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L-Valinium hydrogenphosphite

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Key indicators

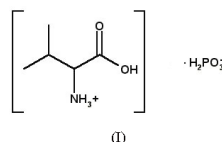
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.038
wR factor = 0.100
Data-to-parameter ratio = 10.8

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the title compound, $\text{C}_5\text{H}_{12}\text{NO}_2^+ \cdot \text{H}_2\text{PO}_3^-$, can be described as a stacking of L-valinium and hydrogenphosphite ions. The stability of such an arrangement results from a network of hydrogen bonds, which maintain the cohesion of the organic–inorganic layers in the crystal. The asymmetric unit contains two valinium residues and two hydrogenphosphite ions, one of which is disordered.

Comment

In recent years, organic–inorganic hybrid materials have attracted considerable attention as preferred materials in non-linear optics (NLO), such as second harmonic generation (SHG) and optical bistability, owing to their large optical nonlinearities (Masse & Zyss, 1991; Zaccaro *et al.*, 1998; Mosset *et al.*, 1996). The very high SHG and NLO properties make these hybrid materials highly attractive for application to frequency doubling of the light produced by semiconductor lasers (Kondo *et al.*, 1988). L-Valinium hydrogenphosphite, (I), results from our systematic investigation of organic–inorganic hybrid materials obtained by interaction between various phosphoric oxyacids and amino acids.

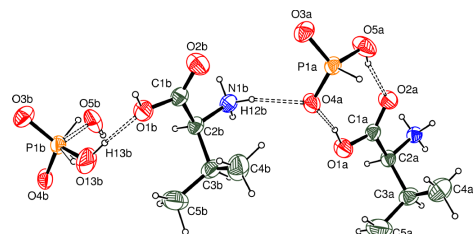


The structure can be described as alternating layers of organic cations ($\text{C}_5\text{H}_{12}\text{NO}_2^+$) and hydrogenphosphite anions (H_2PO_3^-), both layers being parallel to the *ac* plane. The main feature of this stacking is the presence of strong hydrogen bonds, similar to those observed in other ionic compounds (Pecaut & Bagieu-Beucher, 1993; Averbuch-Pouchot, 1993). Within a layer, the distance between the H_2PO_3^- groups is significantly longer [$\text{P}-\text{P} = 4.904(3) \text{ \AA}$], because the $(\text{HPO}_3\text{H})_n$ chain is more stretched. These entities generate, through strong hydrogen bonds, infinite chains of $(\text{HPO}_3\text{H})_n$ parallel to the *b* axis. Hydrogenphosphite groups are hydrogen bonded to the organic cation in two ways, first *via* the carboxylic acid group and second *via* the ammonium groups. We do not observe any hydrogen bonds either between organic cations or between inorganic anions. The valinium residues adopt a *gauche* II conformation and their mean backbone conformation angles $\Psi_1(\text{O}2-\text{C}1-\text{C}2-\text{N}1)$ and $\Psi_2(\text{O}1-\text{C}1-\text{C}2-\text{N}1)$ [$-11.7(2)/168.8(1)$ and $-12.1(2)/167.9(1)^\circ$ for cations *A* and *B* respectively] (Table 1)] are similar to those observed in DL-valinium dihydrogenphosphate (Ravikumar *et al.*, 2002).

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Figure 1

An ORTEP-3 (Farrugia, 1997) view with the atomic labelling scheme showing the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystals of L-valinium hydrogenphosphite were prepared by slow evaporation, at room temperature, of an aqueous solution of L-valine and phosphorous acid in a stoichiometric ratio of 1:1. After six months, crystals appeared as colourless prisms.

Crystal data

$C_5H_{12}NO_2^+ \cdot H_2PO_3^-$	$D_x = 1.408 \text{ Mg m}^{-3}$
$M_r = 199.15$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 12190 reflections
$a = 16.3590(3) \text{ \AA}$	$\theta = 1.4\text{--}26.4^\circ$
$b = 6.2540(2) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$c = 19.4560(3) \text{ \AA}$	$T = 293(2) \text{ K}$
$\beta = 109.238(1)^\circ$	Prism, colourless
$V = 1879.37(8) \text{ \AA}^3$	$0.60 \times 0.40 \times 0.35 \text{ mm}$
$Z = 8$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.065$
φ scans	$\theta_{\text{max}} = 26.4^\circ$
Absorption correction: none	$h = -20 \rightarrow 20$
12190 measured reflections	$k = -7 \rightarrow 7$
3629 independent reflections	$l = -23 \rightarrow 23$
3205 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.5313P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} = 0.034$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
3629 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
335 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

O2a—C1a	1.2218 (19)	O5a—P1a	1.5591 (12)
O1a—C1a	1.2913 (18)	P1b—O13b	1.484 (6)
O4a—P1a	1.5104 (12)	P1b—O5b	1.5369 (16)
O4b—P1b	1.4964 (12)	O1b—C1b	1.3121 (19)
O3a—P1a	1.4855 (11)	O2b—C1b	1.206 (2)
O3b—P1b	1.4930 (12)		
O2a—C1a—O1a	125.70 (14)	O4b—P1b—O5b	109.73 (10)
O13b—P1b—O3b	114.3 (5)	O3a—P1a—O4a	116.11 (7)
O13b—P1b—O4b	110.3 (5)	O3a—P1a—O5a	110.45 (7)
O3b—P1b—O4b	115.76 (7)	O4a—P1a—O5a	109.37 (7)
O3b—P1b—O5b	111.65 (10)	O2b—C1b—O1b	125.42 (14)
O2a—C1a—C2a—N1a	−11.7 (2)	N1b—C2b—C1b—O2b	−12.1 (2)
O1a—C1a—C2a—N1a	168.78 (13)	N1b—C2b—C1b—O1b	167.89 (13)
N1a—C2a—C3a—C4a	74.0 (2)	N1b—C2b—C3b—C4b	80.56 (19)
N1a—C2a—C3a—C5a	−159.58 (18)	N1b—C2b—C3b—C5b	−153.39 (17)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1a—H1a \cdots O4a	0.83 (3)	1.69 (3)	2.506 (2)	167 (3)
O1b—H1b \cdots O4b ⁱ	0.74 (3)	1.82 (3)	2.538 (2)	165 (3)
N1a—H10a \cdots O3b ⁱⁱ	0.87 (2)	1.95 (2)	2.783 (2)	159 (2)
N1b—H11b \cdots O3a ⁱⁱⁱ	0.89 (2)	1.85 (2)	2.724 (2)	170 (2)
N1a—H11a \cdots O4b ^{iv}	0.87 (2)	1.98 (2)	2.837 (2)	169 (2)
N1b—H10b \cdots O3a ^v	0.88 (2)	2.11 (2)	2.845 (2)	141 (2)
N1a—H12a \cdots O3b ^{vi}	0.84 (2)	1.97 (2)	2.802 (2)	170 (2)
N1b—H12b \cdots O4a	0.91 (2)	1.98 (2)	2.852 (2)	159 (2)
O5a—H14a \cdots O2a	0.82	1.82	2.626 (2)	167
O5b—H14b \cdots O2b ⁱⁱⁱ	0.82	2.23	3.026 (2)	165
O13b—H13b \cdots O1b	0.82	1.90	2.681 (11)	160

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

One of the monohydrogenphosphite anions is disordered. The disorder can be described as a rotation of this anion around the axis which bisects the angle O4b—P1b—O3b. The refined model corresponds to a disordered distribution between OH and H, with occupation factors of 0.85 (1) and 0.15 (1). Some of the H atoms were found in difference Fourier maps and were refined with isotropic displacement parameters. The hydroxyl H atoms were constrained, with only torsional freedom. The H atoms of the disordered hydrogenphosphite group were constrained.

Data collection: *KappaCCD Reference Manual* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELX97* (Sheldrick, 1998); program(s) used to refine structure: *SHELX97*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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