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Key indicators

Single-crystal X-ray study

T = 183 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.043

wR factor = 0.117

Data-to-parameter ratio = 13.8

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

Pillared layered hydrogen-bonded network in hexamethylenediammonium hydrogenphosphite

In the structure of the title compound, $\text{C}_6\text{H}_{18}\text{N}_2^{2+} \cdot 2\text{H}_2\text{PO}_3^-$, the hexamethylenediammonium dication has a center of symmetry and the asymmetric unit contains half of the dication and one hydrogenphosphite anion. The $(\text{P}-\text{O}-\text{H} \cdots \text{O}(-\text{P}))$ and $\text{N}-\text{H} \cdots \text{O}(-\text{P})$ hydrogen bonds link ammonium and hydrogenphosphite groups to form a two-dimensional hydrogen-bonded network. Layers are linked covalently into pillars by bifunctional diammonium moieties, making a three-dimensional framework.

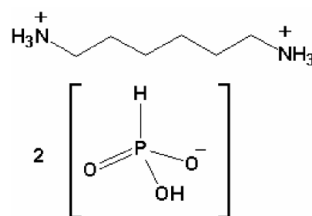
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Comment

Current interest in supramolecular chemistry and materials chemistry has been focused on the search for new synthons and the design of building blocks which can be utilized for the engineering of one-, two- or three-dimensional assemblies.



(I)

These include both organic and organic–inorganic hybrid materials, as well as organometallic moieties. The hydrogen bond plays a key role in this field and a number of hydrogen-bonding synthons have been introduced for the rational design of solids (Braga *et al.*, 1998; Desiraju, 1989; Meleñdez &

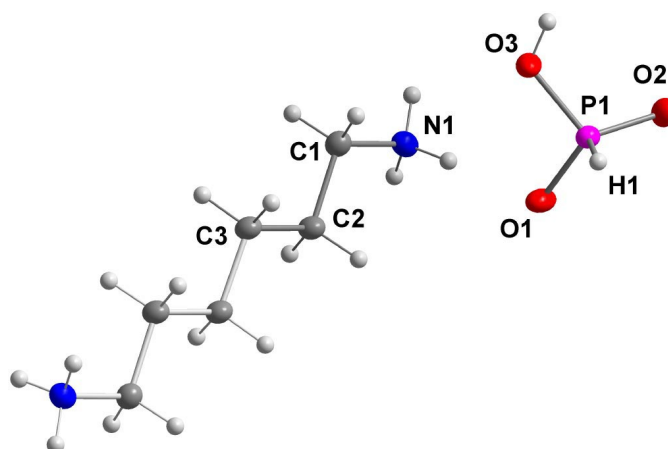


Figure 1

The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. Only symmetry-independent atoms are labelled.

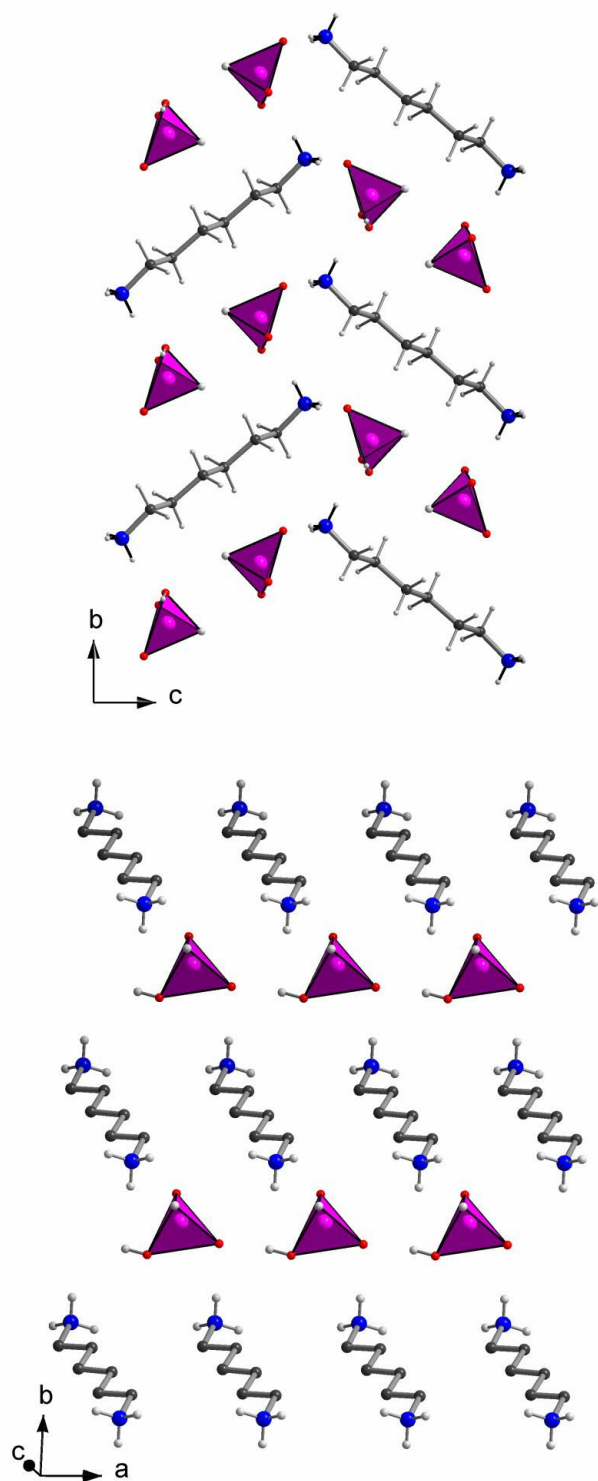


Figure 2
Top: the alternating arrangement of organic dications and hydrogenphosphite tetrahedra. Notice the orientation of hydrogen on the P atom pointing out from the layers. Bottom: a view on to a layer showing the arrangement of polyhedra to form chains parallel to the *a* axis.

Hamilton, 1998). It has been found that phosphonic acids are potentially good candidates for the assembly of hydrogen-bonded networks (Ferguson *et al.*, 1998; Gregson *et al.*, 2000;

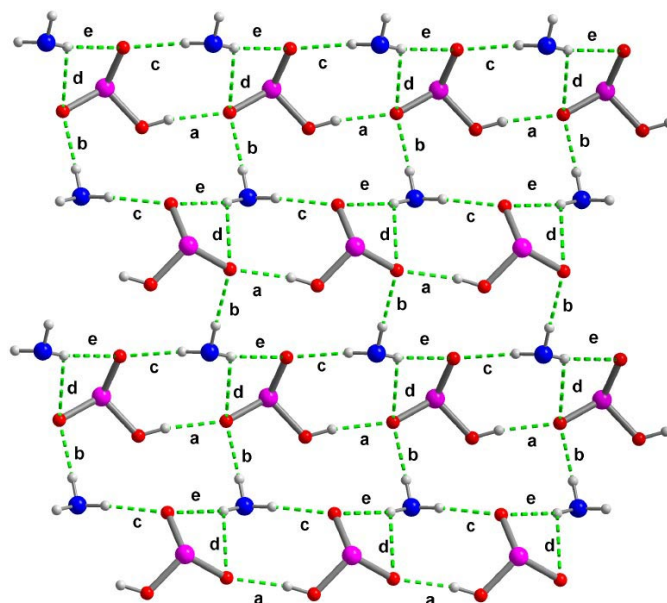


Figure 3
The pattern of the hydrogen-bonding network. The hydrogen-bond notations are given in Table 2. For clarity, C atoms are not shown.

Mahmoudkhani & Langer, 2001; Sharma & Clearfield, 2000; Sharma *et al.*, 2001). Phosphorous acid, the inorganic analogue of phosphonic acids and could behave in a similar manner in view of the architecture of the resulting structure and having the potential for hydrogen-bonding interactions. This requires a systematic investigation and careful analysis of already known structures. For example, in the crystal structures of anilinium hydrogenphosphite (Paixão *et al.*, 2000) and ethylenediammonium hydrogenphosphite (Fleck *et al.*, 2000), the hydrogenphosphite group is involved in hydrogen-bonding networks, forming sheets or layers with a railroad-type section, respectively.

In the crystal structure of the title compound, (I), the hexamethylenediammonium cation is centrosymmetric and the asymmetric unit contains half of the dication and a hydrogenphosphite anion (Fig. 1). The structure exhibits a pillar-like layered hydrogen-bonded network, as shown in Fig. 2. The anion acts as both hydrogen-bond donor (through the O3 atom) and acceptor (through the O1 and O2 atoms). The O2 atom is a bifurcated acceptor of hydrogen bonds *via* the H12 and H13 atoms, while the N1 atom acts as a bifurcated hydrogen-bond donor through the H13 atom. The O1 atom acts as an acceptor of three hydrogen bonds *via* the H3, H11 and H13 atoms (see Table 2 for the hydrogen-bond geometry and notations). The hydrogen-bonding pattern is presented in Fig. 3. Although the first-level graph set, based on the methodology of Bernstein *et al.* (1995) and Grell *et al.* (1999), contains only *D* and *C*(4) descriptors, the second and higher levels comprise several motifs, including chains and rings. The assignment of graph-set descriptors was performed using *PLUTO*, as described by Motherwell *et al.* (1999). The O3 atom acts only as a donor to the O1 atom, hydrogen bond [a], thus forming *C*(4) chain motifs along the *a* axis. A *R*₁²(4) ring motif is formed by the combination of [d] and [e] hydrogen

bonds. A pair of hydrogenphosphite anions and an ammonium cation are linked together *via* [a], [c] and [d] hydrogen bonds, forming an $R_3^2(8)$ ring motif. An $R_3^3(10)$ motif is also formed by [a], [c] and [e] hydrogen bonds. A combination of [a], [b], [e], [c] and [b] hydrogen bonds gives an $R_5^3(12)$ ring motif.

Experimental

The title compound was prepared by the reaction of a solution of phosphorous acid in water, and a solution of 1,6-hexamethylenediamine in water with the molar ratio 2:1 at ambient temperature. Crystals suitable for X-ray diffraction analysis were obtained by very slow evaporation of the solution over a period of several days.

Crystal data

$C_6H_{18}N_2^{2+} \cdot 2H_2PO_3^-$	$D_x = 1.432 \text{ Mg m}^{-3}$
$M_r = 280.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2831 reflections
$a = 4.9330(3) \text{ \AA}$	$\theta = 1-25^\circ$
$b = 8.9074(5) \text{ \AA}$	$\mu = 0.35 \text{ mm}^{-1}$
$c = 14.8407(8) \text{ \AA}$	$T = 183(2) \text{ K}$
$\beta = 94.751(1)^\circ$	Parallelepiped, colorless
$V = 649.86(6) \text{ \AA}^3$	$0.16 \times 0.08 \times 0.02 \text{ mm}$
$Z = 2$	

Data collection

Siemens SMART CCD diffractometer	1284 independent reflections
ω scans	1049 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$R_{\text{int}} = 0.042$
$T_{\text{min}} = 0.946$, $T_{\text{max}} = 0.993$	$\theta_{\text{max}} = 26.1^\circ$
4004 measured reflections	$h = -6 \rightarrow 6$
	$k = -11 \rightarrow 9$
	$l = -16 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 0.4391P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.117$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
1284 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
93 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

P1—O1	1.5060 (19)	P1—O3	1.5686 (19)
P1—O2	1.4974 (19)	P1—H1	1.27 (2)
O1—P1—H1	106.4 (11)	O2—P1—O3	112.83 (10)
O1—P1—O3	105.82 (11)	O3—P1—H1	102.3 (11)
O2—P1—H1	113.1 (11)	P1—O3—H3	118 (3)
O2—P1—O1	115.29 (12)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
[a] O3—H3 \cdots O1 ⁱ	0.80 (2)	1.79 (2)	2.587 (3)	171 (4)
[b] N1—H11 \cdots O1	0.87 (2)	1.91 (2)	2.784 (3)	177 (3)
[c] N1—H12 \cdots O2 ⁱⁱ	0.87 (2)	1.91 (2)	2.781 (3)	173 (3)
[d] N1—H13 \cdots O1 ⁱⁱⁱ	0.87 (2)	2.50 (3)	3.060 (3)	123 (2)
[e] N1—H13 \cdots O2 ⁱⁱⁱ	0.87 (2)	2.18 (2)	3.045 (3)	171 (3)

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

The H atom bonded to the P atom was refined isotropically without restraints. The H atoms of the ammonium and hydroxyl groups were refined isotropically with restrained bond distances of 0.85 and 0.80 \AA , respectively, whereas the other H atoms were constrained to idealized geometries using the appropriate riding model. Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT and SADABS (Sheldrick, 2001); program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2000).

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