

A second polymorph of 2-amino-pyridinium dihydrogenphosphate

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Received 11 July 2005

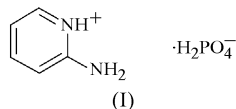
Accepted 3 August 2005

Online 31 August 2005

In the title compound, β - $C_5H_7N_2^+ \cdot H_2PO_4^-$, the tetrahedral dihydrogenphosphate moieties are linked into double chains by $O-H \cdots O$ hydrogen bonds, and the organic species crosslink the chains into sheets by way of $N-H \cdots O$ bonds. The resulting structure is quite different from that of the previously described α polymorph of this stoichiometry [Czapla, Dacko & Waskowska (2003). *J. Phys. Condens. Matter*, **15**, 3793–3803].

Comment

Ammonium phosphates can function as intermediates or by-products in the formation of open-framework metal phosphates templated by organic amines (Oliver *et al.*, 1998; Neeraj *et al.*, 1999; Rao *et al.*, 2000). They show interesting crystal packing motifs, strongly influenced by the interplay of $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds (Demir *et al.*, 2002). We describe here the structure of the title compound, β -($C_5H_7N_2$)(H_2PO_4), (I) (Fig. 1), which was obtained accidentally in the hydrothermal preparation of a 2-amino-pyridinium-templated zincophosphate at 443 K. Compound (I) is a polymorph of a quite different structure of the same stoichiometry (Czapla *et al.*, 2003), hereafter denoted α -($C_5H_7N_2$)(H_2PO_4).



In the tetrahedral dihydrogenphosphate group in (I), the protonated P–O vertices (O1 and O2) show the expected lengthening (Table 1) relative to the other P–O bonds (O3 and O4), which are of similar length as a result of delocalization of the negative charge between them. The pyridine ring is essentially planar (for atoms N1 and C1–C5 the r.m.s. deviation from the least-squares plane is 0.004 Å) and its bond distances and angles are normal.

The crystal packing in (I) is shown in Figs. 2 and 3. In addition to electrostatic forces, hydrogen bonds appear to be a key factor in establishing this structure. The dihydrogenphosphate anions are linked into double chains by way of P–O–H \cdots O–P bonds (Table 2), such that every anion acts as a donor for two hydrogen bonds and an acceptor for two hydrogen bonds. In graph-set notation (Bernstein *et al.*, 1995), an $R_3^3(12)$ loop arises for every triplet of connected tetrahedra. The $P1 \cdots P1^i$ and $P1 \cdots P1^{ii}$ separations are 4.5260 (14) and 4.5357 (17) Å, respectively (see Table 2 for symmetry codes). The chains propagate along [010], generated by the 2_1 screw axis.

(Di)hydrogenphosphate chains can show a surprising variety of hydrogen-bonding motifs. In *N*-(2-hydroxyethyl)-ethylenediammonium hydrogenphosphate monohydrate (Demir *et al.*, 2002), infinite chains of HPO_4^{2-} groups are linked by single P–O–H \cdots O–P connections, whilst in triethanolammonium dihydrogenphosphate (Demir *et al.*, 2003), the $H_2PO_4^-$ moieties are connected by alternating single and double P–O–H \cdots O–P hydrogen-bond links. In 1,3-diaminium hydrogenphosphate hydrate (Kamoun *et al.*, 1991), single phosphate/water chains occur, whereas 1,3-diaminium bis(dihydrogenphosphate) (Kamoun *et al.*, 1992; Marsh, 2004) contains a double tetrahedral chain different from that seen in (I), in which the fundamental symmetry is that of inversion.

In (I), the organic species interacts with the inorganic chains by way of three $N-H \cdots O$ bonds. Two of these bonds are to a single adjacent $H_2PO_4^-$ tetrahedron, and the third is to a similar species displaced in the *a* direction. These interactions

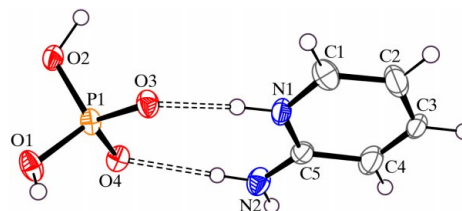


Figure 1

A view of (I), showing 50% probability displacement ellipsoids. Hydrogen bonds are indicated by dashed bonds.

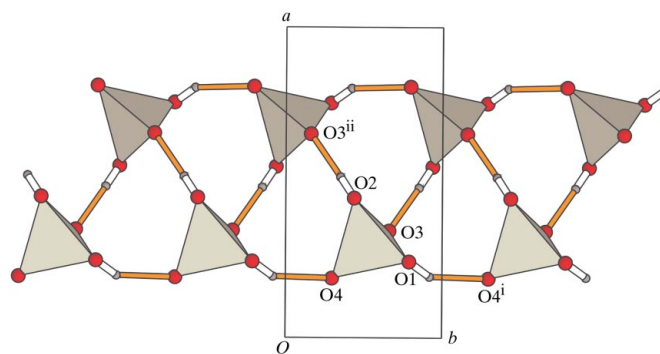


Figure 2

A detail of (I) in a polyhedral representation, showing the connectivity of the dihydrogenphosphate units into [010] chains by way of $O-H \cdots O$ hydrogen bonds ($H \cdots O$ portion shaded). Symmetry codes are as in Table 2.

result in (001) sheets that interact with each other by van der Waals forces. In contrast to the distinctive π - π stacking interactions between closely associated pairs of 2-aminopyridinium rings in the zincophosphate framework $\{(C_5H_7N_2)[Zn(HPO_4)(H_2PO_4)] \cdot H_2O\}_n$, synthesized at room temperature (Yilmaz *et al.*, 2005), there are no significant π - π stacking forces in (I).

The structure of (I) is quite different from that of α -($C_5H_7N_2$)(H_2PO_4) (Czapla *et al.*, 2003), which contains a three-dimensional supramolecular array of $H_2PO_4^-$ groups encapsulating the organic moieties in pseudo-channels in space group $C2/c$. In addition to one well defined P—O—H \cdots O—P hydrogen bond, α -($C_5H_7N_2$)(H_2PO_4) contains two short [2.469 (2) and 2.471 (2) Å] inversion-symmetry-generated pairs of O atoms with which the other dihydrogenphosphate H atoms are associated. These could represent symmetric O \cdots H \cdots O bonds (*i.e.* the H atom occupying the inversion centre) or disordered O—H \cdots O and O \cdots H—O bonds (*i.e.* a double potential well with the H atom shifted away from the inversion centre). The H atoms associated with the short O \cdots O pairs were not located in the X-ray study, but on the basis of the physical properties of α -($C_5H_7N_2$)(H_2PO_4), Czapla *et al.* (2003) suggested that a double potential well was more likely. α -($C_5H_7N_2$)(H_2PO_4) shows a ferroelectric to paraelectric phase transition at 104 K, which is probably associated with rearrangements of the H atoms. We are now investigating this system further to try to clarify this situation.

Although the connectivities of the dihydrogenphosphate tetrahedra are completely different, the α and β forms of ($C_5H_7N_2$)(H_2PO_4) both contain three similar N—H \cdots O interactions [for the α form, mean H \cdots O = 2.02 Å and mean N \cdots O = 2.882 (2) Å; for the β form, mean H \cdots O = 1.98 Å and mean N \cdots O = 2.849 (6) Å]. The β form is slightly more dense than the α form ($\rho = 1.580$ and 1.557 Mg m $^{-3}$, respectively),

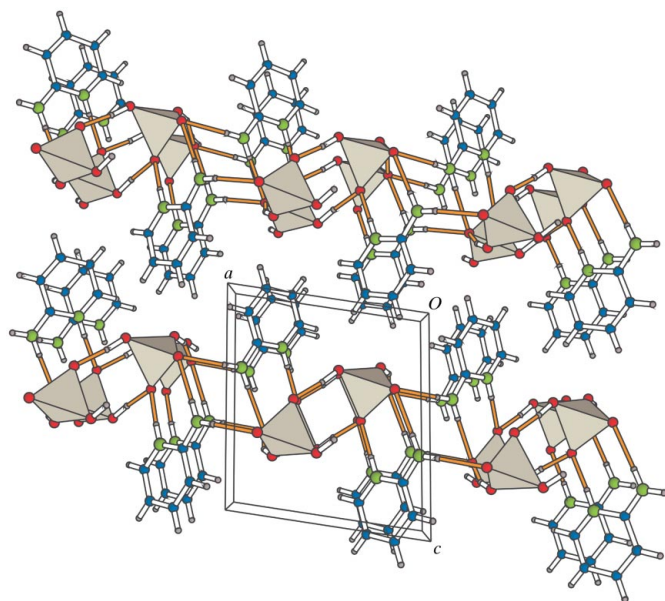


Figure 3
A view down [010] of the unit-cell packing in (I). O—H \cdots O and N—H \cdots O hydrogen bonds are shown with the H \cdots O portion shaded.

perhaps suggesting that it is the more stable form, even though a visual comparison of the structures suggests that van der Waals interactions are more prevalent in the β form.

Experimental

A 0.41 ml aliquot of H_3PO_4 (6 mmol, aqueous, 85 wt%) was mixed with an aqueous suspension (10 ml) of ZnO (0.163 g, 2 mmol) and a clear solution was obtained. An aqueous solution (10 ml) of 2-aminopyridine (0.188 g, 2 mmol) was added to this solution dropwise. The resulting mixture was transferred to a 45 ml Teflon-lined stainless steel reaction vessel, heated at 443 K for 60 h and then cooled to room temperature. Colourless crystals of (I) were isolated by vacuum filtration, washed with a small amount of water and dried in air. All crystals obtained were of the β form (yield 38%). Direct reaction of phosphoric acid and 2-aminopyridine in the absence of ZnO yields the α polymorph, as reported by Czapla *et al.* (2003).

Crystal data

$C_5H_7N_2^+ \cdot H_2PO_4^-$	$D_x = 1.580$ Mg m $^{-3}$
$M_r = 192.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 928 reflections
$a = 9.0502$ (12) Å	$\theta = 2.9$ – 27.5°
$b = 4.5260$ (3) Å	$\mu = 0.32$ mm $^{-1}$
$c = 9.9697$ (11) Å	$T = 120$ (2) K
$\beta = 98.576$ (4) $^\circ$	Rod, colourless
$V = 403.80$ (7) Å 3	$0.32 \times 0.08 \times 0.06$ mm
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	1206 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.090$
Absorption correction: multi-scan	$\theta_{max} = 27.6^\circ$
(SADABS; Bruker, 2003)	$h = -11 \rightarrow 11$
$T_{min} = 0.905$, $T_{max} = 0.978$	$k = -5 \rightarrow 5$
3961 measured reflections	$l = -10 \rightarrow 13$
1719 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.060$	$\Delta\rho_{max} = 0.36$ e Å $^{-3}$
$wR(F^2) = 0.137$	$\Delta\rho_{min} = -0.44$ e Å $^{-3}$
$S = 1.03$	Extinction correction: SHELXL97
1719 reflections	Extinction coefficient: 0.061 (11)
116 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	672 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.0857P]$	Flack parameter: 0.3 (2)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected interatomic distances (Å).

P1—O3	1.514 (3)	P1—O1	1.552 (3)
P1—O4	1.521 (3)	P1—O2	1.560 (4)

Table 2
Hydrogen-bond geometry (Å, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O4 ⁱ	0.80 (3)	1.83 (4)	2.544 (4)	149 (5)
O2—H2 \cdots O3 ⁱⁱ	0.86 (3)	1.69 (3)	2.552 (5)	174 (5)
N1—H7 \cdots O3	0.88	1.82	2.676 (5)	165
N2—H8 \cdots O4	0.88	2.08	2.963 (5)	179
N2—H9 \cdots O4 ⁱⁱⁱ	0.88	2.05	2.908 (5)	166

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

The O-bound H atoms were found in difference maps and their positions were refined with the O–H distance restrained to 0.82 (4) Å. Other H atoms were placed in idealized locations (C–H = 0.95 Å and N–H = 0.88 Å) and refined as riding atoms. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases. The refined value of the Flack (1983) parameter was not definitive. A refinement of the opposite (inverted) absolute structure gave a value of 0.6 (2).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL 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) and *ATOMS* (Shape Software, 2002); software used to prepare material for publication: *SHELXL97*.

The authors would like to thank Ondokuz Mayıs University for financial support and the EPSRC National Crystallography Service (University of Southampton, England) for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1219). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Czapla, Z., Dacko, S. & Waskowska, A. (2003). *J. Phys. Condens. Matter*, **15**, 3793–3803.
- Demir, S., Yilmaz, V. T., Andac, O. & Harrison, W. T. A. (2002). *Acta Cryst. C* **58**, o407–o408.
- Demir, S., Yilmaz, V. T., Andac, O. & Harrison, W. T. A. (2003). *Acta Cryst. E* **59**, o907–o909.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Flack, H. D. (1983). *Acta Cryst. A* **39**, 876–881.
- Kamoun, S., Jouini, A. & Daoud, A. (1991). *Acta Cryst. C* **47**, 117–119.
- Kamoun, S., Jouini, A., Daoud, A., Durif, A. & Guitel, J. C. (1992). *Acta Cryst. C* **48**, 133–135.
- Marsh, R. E. (2004). *Acta Cryst. B* **60**, 252–253.
- Neeraj, S., Natarajan, S. & Rao, C. N. R. (1999). *Angew. Chem. Int. Ed.* **38**, 3480–3483.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Oliver, S., Lough, A. J. & Ozin, G. A. (1998). *Inorg. Chem.* **37**, 5021–5028.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Rao, C. N. R., Natarajan, S. & Neeraj, S. (2000). *J. Solid State Chem.* **152**, 302–321.
- Shape Software (2002). *ATOMS*. Shape Software, 525 Hidden Valley Road, Kingsport, Tennessee, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Yilmaz, V. T., Demir, S., Kazak, C. & Harrison, W. T. A. (2005). *Solid State Sci.* In the press.