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(3-Hydroxy-2-pyridylmethyl)dimethylammonium dihydrogenphosphate

Selcuk Demir,[a] Veysel T. Yilmaz[a]* and William T. A. Harrison[b]

[a]Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit Samsun, Turkey, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: vtyilmaz@omu.edu.tr

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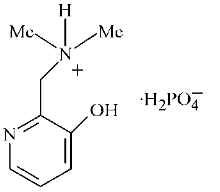
The title compound, $C_8H_{13}N_2O^+\cdot H_2PO_4^-$, is an ionic salt. The organic species is protonated at the N atom of the dimethylaminomethyl group. The dihydrogenphosphate moieties are connected into infinite chains by way of O—H···O links. The $H_2PO_4^-$ group also makes an O—H···N hydrogen bond to the pyridine N atom of the organic species. The organic cations crosslink the phosphate chains into a three-dimensional net work by way of strong N—H···O and O—H···O interactions.

Comment

Organic ammonium phosphates are formed as intermediates or by-products in the syntheses of metal phosphate frameworks templated by organic amines (Oliver *et al.*, 1998; Neeraj *et al.*, 1999; Rao *et al.*, 2000). In the formation of organic templated metal phosphates, the protonated organic amines play an important role. The amines can act as structure-directing agents, usually occupying the available voids or channels, and stabilize the structure through hydrogen bonding and other interactions (Choudhury *et al.*, 2000; Harrison *et al.*, 2002; Yilmaz *et al.*, 2005; Dorn *et al.* 2005). The charge and size of the organic cations also have significant influences on the structure of the anionic inorganic framework.



(I)

The organic ammonium phosphates show interesting crystal packing motifs strongly influenced by N—H···O and O—H···O hydrogen bonds (Demir *et al.*, 2002, 2003*a*,*b*, 2005). Sometimes, a three-dimensional supramolecular array of phosphate ions encapsulates the organic amine cations in channels (Czapla *et al.*, 2003; Dakhlaoui *et al.*, 2004). As a continuation of our work on the preparation and structural characterization of organic ammonium phosphates, in this paper, we report the structure of the title compound, $C_8H_{13}N_2O^+\cdot H_2PO_4^-$, (I) (Fig. 1).

The amine molecule in (I) has two potential N atoms for protonation. Here, the N atom of the 2-dimethylaminomethyl (2-dmam) group is protonated. The inductive effect of the alkyl groups around the 2-dmam N atom presumably favours protonation of this N atom rather than the pyridine N atom. The protonation of the 2-dmam N atom results in a slight lengthening of the three N—C bonds [the mean for (I) is 1.494 (2) Å] relative to the unprotonated form of the amine [mean 1.466 (3) Å; Yilmaz *et al.* 2006]. As expected, the pyridine ring in (I) is essentially planar (for atoms N1 and C1–C5, the r.m.s. deviation from the least-squares plane is 0.003 Å).

For the tetrahedral dihydrogenphosphate group, the protonated P—O vertices (to atoms O3 and O4) show the expected lengthening (Table 1) relative to the other P—O bonds (to atoms O1 and O2), which are of similar length as a result of delocalization of the negative charge between them.

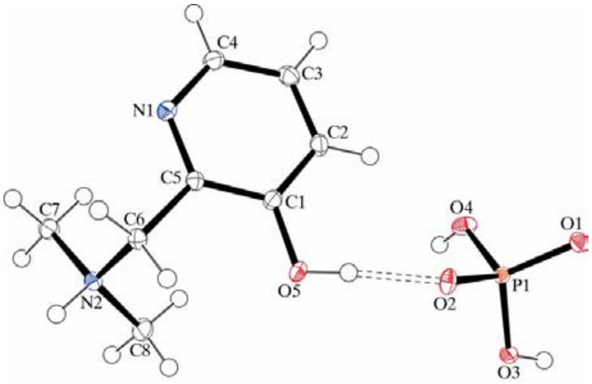


Figure 1
A view of (I), showing 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii and the hydrogen bond is indicated by double dashed lines.

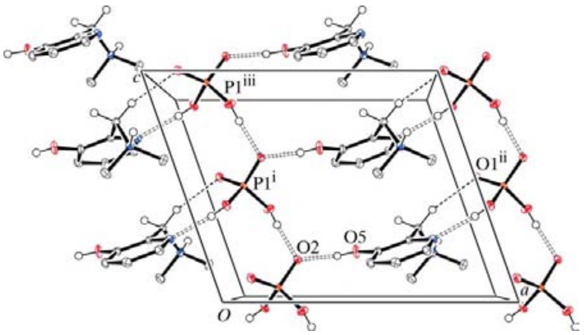


Figure 2
Part of an extended (010) hydrogen-bonded sheet in (I), showing hydrogen-bonded phosphate chains propagating in the *c* direction, cross-linked by phosphate-to-organic O—H···N and organic-to-phosphate O—H···O bonds (double dashed lines) in the *a* direction. The C—H···O interactions are indicated by single dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity (50% probability displacement ellipsoids and arbitrary spheres for H atoms). [Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x, y, z + 1$.]

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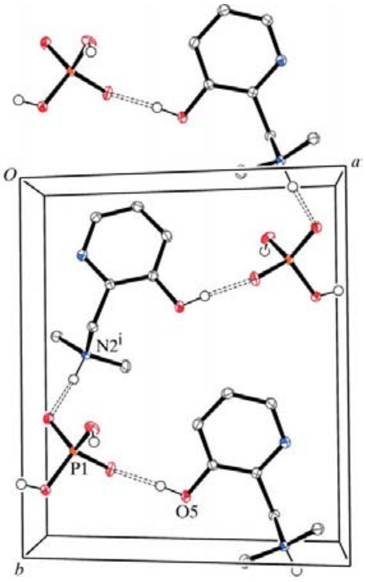

Figure 3
Part of an extended (001) hydrogen-bonding sheet in (I). Only the H atoms involved in hydrogen bonds are shown (50% probability displacement ellipsoids and arbitrary spheres for H atoms). [Symmetry code: (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.]

As well as electrostatic forces, an extensive network of hydrogen bonds, listed in Table 2, appears to be a key factor in the stabilization of this structure. The dihydrogenphosphate anions are linked into one-dimensional chains by way of P—O—H···O═P bonds, running parallel to the *c* axis (*i.e.* generated by the *c*-glide operation). The intrachain P1···P1^{i} separation [symmetry code: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$] is 4.5144 (4) Å, which is similar to those found in β-$(C_5H_7N_2)(H_2PO_4)$ [4.526 (1) and 4.536 (2) Å; Demir *et al.*, 2005]. Unusually, the $H_2PO_4^-$ group in (I) makes an O—H···N hydrogen bond to the organic cation. In related compounds, the dihydrogenphosphate moiety usually makes O—H···O bonds to other anions (Demir *et al.*, 2005).

In turn, the organic cation makes an O—H···O hydrogen bond from its phenol group to a phosphate O atom. This hydrogen bonding results in an extended sheet structure (Fig. 2) propagating in the (010) plane. A short C—H···O interaction (Table 2) may also help to consolidate this extended sheet. Finally, the protonated 2-dmam N atom makes an N—H···O bond to a phosphate O atom displaced in the *b* direction (Fig. 3), resulting in a three-dimensional network. No aromatic π–π stacking interactions are present in (I).

Experimental

H_3PO_4 (0.17 ml, 2.5 mmol) (aqueous 85 wt%) was added dropwise to a solution of 2-(dimethylaminomethyl)-3-hydroxypyridine (0.30 g, 2 mmol) in methanol (30 ml) and stirred at 363 K for 15 min. The resulting mixture was left to crystallize at room temperature. Colourless cubic crystals of the title compound were washed with a small amount of methanol and dried in air.

Crystal data

$C_8H_{13}N_2O^+ \cdot H_2PO_4^-$
$M_r = 250.19$
Monoclinic, $P2_1/c$
$a = 10.7601$ (2) Å
$b = 11.9724$ (2) Å
$c = 8.9122$ (1) Å
$\beta = 109.3578$ (11)°
$V = 1083.20$ (3) Å^3
$Z = 4$
$D_x = 1.534$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4901 reflections
$\theta = 2.9$–27.5°
$\mu = 0.26$ mm^{-1}
$T = 120$ (2) K
Cube, colourless
0.35 × 0.35 × 0.35 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.914$, $T_{max} = 0.914$
22984 measured reflections
2481 independent reflections
2282 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -10 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.070$
$S = 1.05$
2481 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 0.7457P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.034 (2)

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.4980 (9)	P1—O3	1.5726 (9)
P1—O2	1.5139 (9)	P1—O4	1.5731 (9)
O1—P1—O2	114.83 (5)	O1—P1—O4	107.61 (5)
O1—P1—O3	111.14 (5)	O2—P1—O4	108.91 (5)
O2—P1—O3	106.81 (5)	O3—P1—O4	107.28 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···N1^{v}	0.787 (18)	1.955 (18)	2.7243 (14)	166 (2)
O4—H2···O2^{vi}	0.848 (18)	1.749 (18)	2.5813 (13)	167 (2)
N2—H3···O1^{vii}	0.963 (15)	1.661 (16)	2.6187 (13)	173 (1)
O5—H4···O2	0.877 (18)	1.723 (18)	2.5939 (12)	172 (2)
C6—H6*A*···O1^{ii}	0.99	2.30	3.2663 (15)	165

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

N- and O-bound H atoms were found in difference maps and their positions were refined freely. C-bound H atoms were placed in idealized locations (C—H = 0.95–0.99 Å) and refined as riding. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier) was applied and the methyl groups were allowed to rotate to fit the electron density.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3006). Services for accessing these data are described at the back of the journal.

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