Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

[Hydroxy(4-pyridyl)methyl]phosphonic acid monohydrate

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Received 1 July 2002
Accepted 3 July 2002
Online 12 July 2002

Key indicators

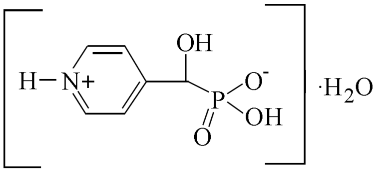
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.103
Data-to-parameter ratio = 12.1

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

The title compound, $C_6H_8O_4NP\cdot H_2O$, contains one phosphonate group and one pyridyl ring connected by a CH(OH) group. The pyridyl N atom and one of the three phosphonate O atoms are protonated. Extensive hydrogen-bonding interactions, as well as π–π-stacking interactions, are found between the molecules, thus generating a three-dimensional supramolecular network structure.

Comment

Metal phosphonates are organic–inorganic hybrid materials that can be designed to possess specific properties; these include ion exchangers, sensors, non-linear optical materials and catalysts (Clearfield, 1998). A number of functional phosphonic acids have been employed to build up novel structures, ranging from one-dimensional chains, through two-dimensional layers to three-dimensional pillared layers or open frameworks. As a potential multidentate ligand, [hydroxy(4-pyridyl)methyl]phosphonic acid is capable of forming extended structures with metal ions. During our efforts to synthesize a cobalt compound by direct reaction of the acid with $CoCl_2$ under hydrothermal conditions, however, good quality single crystals of the unreacted acid were obtained as the monohydrate, (I).



(I)

Fig. 1 shows that the phosphonate group and the pyridyl ring are separated by a CH(OH) group. Consequently, a chiral center is created at atom C6. Among the three phosphonate O atoms, only O3 is protonated; hence the P—O3 distance is 1.5736 (19) Å, much longer than the other two P—O distances (Table 1). The P—C and C—O distances are normal. The CPO_3 tetrahedron is slightly distorted, with the O—P—O(C) angles ranging from 105.61 (12) to 117.98 (11)°. The pyridyl N atom is also protonated in order to balance the overall charge. The neighboring molecules are connected by the hydrogen bonds between the phosphonate O atoms and the hydroxyl O atom, forming an infinite chain along the 2_1 screw axis (Table 2). These chains are held together through hydrogen bonds between O1*W* and the phosphonate O atoms (O1 and O2), forming a chiral layer. π–π-Stacking interactions are also found within the layer, with a centroid-to-centroid distance of 3.61 (2) Å for adjacent pyridyl rings. Neighboring layers are

DOI: 10.1107/S160053680201173X

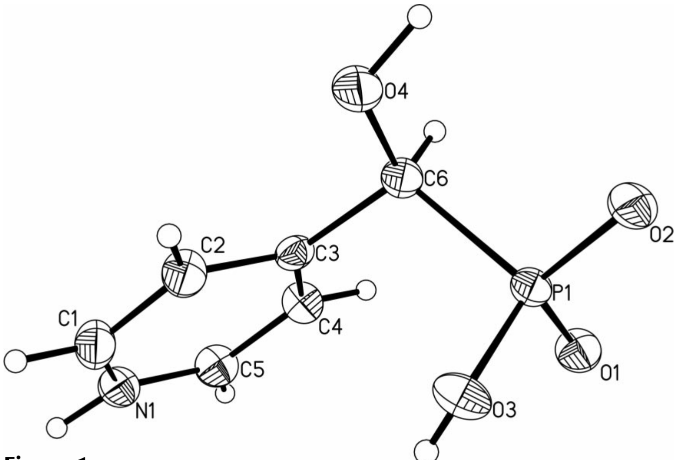


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids.

situated about inversion centers and are linked by hydrogen bonds between atoms O1*W* and N1, thus leading to a racemic three-dimensional supramolecular network (Fig. 2).

Experimental

Colorless single crystals of (I) were obtained by hydrothermal treatment of a mixture of [hydroxy(4-pyridyl)methyl]phosphonic acid (0.0986 g, 0.5 mmol; Bogdan, 1996), $CoCl_2 \cdot 6H_2O$ (0.0623 g, 0.25 mmol) and 8 ml H_2O–EtOH (1:3) at 413 K for 2 d, then cooling slowly to room temperature.

Crystal data

$C_6H_8NO_4P \cdot H_2O$
$M_r = 207.12$
Monoclinic, $P2_1/n$
$a = 6.486$ (1) Å
$b = 15.464$ (3) Å
$c = 8.457$ (2) Å
$\beta = 103.91$ (1)°
$V = 823.3$ (3) Å^3
$Z = 4$
$D_x = 1.671$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1197 reflections
$\theta = 2.6$–23.9°
$\mu = 0.32$ mm^{-1}
$T = 293$ (2) K
Column, colorless
0.30 × 0.25 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.906$, $T_{\max} = 0.966$
4405 measured reflections
1613 independent reflections
1189 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 26.0°$
$h = -8 \rightarrow 7$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.103$
$S = 0.94$
1613 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

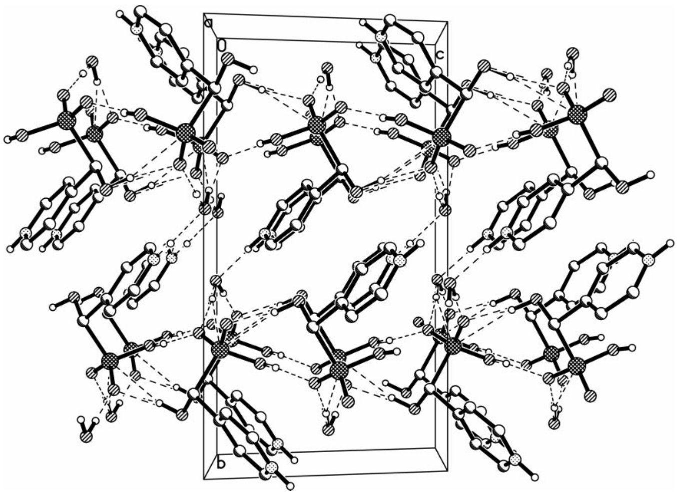


Figure 2
The packing of (I), viewed along the *a* axis.

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.4910 (18)	P1—O3	1.5736 (19)
P1—O2	1.4938 (17)	P1—C6	1.843 (3)
O1—P1—O2	117.98 (11)	O3—P1—C6	105.61 (12)
O1—P1—O3	109.43 (10)	O4—C6—C3	108.7 (2)
O2—P1—O3	107.30 (11)	O4—C6—P1	111.21 (18)
O1—P1—C6	108.79 (11)	C3—C6—P1	109.83 (17)
O2—P1—C6	107.04 (11)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2$^{\rm i}$	0.77 (3)	1.85 (3)	2.617 (2)	174 (3)
O4—H4···O1$^{\rm ii}$	0.95 (3)	1.76 (3)	2.697 (3)	169 (3)
O1*W*—H1*WA*···O2$^{\rm iii}$	0.92 (3)	1.79 (3)	2.705 (3)	173 (3)
O1*W*—H1*WB*···O1$^{\rm iv}$	0.77 (3)	1.97 (3)	2.727 (3)	167 (4)
N1—H1N···O1*W*	0.93 (3)	1.75 (3)	2.669 (3)	170 (3)

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

The positions of all H atoms of the pyridyl ring, except for that on N, were fixed geometrically and distances to H atoms were set by the refinement program (C—H = 0.93–0.98 Å). The other H atoms were found from difference density maps. The bond distances were O—H = 0.77 (3)–0.95 (3) Å and N—H = 0.93 (3) Å.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was funded by the National Natural Science Foundation of China (Nos. 29901003, 29823001 and 20131020) and the Analysis Center of Nanjing University. The authors thank Mr Yong-Jiang Liu for the data collection.

References

Bogdan, B. (1996). *Tetrahedron*, **38**, 12483–12494.
Bruker (1997). *SMART, SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Clearfield, A. (1998). *Progress in Inorganic Chemistry*, edited by K. D. Karlin, Vol. 47, pp. 371–510. New York: John Wiley and Sons Inc.
Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.