organic compounds

2-(Hydroxymethyl)pyridinium dihydrogenphosphate

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The title compound, $C_6H_8NO^+ \cdot H_2PO_4^-$, consists of 2-(hydroxymethyl)pyridinium and dihydrogenphosphate ions. The dihydrogenphosphate moieties are linked into chains by pairs of $P-O-H\cdots O-P$ hydrogen bonds. The 2-(hydroxymethyl)pyridinium cations are connected to the dihydrogenphosphate units by $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds. Weak $\pi-\pi$ interactions help to determine the interchain packing.

Comment

During the synthesis of metal phosphates templated by organic amines (Cheetham *et al.*, 1999), amine phosphates may occur as unexpected by-products and may also act as intermediates in the formation of open-framework structures (Oliver *et al.*, 1998; Neeraj *et al.*, 1999; Rao *et al.*, 2000). In addition, amine phosphates show interesting crystal-packing motifs controlled 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, (I) (Fig. 1).

(I)
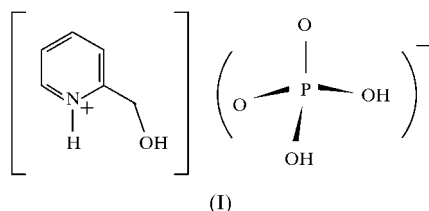
The pyridine ring in (I) is essentially planar (for atoms N1 and C1–C5, the r.m.s. deviation from the best least-squares plane is 0.009 Å), and the bond distances and angles in the cation are comparable to those seen for the neutral molecule coordinated to metal ions (Yilmaz *et al.*, 2002*a,b*). Similar geometric parameters were also observed in $(C_6H_8NO)[RuCl_3(C_6H_6NO)(NO)]$ (Suzuki *et al.*, 1999), in which the organic
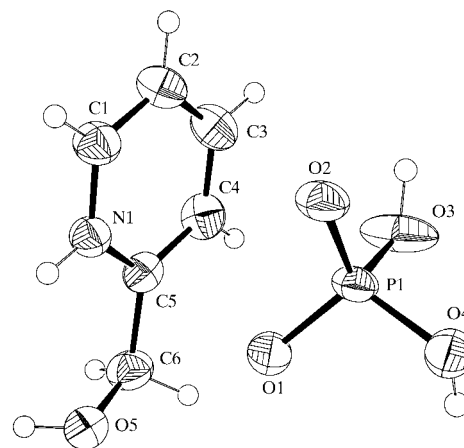

Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

moiety acts as both an $O-H$ deprotonated N,O-chelating ligand to ruthenium and an $N-H$ protonated counter-ion.

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

The crystal packing is shown in Figs. 2 and 3. The dihydrogenphosphate anions are linked by relatively strong, roughly parallel, pairs of $P-O-H\cdots O-P$ and $P-O\cdots H-O-P$ hydrogen bonds, thus creating a polymeric chain that
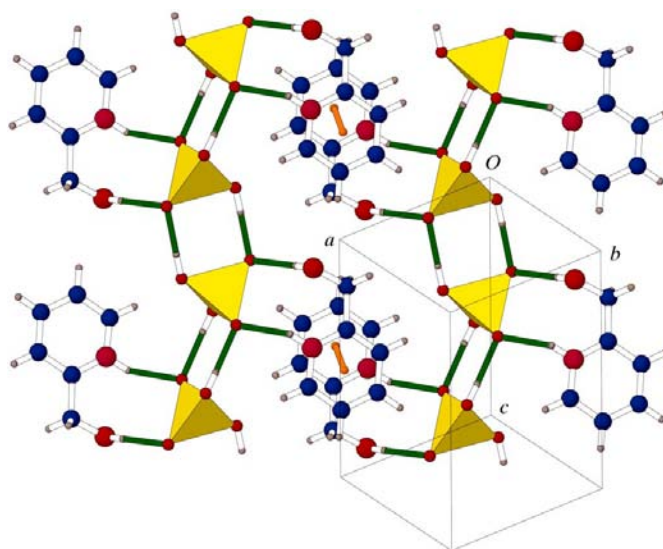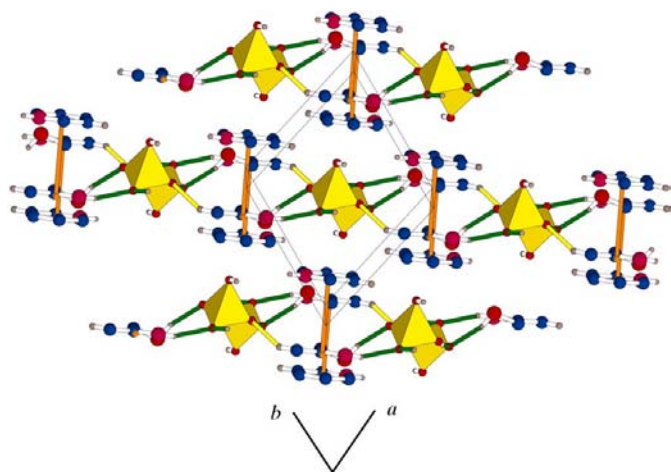

Figure 2
Part of the structure of (I), showing the connectivity of the dihydrogenphosphate units (shaded tetrahedra) into [001] chains *via* pairs of $O-H\cdots O$ hydrogen bonds ($H\cdots O$ portion shaded; shown as green in the online version). Each organic moiety is pendant to a particular $H_2PO_4^-$ group. Adjacent chains interact *via* weak $\pi-\pi$ stacking interactions (lines linking pyridine-ring centroids; shown as orange online). Sphere radii are arbitrary. (C, N, O and H atoms are shown as blue, green, red and grey spheres, respectively, in the online version.)

Figure 3
The unit-cell packing in (I), viewed along [001]. All H atoms bound to C atoms (except atom H14) have been omitted for clarity. Atom and bond colours are as in Fig. 2, with H14···O3 bonds coloured light grey (yellow in the online version).

room temperature. The colourless transparent crystals of (I) that formed from the mixture were washed with a small amount of water and acetone, and finally dried in air.

Crystal data

$C_6H_8NO^+ \cdot H_2PO_4^-$	$Z = 2$
$M_r = 207.12$	$D_x = 1.608$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.8826$ (4) Å	Cell parameters from 2793
$b = 8.0041$ (4) Å	reflections
$c = 8.2092$ (5) Å	$\theta = 2.8$–30.0°
$\alpha = 65.5050$ (1)°	$\mu = 0.31$ mm^{-1}
$\beta = 69.5660$ (1)°	$T = 293$ (2) K
$\gamma = 69.0370$ (1)°	Chunk, colourless
$V = 427.67$ (4) Å^3	$0.39 \times 0.37 \times 0.28$ mm

Data collection

Bruker SMART1000 CCD diffractometer	2447 independent reflections
	2150 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.012$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$\theta_{max} = 30.0°$
	$h = -9 \rightarrow 11$
$T_{min} = 0.884$, $T_{max} = 0.918$	$k = -10 \rightarrow 11$
3828 measured reflections	$l = -7 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0759P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.0416P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
2447 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
118 parameters	$\Delta\rho_{min} = -0.45$ e Å^{-3}
H-atom parameters constrained	

propagates along [001]. Along the chain, these bonds alternate between P—O3—H3···O2—P and P—O2···H3—O2—P pairs, and between P—O4—H4···O1—P and P—O1···H4—O4—P pairs. By comparison, in *N*-(2-hydroxyethyl)ethylene-diammonium hydrogenphosphate monohydrate (Demir *et al.*, 2002), infinite chains of HPO$_4$ groups are linked by a single P—O—H···O—P connection, while in triethanolammonium dihydrogenphosphate (Demir *et al.*, 2003), the H$_2$PO$_4^-$ moieties are connected by alternating single and double P—O—H···O—P hydrogen-bond links.

In (I), the 2-(hydroxymethyl)pyridinium cations are pendant to the phosphate chains; each C$_6$H$_8$NO$^+$ cation is bonded to its neighbouring H$_2$PO$_4^-$ unit by both an N1—H1···O1 and an O5—H5···O2 hydrogen bond. The first of these links (Table 2) may be acute because of a weak intra-molecular N1—H1···O5 hydrogen bond [N—H = 0.89 Å, H···O = 2.40 Å, N···O = 2.736 (2) Å and N—H···O = 103°].

Adjacent chains interact *via* van der Waals forces and relatively weak π–π ring-stacking interactions [ring-centroid separation = 3.829 Å; the adjacent ring is generated by the symmetry code $(-x, -y, 1 - z)$]. The pattern of π–π stacking (Fig. 2) between adjacent chains results in a head-to-tail configuration for the participating 2-(hydroxymethyl)-pyridinium cations, although it is not clear that the π–π interaction alone actually drives this motif. This configuration results in extended (110) sheets (Fig. 3). If it is not an artefact of the crystal packing, a weak C4—H14···O3 bond (Table 2) provides further cohesion between neighbouring chains in the (110) sheets.

Experimental

H$_3$PO$_4$ (0.814 ml, 12 mmol; aqueous 85 wt%) was added dropwise to an aqueous solution (20 ml) of ethylene glycol (20%) and 2-(hydroxymethyl)pyridine (1.012 ml, 10 mmol), and the resulting mixture was stirred for 2 h at 323 K and then left to crystallize at

Table 1
Selected interatomic distances (Å).

P1—O1	1.5054 (10)	P1—O3	1.5634 (11)
P1—O2	1.5072 (9)	P1—O4	1.5668 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2^i	0.87	1.67	2.5386 (14)	173
O4—H4···O1^{ii}	0.79	1.78	2.5667 (14)	176
O5—H5···O2^{iii}	0.89	1.83	2.7071 (15)	165
N1—H1···O1^{iii}	0.89	1.89	2.7172 (16)	153
C4—H14···O3^{iv}	0.93	2.52	3.3472 (19)	148

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 1 - y, 1 - z$; (iv) $1 - x, -y, 1 - z$.

Hydroxy and amine H atoms were found in difference maps and were refined by allowing them to ride in these positions. H atoms bonded to C atoms were placed in calculated positions 0.97 Å from their parent atoms and modelled as riding. The U_{iso}(H) values were constrained to be $1.2U_{eq}$ of the values of the parent atom in all cases.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

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