

Guanidinium dihydrogen phosphite

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{P}-\text{O}) = 0.001$ Å
 R factor = 0.029
 wR factor = 0.075
Data-to-parameter ratio = 25.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The structure of the title compound, $\text{CH}_6\text{N}_3^+\cdot\text{H}_2\text{PO}_3^-$, originally determined by Krumbe & Haussuhl [*Z. Kristallogr.* (1987), **178**, 132–134], has been redetermined. The intermolecular packing is controlled by $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, resulting in a non-centrosymmetric three-dimensional structure.

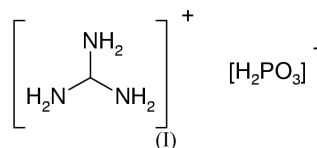
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Comment

Amine phosphates have recently been proposed as key intermediates in the synthesis of organically templated open frameworks (Rao *et al.*, 2000). In addition, they show interesting crystal-packing motifs controlled by the interplay of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Demir *et al.*, 2002). Less is known about the crystal structures of amine–hydrogen phosphite complexes which involve the $[\text{HPO}_3]^{2-}$ ion or its protonated derivative, $[\text{H}_2\text{PO}_3]^-$. Here we report the crystal structure of guanidinium dihydrogen phosphite, $\text{CH}_6\text{N}_3^+\cdot\text{H}_2\text{PO}_3^-$, (I) (Fig. 1). This phase was first prepared and characterized by Krumbe & Haussuhl (1987), but a redetermination was considered worthwhile, as atomic parameters were not published.

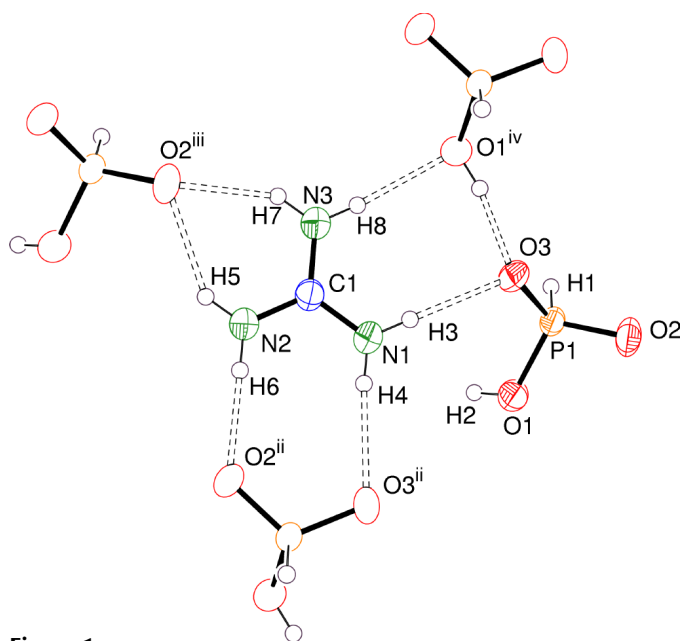


The CH_6N_3^+ cation [$d_{\text{av}}(\text{C}-\text{N}) = 1.325$ (2) Å; $\theta_{\text{av}}(\text{N}-\text{C}-\text{N}) = 120.0$ (2)°] shows its usual ‘propeller’ shape approximating to D_{3h} local symmetry (Harrison & Phillips, 1997), indicating that the usual bonding model for this species, with a C–N bond order of 1.33, is appropriate here. The dihydrogen phosphite anion possesses typical (Doran *et al.*, 2001) geometrical parameters [$d_{\text{av}}(\text{P}-\text{O}) = 1.523$ (2) Å; $\theta_{\text{av}}(\text{O}-\text{P}-\text{O}) = 111.2$ (2)°], with the P–O1H vertex significantly lengthened compared with the other P–O bonds.

The unit-cell packing (Fig. 2) involves chains of $[\text{H}_2\text{PO}_3]^-$ groups propagating in the polar [010] direction, linked together *via* $\text{O1}-\text{H2}\cdots\text{O3}$ hydrogen bonds. All six of the guanidinium H atoms are involved in $\text{N}-\text{H}\cdots\text{O}$ interactions (Figs. 1 and 2); O1 accepts one, O2 three, and O3 two $\text{N}-\text{H}\cdots\text{O}$ bonds. The resulting $\text{O}(\text{PH}_3)$ coordinations for O2 and O3 are approximately tetrahedral. As expected (Doran *et al.*, 2001), the P–H vertex is not involved in the hydrogen-bonding scheme.

Experimental

$(\text{CH}_6\text{N}_3)_2(\text{CO}_3)$ (0.91 g, 0.005 mmol) and H_3PO_3 (0.82 g, 0.01 mmol) were dissolved in 20 ml distilled water. Block-shaped crystals of (I) grew over the course of a few days as the solvent evaporated.


Figure 1

Fragment of (I) (50% displacement ellipsoids and arbitrary spheres for the H atoms), showing the atom-labelling scheme and hydrogen-bonding interactions (dashed lines). Symmetry-generated hydrogen phosphite moieties are indicated by unshaded ellipsoids; symmetry codes are as in Table 2. Note how each roughly parallel pair of guanidinium N—H bonds (H3 + H5; H6 + H8; H4 + H7) hydrogen bonds to a different acceptor configuration.

Crystal data

$\text{CH}_6\text{N}_3^+\cdot\text{H}_2\text{PO}_3^-$
 $M_r = 141.07$
 Monoclinic, $P2_1$
 $a = 4.5268$ (3) Å
 $b = 7.4711$ (5) Å
 $c = 9.1856$ (6) Å
 $\beta = 100.631$ (2)°
 $V = 305.33$ (3) Å³
 $Z = 2$

$D_x = 1.534$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2092 reflections
 $\theta = 2.3$ – 32.3 °
 $\mu = 0.38$ mm⁻¹
 $T = 293$ (2) K
 Block, colourless
 $0.32 \times 0.21 \times 0.16$ mm

Data collection

Bruker SMART1000 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.891$, $T_{\max} = 0.944$
 3144 measured reflections

1836 independent reflections
 1691 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$
 $\theta_{\max} = 32.5$ °
 $h = -4 \rightarrow 6$
 $k = -11 \rightarrow 10$
 $l = -13 \rightarrow 13$

Refinement

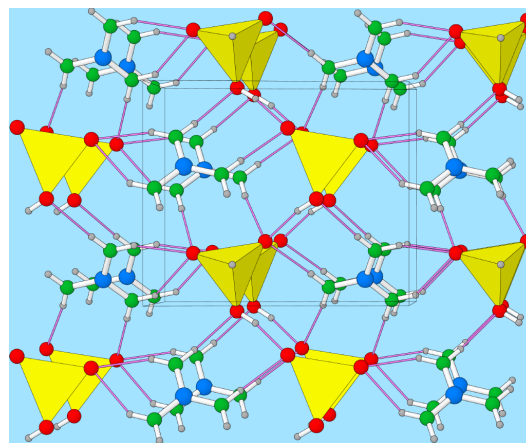
Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.076$
 $S = 0.99$
 1836 reflections
 73 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.28$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³
 Absolute structure: Flack (1983),
 1055 Friedel pairs
 Flack parameter = -0.03 (9)

Table 1

Selected geometric parameters (Å, °).

P1—O2	1.4878 (11)	C1—N3	1.321 (2)
P1—O3	1.5073 (11)	C1—N2	1.3227 (19)
P1—O1	1.5736 (13)	C1—N1	1.3314 (19)


Figure 2

The crystal packing in (I), viewed approximately down [100], with the dihydrogen phosphite tetrahedra coloured yellow. The coloured spheres, of arbitrary radii, represent O atoms (red), C atoms (blue), N atoms (green), and H atoms (grey). Hydrogen bonds are highlighted in pink.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H2 \cdots O3 ⁱ	0.82	1.75	2.5602 (17)	169
N1—H4 \cdots O3 ⁱⁱ	0.86	2.18	3.039 (2)	174
N1—H3 \cdots O3	0.86	2.12	2.9837 (19)	178
N2—H6 \cdots O2 ⁱⁱ	0.86	1.96	2.820 (2)	179
N2—H5 \cdots O2 ⁱⁱⁱ	0.86	2.14	2.8907 (19)	146
N3—H8 \cdots O1 ^{iv}	0.86	2.15	3.005 (2)	176
N3—H7 \cdots O2 ⁱⁱⁱ	0.86	2.11	2.8714 (19)	147

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

Atom H2 was located in a difference map and the other H atoms were placed in calculated positions [$d(\text{N}-\text{H}) = 0.86$ Å and $d(\text{P}-\text{H}) = 1.32$ Å]. The H atoms were included in the refinement in the riding-motion approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97; molecular graphics: ORTEP-3 (Farrugia, 1997) and ATOMS (Shape Software, 1999); software used to prepare material for publication: SHELXL97.

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