# organic papers

# Phosphoric acid imidazolium dihydrogenphosphate

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The title compound, $H_3PO_4 \cdot C_3H_5N_2^+ \cdot H_2PO_4^-$, was synthesized during an investigation of the intercalation of imidazole into a series of $VOPO_4$ compounds. The asymmetric unit contains two phosphate species, which are disordered $H_2PO_4^-$ and $H_3PO_4$, and one imidazolium cation, and has significant hydrogen bonding.

## Comment

Recently, there has been much interest in vanadium phosphate-based compounds, due mostly to their potential application as battery materials, electrochromic displays and catalysts (Padhi *et al.*, 1997; Song *et al.*, 2005; Whittingham, 2004; Whittingham *et al.*, 2005). Since the early 1980s, a new class of ionic liquids, based on imidazole (Imd), has also attracted great interest due to their potential commercial and environmental advantages (Seddon, 1997). These ionic liquids are solvent-free, allowing them, potentially, to behave in a very different manner from conventional ionic electrolytic solutions. They are also capable of operating over a wide range of temperature, from ambient to well over 373 K. The possible use of an imidazolium salt, Imd$X$, mixed with the corresponding lithium salt, Li$X$, could be very attractive for advanced lithium batteries. Such a battery might contain a lithium-containing anode material, an imidazolium electrolyte and a cathode containing a layered-structure vanadium oxide or phosphate. However, a concern with such a system is the possible intercalation of the imidazolium cations between the layers of the oxide/phosphate structures. Such intercalation compounds have not previously been reported. While studying these possible reactions, we accidentally synthesized the title compound, (I), containing only imidazolium cations and phosphoric/phosphate species. This paper describes the crystal structure of this compound.



(I)
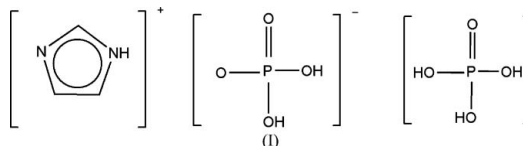
Colourless crystals of (I) were found to crystallize in the monoclinic system. The structure is of an ionic type with hydrogen bonding (Figs. 1 and 2). It contains two phosphate groups and one imidazolium cation. Some of the H atoms are disordered between the two phosphate groups so they are a disordered mixture of $H_2PO_4^-$ and $H_3PO_4$. This disorder provides H atoms for all the short O—O distances ($\sim$2.5 Å), making them hydrogen bonds (Table 2). The imidazolium
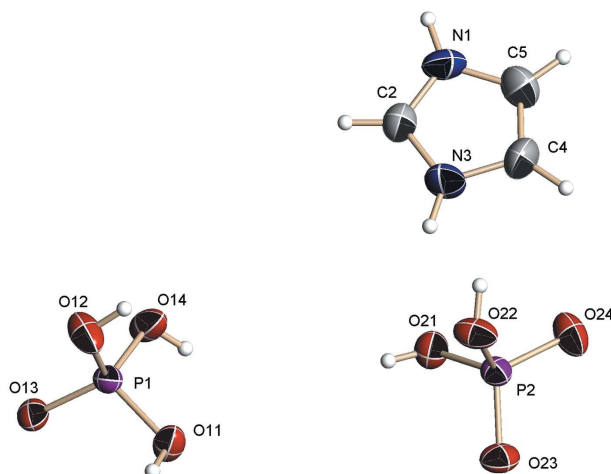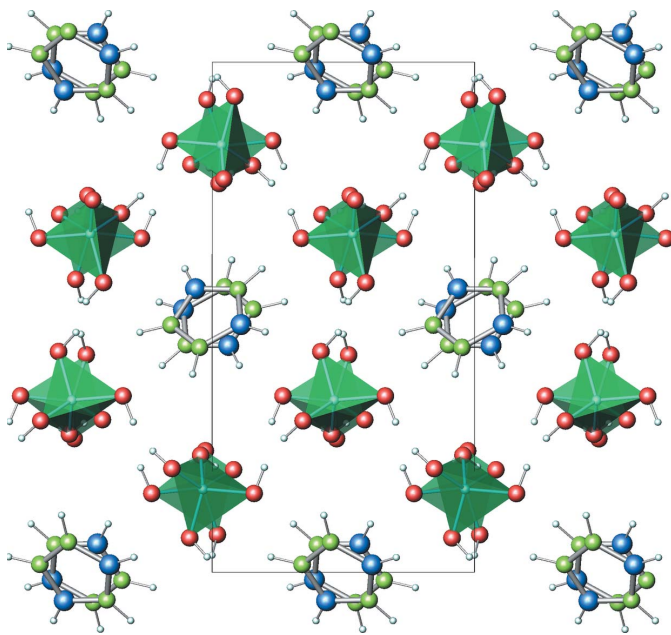
**Figure 1**
A view of the asymmetric unit of (I), showing the numbering scheme employed. Displacement ellipsoids are shown at the 50% probability level and H atoms are displayed with arbitrarily small radii. One component of the H-atom disorder is shown.



**Figure 2**
A view showing the packing of the components of (I). H atoms have been omitted.

cation is also disordered between two orientations in about a 3:1 ratio. The strong hydrogen bonding in this structure is in addition to the electrostatic interactions between the phosphate anions and the imidazolium cations. Both $PO_4$ tetrahedra (Table 1) have two short P—O distances in the range 1.50–1.51 Å, while the other two lie between 1.54 and 1.56 Å.

## Experimental

Several approaches have been used for the synthesis of $VOPO_4 \cdot 2H_2O$, the starting material in this study. The conventional approach involves the prolonged refluxing of $V_2O_5$ in aqueous phosphoric acid (Ladwig, 1965). A more rapid method uses a sonochemical approach (Park *et al.*, 2001). In order to optimize the

possible reactions, we decided to make a highly porous phosphate of formula $VOPO_4 \cdot 2H_2O$ by reacting foam gel $V_2O_5$ (Chandrappa *et al.*, 2002) with phosphoric acid. The title compound was isolated from a mixture of excess imidazole and the above $VOPO_4 \cdot 2H_2O$ in a 3:1 molar ratio. This mixture was allowed to stand for 30 d under ambient conditions. Crystals began to grow at the surface of a greenish solid precipitate in the beaker. The title compound was obtained by careful removal of a single crystal from the mixture.

### Crystal data

| | |
|---|---|
| $H_3PO_4 \cdot C_3H_5N_2{}^+ \cdot H_2PO_4{}^-$ | $D_x = 1.749$ Mg m$^{-3}$ |
| $M_r = 264.07$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 3640 |
| $a = 9.138$ (4) Å | reflections |
| $b = 14.605$ (6) Å | $\theta = 2.6$–31.3° |
| $c = 7.516$ (3) Å | $\mu = 0.46$ mm$^{-1}$ |
| $\beta = 91.447$ (6)° | $T = 296$ (2) K |
| $V = 1002.8$ (7) Å$^3$ | Prism, colourless |
| $Z = 4$ | $0.36 \times 0.28 \times 0.24$ mm |

### Data collection

| | |
|---|---|
| Bruker APEX CCD area-detector | 2291 independent reflections |
| diffractometer | 1895 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.025$ |
| Absorption correction: multi-scan | $\theta_{max} = 27.5°$ |
| (*SADABS*; Sheldrick, 1996) | $h = -11 \rightarrow 8$ |
| $T_{min} = 0.802$, $T_{max} = 0.895$ | $k = -16 \rightarrow 18$ |
| 6101 measured reflections | $l = -9 \rightarrow 9$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o{}^2) + (0.003P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | $+ 1.182P]$ |
| $wR(F^2) = 0.079$ | where $P = [\text{-max}(F_o{}^2,0) + 2F_c{}^2]/3$ |
| $S = 1.00$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2291 reflections | $\Delta\rho_{max} = 0.28$ e Å$^{-3}$ |
| 162 parameters | $\Delta\rho_{min} = -0.36$ e Å$^{-3}$ |
| H-atom parameters constrained | Extinction correction: *SHELXL97* |
| | (Sheldrick, 1997) |
| | Extinction coefficient: 0.0192 (9) |

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| N1—C2 | 1.303 (5) | P1—O12 | 1.5405 (16) |
| N1—C5 | 1.351 (6) | P1—O11 | 1.5530 (16) |
| C2—N3 | 1.311 (4) | P2—O23 | 1.5010 (16) |
| N3—C4 | 1.369 (6) | P2—O24 | 1.5112 (17) |
| C4—C5 | 1.299 (7) | P2—O22 | 1.5464 (16) |
| P1—O13 | 1.4965 (16) | P2—O21 | 1.5565 (17) |
| P1—O14 | 1.5125 (16) | | |

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| N1—H1⋯O14[i] | 0.86 | 1.97 | 2.827 (4) | 177 |
| N3—H3⋯O21 | 0.86 | 2.16 | 2.986 (4) | 160 |
| O11—H11⋯O13[ii] | 0.82 | 1.79 | 2.587 (2) | 162 |
| O12—H12⋯O23[iii] | 0.82 | 1.79 | 2.554 (2) | 155 |
| O13—H13⋯O11[iv] | 0.82 | 1.82 | 2.587 (2) | 155 |
| O14—H14⋯O14[v] | 0.82 | 1.67 | 2.461 (3) | 162 |
| O21—H21⋯O23[iv] | 0.82 | 1.80 | 2.602 (2) | 165 |
| O22—H22⋯O13 | 0.82 | 1.76 | 2.561 (2) | 164 |
| O24—H24⋯O24[vi] | 0.82 | 1.67 | 2.441 (4) | 156 |

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

Both disordered imidazolium ions overlap and their geometry was constrained only during the initial refinement, while in the final

refinement they were freely refined.The H atoms of the phosphate groups were located in a difference Fourier map and refined independently. On introducing partially occupied H atoms into the $PO_4$ groups, refinement of the H-atom positions was constrained, but the $U_{iso}$(H) values were refined freely. The H atoms of the imidazolium ions were refined within a rigid-body model riding on their parent C or N atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{iso}$(H) = $1.2U_{eq}$(C,N).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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