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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.061
 wR factor = 0.161
Data-to-parameter ratio = 13.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.[(1*H*-Benzimidazol-2-ylmethyl)iminodimethylene]-
diphosphonic acid dihydrate

The title compound, $\text{C}_9\text{H}_{15}\text{O}_6\text{N}_3\text{P}_2 \cdot 2\text{H}_2\text{O}$, contains two phosphonic acid groups and one benzimidazole group connected by an $\text{N}(\text{CH}_2)_3$ group. One of the benzimidazole N atoms and two phosphonic acid O atoms of each PO_3 group are protonated. Extensive hydrogen-bonding interactions, as well as π - π stacking interactions, are found between the molecules, leading to a three-dimensional supramolecular network structure.

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Comment

Metal phosphonates are organic–inorganic hybrid materials that are important because of their potential applications in ion exchange, sensors, catalysis and molecular recognition (Clearfield, 1998). A number of multifunctional phosphonic acids have been used for building novel structures, ranging from zero-dimensional molecules to three-dimensional frameworks. As a potential multidentate ligand, [(1*H*-benzimidazol-2-ylmethyl)iminodimethylene]diphosphonic acid (bibmpH_4) is potentially able to form various structures with metal ions. Five isomorphous compounds with chain structures have been obtained through hydrothermal reactions of bibmpH_4 and metal sources (Cao *et al.*, 2006). During our efforts to synthesize a manganese compound by direct reaction of bibmpH_4 with $\text{Mn}(\text{ClO}_4)_2$ in aqueous solution, however, excellent quality single crystals of the unreacted acid were obtained as the title dihydrate, (I).

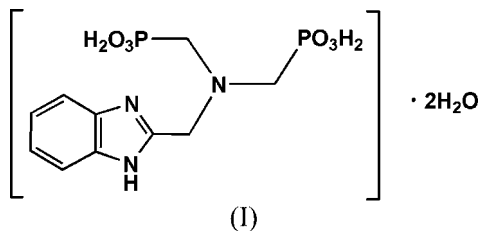


Fig. 1 shows the structure of compound (I) with the atomic labelling scheme. Of the three phosphonate O atoms connected to each of P1 and P2, atoms O2, O3, O5 and O6 are protonated. Hence, the P1–O2, P1–O3, P2–O5 and P2–O6 distances of 1.564 (3), 1.546 (3), 1.537 (3) and 1.567 (3) Å, respectively, are much longer than the other P1–O1 [1.509 (3) Å] and P2–O4 [1.507 (3) Å] distances. The P–C and C–O distances are normal. The CPO_3 tetrahedra are slightly distorted, with the O–P–O(C) angles ranging from 103.53 (15) to 116.84 (17)°.

Neighbouring molecules are connected by very strong hydrogen bonds (Table 1) between phosphonate atoms O2

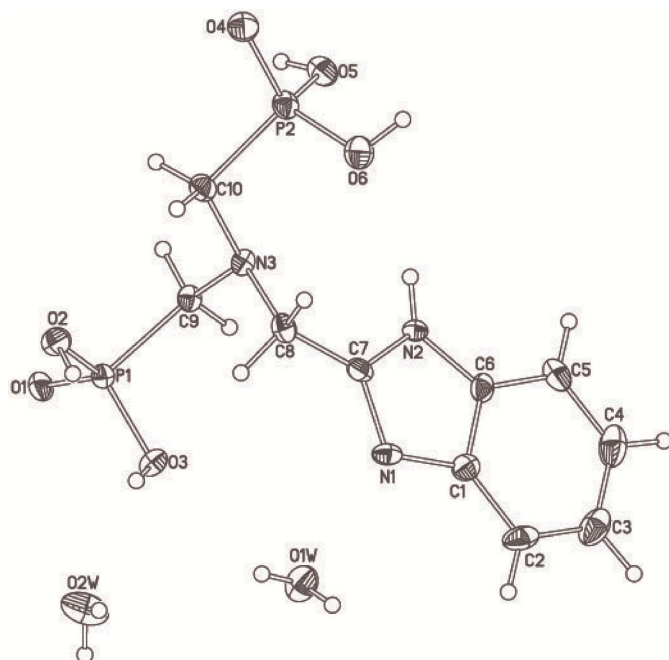


Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. C-bound H atoms have been omitted for clarity.

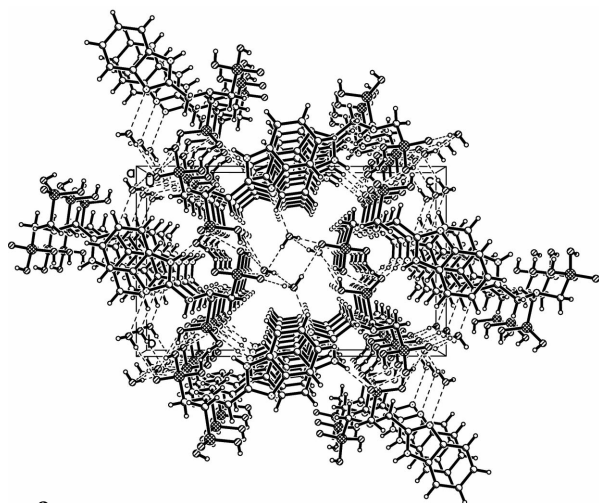


Figure 2
The crystal packing, viewed along the *a* axis. C-bound H atoms have been omitted for clarity. Dashed lines indicate hydrogen bonds.

and O6, forming an infinite chain along the *b* axis. These chains are held together through hydrogen bonds between atoms N2 and O1, and between atom O2W and the phosphonate O atoms, forming a layer in the *ab* plane.

Neighbouring layers are linked by hydrogen bonds between atoms O1W and O4 from different layers. π - π stacking interactions are also found between these layers along the *a* axis, with centroid-to-centroid distances between adjacent benzene rings of 3.627 (2) and 3.955 (2) Å. Therefore, a three-dimensional supramolecular network is formed with one-dimensional channels generated along the *a* axis. The solvent water molecules O1W and O2W reside within the channels.

Experimental

(Benzimidazol-2-ylmethyl)iminobis(methylenephosphonic acid) (bibmpH₄) was synthesized according to the literature procedure of Yoshikawa (1995). A mixture of bibmpH₄ (0.081 g, 0.25 mmol), manganese(II) perchlorate (0.0905 g, 0.25 mmol) and water (10 ml) was stirred at room temperature for 10 min. The filtrate was kept at room temperature for 2 d, after which colourless block crystals of (I) were collected. Analysis, calculated for (I): C 32.70, H 4.09, N 11.44%; found: C 32.21, H 4.94, N 11.23%.

Crystal data

C₁₀H₁₅N₃O₆P₂·2H₂O
M_r = 371.22
 Monoclinic, *P*2₁/*c*
a = 7.0336 (8) Å
b = 11.5822 (13) Å
c = 18.935 (2) Å
 β = 91.252 (2)°
V = 1542.2 (3) Å³

Z = 4
D_x = 1.599 Mg m⁻³
 Mo *K*α radiation
 μ = 0.33 mm⁻¹
T = 298 (2) K
 Block, colourless
 0.32 × 0.28 × 0.26 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.91, *T_{max}* = 0.92

8348 measured reflections
 3025 independent reflections
 2151 reflections with *I* > 2σ(*I*)
R_{int} = 0.052
 θ_{\max} = 26.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.061
wR (*F*²) = 0.161
S = 0.95
 3025 reflections
 226 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1074P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.66 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.64 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2W—H2WB...O1W ⁱ	0.80 (7)	2.28 (7)	3.051 (5)	163 (6)
O1W—H1WA...O4 ⁱⁱ	0.85 (6)	1.98 (6)	2.823 (4)	173 (5)
O2W—H2WA...O4 ⁱⁱⁱ	0.87 (6)	1.90 (7)	2.722 (5)	158 (6)
O1W—H1WB...O4 ⁱⁱⁱ	0.80 (6)	2.20 (6)	2.965 (4)	159 (5)
O2—H2A...O6 ⁱⁱⁱ	0.88 (5)	1.56 (5)	2.359 (4)	148 (4)
O5—H5A...O2W ^{iv}	0.82 (5)	2.51 (5)	3.302 (5)	162 (5)
N2—H2C...O1 ^{iv}	0.86	1.93	2.770 (4)	165

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

All H atoms on C and N atoms were placed in calculated positions and included as part of a riding model, with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom. O-bound H atoms were refined freely.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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