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3-Pyridylmethylphosphonic acid monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.004 Å
R factor = 0.052
wR factor = 0.146
Data-to-parameter ratio = 11.4

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

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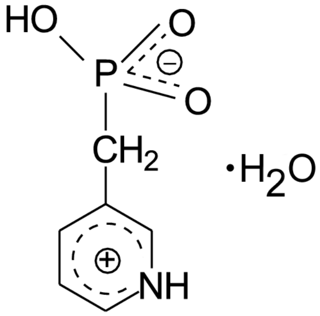
The title molecule, $C_6H_8NO_3P\cdot H_2O$, has a zwitterionic structure. The crystal-packing properties are influenced by the presence of water molecules in the crystal lattice and are stabilized by stacking interactions between pyridyl rings. Hydrogen bonds link the molecules in a three-dimensional network.

Comment

The investigation presented in this paper is part of systematic studies of organophosphorus derivatives of pyridine. Here we describe the crystal structure of 3-pyridylmethylphosphonic acid monohydrate, (I). In previous papers, the structures of 2-pyridylmethylphosphonic acid, (II) (Gałdecki & Wolf, 1990), and 4-pyridylmethylphosphonic acid monohydrate, (III) (Wolf *et al.*, 1996), were reported. Knowledge of the structure of these compounds will help to design and synthesize new platinum(II) complexes with cytotoxic activity using them as ligands. Platinum(II) complexes of phosphonate ligands exhibit significant antitumour activity (Klenner *et al.*, 1993; Bloemink *et al.*, 1994).



(I)

The title molecule exists as a zwitterion. Negative charge is spread over the O2—P1—O3 fragment of the phosphonic group while the positive charge, formally located on the N atom, is delocalized over the pyridyl ring.

The most interesting feature of (I) is the significant difference between the P1—O2 and P1—O3 bond lengths, as large as 10*σ*, while the corresponding values in the previous reported structures, (II) and (III), are not significantly different, 1.500 (4) and 1.507 (3) Å, and 1.506 (2) and 1.5039 (14) Å, respectively. However, the above-mentioned values for bond distances P1—O2 and P1—O3 in (I) are within the range for delocalized bond lengths 1.473–1.534 Å (mean value 1.501 Å) in aminophosphonic acids (Choi & McPartlin, 2000).

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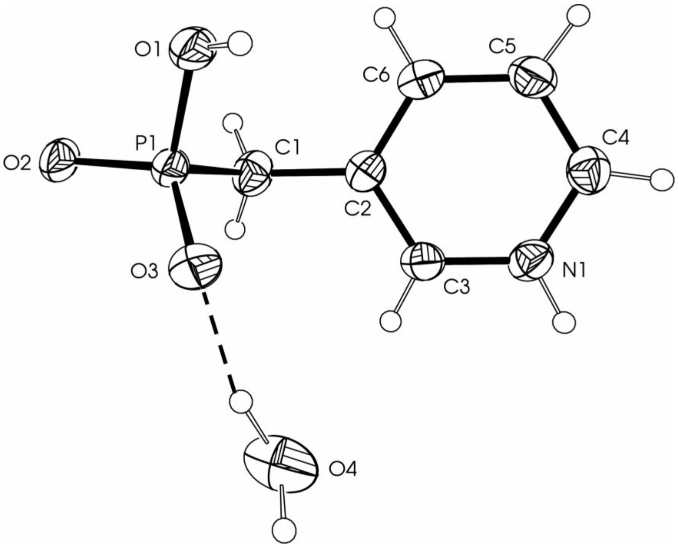

Figure 1
The structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

Analysis of the structural data indicates that the coordination around the P atom is nearly tetrahedral, with the angles varying from 105.03 (10) to 116.84 (11)°.

Table 2 presents the hydrogen-bonding geometry and C—H···O interactions, with H···O contacts significantly less than the sum of the van der Waals radii (Taylor & Kennard, 1982).

The crystal-packing properties are influenced by the presence of water molecules in the crystal lattice. The solvent water molecule is a donor of two hydrogen bonds and is involved in two C—H···O interactions.

Considering the above P—O distances, it should be noticed that they correspond to three different environments (in order of decreasing bond distances): O1 is protonated and a donor in one O—H···O interaction; O2 is an acceptor in two (O—H···O and N—H···O) interactions; O3 is an acceptor in three (two O—H···O and one C—H···O) interactions.

Apart from the typical hydrogen bonds, aromatic π–π-stacking interactions between pyridyl rings are found. They additionally stabilize the molecular packing of (I). The distances between the centroids of the pyridyl rings are $Cg1\cdots Cg2(1-x, 1-y, 1-z)$ = 3.738 (4) Å and $Cg1\cdots Cg3(-x, 1-y, 1-z)$ = 4.021 (4) Å. The perpendicular distances between the rings are 3.514 (4) and 3.459 (4) Å, respectively.

The conformation of the non-H skeleton of the title molecule is described by the torsion angles summarized in Table 1.

Experimental

The title compound was synthesized in one step by the acidolysis of diethyl 3-pyridylmethylphosphonate with hydrobromic acid in acetic acid (Wasilewski *et al.*, 1976; Ochocki *et al.*, 1997) and was recrystallized from a water/ethanol mixture (1:1 by volume). The purity of the product was confirmed by ^{1}H NMR analysis.

Crystal data

$C_6H_8NO_3P\cdot H_2O$
M_r = 191.12
Monoclinic, $P2_1/n$
a = 7.0554 (7) Å
b = 14.0106 (13) Å
c = 8.5228 (15) Å
β = 103.444 (12)°
V = 819.40 (18) Å^3
Z = 4
D_x = 1.549 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 20.0–37.8°
μ = 2.84 mm^{-1}
T = 293 (2) K
Cylinder, colourless
0.15 mm (radius)

Data collection

Kuma KM-4 diffractometer
ω scans
Absorption correction: cylindrical (*CYLABS*; Nardelli, 1996*a*)
$T_{\min}$ = 0.491, $T_{\max}$ = 0.527
2917 measured reflections
1410 independent reflections
1302 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.061
$\theta_{\max}$ = 67.1°
$h = -7 \rightarrow 8$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.146
S = 1.11
1410 reflections
124 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 0.3766P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.007
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.025 (2)

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.4860 (18)	C2—C6	1.392 (3)
P1—O2	1.5150 (17)	C3—N1	1.340 (3)
P1—O1	1.5655 (18)	N1—C4	1.334 (3)
P1—C1	1.799 (3)	C4—C5	1.366 (4)
C1—C2	1.502 (3)	C5—C6	1.383 (4)
C2—C3	1.383 (4)		
O3—P1—O2	116.84 (11)	O2—P1—C1	106.60 (12)
O3—P1—O1	112.23 (12)	O1—P1—C1	105.92 (12)
O2—P1—O1	105.03 (10)	C2—C1—P1	114.42 (17)
O3—P1—C1	109.52 (12)		
O3—P1—C1—C2	−58.1 (2)	P1—C1—C2—C3	93.1 (3)
O2—P1—C1—C2	174.66 (18)	P1—C1—C2—C6	−86.7 (3)
O1—P1—C1—C2	63.2 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O2$^{\rm i}$	0.74 (3)	1.87 (3)	2.598 (3)	170 (4)
N1—H1···O2$^{\rm ii}$	0.89 (3)	1.78 (3)	2.644 (3)	163 (3)
O4—H401···O3$^{\rm iii}$	0.97 (3)	1.82 (4)	2.787 (4)	171 (4)
O4—H402···O3	0.95 (3)	1.87 (3)	2.806 (3)	166 (3)
C3—H3···O4	0.93	2.44	3.227 (4)	142
C1—H101···O4$^{\rm iv}$	0.97	2.38	3.309 (4)	159
C4—H4···O3$^{\rm v}$	0.93	2.44	3.313 (3)	156

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

H atoms of the pyridyl and methylene groups, except H1, were geometrically placed and refined using a riding model with isotropic displacement parameters equal to $1.2U_{\rm eq}$ of the attached C atom. H atoms involved in hydrogen bonds were located from a difference map and refined isotropically. Atoms H401 and H402 of the solvent water molecule were refined with the O—H distances restrained to 0.95 (3) Å (U_{iso} = 1.5U_{eq} of atom O4).

Data collection: *KM*-4 *Data Collection Program* (Kuma, 1998); cell refinement: *KM*-4 *Data Collection Program*; data reduction: *DATAPROC* (Kuma, 1996); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *PARST*97 (Nardelli, 1996*b*).

References

Bloemink, M. J., Dorebos, J. P., Heeterbrij, R. J., Keppler, B. K., Reedijk, J. & Zahn, H. (1994). *Inorg. Chem.* **33**, 1127.

Choi, N. & McPartlin, M. (2000). *Aminophosphonic and Aninophosphinic Acids. Chemistry and Biological Activity*, edited by H. R. Hudson and V. P. Kukhar, pp. 327–361. New York: Wiley and Sons Ltd.

Gałdecki, Z. & Wolf, W. M. (1990). *Acta Cryst.* C**46**, 271–273.

Klenner, T., Valenzuela-Paz, P., Amelung, F., Münch, H., Zahn, H., Keppler, B. K. & Blum, H. (1993). *Metal Complexes in Cancer Chemotherapy*, edited by B. K. Keppler, pp. 87–127. Weinheim: VCH.

Kuma (1996). *DATAPROC*. Kuma Diffraction. Kuma Diffraction, Wrocław, Poland.

Kuma (1998). *KM*-4 *Data Collection Program*. Version 10.2.1. Kuma Diffraction, Wrocław, Poland.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Nardelli, M. (1996*a*). *CYLABS*. University of Parma, Italy.

Nardelli, M. (1996*b*). *J. Appl. Cryst.* **29**, 296–300.

Ochocki, J., Erxleben, A. & Lippert, B. (1997). *J. Heterocycl. Chem.* **34**, 1179.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Wasilewski, C., Sobczak, A. & Szewczyk, J. (1976). *Pol. J. Chem.* **50**, 1795.

Wolf, W. M., Gałdecki, Z. & Gałdecka, E. (1996). *Pol. J. Chem.* **70**, 777–782.