

## Piperizinium hydrogen phosphite monohydrate

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## Key indicators

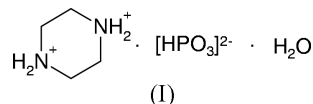
Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.042  
 $wR$  factor = 0.131  
Data-to-parameter ratio = 24.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_6\text{H}_{12}\text{N}_2^{2+} \cdot \text{HPO}_3^{2-} \cdot \text{H}_2\text{O}$ , contains doubly protonated piperizinium cations, hydrogen phosphite anions and water molecules. The component species have normal geometrical parameters and interact by way of  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds, resulting in [010] chains of alternating  $[\text{HPO}_3]^{2-}$  and  $\text{H}_2\text{O}$  species, crosslinked by the organic moieties. A possible  $\text{C}-\text{H} \cdots \text{O}$  interaction is also present.

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## Comment

The crystal structures of (protonated) amine hydrogen phosphites containing  $[\text{HPO}_3]^{2-}$  or  $[\text{H}_2\text{PO}_3]^-$  oxo-anions are of crystallochemical interest in terms of the interplay between the hydrogen bonds linking the cations, anions, and, if applicable, water molecules together (Averbuch-Pouchot, 1993*a,b*; Harrison, 2003*a,b*).



The asymmetric unit of the title compound, (I), consists of two half-molecule  $\{\text{C}_2\text{H}_6\text{N}\}$  fragments of  $(\text{C}_4\text{H}_{12}\text{N}_2)^{2+}$  piperizinium cations, an  $[\text{HPO}_3]^{2-}$  hydrogen phosphite group and a water molecule. Inversion symmetry (Fig. 1) generates the two complete piperizinium cations, and the water O atom is disordered over two adjacent sites (see *Experimental*). The

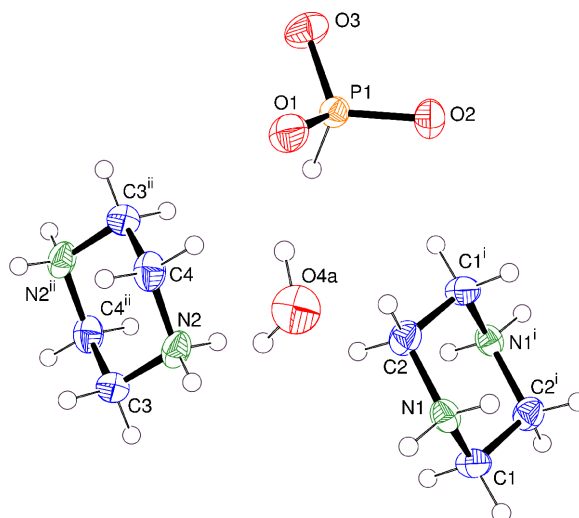
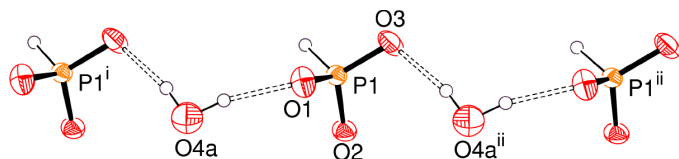
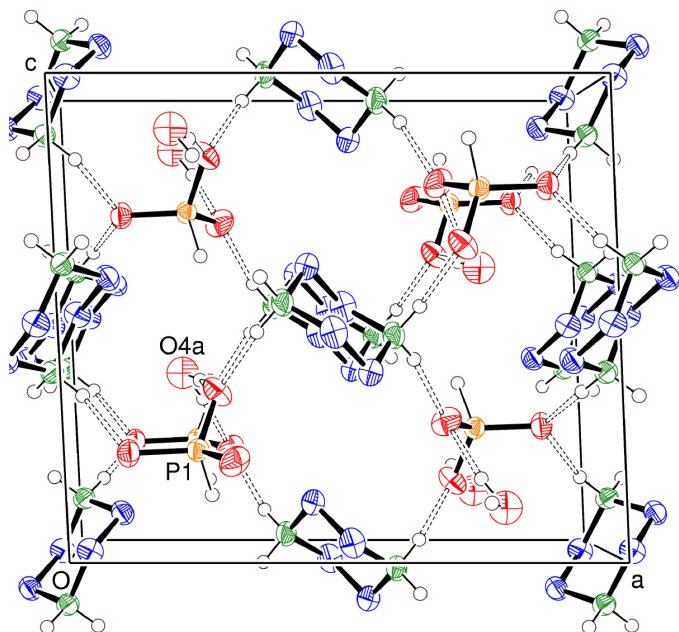


Figure 1

View of (I) (50% displacement ellipsoids; H atoms are drawn as small spheres of arbitrary radius). The disordered O4*b* species is omitted. Symmetry codes: (i)  $-x, 1 - y, -z$ ; (ii)  $1 - x, 1 - y, -z$ .



**Figure 2**  
Detail of a [010] hydrogen phosphite-water chain with the H...O components of the hydrogen bonds indicated by dashed lines (atom O4b not shown). Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $x, y - 1, z$ .



**Figure 3**  
Unit-cell packing in (I) projected onto (010). The H...O components of the hydrogen bonds are indicated by dashed lines. O4b and all C-H H atoms are omitted for clarity.

hydrogen phosphite group shows its usual (Harrison, 2003a) pseudo-pyramidal geometry [mean  $d(\text{P}-\text{O}) = 1.521(2) \text{ \AA}$ ; mean  $\theta(\text{O}-\text{P}-\text{O}) = 112.48(9)^\circ$ ] and the organic species adopt typical chair conformations.

As well as electrostatic forces, the component species in (I) interact by means of O-H...O and N-H...O hydrogen bonds (Table 2), and possibly a C-H...O interaction (see below). Infinite chains of alternating  $[\text{HPO}_3]^{2-}$  and  $\text{H}_2\text{O}$  moieties are formed (Fig. 2) along [010] as a result of the water-to-phosphite O-H...O hydrogen bonds, with the repeating units generated by translation symmetry. The resulting  $\text{P1}\cdots\text{P1}^{\text{iii}}$  (Fig. 2; see Table 2 for symmetry code) separation of  $6.5706(7) \text{ \AA}$  is naturally much larger than the typical P...P separations ( $4.7\text{--}4.9 \text{ \AA}$ ) seen when  $[\text{H}_2\text{PO}_3]^-$  dihydrogen phosphite units link together by way of P-O-H...O-P interactions without an intervening water molecule (Averbuch-Pouchot, 1993a, Harrison, 2003a).

The piperizinium cations crosslink the [010]  $[\text{HPO}_3]^{2-}\text{-H}_2\text{O}$  chains by way of the N-H...O hydrogen bonds (Table 2), with all four bonds close to linear [mean  $\theta(\text{N}-\text{H}\cdots\text{O}) = 168^\circ$ ]. A short  $\text{C1}-\text{H5}\cdots\text{O4a}^{\text{iv}}$  (Table 2) interaction was identified in a PLATON (Spek, 2003) analysis of (I). If it is not merely a packing artefact, it may provide some additional coherence

between the piperizinium cations and the water component of the  $[\text{HPO}_3]^{2-}\text{-H}_2\text{O}$  [010] chains, although its role, if any, in the disordering of the water molecule O4 atom is not obvious.

## Experimental

$\text{H}_3\text{PO}_3$  (0.82 g; 1 mmol) and piperazine hexahydrate (1.92 g; 0.01 mmol) were dissolved in 10 ml deionized water, resulting in a clear solution. Block-shaped crystals of (I) grew as the water evaporated over several days.

### Crystal data

$\text{C}_6\text{H}_{12}\text{N}_2^{2+}\cdot\text{HPO}_3^{2-}\cdot\text{H}_2\text{O}$   
 $M_r = 186.15$   
Monoclinic,  $P2_1/c$   
 $a = 12.2476(8) \text{ \AA}$   
 $b = 6.5706(4) \text{ \AA}$   
 $c = 10.6592(8) \text{ \AA}$   
 $\beta = 92.744(1)^\circ$   
 $V = 856.8(1) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.443 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 2470 reflections  
 $\theta = 3.3\text{--}29.8^\circ$   
 $\mu = 0.30 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
Block, colourless  
 $0.27 \times 0.23 \times 0.19 \text{ mm}$

### Data collection

Bruker SMART1000 CCD diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1999)  
 $T_{\text{min}} = 0.925, T_{\text{max}} = 0.949$   
6211 measured reflections

2468 independent reflections  
1930 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -17 \rightarrow 16$   
 $k = -8 \rightarrow 9$   
 $l = -14 \rightarrow 12$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.131$   
 $S = 1.02$   
2468 reflections  
100 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0845P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

**Table 1**

Selected bond lengths ( $\text{\AA}$ ) for (I).

P1—O3	1.5151 (13)	P1—O1	1.5234 (14)
P1—O2	1.5230 (12)		

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ ) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H2...O2 <sup>i</sup>	0.90	1.84	2.7147 (19)	164
N1—H3...O2 <sup>ii</sup>	0.90	1.81	2.7043 (19)	172
N2—H8...O3 <sup>iii</sup>	0.90	1.77	2.642 (2)	163
N2—H9...O1 <sup>iii</sup>	0.90	1.78	2.676 (2)	171
O4a—H14...O1	0.95	1.90	2.840 (4)	167
O4a—H15...O3 <sup>iii</sup>	0.93	1.90	2.811 (4)	168
O4b—H14...O1	0.93	1.90	2.752 (4)	151
O4b—H15...O3 <sup>iii</sup>	0.96	1.90	2.765 (4)	149
C1—H5...O4a <sup>iv</sup>	0.97	2.38	3.300 (5)	159

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

The water O atom was modelled as being disordered over two adjacent sites with isotropic displacement factors [ $d(\text{O4a}\cdots\text{O4b}) = 0.638(5) \text{ \AA}$ ; fractional site occupancies = 0.563 (14) and 0.437 (14) for O4a and O4b, respectively, with their sum constrained to unity]. The present data did not reveal H-atom sites that could be unambiguously associated with either O4a or O4b; instead, two distinct features in

the difference map provided H-atom sites that were reasonable for both O4a and O4b (see Table 2). These O—H H atoms were refined by riding on O4a in their as-found positions. The N—H H atoms were found in difference maps and refined by riding in their idealized positions [ $d(\text{N—H}) = 0.90 \text{ \AA}$ ]. The H atoms bonded to C and P were placed in calculated positions [ $d(\text{C—H}) = 0.97 \text{ \AA}$ ;  $d(\text{P—H}) = 1.32 \text{ \AA}$ ] and refined by riding. For all H atoms, the constraint  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$  was applied.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *ORTEP-3* (Farrugia,

1997); software used to prepare material for publication: *SHELXL97*.

## References

- Averbuch-Pouchot, M. T. (1993a) *Acta Cryst.* **C49**, 813–815.  
Averbuch-Pouchot, M. T. (1993b) *Acta Cryst.* **C49**, 815–818.  
Bruker (1999). *SMART* (Version 5.624), *SAINTE-Plus* (Version 6.02A) and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565–565.  
Harrison, W. T. A. (2003a) *Acta Cryst.* **E59**, o769–o770.  
Harrison, W. T. A. (2003b) *Acta Cryst.* **E59**, o1267–o1269.  
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

## supporting information

*Acta Cryst.* (2004). E60, o1577–o1579 [https://doi.org/10.1107/S1600536804020185]

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(I)

*Crystal data*

$(C_6H_{12}N_2)^{2+} \cdot [HPO_3]^{2-} \cdot H_2O$

$M_r = 186.15$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 12.2476$  (8) Å

$b = 6.5706$  (4) Å

$c = 10.6592$  (8) Å

$\beta = 92.744$  (1)°

$V = 856.8$  (1) Å<sup>3</sup>

$Z = 4$

$F(000) = 400$

$D_x = 1.443$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2470 reflections

$\theta = 3.3$ – $29.8^\circ$

$\mu = 0.30$  mm<sup>-1</sup>

$T = 293$  K

Block, colourless

$0.27 \times 0.23 \times 0.19$  mm

*Data collection*

Bruker SMART1000 CCD  
diffractometer

Radiation source: normal-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 1999)

$T_{\min} = 0.925$ ,  $T_{\max} = 0.949$

6211 measured reflections

2468 independent reflections

1930 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 30.0^\circ$ ,  $\theta_{\min} = 3.3^\circ$

$h = -17 \rightarrow 16$

$k = -8 \rightarrow 9$

$l = -14 \rightarrow 12$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.131$

$S = 1.02$

2468 reflections

100 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difmap (O-H and N-H)  
and geom (C-H and P-H)

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.78$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.44$  e Å<sup>-3</sup>

*Special details*

**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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
P1	0.23916 (3)	-0.02316 (6)	0.23270 (4)	0.02544 (15)	
H1	0.2609	0.0944	0.1366	0.031*	
O1	0.27883 (11)	0.0919 (2)	0.35030 (14)	0.0398 (3)	
O2	0.11571 (10)	-0.0529 (2)	0.22692 (13)	0.0335 (3)	
O3	0.30154 (11)	-0.2194 (2)	0.21505 (14)	0.0420 (4)	
N1	0.01729 (11)	0.6267 (2)	0.10922 (13)	0.0272 (3)	
H2	-0.0364	0.5840	0.1576	0.033*	
H3	0.0549	0.7250	0.1512	0.033*	
C1	-0.03148 (15)	0.7113 (3)	-0.01021 (17)	0.0318 (4)	
H4	0.0258	0.7674	-0.0596	0.038*	
H5	-0.0817	0.8203	0.0082	0.038*	
C2	0.09189 (15)	0.4532 (3)	0.08474 (18)	0.0321 (4)	
H6	0.1205	0.3975	0.1639	0.039*	
H7	0.1530	0.5012	0.0383	0.039*	
N2	0.39969 (11)	0.5910 (2)	0.03315 (15)	0.0339 (4)	
H8	0.3613	0.6719	0.0831	0.041*	
H9	0.3531	0.5391	-0.0264	0.041*	
C3	0.48414 (15)	0.7131 (3)	-0.0271 (2)	0.0377 (4)	
H10	0.5317	0.7769	0.0368	0.045*	
H11	0.4496	0.8195	-0.0780	0.045*	
C4	0.44956 (15)	0.4235 (3)	0.10849 (19)	0.0372 (4)	
H12	0.3926	0.3446	0.1458	0.045*	
H13	0.4964	0.4794	0.1759	0.045*	
O4A	0.2172 (5)	0.5036 (5)	0.3865 (3)	0.0557 (14)*	0.563 (14)
H14	0.2488	0.3733	0.3721	0.067*	
H15	0.2536	0.5828	0.3296	0.067*	
O4B	0.2678 (6)	0.5011 (6)	0.4032 (4)	0.0507 (17)*	0.437 (14)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
P1	0.0236 (2)	0.0260 (2)	0.0267 (2)	0.00143 (15)	0.00188 (16)	0.00038 (16)
O1	0.0408 (7)	0.0355 (7)	0.0416 (8)	0.0016 (6)	-0.0139 (6)	-0.0054 (6)
O2	0.0250 (6)	0.0369 (7)	0.0388 (7)	-0.0022 (5)	0.0023 (5)	-0.0088 (5)
O3	0.0453 (8)	0.0385 (8)	0.0431 (8)	0.0168 (6)	0.0109 (6)	-0.0020 (6)
N1	0.0276 (7)	0.0276 (7)	0.0264 (7)	-0.0051 (5)	0.0022 (5)	-0.0039 (5)
C1	0.0364 (8)	0.0248 (8)	0.0339 (9)	0.0031 (7)	-0.0010 (7)	0.0004 (7)
C2	0.0282 (8)	0.0357 (9)	0.0319 (9)	0.0025 (7)	-0.0033 (7)	-0.0021 (7)
N2	0.0235 (7)	0.0417 (9)	0.0365 (8)	0.0052 (6)	0.0004 (6)	-0.0117 (7)
C3	0.0351 (9)	0.0280 (9)	0.0496 (11)	0.0007 (7)	-0.0025 (8)	-0.0020 (8)

C4	0.0293 (8)	0.0467 (11)	0.0357 (10)	-0.0037 (7)	0.0035 (7)	0.0015 (8)
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*Geometric parameters (Å, °)*

P1—O3	1.5151 (13)	N2—C3	1.479 (2)
P1—O2	1.5230 (12)	N2—H8	0.9000
P1—O1	1.5234 (14)	N2—H9	0.9000
P1—H1	1.3200	C3—C4 <sup>ii</sup>	1.512 (3)
N1—C1	1.488 (2)	C3—H10	0.9700
N1—C2	1.492 (2)	C3—H11	0.9700
N1—H2	0.9000	C4—C3 <sup>ii</sup>	1.512 (3)
N1—H3	0.9000	C4—H12	0.9700
C1—C2 <sup>i</sup>	1.513 (2)	C4—H13	0.9700
C1—H4	0.9700	O4A—O4B	0.638 (5)
C1—H5	0.9700	O4A—H14	0.9549
C2—C1 <sup>i</sup>	1.513 (2)	O4A—H15	0.9296
C2—H6	0.9700	O4B—H14	0.9285
C2—H7	0.9700	O4B—H15	0.9594
N2—C4	1.477 (3)		
O3—P1—O2	113.03 (8)	C4—N2—C3	111.13 (14)
O3—P1—O1	112.44 (8)	C4—N2—H8	109.4
O2—P1—O1	111.96 (8)	C3—N2—H8	109.4
O3—P1—H1	106.3	C4—N2—H9	109.4
O2—P1—H1	106.3	C3—N2—H9	109.4
O1—P1—H1	106.3	H8—N2—H9	108.0
C1—N1—C2	111.10 (13)	N2—C3—C4 <sup>ii</sup>	109.44 (15)
C1—N1—H2	109.4	N2—C3—H10	109.8
C2—N1—H2	109.4	C4 <sup>ii</sup> —C3—H10	109.8
C1—N1—H3	109.4	N2—C3—H11	109.8
C2—N1—H3	109.4	C4 <sup>ii</sup> —C3—H11	109.8
H2—N1—H3	108.0	H10—C3—H11	108.2
N1—C1—C2 <sup>i</sup>	110.40 (14)	N2—C4—C3 <sup>ii</sup>	110.48 (16)
N1—C1—H4	109.6	N2—C4—H12	109.6
C2 <sup>i</sup> —C1—H4	109.6	C3 <sup>ii</sup> —C4—H12	109.6
N1—C1—H5	109.6	N2—C4—H13	109.6
C2 <sup>i</sup> —C1—H5	109.6	C3 <sup>ii</sup> —C4—H13	109.6
H4—C1—H5	108.1	H12—C4—H13	108.1
N1—C2—C1 <sup>i</sup>	110.45 (14)	O4B—O4A—H14	68.0
N1—C2—H6	109.6	O4B—O4A—H15	72.8
C1 <sup>i</sup> —C2—H6	109.6	H14—O4A—H15	100.7
N1—C2—H7	109.6	O4A—O4B—H14	72.5
C1 <sup>i</sup> —C2—H7	109.6	O4A—O4B—H15	67.8
H6—C2—H7	108.1	H14—O4B—H15	100.5

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

*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>
N1—H2 $\cdots$ O2 <sup>iii</sup>	0.90	1.84	2.7147 (19)	164
N1—H3 $\cdots$ O2 <sup>iv</sup>	0.90	1.81	2.7043 (19)	172
N2—H8 $\cdots$ O3 <sup>iv</sup>	0.90	1.77	2.642 (2)	163
N2—H9 $\cdots$ O1 <sup>v</sup>	0.90	1.78	2.676 (2)	171
O4 <i>A</i> —H14 $\cdots$ O1	0.95	1.90	2.840 (4)	167
O4 <i>A</i> —H15 $\cdots$ O3 <sup>iv</sup>	0.93	1.90	2.811 (4)	168
O4 <i>B</i> —H14 $\cdots$ O1	0.93	1.90	2.752 (4)	151
O4 <i>B</i> —H15 $\cdots$ O3 <sup>iv</sup>	0.96	1.90	2.765 (4)	149
C1—H5 $\cdots$ O4 <i>A</i> <sup>iii</sup>	0.97	2.38	3.300 (5)	159

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