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L-Valinium hydrogenphosphite

Leulmi Bendheif,
Nourredine Benali-Cherif,*
Lamia Benguedouar,
Karim Bouchouit and
Hocine Merazig

Laboratoire de Chimie Moléculaire, du Contrôle de l'Environnement et des Mesures Physico-Chimiques, Faculté des Sciences, Département de Chimie, Université Mentouri de Constantine, 25000 Constantine, Algeria

Correspondence e-mail:
benalicherif@hotmail.com

The crystal structure of the title compound, $C_5H_{12}NO_2^+\cdot H_2PO_3^-$, 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.

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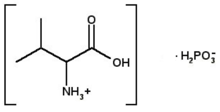
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
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.

Comment

In recent years, organic–inorganic hybrid materials have attracted considerable attention as prefered materials in non-linear optics (NLO), such as second harmonic generation (SHG) and optical bistability, owing to their large optical non-linearities (Masse & Zyss, 1991; Zaccaro *et al.*, 1998; Mosset *et al.*, 1996). The very high SGH 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.



(I)

The structure can be described as alternating layers of organic cations ($C_5H_{12}NO_2^+$) 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 [P—P = 4.904 (3) Å], because the $(HPO_3H)_n$ chain is more stretched. These entities generate, through strong hydrogen bonds, infinite chains of $(HPO_3H)_n$ 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 Ψ_1(O2—C1—C2—N1) and Ψ_2(O1—C1—C2—N1) [−11.7 (2)/168.8 (1) and −12.1 (2)/167.9 (1)° 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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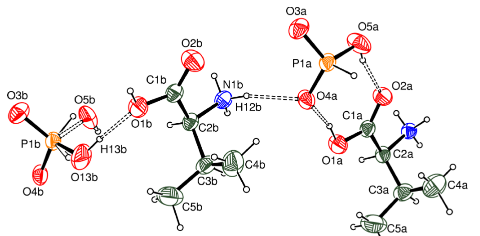

Figure 1
An *ORTEP*-3 (Farrugia, 1997) view with the atomic labelling scheme showing the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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

$C_5H_{12}NO_2^+ \cdot H_2PO_3^-$
$M_r = 199.15$
Monoclinic, $P2_1/n$
$a = 16.3590$ (3) Å
$b = 6.2540$ (2) Å
$c = 19.4560$ (3) Å
$\beta = 109.238$ (1)°
$V = 1879.37$ (8) Å^3
$Z = 8$

$D_x = 1.408$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12190 reflections
$\theta = 1.4$–26.4°
$\mu = 0.28$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.60 × 0.40 × 0.35 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: none
12190 measured reflections
3629 independent reflections
3205 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.065$
$\theta_{\rm max} = 26.4°$
$h = -20 \rightarrow 20$
$k = -7 \rightarrow 7$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.100$
$S = 1.06$
3629 reflections
335 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.5313P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.034$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2*a*—C1*a*	1.2218 (19)	O5*a*—P1*a*	1.5591 (12)
O1*a*—C1*a*	1.2913 (18)	P1*b*—O13*b*	1.484 (6)
O4*a*—P1*a*	1.5104 (12)	P1*b*—O5*b*	1.5369 (16)
O4*b*—P1*b*	1.4964 (12)	O1*b*—C1*b*	1.3121 (19)
O3*a*—P1*a*	1.4855 (11)	O2*b*—C1*b*	1.206 (2)
O3*b*—P1*b*	1.4930 (12)		
O2*a*—C1*a*—O1*a*	125.70 (14)	O4*b*—P1*b*—O5*b*	109.73 (10)
O13*b*—P1*b*—O3*b*	114.3 (5)	O3*a*—P1*a*—O4*a*	116.11 (7)
O13*b*—P1*b*—O4*b*	110.3 (5)	O3*a*—P1*a*—O5*a*	110.45 (7)
O3*b*—P1*b*—O4*b*	115.76 (7)	O4*a*—P1*a*—O5*a*	109.37 (7)
O3*b*—P1*b*—O5*b*	111.65 (10)	O2*b*—C1*b*—O1*b*	125.42 (14)
O2*a*—C1*a*—C2*a*—N1*a*	−11.7 (2)	N1*b*—C2*b*—C1*b*—O2*b*	−12.1 (2)
O1*a*—C1*a*—C2*a*—N1*a*	168.78 (13)	N1*b*—C2*b*—C1*b*—O1*b*	167.89 (13)
N1*a*—C2*a*—C3*a*—C4*a*	74.0 (2)	N1*b*—C2*b*—C3*b*—C4*b*	80.56 (19)
N1*a*—C2*a*—C3*a*—C5*a*	−159.58 (18)	N1*b*—C2*b*—C3*b*—C5*b*	−153.39 (17)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*a*—H1*a*⋯O4*a*	0.83 (3)	1.69 (3)	2.506 (2)	167 (3)
O1*b*—H1*b*⋯O4*b*$^{\rm i}$	0.74 (3)	1.82 (3)	2.538 (2)	165 (3)
N1*a*—H10*a*⋯O3*b*$^{\rm ii}$	0.87 (2)	1.95 (2)	2.783 (2)	159 (2)
N1*b*—H11*b*⋯O3*a*$^{\rm iii}$	0.89 (2)	1.85 (2)	2.724 (2)	170 (2)
N1*a*—H11*a*⋯O4*b*$^{\rm iv}$	0.87 (2)	1.98 (2)	2.837 (2)	169 (2)
N1*b*—H10*b*⋯O3*a*$^{\rm v}$	0.88 (2)	2.11 (2)	2.845 (2)	141 (2)
N1*a*—H12*a*⋯O3*b*$^{\rm vi}$	0.84 (2)	1.97 (2)	2.802 (2)	170 (2)
N1*b*—H12*b*⋯O4*a*	0.91 (2)	1.98 (2)	2.852 (2)	159 (2)
O5*a*—H14*a*⋯O2*a*	0.82	1.82	2.626 (2)	167
O5*b*—H14*b*⋯O2*b*$^{\rm iii}$	0.82	2.23	3.026 (2)	165
O13*b*—H13*b*⋯O1*b*	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) $\frac{1}{2}+x, \frac{5}{2}-y, z-\frac{1}{2}$; (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 O4*b*—P1*b*—O3*b*. 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: *SHELX*97 (Sheldrick, 1998); program(s) used to refine structure: *SHELX*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Averbuch-Pouchot, M. T. (1993). *Acta Cryst.* C**49**, 815–818.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kondo, T., Ogasawara, N. & Ito, R. (1988). *Acta Cryst.* C**44**, 102–104.
Masse, R. & Zyss, J. (1991). *Mol. Eng.* **1**, 141–152.
Mosset, A., Baruchel, P., Lecante, P., Trombe, J. C., Ahamdane, H. & Bensamka, F. (1996). *J. Mater. Chem.* **26**, 503–508.
Nonius (1998). *KappaCCD Reference Manual.* Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Pecaut, J. & Bagieu-Beucher, M. (1993). *Acta Cryst.* C**49**, 834–837.
Ravikumar, B. S., Sridhar, B. & Rajaram, R. K. (2002) *Acta Cryst.* E**58**, o879–o881.
Sheldrick, G. M. (1998). *SHELX*97, which includes *SHELXS*97 and *SHELXL*97. Release 97-2. University of Göttingen, Germany.
Zaccaro, J., Bagieu-Beucher, M., Espesso, J. & Ibanez, A. (1998). *J. Cryst. Growth*, **186**, 224–232.