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4-Carbamoylpyridinium dihydrogen phosphate

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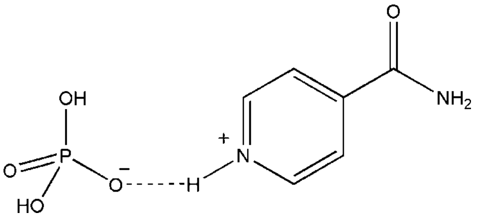
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.024; wR factor = 0.086; data-to-parameter ratio = 11.4.

The crystal structure of the title compound, $C_6H_7N_2O^+\cdot H_2PO_4^-$, indicates that the anion is connected to the cation *via* an intermolecular N—H⋯O hydrogen bond. There are other intermolecular N—H⋯O and O—H⋯O hydrogen bonds as well as weak C—H⋯O hydrogen bonds in the crystal structure.

Related literature

For related literature, see: Allen (2002); Chieh & Palenik (1971); Chippindale (2006); Gholivand & Pourayoubi (2004); Gholivand *et al.* (2005); Kortz (2000); Oh *et al.* (2006); Okabe *et al.* (1993); Pope *et al.* (2005); Steiner (2002); Szemes *et al.* (1996).



Experimental

Crystal data

$C_6H_7N_2O^+\cdot H_2PO_4^-$
M_r = 220.12
Monoclinic, Cc
a = 4.7748 (7) Å
b = 23.629 (7) Å
c = 8.340 (3) Å
β = 103.94 (3)°
V = 913.2 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 293 (2) K
0.35 × 0.25 × 0.06 mm

Data collection

STOE IPDS II diffractometer
Absorption correction: numerical (shape of crystal determined optically)
T_{min} = 0.910, T_{max} = 0.980
4586 measured reflections
1858 independent reflections
1820 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.086
S = 1.27
1858 reflections
163 parameters
2 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Absolute structure: Flack (1983), with 3363 Friedel pairs
Flack parameter: 0.14 (11)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O5^{i}	0.92 (4)	1.74 (2)	2.643 (6)	169 (2)
N2—H2A⋯O6^{ii}	0.96 (4)	1.97 (2)	2.928 (8)	177 (2)
N2—H2B⋯O2^{iii}	0.87 (5)	2.09 (2)	2.936 (7)	162 (2)
O3—H3B⋯O5^{iv}	0.81 (4)	1.83 (1)	2.628 (7)	171 (2)
O4—H4B⋯O6^{iii}	0.76 (5)	1.79 (1)	2.524 (8)	162 (2)
C3—H3A⋯O2^{v}	0.93 (3)	2.33 (1)	2.229 (7)	162 (2)
C4—H4A⋯O6^{iii}	0.88 (4)	2.33 (1)	2.158 (6)	159 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2188).

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supplementary materials

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4-Carbamoylpyridinium dihydrogen phosphate

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Comment

Research on phosphate compounds has attracted attention due to their applications as O-donor ligands in coordination chemistry (Szemes *et al.*, 1996; Kortz *et al.*, 2000; Pope *et al.*, 2005; Chippindale, 2006; Oh *et al.*, 2006). The crystal structures of two phosphate compounds (Chieh & Palenik, 1971; Okabe *et al.*, 1993) a dichlorophosphate (Gholivand & Pourayoubi, 2004) and a dioxophosphate (Gholivand *et al.*, 2005) have been reported. Recently, considerable attention has been paid to the subtle manipulation of hydrogen bonding in solid state structures (Steiner, 2002).

We have synthesized the title compound and report here its crystal structure. An *ORTEP* view of the molecular structure is presented in Fig. 1. The cation and anion are connected to each other *via* the intermolecular hydrogen bond N1—H1···O5.

In the anion, the bond lengths are P1—O3 1.571 (2), P1—O4 1.550 (2), P1—O5 1.508 (2) and P1—O6 1.498 (2) Å. These are in excellent agreement with the values found in the Cambridge Structural Database (Version of November, 2006; 313 hits; Allen, 2002): P—OH 1.550, P═O 1.504 and $P—O^-$ 1.504 Å. The coordination geometry around the phosphorus atom is slightly distorted tetrahedral. The sum of the angles around the atoms N1 and N2 are 359.5° and 358°, respectively. These results show that the nitrogen atoms deviate slightly from planarity (*i.e.* from 360.0°).

The packing diagram of the title compound (Fig. 2) shows the four cations and anions in the unit cell. Each $H_2PO_4^-$ anion is connected to other anions by intermolecular O3—H3B···O5 and O4—H4B···O6 hydrogen bonds, whereas the 4-pyridinium carboxylic acid amide cation is linked to another cation by the intermolecular N2—H2B···O2 hydrogen bond. All these hydrogen bonds, together with weak intermolecular C3—H3A···O2 and C4—-H4A···O6 hydrogen bonds produce a three dimensional polymeric chain in the crystal structure (Table 1).

Experimental

To a stirred suspension of phosphorus pentachloride (2.08 g, 10 mmol) in dry CCl_4 (35 ml), 4-pyridinecarboxylic acid amide (1.22 g, 10 mmol) was added at 298 K. The mixture was then heated at the reflux temperature (353–355 K) for 24 h. The mixture was cooled to room temperature and the reaction flask was placed in an ice bath. Formic acid (0.46 g, 10 mmol) was added dropwise to the mixture to release CO and HCl and finally to oxidize the phosphoramidate. After stirring for 24 h, a white precipitate was obtained, which was filtered and washed with H_2O (40 ml) and dried in air. The white precipitate (0.406 g, 2 mmol) was added to Hg_2Cl_2 (0.472 g,1 mmol) in hot ethanol (20 ml) to synthesize the Hg complex; however, catalytic hydrolysis of the phosphoramidate occurred. The product of this reaction was filtered and washed with ethanol (10 ml) and then recrystallized from distilled water at 298 K (yield 65%; m.p. 429–431 K).

Refinement

All H atoms were located in a difference synthesis and refined isotropically [C—H = 0.88 (4) − 0.95 (4) Å, N—H = 0.87 (5) − 0.96 (4) Å, and O—H = 0.76 (5) − 0.81 (4) Å].

Figures

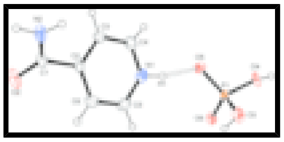

Fig. 1. *ORTEP* view of the structure of the title compound, indicating the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

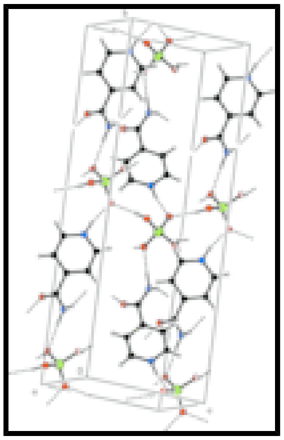

Fig. 2. A packing diagram of the crystal structure, in which the hydrogen bonds are shown as dashed lines.

4-carbamoylpyridinium dihydrogen phosphate

Crystal data

$C_6H_7N_2O^+ \cdot H_2PO_4^-$

$M_r = 220.12$

Monoclinic, *Cc*

$a = 4.7748$ (7) Å

$b = 23.629$ (7) Å

$c = 8.340$ (3) Å

$\beta = 103.94$ (3)°

$V = 913.2$ (5) Å^3

$Z = 4$

$F_{000} = 456$

$D_x = 1.601$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 2500 reflections

$\theta = 1.8$–27.9°

$\mu = 0.30$ mm^{-1}

$T = 293$ (2) K

Block, colourless

0.35 × 0.25 × 0.06 mm

Data collection

STOE IPDS II
diffractometer

rotation method scans

Absorption correction: numerical
(shape of crystal determined optically)

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 27.9$°

$\theta_{\text{min}} = 1.7$°

$T_{\min} = 0.910$, $T_{\max} = 0.980$	$h = -5\rightarrow 6$
4586 measured reflections	$k = -30\rightarrow 30$
1858 independent reflections	$l = -10\rightarrow 10$
1820 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	All H-atom parameters refined
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 0.979P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$(\Delta/\sigma)_{\max} = 0.004$
$wR(F^2) = 0.086$	$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$S = 1.27$	$\Delta\rho_{\min} = -0.26$ e Å^{-3}
1858 reflections	Extinction correction: none
163 parameters	Absolute structure: Flack (1983), 3363 Friedel pairs
2 restraints	Flack parameter: 0.14 (11)

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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.4437 (6)	0.24832 (11)	−0.4892 (4)	0.0339 (6)
C2	0.3191 (6)	0.19021 (10)	−0.4761 (3)	0.0278 (5)
C3	0.1908 (7)	0.17827 (11)	−0.3488 (4)	0.0345 (6)
H3A	0.177 (7)	0.2049 (13)	−0.269 (4)	0.027 (7)*
C4	0.0827 (7)	0.12493 (12)	−0.3384 (4)	0.0377 (6)
H4A	0.001 (8)	0.1135 (15)	−0.261 (5)	0.041 (9)*
C5	0.2227 (8)	0.09561 (12)	−0.5738 (4)	0.0423 (8)
H5	0.234 (9)	0.0650 (15)	−0.645 (5)	0.043 (9)*
C6	0.3409 (8)	0.14827 (13)	−0.5879 (4)	0.0393 (6)
H6	0.442 (10)	0.1551 (17)	−0.669 (5)	0.061 (12)*
N1	0.0962 (6)	0.08611 (10)	−0.4504 (3)	0.0359 (5)
H1	−0.003 (9)	0.0540 (19)	−0.437 (5)	0.062 (12)*
N2	0.2814 (6)	0.29148 (11)	−0.4720 (5)	0.0490 (8)
H2A	0.339 (9)	0.3298 (16)	−0.484 (5)	0.046 (9)*
H2B	0.099 (11)	0.2873 (19)	−0.475 (6)	0.067 (14)*
O2	0.6852 (6)	0.25244 (9)	−0.5158 (4)	0.0563 (8)
O3	−0.4720 (5)	−0.03277 (10)	−0.6565 (3)	0.0440 (5)
H3B	−0.377 (10)	−0.0199 (18)	−0.716 (5)	0.062 (13)*
O4	−0.5034 (5)	−0.08807 (9)	−0.4108 (3)	0.0374 (5)
H4B	−0.663 (11)	−0.0822 (18)	−0.444 (6)	0.059 (14)*

O5	−0.1924 (5)	−0.00130 (8)	−0.3746 (3)	0.0404 (5)
O6	−0.0475 (5)	−0.09051 (8)	−0.4977 (3)	0.0341 (4)
P1	−0.29004 (11)	−0.05229 (2)	−0.48238 (8)	0.02305 (15)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0295 (14)	0.0300 (13)	0.0434 (14)	−0.0039 (10)	0.0113 (11)	0.0071 (11)
C2	0.0255 (12)	0.0250 (11)	0.0342 (12)	−0.0009 (9)	0.0098 (11)	0.0037 (9)
C3	0.0448 (17)	0.0278 (12)	0.0346 (14)	−0.0012 (11)	0.0169 (13)	−0.0006 (10)
C4	0.0470 (18)	0.0334 (14)	0.0364 (14)	−0.0024 (12)	0.0170 (14)	0.0087 (11)
C5	0.060 (2)	0.0305 (14)	0.0369 (16)	−0.0009 (13)	0.0126 (16)	−0.0068 (11)
C6	0.0517 (19)	0.0347 (14)	0.0368 (15)	0.0016 (13)	0.0213 (14)	0.0007 (11)
N1	0.0416 (14)	0.0236 (10)	0.0401 (13)	−0.0055 (9)	0.0050 (11)	0.0049 (9)
N2	0.0386 (17)	0.0236 (10)	0.090 (2)	−0.0046 (8)	0.0256 (18)	0.0017 (12)
O2	0.0342 (12)	0.0442 (11)	0.097 (2)	−0.0012 (10)	0.0272 (15)	0.0221 (12)
O3	0.0345 (12)	0.0595 (13)	0.0350 (11)	−0.0087 (10)	0.0028 (9)	0.0145 (10)
O4	0.0218 (11)	0.0431 (11)	0.0477 (13)	−0.0055 (8)	0.0092 (9)	0.0164 (9)
O5	0.0518 (13)	0.0302 (9)	0.0441 (11)	−0.0118 (9)	0.0213 (10)	−0.0122 (8)
O6	0.0266 (10)	0.0308 (9)	0.0465 (12)	−0.0011 (7)	0.0116 (9)	−0.0015 (8)
P1	0.0231 (3)	0.0211 (2)	0.0264 (3)	−0.0036 (2)	0.0086 (2)	0.0005 (2)

Geometric parameters (Å, °)

C1—O2	1.230 (4)	C5—H5	0.95 (4)
C1—N2	1.310 (4)	C6—H6	0.93 (4)
C1—C2	1.511 (3)	N1—H1	0.92 (4)
C2—C3	1.376 (3)	N2—H2A	0.96 (4)
C2—C6	1.382 (4)	N2—H2B	0.87 (5)
C3—C4	1.373 (4)	O3—P1	1.571 (2)
C3—H3A	0.93 (3)	O3—H3B	0.81 (4)
C4—N1	1.322 (4)	O4—P1	1.550 (2)
C4—H4A	0.88 (4)	O4—H4B	0.76 (5)
C5—N1	1.332 (4)	O5—P1	1.5084 (19)
C5—C6	1.383 (4)	O6—P1	1.498 (2)
O2—C1—N2	124.3 (3)	C2—C6—H6	120 (3)
O2—C1—C2	119.2 (2)	C5—C6—H6	121 (3)
N2—C1—C2	116.5 (2)	C4—N1—C5	122.5 (3)
C3—C2—C6	119.6 (2)	C4—N1—H1	112 (3)
C3—C2—C1	119.9 (2)	C5—N1—H1	125 (3)
C6—C2—C1	120.5 (2)	C1—N2—H2A	122 (2)
C4—C3—C2	118.7 (2)	C1—N2—H2B	121 (3)
C4—C3—H3A	119.1 (18)	H2A—N2—H2B	115 (4)
C2—C3—H3A	122.1 (18)	P1—O3—H3B	114 (3)
N1—C4—C3	120.7 (3)	P1—O4—H4B	117 (3)
N1—C4—H4A	114 (2)	O6—P1—O5	113.46 (13)
C3—C4—H4A	125 (2)	O6—P1—O4	107.30 (11)
N1—C5—C6	119.2 (3)	O5—P1—O4	110.09 (13)

N1—C5—H5	118 (2)	O6—P1—O3	111.38 (13)
C6—C5—H5	123 (2)	O5—P1—O3	109.83 (14)
C2—C6—C5	119.3 (3)	O4—P1—O3	104.35 (13)
O2—C1—C2—C3	133.7 (3)	C2—C3—C4—N1	−1.4 (5)
N2—C1—C2—C3	−46.7 (4)	C3—C2—C6—C5	2.7 (5)
O2—C1—C2—C6	−44.2 (4)	C1—C2—C6—C5	−179.4 (3)
N2—C1—C2—C6	135.4 (3)	N1—C5—C6—C2	−1.5 (5)
C6—C2—C3—C4	−1.2 (4)	C3—C4—N1—C5	2.6 (5)
C1—C2—C3—C4	−179.2 (3)	C6—C5—N1—C4	−1.1 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5$^{\rm i}$	0.92 (4)	1.74 (2)	2.643 (6)	169 (2)
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Fig. 1

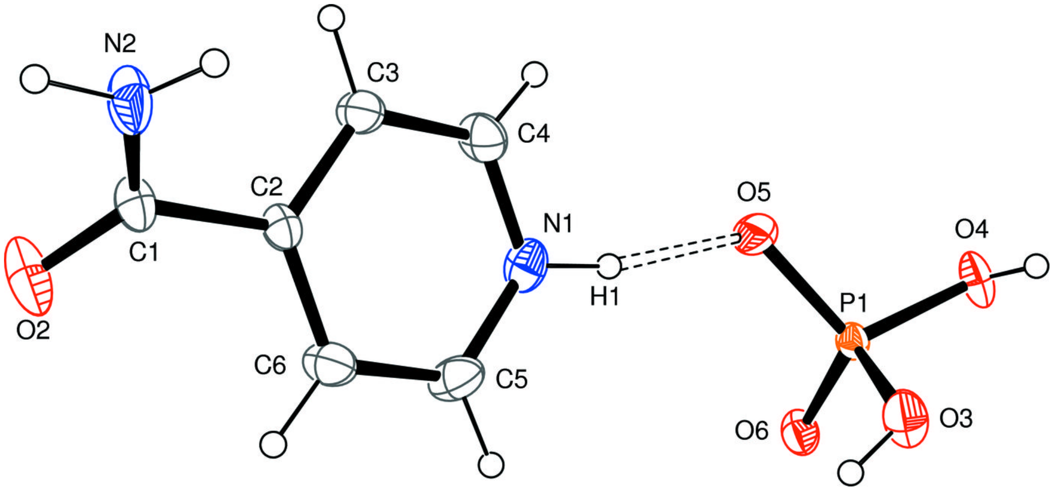

Fig. 2