crystal structure form an intricate three-dimensional supra-molecular network.

## Related literature

For the structures of organophosphonates, see: Clearfield (2002); Finn *et al.* (2003). For similar bisphosphonates, see: Fernández *et al.* (2003); For complexes with 1-aminoethylidene-1,1-diphosphonic acid, see: Yin *et al.* (2005); Ding *et al.* (2006); Li *et al.* (2008). For the synthesis, see: Chai *et al.* (1980).



## Experimental

### Crystal data

 $\text{H}_3\text{O}^+\cdot\text{C}_2\text{H}_8\text{N}_2\text{O}_6\text{P}_2^-$   
 $M_r = 223.06$   
 Monoclinic,  $P2_1/c$   
 $a = 7.3372$  (6) Å  
 $b = 10.6553$  (8) Å  
 $c = 10.6128$  (8) Å  
 $\beta = 97.705$  (1)°

 $V = 822.22$  (11) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.53$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.36 \times 0.27 \times 0.18$  mm

### Data collection

 Bruker SMART 4K CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)  
 $T_{\min} = 0.831$ ,  $T_{\max} = 0.910$   
 5340 measured reflections  
 1972 independent reflections  
 1837 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.097$   
 $S = 1.10$   
 1972 reflections  
 136 parameters  
 4 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.61$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1C}\cdots\text{O2}^{\text{I}}$	0.89	1.98	2.809 (2)	155
$\text{N1}-\text{H1A}\cdots\text{O5}^{\text{I}}$	0.89	1.90	2.713 (2)	151
$\text{N1}-\text{H1B}\cdots\text{O3}^{\text{II}}$	0.89	2.01	2.824 (2)	152
$\text{O4}-\text{H3}\cdots\text{O3}^{\text{II}}$	0.73 (4)	1.86 (4)	2.591 (2)	176 (4)
$\text{O1}-\text{H4}\cdots\text{O6}^{\text{III}}$	0.71 (3)	1.84 (3)	2.550 (2)	172 (4)
$\text{O1W}-\text{H5}\cdots\text{O5}^{\text{IV}}$	0.893 (10)	1.954 (15)	2.804 (2)	159 (3)
$\text{O1W}-\text{H8}\cdots\text{O1}^{\text{V}}$	0.888 (10)	2.64 (4)	3.061 (2)	110 (3)
$\text{O1W}-\text{H8}\cdots\text{O3}^{\text{VI}}$	0.888 (10)	2.27 (2)	3.041 (2)	145 (3)
$\text{O1W}-\text{H6}\cdots\text{O2}^{\text{VII}}$	0.896 (10)	1.935 (11)	2.828 (2)	175 (3)
$\text{O1W}-\text{H7}\cdots\text{O6}^{\text{III}}$	0.900 (10)	1.920 (11)	2.815 (2)	173 (3)

 Symmetry codes: (i)  $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 2, -y + 1, -z$ ; (iii)  $x - 1, y, z$ ; (iv)  $-x + 2, -y + 1, -z + 1$ ; (v)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (vi)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (vii)  $-x + 1, -y + 1, -z + 1$ .

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008b); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008b); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2053).

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## supporting information

*Acta Cryst.* (2009). E65, o787 [doi:10.1107/S1600536809008770]

## Hydroxonium 1-ammonioethane-1,1-diylidiphosphonate

Ming Li, Wen Wen, Wuzu Ha and Liang Chang

### S1. Comment

Organophosphonic acids and their compounds have attracted tremendous interest. A series of phosphonate hybrid materials have been prepared and show potential applications in catalysts, sensors, sorbents, magnetic and luminescent materials. Such materials also illustrate a variety of structures from one-dimensional chains, two-dimensional layers to three-dimensional porous frameworks. (Finn *et al.*, 2003). Introduction of some functional groups to phosphonic acids, such as crown ether,  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NR}_2$  or mixed groups will modify their complexing ability and construct a great number of novel phosphonates (Clearfield, 2002). Compared with other phosphonic acids, 1-aminoethylidene-1,1-di-phosphonic acid ( $\text{AEDPH}_4$ ) is easier to synthesize. However, little attention has been paid to the structural study of metal-AEDP compounds (Yin *et al.*, 2005; Ding *et al.*, 2006). In our recent paper, it is found that  $\text{AEDPH}_4$  is inclined to transfer one proton to the amino group, which is in agreement with Fernández's results on similar bisphosphonates. (Li *et al.*, 2008; Fernández *et al.*, 2003). Deprotonation of it will result in predictable hydrogen aggregates from stronger  $\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{P}$  to weaker  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds. Herein, we report its structure, (I).

The asymmetric unit of (I) is built up from one deprotonated  $\text{AEDPH}_3$  anion and a disordered  $\text{H}_3\text{O}^+$  cation, which are linked through four types of  $\text{Ow}-\text{H}\cdots\text{O}$  hydrogen bonds (Fig. 1, Table 1). Two of the four protons of phosphonates are used in protonation, one for the amino group, the other for the  $\text{H}_3\text{O}^+$  cation. The combination of different hydrogen bond interactions,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  results in the formation of an intricate three dimensional supramolecular network (Fig.2, Table 1).

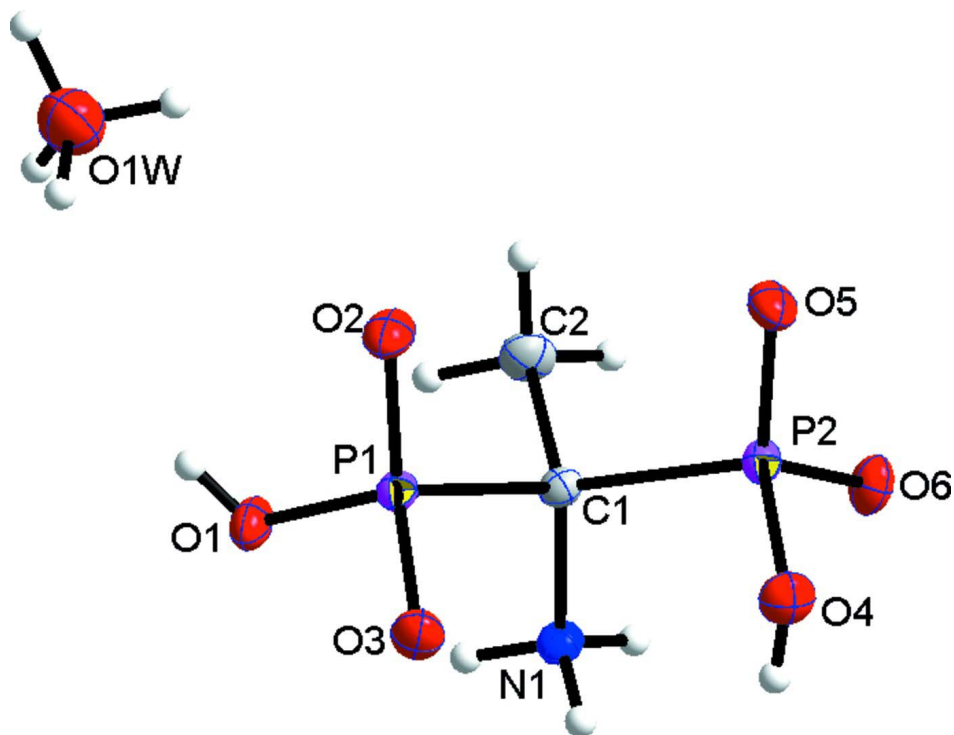
### S2. Experimental

The  $\text{AEDPH}_4$  was synthesized according to the US Patent 4239695 (Chai *et al.*, 1980). It was crystallized directly from the  $\text{AEDPH}_4$  aqueous solution. When the mixture was heated for 24h, colorless crystals were obtained.

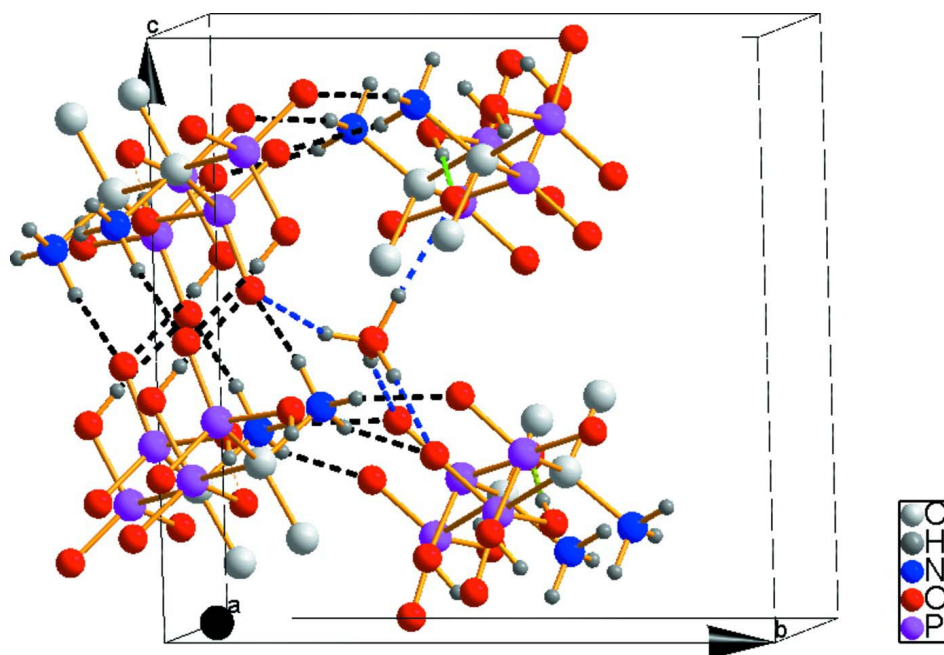
### S3. Refinement

All H atoms attached to C and N atoms were fixed geometrically and treated as riding with  $\text{C}-\text{H} = 0.96 \text{ \AA}$  (C),  $\text{N}-\text{H} = 0.89 \text{ \AA}$  with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}, \text{N})$ . The H atoms of hydroxyl were located in difference Fourier maps and included in the subsequent refinement.

The three hydrogen atoms of the  $\text{H}_3\text{O}^+$  cation are statistically distributed over four positions with occupation factor of 0.75, building a pseudo tetrahedron.

**Figure 1**

The asymmetric unit of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

**Figure 2**

Partial packing view of compound (I), showing the formation of the three dimensional network built from hydrogen bonds. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

## Hydroxonium 1-ammonioethane-1,1-diylidiphosphonate

## Crystal data

 $\text{H}_3\text{O}^+\cdot\text{C}_2\text{H}_8\text{N}_2\text{O}_6\text{P}_2^-$  $M_r = 223.06$ Monoclinic,  $P2_1/c$ 

Hall symbol: -P 2ybc

 $a = 7.3372$  (6) Å $b = 10.6553$  (8) Å $c = 10.6128$  (8) Å $\beta = 97.705$  (1)° $V = 822.22$  (11) Å<sup>3</sup> $Z = 4$  $F(000) = 464$  $D_x = 1.802$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3640 reflections

 $\theta = 2.7\text{--}29.8^\circ$  $\mu = 0.53$  mm<sup>-1</sup> $T = 293$  K

Plate, colorless

 $0.36 \times 0.27 \times 0.18$  mm

## Data collection

Bruker SMART 4K CCD area-detector  
diffractometer

Graphite monochromator

 $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 2008a)

 $T_{\min} = 0.831$ ,  $T_{\max} = 0.910$ 

5340 measured reflections

1972 independent reflections

1837 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.015$  $\theta_{\max} = 28.0^\circ$ ,  $\theta_{\min} = 2.7^\circ$  $h = -9 \rightarrow 9$  $k = -9 \rightarrow 14$  $l = -13 \rightarrow 11$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$  $wR(F^2) = 0.097$  $S = 1.10$ 

1972 reflections

136 parameters

4 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from  
neighbouring sitesH atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.8715P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.40$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.61$  e Å<sup>-3</sup>Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ 

Extinction coefficient: 0.023 (2)

## 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 (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.9948 (2)	0.56114 (16)	0.24265 (16)	0.0131 (3)	
C2	0.9672 (3)	0.62357 (19)	0.36861 (18)	0.0209 (4)	
H2A	1.0741	0.6722	0.3993	0.031*	
H2B	0.9488	0.5602	0.4299	0.031*	
H2C	0.8615	0.6774	0.3556	0.031*	
N1	1.0165 (2)	0.66564 (14)	0.14939 (14)	0.0152 (3)	

H1A	0.9151	0.7124	0.1391	0.023*	
H1B	1.0347	0.6329	0.0750	0.023*	
H1C	1.1124	0.7131	0.1792	0.023*	
O1W	0.4462 (2)	0.70203 (18)	0.52441 (17)	0.0363 (4)	
O1	0.63612 (19)	0.57626 (13)	0.17124 (14)	0.0209 (3)	
O2	0.75556 (18)	0.37252 (13)	0.27913 (13)	0.0208 (3)	
O3	0.80235 (18)	0.42568 (13)	0.05066 (12)	0.0208 (3)	
O4	1.23166 (19)	0.41015 (14)	0.13108 (14)	0.0209 (3)	
O5	1.20389 (18)	0.37077 (13)	0.35944 (13)	0.0204 (3)	
O6	1.36080 (17)	0.56986 (13)	0.29441 (13)	0.0199 (3)	
P1	0.78594 (6)	0.47061 (4)	0.18354 (4)	0.01339 (15)	
P2	1.21301 (6)	0.47175 (4)	0.26319 (4)	0.01358 (15)	
H3	1.227 (5)	0.456 (3)	0.079 (3)	0.051 (10)*	
H4	0.562 (5)	0.568 (3)	0.208 (3)	0.049 (10)*	
H5	0.5658 (17)	0.698 (3)	0.554 (3)	0.018 (7)*	0.75
H6	0.386 (4)	0.673 (3)	0.587 (2)	0.018 (7)*	0.75
H7	0.426 (4)	0.663 (2)	0.4485 (15)	0.013 (7)*	0.75
H8	0.422 (5)	0.7827 (13)	0.509 (4)	0.038 (10)*	0.75

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0145 (7)	0.0114 (7)	0.0138 (7)	-0.0006 (6)	0.0032 (6)	0.0007 (6)
C2	0.0254 (9)	0.0214 (9)	0.0164 (8)	0.0030 (7)	0.0042 (7)	-0.0040 (7)
N1	0.0165 (7)	0.0123 (7)	0.0173 (7)	-0.0002 (5)	0.0040 (5)	0.0017 (5)
O1W	0.0356 (9)	0.0393 (10)	0.0331 (9)	0.0008 (8)	0.0010 (7)	-0.0001 (7)
O1	0.0155 (6)	0.0200 (7)	0.0283 (7)	0.0043 (5)	0.0073 (5)	0.0065 (5)
O2	0.0210 (6)	0.0164 (6)	0.0261 (7)	0.0001 (5)	0.0068 (5)	0.0073 (5)
O3	0.0217 (6)	0.0236 (7)	0.0169 (6)	-0.0005 (5)	0.0022 (5)	-0.0037 (5)
O4	0.0248 (7)	0.0184 (7)	0.0201 (7)	0.0019 (5)	0.0051 (5)	-0.0036 (5)
O5	0.0191 (6)	0.0189 (6)	0.0227 (7)	0.0010 (5)	0.0005 (5)	0.0066 (5)
O6	0.0148 (6)	0.0193 (6)	0.0259 (7)	-0.0038 (5)	0.0037 (5)	-0.0049 (5)
P1	0.0127 (2)	0.0124 (2)	0.0152 (2)	-0.00029 (15)	0.00251 (16)	0.00126 (15)
P2	0.0123 (2)	0.0125 (2)	0.0158 (2)	0.00017 (15)	0.00167 (16)	0.00006 (15)

*Geometric parameters (Å, °)*

C1—N1	1.512 (2)	O1W—H6	0.896 (10)
C1—C2	1.531 (2)	O1W—H7	0.900 (10)
C1—P1	1.8479 (17)	O1W—H8	0.888 (10)
C1—P2	1.8505 (17)	O1—P1	1.5666 (14)
C2—H2A	0.9600	O1—H4	0.71 (3)
C2—H2B	0.9600	O2—P1	1.4940 (13)
C2—H2C	0.9600	O3—P1	1.5093 (13)
N1—H1A	0.8900	O4—P2	1.5706 (14)
N1—H1B	0.8900	O4—H3	0.73 (4)
N1—H1C	0.8900	O5—P2	1.4914 (13)
O1W—H5	0.893 (10)	O6—P2	1.5106 (13)

N1—C1—C2	106.82 (14)	H5—O1W—H7	109 (3)
N1—C1—P1	108.51 (11)	H6—O1W—H7	118 (3)
C2—C1—P1	108.82 (12)	H5—O1W—H8	106 (3)
N1—C1—P2	106.91 (11)	H6—O1W—H8	111 (3)
C2—C1—P2	109.54 (12)	H7—O1W—H8	106 (3)
P1—C1—P2	115.87 (9)	P1—O1—H4	116 (3)
C1—C2—H2A	109.5	P2—O4—H3	113 (3)
C1—C2—H2B	109.5	O2—P1—O3	116.77 (8)
H2A—C2—H2B	109.5	O2—P1—O1	113.10 (8)
C1—C2—H2C	109.5	O3—P1—O1	107.04 (8)
H2A—C2—H2C	109.5	O2—P1—C1	109.10 (8)
H2B—C2—H2C	109.5	O3—P1—C1	108.44 (8)
C1—N1—H1A	109.5	O1—P1—C1	101.18 (8)
C1—N1—H1B	109.5	O5—P2—O6	116.47 (8)
H1A—N1—H1B	109.5	O5—P2—O4	109.10 (8)
C1—N1—H1C	109.5	O6—P2—O4	109.82 (8)
H1A—N1—H1C	109.5	O5—P2—C1	109.54 (8)
H1B—N1—H1C	109.5	O6—P2—C1	104.71 (8)
H5—O1W—H6	107 (3)	O4—P2—C1	106.71 (8)
N1—C1—P1—O2	-176.13 (11)	N1—C1—P2—O5	177.18 (11)
C2—C1—P1—O2	-60.25 (14)	C2—C1—P2—O5	61.79 (14)
P2—C1—P1—O2	63.66 (11)	P1—C1—P2—O5	-61.75 (11)
N1—C1—P1—O3	55.70 (13)	N1—C1—P2—O6	51.57 (12)
C2—C1—P1—O3	171.58 (12)	C2—C1—P2—O6	-63.82 (13)
P2—C1—P1—O3	-64.51 (11)	P1—C1—P2—O6	172.64 (9)
N1—C1—P1—O1	-56.68 (12)	N1—C1—P2—O4	-64.85 (12)
C2—C1—P1—O1	59.20 (13)	C2—C1—P2—O4	179.76 (12)
P2—C1—P1—O1	-176.89 (9)	P1—C1—P2—O4	56.22 (11)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1C $\cdots$ O2 <sup>i</sup>	0.89	1.98	2.809 (2)	155
N1—H1A $\cdots$ O5 <sup>i</sup>	0.89	1.90	2.713 (2)	151
N1—H1B $\cdots$ O3 <sup>ii</sup>	0.89	2.01	2.824 (2)	152
O4—H3 $\cdots$ O3 <sup>ii</sup>	0.73 (4)	1.86 (4)	2.591 (2)	176 (4)
O1—H4 $\cdots$ O6 <sup>iii</sup>	0.71 (3)	1.84 (3)	2.550 (2)	172 (4)
O1W—H5 $\cdots$ O5 <sup>iv</sup>	0.89 (1)	1.95 (2)	2.804 (2)	159 (3)
O1W—H8 $\cdots$ O1 <sup>v</sup>	0.89 (1)	2.64 (4)	3.061 (2)	110 (3)
O1W—H8 $\cdots$ O3 <sup>vi</sup>	0.89 (1)	2.27 (2)	3.041 (2)	145 (3)
O1W—H6 $\cdots$ O2 <sup>vii</sup>	0.90 (1)	1.94 (1)	2.828 (2)	175 (3)
O1W—H7 $\cdots$ O6 <sup>iii</sup>	0.90 (1)	1.92 (1)	2.815 (2)	173 (3)

Symmetry codes: (i)  $-x+2, y+1/2, -z+1/2$ ; (ii)  $-x+2, -y+1, -z$ ; (iii)  $x-1, y, z$ ; (iv)  $-x+2, -y+1, -z+1$ ; (v)  $x, -y+3/2, z+1/2$ ; (vi)  $-x+1, y+1/2, -z+1/2$ ; (vii)  $-x+1, -y+1, -z+1$ .