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Piperizinium hydrogen phosphite monohydrate

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The title compound, $C_6H_{12}N_2^{2+}\cdot HPO_3^{2-}\cdot H_2O$, contains doubly protonated piperizinium cations, hydrogen phosphite anions and water molecules. The component species have normal geometrical parameters and interact by way of N—H···O and O—H···O hydrogen bonds, resulting in [010] chains of alternating $[HPO_3]^{2-}$ and H_2O species, crosslinked by the organic moieties. A possible C—H···O interaction is also present.

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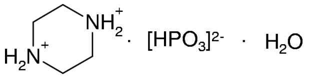
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.131
Data-to-parameter ratio = 24.7

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

Comment

The crystal structures of (protonated) amine hydrogen phosphites containing $[HPO_3]^{2-}$ or $[H_2PO_3]^{-}$ oxo-anions are of crystallochemical interest in terms of the interplay between the hydrogen bonds linking the cations, anions, and, if applicable, water molecules together (Averbuch-Pouchot, 1993*a*,*b*; Harrison, 2003*a*,*b*).



(I)

The asymmetric unit of the title compound, (I), consists of two half-molecule $\{C_2H_6N\}$ fragments of $(C_4H_{12}N_2)^{2+}$ piperizinium cations, an $[HPO_3]^{2-}$ hydrogen phosphite group and a water molecule. Inversion symmetry (Fig. 1) generates the two complete piperizinium cations, and the water O atom is disordered over two adjacent sites (see *Experimental*). The

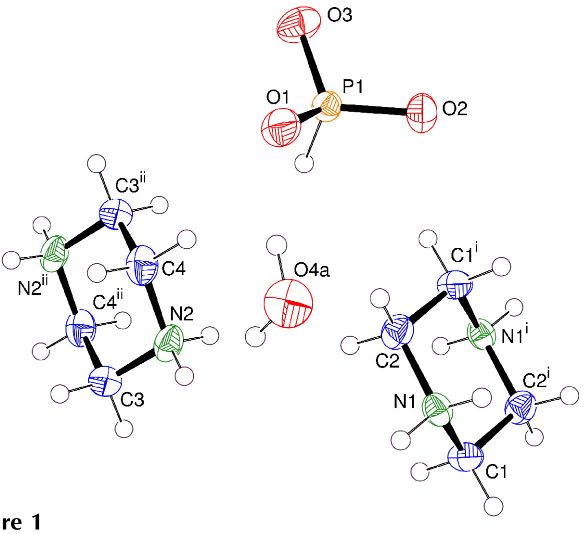


Figure 1
View of (I) (50% displacement ellipsoids; H atoms are drawn as small spheres of arbitrary radius). The disordered O4*b* species is omitted. Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$.

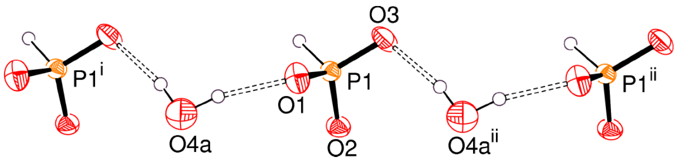


Figure 2
Detail of a [010] hydrogen phosphite–water chain with the H···O components of the hydrogen bonds indicated by dashed lines (atom O4*b* not shown). Symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x*, *y* − 1, *z*.

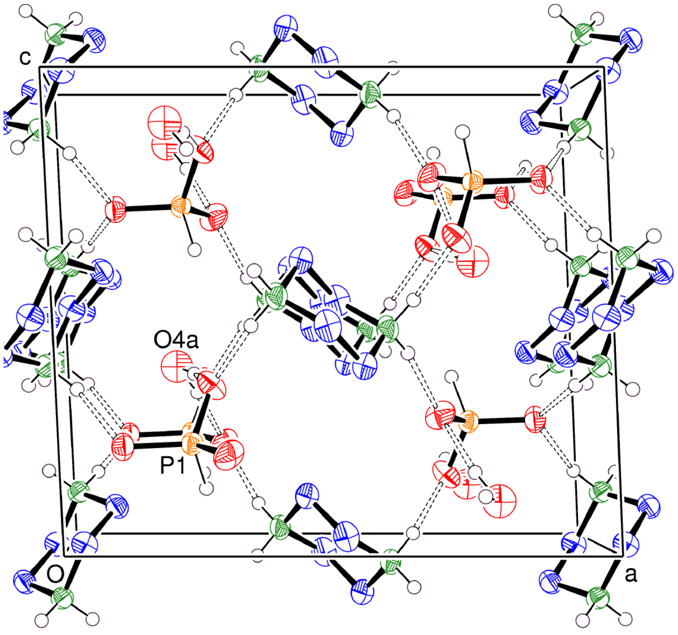


Figure 3
Unit-cell packing in (I) projected onto (010). The H···O components of the hydrogen bonds are indicated by dashed lines. O4*b* and all C—H H atoms are omitted for clarity.

hydrogen phosphite group shows its usual (Harrison, 2003*a*) pseudo-pyramidal geometry [mean d(P—O) = 1.521 (2) Å; mean θ(O—P—O) = 112.48 (9)°] and the organic species adopt typical chair conformations.

As well as electrostatic forces, the component species in (I) interact by means of O—H···O and N—H···O hydrogen bonds (Table 2), and possibly a C—H···O interaction (see below). Infinite chains of alternating $[HPO_3]^{2-}$ and H_2O moieties are formed (Fig. 2) along [010] as a result of the water-to-phosphite O—H···O hydrogen bonds, with the repeating units generated by translation symmetry. The resulting P1···P1^{ii} (Fig. 2; see Table 2 for symmetry code) separation of 6.5706 (7) Å is naturally much larger than the typical P···P separations (4.7–4.9 Å) seen when $[H_2PO_3]^-$ dihydrogen phosphite units link together by way of P—O—H···O—P interactions without an intervening water molecule (Averbuch-Pouchot, 1993*a*, Harrison, 2003*a*).

The piperizinium cations crosslink the [010] $[HPO_3]^{2-}$–H_2O chains by way of the N—H···O hydrogen bonds (Table 2), with all four bonds close to linear [mean θ(N—H···O) = 168°]. A short C1—H5···O4*a*^{iv} (Table 2) interaction was identified in a *PLATON* (Spek, 2003) analysis of (I). If it is not merely a packing artefact, it may provide some additional coherence between the piperizinium cations and the water component of the $[HPO_3]^{2-}$–H_2O [010] chains, although its role, if any, in the disordering of the water molecule O4 atom is not obvious.

Experimental

H_3PO_3 (0.82 g; 1 mmol) and piperizine hexahydrate (1.92 g; 0.01 mmol) were dissolved in 10 ml deionized water, resulting in a clear solution. Block-shaped crystals of (I) grew as the water evaporated over several days.

Crystal data

$C_6H_{12}N_2^{2+}\cdot HPO_3^{2-}\cdot H_2O$
$M_r = 186.15$
Monoclinic, $P2_1/c$
$a = 12.2476$ (8) Å
$b = 6.5706$ (4) Å
$c = 10.6592$ (8) Å
$\beta = 92.744$ (1)°
$V = 856.8$ (1) Å^3
$Z = 4$

$D_x = 1.443$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2470 reflections
$\theta = 3.3$–29.8°
$\mu = 0.30$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.27 × 0.23 × 0.19 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.925$, $T_{max} = 0.949$
6211 measured reflections

2468 independent reflections
1930 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 30.0°$
$h = -17 \rightarrow 16$
$k = -8 \rightarrow 9$
$l = -14 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.131$
$S = 1.02$
2468 reflections
100 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

P1—O3	1.5151 (13)	P1—O1	1.5234 (14)
P1—O2	1.5230 (12)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···O2^i	0.90	1.84	2.7147 (19)	164
N1—H3···O2^{ii}	0.90	1.81	2.7043 (19)	172
N2—H8···O3^{ii}	0.90	1.77	2.642 (2)	163
N2—H9···O1^{iii}	0.90	1.78	2.676 (2)	171
O4*a*—H14···O1	0.95	1.90	2.840 (4)	167
O4*a*—H15···O3^{ii}	0.93	1.90	2.811 (4)	168
O4*b*—H14···O1	0.93	1.90	2.752 (4)	151
O4*b*—H15···O3^{ii}	0.96	1.90	2.765 (4)	149
C1—H5···O4*a*^{iv}	0.97	2.38	3.300 (5)	159

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

The water O atom was modelled as being disordered over two adjacent sites with isotropic displacement factors [d(O4*a*···O4*b*) = 0.638 (5) Å; fractional site occupancies = 0.563 (14) and 0.437 (14) for O4a and O4*b*, respectively, with their sum constrained to unity]. The present data did not reveal H-atom sites that could be unambiguously associated with either O4a or O4*b*; instead, two distinct features in the difference map provided H-atom sites that were reasonable for both O4*a* and O4*b* (see Table 2). These O—H H atoms were refined by riding on O4*a* in their as-found positions. The N—H H atoms were found in difference maps and refined by riding in their idealized positions [d(N—H) = 0.90 Å]. The H atoms bonded to C and P were placed in calculated positions [d(C—H) = 0.97 Å; d(P—H) = 1.32 Å] and refined by riding. For all H atoms, the constraint $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(carrier atom) was applied.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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