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3-Amino-2-chloropyridinium dihydrogenphosphate

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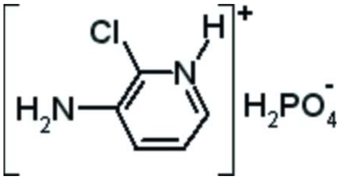
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.085; data-to-parameter ratio = 12.4.

The crystal structure of the title compound, $C_5H_6ClN_2^+\cdot H_2PO_4^-$, can be described as a stacking of 3-amino-2-chloropyridinium cations and dihydrogenphosphate anions. As well as electrostatic van der Waals interactions, the component species interact by means of multiple hydrogen bonds. The $H_2PO_4^-$ units are linked into polymeric chains propagating along the c axis by way of O—H···O hydrogen bonds. The organic cations are anchored between planes parallel to ac, linking the chains into a three-dimensional network.

Related literature

For related literature, see: Adams (1977); Blessing (1986); Desiraju (1989, 1995); Hebert (1978); Masse & Durif (1990); Nelmes & Choudhary (1978); Spek (2003).



Experimental

Crystal data

$C_5H_6ClN_2^+\cdot H_2PO_4^-$
M_r = 226.55
Monoclinic, $P2_1/c$
a = 7.391 (2) Å
b = 16.230 (3) Å
c = 7.504 (4) Å
β = 97.73 (3)°
V = 891.9 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 293 (2) K
0.21 × 0.19 × 0.17 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: none
3120 measured reflections
1568 independent reflections
1467 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022
2 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.085
S = 1.08
1568 reflections
126 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.32 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4$^{\rm i}$	0.82	1.81	2.611 (3)	164
O2—H2···O3$^{\rm ii}$	0.82	1.83	2.646 (3)	177
N1—H11···O3$^{\rm iii}$	0.86	1.73	2.577 (3)	168
N2—H21···Cl	0.87 (3)	2.66 (3)	3.008 (3)	105 (2)
N2—H21···O4	0.87 (3)	2.28 (3)	3.052 (3)	149 (3)
N2—H22···O4$^{\rm iv}$	0.90 (3)	2.02 (3)	2.915 (3)	173 (3)
C3—H3···O2$^{\rm iv}$	0.93	2.54	3.446 (3)	166
C4—H4···O1$^{\rm v}$	0.93	2.47	3.164 (3)	132

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2010).

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supplementary materials

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3-Amino-2-chloropyridinium dihydrogenphosphate

K. Hamed, **A. Samah** and **R. Mohamed**

Comment

Chemistry of organic-inorganic hybrid materials continue to be a focus area in material science. In the last few years, a considerable stategy employed in crystal engineering, is to take advantage of hydrogen bond interactions. Indeed, hydrogen bonds are of value not only because they are recognised as the most powerful force to generate interesting supramolecular networks (Desiraju, 1989; Desiraju, 1995)) but also because of their widespread biological occurrence (Adams, (1977); Nelmes & Choudhary (1978); Blessing, (1986)). As part of our continuing interest in this field, we have synthesized a new compound, 3-amino-2-chloropiridinium dihydrogenmonophosphate (I),

The Crystal structure of (I), consists of dihydrogenmonophosphate anions, and 3-amino-2-chloropiridinium cations. The asymmetric unit contains one crystallographically independent cation and an anion (Fig. 1). The $H_2PO_4^-$ anion shows its normal tetrahedral geometry with the protonated P1—O1 and P1—O2 vertices showing their expected lengthening relative to the unprotonated P—O bonds (Table 1). The 3-amino-2-cloropyridinium cation shows no unusual geometrical features. The anions are linked into polymeric chains of single tetrahedra propagating along [001] by way of the O1—H1···O4 and O2—H2···O3 hydrogen bonds. Similar chains have been seen in amphetamine dihydrogenmonophosphate (Hebert,1978) and in *L*,b-methyl alaninium dihydrogenmonophosphate (Masse & Durif, 1990). These polymeric chains are interconnected by means of N—H···O hydrogen bonds originating from the NH_2 groups of organic cation, to form infinite layers parallel to the ac plane and centred at y = 0 and y =1/2, as shown in Fig. 2. Charge compensation of these layers is achieved by the incorporation of the protonated pyridinium cation in the inetrlayer spaces. The cationic units interact with the anionic framework through different interactions (electrostatic, H-bonds and Van Der Waals) to make up into three dimensional infinite network. The organic and the inorganic species interact by way of three types of hydrogen bonds. The first one O—H···.O, involving short contacts H···.O of lengths 1.81 Å and 1.83 Å, connects the $H_2PO_4^-$ anions to develop the corrugated chains along the c direction. The second type N—H···.O, with N···O distances ranging from 2.577 (3) Å to 3.052 (3) Å, interconnects two successive chains, while the pertinent angles fall in the interval 149° to 173°. A PLATON (Spek, 2003) analysis of (I) indicated the presence of a third type of weak C—H···O contacts that ensure the cohesion of the ionic groups, giving rise to three-dimensional complex network of hydrogen bonds. It is worth noticing, the presence of a weak intramolecular bonding identified by PLATON (Spek, 2003) analysis (N2—H21···Cl = 2.66 (3) Å), occuring between NH_2 group adjacent to Cl group to reinforce the pyridinium cation.

Experimental

Single crystals of $C_5H_6N_2ClH_2PO_4$ were prepared by adding drop by drop 0.25 mmol of orthophosphoric acid in 50 ml of water, to a solution of 3-amino-2chloro pyridine (m = 0.5 g, 3.88 mmol) in ethanol. The solution thus obtained was slowly evaporated at room temperature, until the formation of crystals of (I) of good quality.

Figures

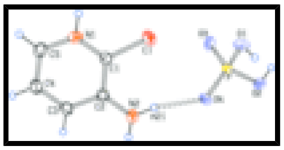

Fig. 1. ORTEP-3 (Farrugia,1999) view of (I) with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level

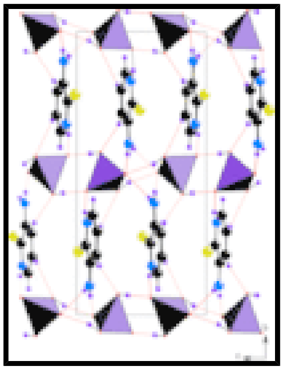

Fig. 2. Projection of (I) along c axis.

3-Amino-2-chloropyridinium dihydrogenphosphate

Crystal data

$C_5H_6ClN_2^{+}\cdot H_2P_1O_4^{-}$

$M_r = 226.55$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.391$ (2) Å

$b = 16.230$ (3) Å

$c = 7.504$ (4) Å

$\beta = 97.73$ (3)°

$V = 891.9$ (6) Å^3

$Z = 4$

$F_{000} = 464$

$D_x = 1.687$ Mg m^{-3}

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

Cell parameters from 25 reflections

$\theta = 8$–10°

$\mu = 0.59$ mm^{-1}

$T = 293$ (2) K

Prism, colorless

0.21 × 0.19 × 0.17 mm

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ K

non–profiled ω scans

Absorption correction: None

3120 measured reflections

1568 independent reflections

1467 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.022$

$\theta_{\rm max} = 25$°

$\theta_{\rm min} = 2$°

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 19$

$l = -8 \rightarrow 8$

2 standard reflections

every 120 min

intensity decay: 1%

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.5528P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$(\Delta/\sigma)_{max} = 0.0001$
$wR(F^2) = 0.085$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.39$ e Å^{-3}
1568 reflections	Extinction correction: none
126 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

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.

H atoms bonded to N2 were allowed to refine while the rest of the H-atoms were treated as riding, with C—H = 0.93 A ° , N—H =0.86 A ° and O—H = 0.82 A ° , and with Uiso(H) = 1.2Ueq(C,*N*) and 1.5Ueq(O).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
P	0.40091 (7)	0.51420 (3)	0.23747 (7)	0.03013 (17)
Cl	0.32834 (7)	0.72253 (4)	0.51245 (8)	0.04714 (19)
O1	0.5783 (2)	0.55975 (10)	0.3199 (2)	0.0455 (4)
H1	0.6305	0.5327	0.4038	0.068*
O2	0.4582 (2)	0.42619 (8)	0.1812 (2)	0.0424 (4)
H2	0.5285	0.4302	0.1059	0.064*
O3	0.3260 (2)	0.56276 (9)	0.0720 (2)	0.0439 (4)
O4	0.27281 (19)	0.50273 (9)	0.3745 (2)	0.0374 (3)
N1	0.0778 (2)	0.82641 (10)	0.5819 (2)	0.0357 (4)
H11	0.1582	0.8624	0.5625	0.043*
N2	0.0393 (3)	0.60423 (12)	0.5991 (3)	0.0482 (5)
H22	−0.050 (4)	0.5675 (16)	0.606 (3)	0.046 (7)*
H21	0.138 (4)	0.5870 (17)	0.561 (4)	0.056 (8)*

C1	0.1183 (3)	0.74668 (12)	0.5701 (3)	0.0322 (4)
C2	−0.0037 (3)	0.68483 (12)	0.6048 (3)	0.0325 (4)
C3	−0.1721 (3)	0.71241 (12)	0.6491 (3)	0.0370 (5)
H3	−0.2588	0.6740	0.6737	0.044*
C4	−0.2113 (3)	0.79467 (13)	0.6568 (3)	0.0418 (5)
H4	−0.3243	0.8118	0.6847	0.050*
C5	−0.0826 (3)	0.85219 (13)	0.6228 (3)	0.0415 (5)
H5	−0.1077	0.9082	0.6284	0.050*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P	0.0342 (3)	0.0262 (3)	0.0324 (3)	0.00296 (18)	0.0132 (2)	0.00355 (18)
Cl	0.0324 (3)	0.0520 (3)	0.0595 (4)	−0.0018 (2)	0.0151 (2)	−0.0031 (3)
O1	0.0473 (9)	0.0466 (9)	0.0440 (9)	−0.0149 (7)	0.0113 (7)	0.0093 (7)
O2	0.0565 (9)	0.0285 (7)	0.0471 (9)	0.0075 (6)	0.0247 (7)	0.0042 (6)
O3	0.0531 (9)	0.0438 (8)	0.0375 (8)	0.0213 (7)	0.0161 (7)	0.0093 (6)
O4	0.0366 (7)	0.0408 (8)	0.0383 (8)	−0.0012 (6)	0.0174 (6)	0.0004 (6)
N1	0.0394 (9)	0.0308 (9)	0.0369 (9)	−0.0086 (7)	0.0050 (7)	−0.0011 (7)
N2	0.0422 (11)	0.0303 (9)	0.0761 (15)	0.0001 (8)	0.0229 (10)	−0.0013 (9)
C1	0.0307 (9)	0.0344 (10)	0.0318 (10)	−0.0019 (8)	0.0051 (7)	−0.0018 (8)
C2	0.0329 (10)	0.0320 (10)	0.0330 (10)	−0.0021 (8)	0.0058 (8)	−0.0013 (8)
C3	0.0345 (10)	0.0362 (11)	0.0418 (11)	−0.0050 (8)	0.0110 (9)	−0.0043 (9)
C4	0.0347 (11)	0.0404 (11)	0.0519 (13)	0.0007 (9)	0.0116 (9)	−0.0089 (10)
C5	0.0433 (12)	0.0321 (10)	0.0496 (12)	0.0008 (9)	0.0079 (9)	−0.0061 (9)

Geometric parameters (Å, °)

P—O4	1.5001 (15)	C1—C2	1.397 (3)
P—O3	1.5116 (16)	C2—C3	1.404 (3)
P—O1	1.5591 (16)	C3—C4	1.369 (3)
P—O2	1.5641 (14)	C4—C5	1.381 (3)
O1—H1	0.8200	N2—H22	0.90 (3)
O2—H2	0.8200	N2—H21	0.87 (3)
Cl—C1	1.712 (2)	C3—H3	0.9300
N1—H11	0.8600	C4—C5	1.381 (3)
N1—C5	1.332 (3)	C4—H4	0.9300
N1—C1	1.334 (3)	C5—H5	0.9300
N2—C2	1.348 (3)		

O4—P—O3	115.62 (9)	N1—C5—C4	119.14 (19)
O4—P—O1	111.20 (9)	P—O1—H1	109.5
O3—P—O1	105.94 (9)	P—O2—H2	109.5
O4—P—O2	106.88 (8)	C5—N1—H11	118.8
O3—P—O2	109.68 (9)	C1—N1—H11	118.8
O1—P—O2	107.25 (9)	C2—N2—H22	117.7 (16)
C5—N1—C1	122.31 (17)	C2—N2—H21	122.5 (18)
N1—C1—C2	121.94 (18)	H22—N2—H21	118 (2)
N1—C1—Cl	117.24 (15)	C4—C3—H3	119.3

C2—C1—Cl	120.82 (15)	C2—C3—H3	119.3
N2—C2—C1	122.07 (19)	C3—C4—H4	120.1
N2—C2—C3	122.47 (19)	C5—C4—H4	120.1
C1—C2—C3	115.45 (18)	N1—C5—H5	120.4
C4—C3—C2	121.34 (19)	C4—C5—H5	120.4
C3—C4—C5	119.8 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4^{i}	0.82	1.81	2.611 (3)	164
O2—H2···O3^{ii}	0.82	1.83	2.646 (3)	177
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N2—H21···O4	0.87 (3)	2.28 (3)	3.052 (3)	149 (3)
N2—H22···O4^{iv}	0.90 (3)	2.02 (3)	2.915 (3)	173 (3)
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C4—H4···O1^{v}	0.93	2.47	3.164 (3)	132

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*; (iii) *x*, −*y*+3/2, *z*+1/2; (iv) −*x*, −*y*+1, −*z*+1; (v) *x*−1, −*y*+3/2, *z*+1/2.

Fig. 1

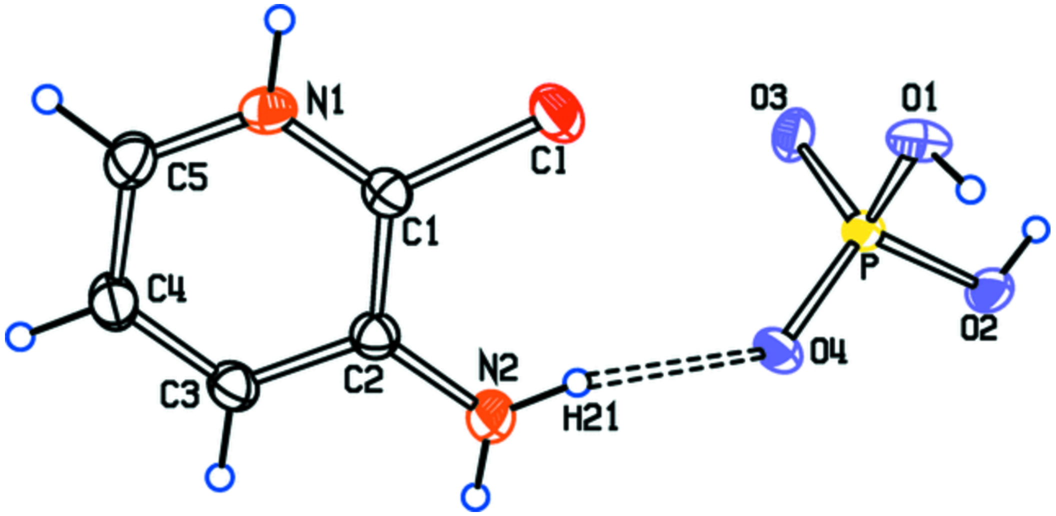

Fig. 2