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Bis(3-carbamoylpyridin-1-ium) phosphite mono- hydrate

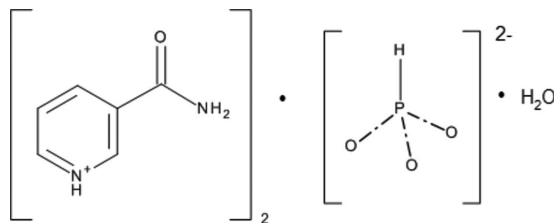
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Two of the constituent molecules in the title structure, $2\text{C}_6\text{H}_7\text{N}_2\text{O}^+\cdot\text{HPO}_3^{2-}\cdot\text{H}_2\text{O}$, *i.e.* the phosphite anion and the water molecule, are situated on a symmetry plane. The molecules are held together by moderate $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$, and weak $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}_{\text{carbonyl}}$ hydrogen bonds in which the amide and secondary amine groups, and the water molecules are involved. The structural features are usual, among them the H atom bonded to the P atom avoids hydrogen bonding.

1. Chemical context

Nicotinamide (pyridine-2-carboxamide) is a biologically important molecule, being the active part of vitamin B3 and nicotinamide adenine dinucleotide (NAD) (*e.g.* Wald, 1991; Williamson *et al.*, 1967).

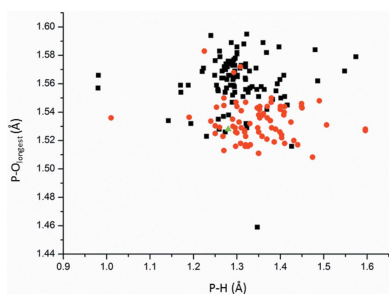


However, interest in the preparation of the title hydrated salt was called for with respect to an investigation of the configuration of the $-\text{NH}_2$ group and its dependence on its environment.

It was hoped that 3-carbamoylpyridine (nicotinamide) would make a salt or a co-crystal with phosphorous acid, H_3PO_3 . It is difficult to predict which of these two forms would be preferred, because of a small difference of $\Delta\text{p}K_a = \text{p}K_a(\text{base}) - \text{p}K_a(\text{acid})$ (Childs *et al.*, 2007). [The $\text{p}K_a$ values for 3-carbamoylpyridine and H_3PO_3 are 3.3 and 1.3 (first degree), respectively (CRC Handbook, 2009).]

2. Structural commentary

The title molecules are shown in Fig. 1. The resulting structure turned out to be a monohydrated salt. Table 1 lists the hydrogen bonds, which are shown in Fig. 2. The secondary amine hydrogen H1n1 is involved in the strongest hydrogen bond present in the structure ($\text{N1}-\text{H1n1}\cdots\text{O3}^i$). Its parameters indicate that this hydrogen bond is situated on the boundary between strong and moderate hydrogen bonds (Gilli & Gilli, 2009). The amide hydrogen H1n2 is donated to the water oxygen, while H2n2 is donated to atom O3 of the phosphite anion. Atom O2 is an acceptor of water hydrogen H1ow. Water hydrogen H2ow is donated to a pair of O3



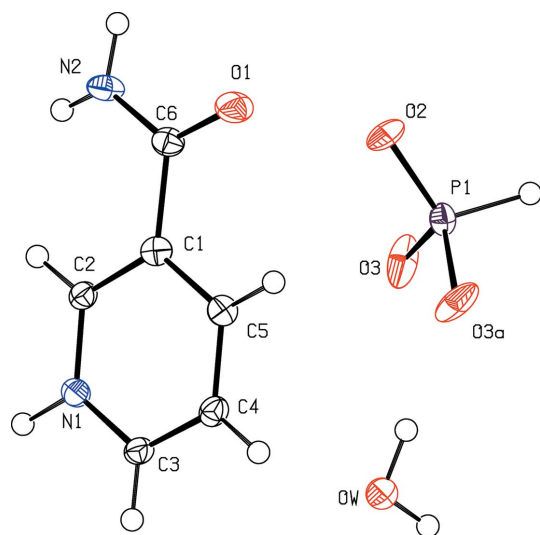


Figure 1
The title molecule, with anisotropic atomic displacement ellipsoids shown at the 50% probability level (*PLATON*; Spek, 2009).

atoms. The carbonyl oxygen O1 is an acceptor of two weak C–H···O hydrogen bonds, namely C3–H1c3···O1ⁱⁱ and C4–H1c4···O1ⁱⁱⁱ. The water oxygen atom is also an acceptor of hydrogen H1c2 (see Table 1).

Phosphite and fluorophosphonate, as well hydrogen phosphite and hydrogen fluorophosphonate, are similar molecules. Either molecule can be involved, not only in isostructural compounds, but even in mixed crystals (Fábry *et al.*, 2012). Similarity regarding not only the shape of the molecules but also the avoidance both of P-bonded fluorines and hydrogens of involvement in strong or moderate hydrogen bonds (Matulková *et al.*, 2017). The latter article shows a plot of the

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

D–H···A	D–H	H···A	D···A	D–H···A
C2–H1c2···Ow ⁱ	0.95	2.64	3.5777 (14)	168
C3–H1c3···O1 ⁱⁱ	0.95	2.56	3.4790 (17)	164
C4–H1c4···O1 ⁱⁱⁱ	0.95	2.56	3.1948 (13)	125
N1–H1n1···O3 ^{iv}	1.053 (15)	1.455 (15)	2.508 (3)	178.1 (14)
N2–H1n2···Ow ⁱ	0.849 (16)	2.140 (16)	2.9513 (13)	159.8 (18)
N2–H2n2···O3 ^v	0.889 (18)	1.955 (18)	2.823 (3)	165.2 (15)
Ow–H1ow···O2 ^{vi}	0.84 (2)	1.82 (2)	2.657 (4)	172 (2)
Ow–H2ow···O3	0.96 (3)	2.42 (2)	3.263 (3)	146.8 (9)
Ow–H2ow···O3 ^{vii}	0.96 (3)	2.42 (2)	3.263 (3)	146.8 (9)

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

dependence of P–F distance on the longest P–O distance in fluorphosphonate and hydrogen fluorphosphonate molecules. The P–F distance tends to be longer in $[\text{FPO}_3]^{2-}$ than in $[\text{HFPO}_3]^-$. Fig. 3 shows a similar plot for the phosphites and hydrogen phosphites between both molecules despite the larger spread of P–H distances in phosphite molecules because of the lower accuracy of the H-atom determinations by X-ray diffraction experiments. The reason why the P–H bond tends to be longer follows from the conservation of the overall bond valence sum of the central P⁵⁺ or P³⁺ atom. It is worth pointing out that the tabulated value of the bond valence parameter for the P–H bond seems to yield too high values. For example, for the important values of the P–H distances, *i.e.* 1.28, 1.33 and 1.37 Å (*cf.* Fig. 3), the bond valences (Bresle & O’Keeffe, 1991) are 1.42, 1.24 and 1.11, respectively. The P–H bond valence parameters are going to be checked as part of future work.

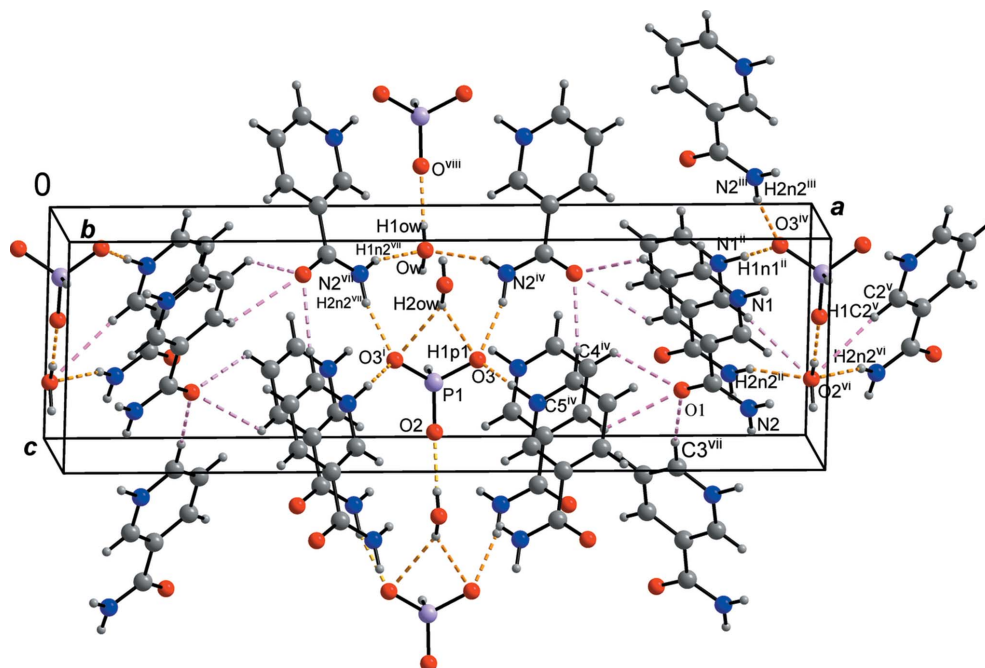


Figure 2
View of the title structure. C, H, N, O and P atoms are represented by gray, small gray, blue, red and violet circles, respectively. [Symmetry codes: (i) $-x + 1, y, z$; (ii) $x, y - 1, z$; (iii) $x, y - 1, z$; (iv) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (v) $-x + 2, y - 1, z$; (vi) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (vii) $x - \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (viii) $x, y - 1, z - 1$.] The hydrogen bonds are shown as yellow dashed lines (*DIAMOND*; Brandenburg & Putz, 2005).

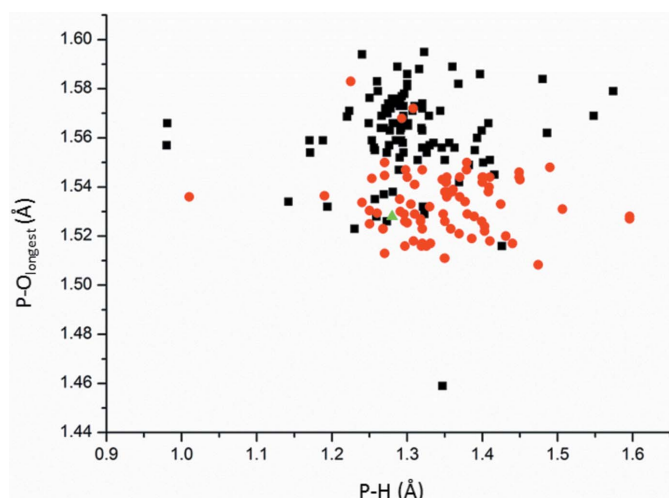


Figure 3
The dependence of the longest P–O distance (Å) on the P–H distance (Å) in hydrogen phosphites (red circles); phosphites are represented by black squares and the title phosphite structure by a green triangle.

The C–NH₂ group tends to be fairly planar for short C–N bonds (Fábry *et al.*, 2014). In agreement with a short C–N bond length [C6–N2 = 1.3232 (18) Å] in the title structure, the best plane through C6/N2/H1n2/H2n2 reveals a maximum deviation of about 0.05 (2) Å for each hydrogen, while $\xi^2 = 12.6$.

3. Supramolecular features

In the crystal, the most important graph-set motif (Etter *et al.*, 1990) present is an $R_4^3(10)$ ring motif, which is composed of atoms P1–O3^{iv}··H2n2^{iv}–N2^{iv}–H1n2^{iv}··Ow··H1n2^{vii}–N2^{vii}–H2n2^{vii}··O3ⁱ (Table 1 and Fig. 2; symmetry codes are given in the figure caption). The phosphite anion and the water molecule are linked by O_{water}–H··O_{phosphite} hydrogen bonds, forming chains propagating along [001]. The cations are linked to these chains *via* N–H··O hydrogen bonds, forming layers parallel to the *bc* plane, as shown in Fig. 2. The layers are linked by C–H··O hydrogen bonds, resulting in the formation of a supramolecular three-dimensional structure.

4. Database survey

The applied crystallographic databases were the Cambridge Crystallographic Database (Version 5.39, with updates to May 2018; Groom *et al.*, 2016) and the Inorganic Crystal Structure Database (June 2018; ICSD, 2018). The search was carried out for all phosphites or hydrogen phosphites with a cation of one kind.

5. Synthesis and crystallization

The title structure was prepared by slow evaporation of a water solution (18 ml) of equimolar amounts of nicotinamide (1.49 g) and phosphorous acid (1 g). Colourless crystals were isolated after two months.

Table 2
Experimental details.

Crystal data	
Chemical formula	2C ₆ H ₇ N ₂ O ⁺ ·HPO ₃ ²⁻ ·H ₂ O
<i>M_r</i>	344.3
Crystal system, space group	Orthorhombic, <i>Pmn</i> 2 ₁
Temperature (K)	95
<i>a</i> , <i>b</i> , <i>c</i> (Å)	22.9297 (4), 4.5910 (1), 7.0900 (1)
<i>V</i> (Å ³)	746.37 (2)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	2.01
Crystal size (mm)	0.45 × 0.16 × 0.06
Data collection	
Diffractometer	Rigaku OD SuperNova Dual source diffractometer with an AtlasS2 detector
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2017)
<i>T</i> _{min} , <i>T</i> _{max}	0.599, 0.831
No. of measured, independent and observed [<i>I</i> > 3σ(<i>I</i>)] reflections	10796, 1592, 1588
<i>R</i> _{int}	0.021
(sin θ/λ) _{max} (Å ⁻¹)	0.630
Refinement	
<i>R</i> [<i>F</i> > 3σ(<i>F</i>)], <i>wR</i> (<i>F</i>), <i>S</i>	0.019, 0.054, 2.21
No. of reflections	1592
No. of parameters	181
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.14, -0.15
Absolute structure	Since the Flack parameter turned out to equal to 0.012(13) in the final stage of refinement it was set to 0. 726 Friedel pairs used in the refinement.
Absolute structure parameter	0.0

Computer programs: *CrysAlis PRO* (Rigaku OD, 2017), *SIR2014* (Burla *et al.*, 2015), *JANA2006* (Petříček *et al.*, 2014), *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg & Putz, 2005).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were discernible in the difference electron-density map. The aryl H atoms were constrained by the constraints C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Water hydrogen H2ow was refined freely, while H1ow was restrained with a distance restraint of 0.84 Å with elasticity 0.02 Å (Müller, 2009), and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The hydrogens of the primary amine N2 group and the secondary amine N1 group were constrained by $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The P–H hydrogen was refined isotropically. Three reflections, *i.e.* 95 $\bar{2}$, 10,5 $\bar{2}$ and 11,5 $\bar{2}$, were discarded from the refinement because $|I(\text{obs}) - I(\text{calc})|/\sigma(I) > 20$.

Since the phosphite oxygens revealed large displacement ellipsoids, the anharmonic displacement parameters upto the fourth grade were included for atoms P1, O2 and O3. (The refinement with the harmonic approximation resulted in $R_{\text{obs}} = 0.0242$, $R_{w\text{obs}} = 0.0773$, $R_{\text{all}} = 0.0243$, $R_{w\text{all}} = 0.0774$ and $S = 3.13$, with number of parameters = 127. With application of anharmonic approximation, $R_{\text{obs}} = 0.0188$, $R_{w\text{obs}} = 0.0535$,

$R_{\text{all}} = 0.0188$, $Rw_{\text{all}} = 0.0535$ and $S = 2.21$, with number of parameters = 181. The respective values of the third- and fourth-order components of the displacement tensor are given in the CIF.)

Refinement with the assumption of the presence of inversion twinning resulted in a Flack parameter of 0.012 (13) (726 Friedel pairs used in the refinement). Therefore, the crystal was considered as single-domained in the final stage of the refinement, the results of which are presented here.

Acknowledgements

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Bis(3-carbamoylpyridin-1-ium) phosphite monohydrate

Jan Fábry

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2017); cell refinement: *CrysAlis PRO* (Rigaku OD, 2017); data reduction: *CrysAlis PRO* (Rigaku OD, 2017); program(s) used to solve structure: *SIR2014* (Burla *et al.*, 2015); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006* (Petříček *et al.*, 2014).

Bis(3-carbamoylpyridin-1-ium) phosphite monohydrate

Crystal data

$2\text{C}_6\text{H}_7\text{N}_2\text{O}^+\cdot\text{HPO}_3^{2-}\cdot\text{H}_2\text{O}$

$M_r = 344.3$

Orthorhombic, *Pmn*2₁

Hall symbol: P -2x;-2yac;2zac

$a = 22.9297$ (4) Å

$b = 4.5910$ (1) Å

$c = 7.0900$ (1) Å

$V = 746.37$ (2) Å³

$Z = 2$

$F(000) = 360$

$D_x = 1.532$ Mg m⁻³

Cu *K*α radiation, $\lambda = 1.54184$ Å

Cell parameters from 9530 reflections

$\theta = 6.5\text{--}75.9^\circ$

$\mu = 2.01$ mm⁻¹

$T = 95$ K

Plate, colourless

$0.45 \times 0.16 \times 0.06$ mm

Data collection

Rigaku OD SuperNova Dual source
diffractometer with an AtlasS2 detector

Radiation source: micro-focus sealed X-ray
tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 5.2027 pixels mm⁻¹

ω / scans

Absorption correction: multi-scan
(*CrysAlis PRO*; Rigaku OD, 2017)

$T_{\min} = 0.599$, $T_{\max} = 0.831$

10796 measured reflections

1592 independent reflections

1588 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 76.3^\circ$, $\theta_{\min} = 3.9^\circ$

$h = -28 \rightarrow 28$

$k = -5 \rightarrow 5$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

$R[F > 3\sigma(F)] = 0.019$

$wR(F) = 0.054$

$S = 2.21$

1592 reflections

181 parameters

1 restraint

22 constraints

H atoms treated by a mixture of independent
and constrained refinement

Weighting scheme based on measured s.u.'s $w =$
 $1/(\sigma^2(I) + 0.0004I^2)$

$(\Delta/\sigma)_{\max} = 0.035$

$\Delta\rho_{\max} = 0.14$ e Å⁻³

$\Delta\rho_{\min} = -0.15$ e Å⁻³

Extinction correction: B-C type 1 Lorentzian
isotropic (Becker & Coppens, 1974)

Extinction coefficient: 910 (160)

Absolute structure: Since the Flack parameter
turned out to equal to 0.012(13) in the final
stage of refinement it was set to 0. 726 Friedel
pairs used in the refinement.

Absolute structure parameter: 0.0

Special details

Refinement. This part differs from the original article by Thanigaimani *et al.* (2006). It also differs from the refinement by Thanigaimani *et al.* (2006) by a different threshold for the consideration of the observed diffractions: $F^2 > 3\sigma(F^2)$ has been used as criterion for observed diffractions by *JANA2006* which was used for the calculation of the corrected structural model.

Three diffractions 9 5 -2, 10 5 -2, 11 5 -2 were discarded from the refinement because $|I(\text{obs})-I(\text{calc})|/\sigma(I) > 20$. Since the Flack parameter turned out to equal to 0.012 (13) in the final stage of refinement it was set to 0. 726 Friedel pairs used in the refinement.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.84788 (5)	0.8441 (2)	0.47478 (18)	0.0157 (3)
C2	0.88464 (4)	1.0560 (2)	0.40131 (18)	0.0159 (3)
H1c2	0.916985	1.121048	0.473657	0.0191*
N1	0.87528 (4)	1.1699 (2)	0.23035 (17)	0.0168 (2)
H1n1	0.9056 (7)	1.320 (3)	0.175 (2)	0.0202*
C3	0.82992 (5)	1.0852 (2)	0.1232 (2)	0.0169 (3)
H1c3	0.824169	1.170176	0.002456	0.0202*
C4	0.79162 (5)	0.8751 (2)	0.1879 (2)	0.0178 (3)
H1c4	0.759552	0.814668	0.112553	0.0213*
C5	0.80087 (4)	0.7536 (2)	0.36522 (18)	0.0168 (3)
H1c5	0.77504	0.608615	0.411623	0.0201*
C6	0.85727 (5)	0.7074 (3)	0.66613 (19)	0.0173 (3)
O1	0.82199 (4)	0.52392 (19)	0.72395 (16)	0.0271 (2)
N2	0.90344 (4)	0.7930 (2)	0.76358 (18)	0.0202 (3)
H1n2	0.9281 (7)	0.917 (3)	0.724 (3)	0.0243*
H2n2	0.9105 (7)	0.698 (4)	0.871 (3)	0.0243*
P1	0.5	0.3758 (3)	0.7085 (2)	0.0181 (6)
H1p1	0.5	0.092 (5)	0.698 (4)	0.034 (6)*
O2	0.5	0.4732 (8)	0.9100 (6)	0.0287 (14)
O3	0.55414 (11)	0.4668 (5)	0.5974 (3)	0.0350 (8)
Ow	0.5	0.7861 (2)	0.22531 (19)	0.0219 (3)
H1ow	0.5	0.672 (5)	0.132 (3)	0.0328*
H2ow	0.5	0.658 (6)	0.332 (4)	0.0328*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0143 (4)	0.0170 (5)	0.0159 (5)	0.0034 (3)	0.0021 (4)	-0.0004 (4)
C2	0.0157 (4)	0.0167 (5)	0.0152 (5)	0.0009 (4)	-0.0018 (4)	-0.0008 (4)
N1	0.0174 (4)	0.0158 (4)	0.0172 (4)	0.0004 (3)	-0.0006 (4)	0.0018 (4)
C3	0.0183 (4)	0.0170 (5)	0.0153 (5)	0.0020 (4)	-0.0026 (4)	0.0000 (4)
C4	0.0163 (4)	0.0189 (5)	0.0182 (5)	0.0008 (3)	-0.0032 (4)	-0.0018 (4)
C5	0.0142 (4)	0.0177 (5)	0.0184 (5)	-0.0001 (4)	0.0019 (3)	-0.0001 (4)
C6	0.0176 (5)	0.0183 (5)	0.0161 (5)	0.0013 (4)	0.0026 (3)	0.0014 (4)
O1	0.0275 (4)	0.0331 (4)	0.0207 (4)	-0.0115 (3)	-0.0015 (4)	0.0082 (4)
N2	0.0179 (4)	0.0265 (5)	0.0162 (4)	-0.0015 (4)	-0.0011 (3)	0.0072 (4)
P1	0.0192 (11)	0.0147 (7)	0.0205 (12)	0	0	-0.0018 (8)

O2	0.038 (3)	0.040 (2)	0.008 (2)	0	0	-0.0080 (19)
O3	0.0349 (14)	0.0382 (15)	0.0318 (15)	-0.0234 (11)	0.0241 (13)	-0.0182 (12)
Ow	0.0283 (5)	0.0185 (5)	0.0188 (5)	0	0	-0.0010 (5)

Geometric parameters (Å, °)

C1—C2	1.3884 (15)	C5—H1c5	0.95
C1—C5	1.3920 (16)	C6—O1	1.2379 (15)
C1—C6	1.5103 (18)	C6—N2	1.3237 (16)
C2—H1c2	0.95	N2—H1n2	0.849 (16)
C2—N1	1.3375 (17)	N2—H2n2	0.889 (18)
N1—H1n1	1.053 (15)	H1n2—H2n2	1.50 (2)
N1—C3	1.3455 (16)	P1—H1p1	1.30 (3)
H1n1—O3 ⁱ	1.455 (15)	P1—O2	1.497 (4)
C3—H1c3	0.9501	P1—O3	1.528 (3)
C3—C4	1.3827 (15)	P1—O3 ⁱⁱ	1.528 (3)
C4—H1c4	0.95	Ow—H1ow	0.84 (2)
C4—C5	1.3917 (18)	Ow—H2ow	0.96 (3)
C2—C1—C5	118.02 (11)	C1—C5—H1c5	119.91
C2—C1—C6	122.79 (10)	C4—C5—H1c5	119.91
C5—C1—C6	119.19 (10)	C1—C6—O1	119.15 (11)
C1—C2—H1c2	119.45	C1—C6—N2	117.36 (10)
C1—C2—N1	121.10 (10)	O1—C6—N2	123.49 (13)
H1c2—C2—N1	119.45	C6—N2—H1n2	124.0 (12)
C2—N1—H1n1	119.1 (9)	C6—N2—H2n2	116.4 (11)
C2—N1—C3	121.51 (10)	H1n2—N2—H2n2	119.2 (16)
H1n1—N1—C3	119.3 (9)	H1p1—P1—O2	110.6 (13)
N1—H1n1—O3 ⁱ	178.1 (14)	H1p1—P1—O3	104.1 (7)
N1—C3—H1c3	119.82	H1p1—P1—O3 ⁱⁱ	104.1 (7)
N1—C3—C4	120.37 (12)	O2—P1—O3	114.21 (12)
H1c3—C3—C4	119.82	O2—P1—O3 ⁱⁱ	114.21 (12)
C3—C4—H1c4	120.58	O3—P1—O3 ⁱⁱ	108.64 (15)
C3—C4—C5	118.82 (11)	H1n1 ⁱⁱⁱ —O3—P1	120.3 (6)
H1c4—C4—C5	120.59	H1ow—Ow—H2ow	104 (2)
C1—C5—C4	120.18 (10)		

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

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>
C2—H1c2 \cdots Ow ⁱⁱⁱ	0.95	2.64	3.5777 (14)	167.77
C3—H1c3 \cdots O1 ^{iv}	0.95	2.56	3.4790 (17)	163.62
C4—H1c4 \cdots O1 ^v	0.95	2.56	3.1948 (13)	124.74
N1—H1n1 \cdots O3 ⁱ	1.053 (15)	1.455 (15)	2.508 (3)	178.1 (14)
N2—H1n2 \cdots Ow ⁱⁱⁱ	0.849 (16)	2.140 (16)	2.9513 (13)	159.8 (18)
N2—H2n2 \cdots O3 ^{vi}	0.889 (18)	1.955 (18)	2.823 (3)	165.2 (15)
Ow—H1ow \cdots O2 ^{vii}	0.84 (2)	1.82 (2)	2.657 (4)	172 (2)

O _w —H2 _{ow} ···O ³	0.96 (3)	2.42 (2)	3.263 (3)	146.8 (9)
O _w —H2 _{ow} ···O ³ⁱⁱ	0.96 (3)	2.42 (2)	3.263 (3)	146.8 (9)

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