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Bis(melaminium) hydrogen phosphite tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.001 Å
R factor = 0.037
wR factor = 0.102
Data-to-parameter ratio = 15.6

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

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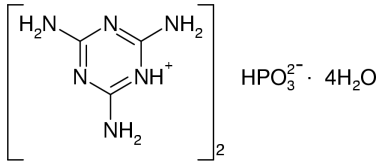
The title compound, $2C_3H_7N_6^+\cdot HPO_3^{2-}\cdot 4H_2O$, crystallizes as a layered structure. The intermolecular packing appears to be controlled by hydrogen bonds and π–π stacking.

Comment

The title compound, bis(melaminium) hydrogen phosphite tetrahydrate, (I) (Fig. 1), arose as an unexpected by-product during our synthetic investigations of organically templated zinc hydrogen phosphites (Rodgers & Harrison, 2000; Harrison, 2001).



(I)

There are two distinct melaminium (2,4,6-triamino-1,3,5-triazine-1-ium) cations, both of which are singly protonated at a ring N atom. Their average ring and terminal C—N bond lengths are 1.348 (2) and 1.318 (2) Å, respectively. The C—N—C bond angles at the protonated ring N atoms (N2 and N7) are somewhat larger than the equivalent angles for the non-protonated ring N atoms, as seen for similar materials (Janczak & Perpétuo, 2001). Both melaminium cations are essentially planar (non-H atom r.m.s. deviations from the least-squares planes are 0.011 and 0.012 Å for the C1- and C4-containing molecules, respectively). For the hydrogen phosphite anion, the average P—O separation of 1.516 (2) Å and the average O—P—O bond angle of 112.2 (2)° compare well with those seen (1.516 Å and 111.2°, respectively) in $[H_2N(CH_2)_2NH_2\}_{]0.5}ZnHPO_3$ (Rodgers & Harrison, 2000).

The packing in this phase (Figs. 2 and 3) is dominated by a combination of hydrogen bonding (Table 2) and π–π-stacking effects, resulting in a structure with strongly layered character. In any (100) sheet, adjacent melaminium cations are linked into zigzag chains in the *c* direction, by way of side-by-side pairs of N—H···N links (Fig. 2). This 'synthon' bonding motif has also been seen in melaminium chloride hemihydrate (Janczak & Perpétuo, 2001) and melaminium acetate acetic acid solvate monohydrate (Perpétuo & Janczak, 2002). The melaminium chains are crosslinked in the *b* direction by the hydrogen phosphite moieties, by way of N—H···O bonds. As expected, the phosphite (P—H) H atom is not involved in hydrogen bonding (Harrison, 2001). The four water molecules each form two H bonds (as O—H···N or O—H···O) and also act as acceptors for hydrogen bonds from melaminium cations or other water molecules. Overall, each melaminium cation makes seven hydrogen bonds and acts as an acceptor for two

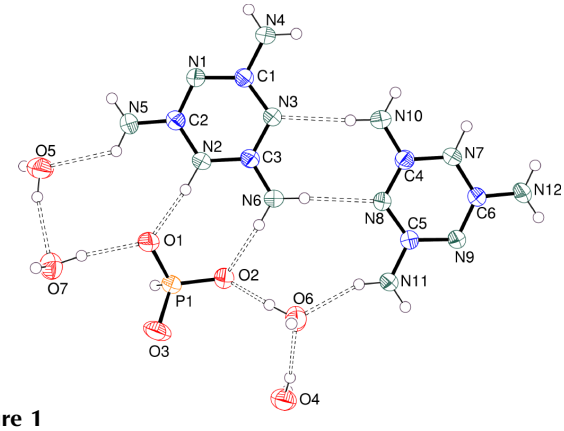


Figure 1
The asymmetric unit of (I) (50% displacement ellipsoids and arbitrary spheres for the H atoms), with hydrogen bonds indicated by dashed lines.

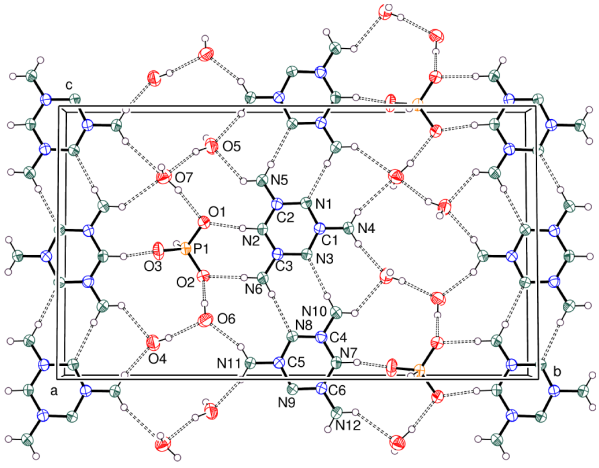


Figure 2
Hydrogen-bonding scheme (dashed lines) for part of a (100) sheet in (I) (50% displacement ellipsoids and arbitrary spheres for the H atoms).

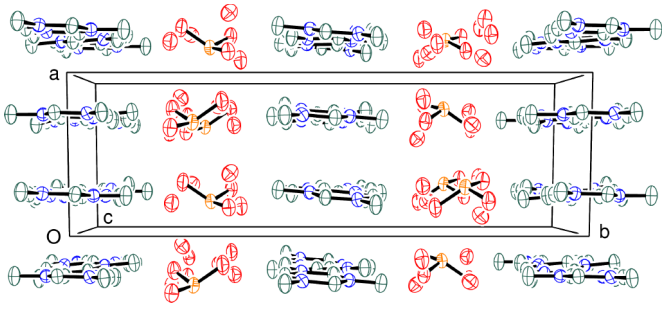


Figure 3
Packing diagram for (I), viewed approximately down [001] (50% displacement ellipsoids, atom colours as in Fig. 1, and H atoms omitted for clarity).

more, assuming a maximum H···N or H···O contact of 2.5 Å.

Intersheet bonding in the [100] direction involves probable π–π-stacking interactions of the melaminium species [shortest intersheet C···N separation = 3.375 (2) Å for C3···N3^{i}; symmetry code: (i) $-x, -y, -z$]. Even stronger melaminium-melaminium π–π-stacking interactions have been observed in related compounds (Perpétuo & Janczak, 2002). In addition, there are intersheet O—H···O hydrogen bonds involving atoms H41, H51, H61, and H72 (Table 2). The acceptor species for these interactions are three phosphite O atoms and one water molecule O atom.

Experimental

A mixture of 0.407 g (5 mmol) ZnO, 0.820 g (10 mmol) H_3PO_3, 0.631 g (5 mmol) melamine, and 20 ml H_2O was sealed in a plastic bottle and heated to 353 K for 5 d. After cooling to room temperature, transparent plate-shaped crystals of the title compound were recovered by vacuum filtration and washing with water and acetone.

Crystal data

$2C_3H_7N_6^+\cdot HPO_3^{2-}\cdot 4H_2O$
M_r = 406.33
Monoclinic, $P2_1/n$
a = 6.7702 (3) Å
b = 21.4106 (11) Å
c = 12.3411 (6) Å
β = 98.108 (10)°
V = 1771.01 (15) Å^3
Z = 4
D_x = 1.524 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4112 reflections
θ = 3.2–27.5°
μ = 0.22 mm^{-1}
T = 293 (2) K
Plate, colourless
0.43 × 0.26 × 0.01 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.913, T_{max} = 0.998
13097 measured reflections
4053 independent reflections
2841 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 27.5°
$h = -8 \rightarrow 8$
$k = -27 \rightarrow 27$
$l = -11 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.102
S = 0.96
4053 reflections
259 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.3305 (19)	N8—C4	1.3281 (19)
N1—C1	1.3516 (19)	N8—C5	1.3491 (19)
N2—C2	1.356 (2)	N9—C6	1.3292 (19)
N2—C3	1.365 (2)	N9—C5	1.3620 (19)
N3—C3	1.3351 (19)	N10—C4	1.318 (2)
N3—C1	1.3502 (19)	N11—C5	1.3192 (19)
N4—C1	1.3248 (19)	N12—C6	1.322 (2)
N5—C2	1.317 (2)	P1—O3	1.5080 (13)
N6—C3	1.309 (2)	P1—O2	1.5154 (12)
N7—C6	1.355 (2)	P1—O1	1.5242 (12)
N7—C4	1.359 (2)	P1—H1	1.32
C2—N1—C1	115.54 (13)	C6—N9—C5	115.36 (13)
C2—N2—C3	119.40 (13)	N10—C4—N8	120.18 (15)
C3—N3—C1	115.59 (13)	N10—C4—N7	117.95 (13)
N4—C1—N3	116.97 (14)	N8—C4—N7	121.87 (14)
N4—C1—N1	116.77 (14)	N11—C5—N8	117.79 (14)
N3—C1—N1	126.25 (13)	N11—C5—N9	116.39 (14)
N5—C2—N1	119.98 (15)	N8—C5—N9	125.81 (13)
N5—C2—N2	118.18 (13)	N12—C6—N9	120.03 (14)
N1—C2—N2	121.83 (14)	N12—C6—N7	117.98 (14)
N6—C3—N3	120.89 (14)	N9—C6—N7	121.98 (14)
N6—C3—N2	117.73 (14)	O3—P1—O2	113.31 (8)
N3—C3—N2	121.37 (14)	O3—P1—O1	111.77 (8)
C6—N7—C4	119.24 (13)	O2—P1—O1	111.54 (7)
C4—N8—C5	115.69 (13)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H3···O1	0.92	1.80	2.7171 (17)	174
N4—H4A···O4^{i}	0.86	2.03	2.873 (2)	169
N4—H4B···O7^{ii}	0.86	2.51	3.335 (2)	162
N5—H5A···N9^{iii}	0.86	2.14	2.991 (2)	173
N5—H5B···O5	0.86	2.31	2.9200 (19)	128
N6—H6A···N8	0.86	2.19	3.0444 (19)	177
N6—H6B···O2	0.86	1.98	2.8141 (17)	164
N7—H7···O3^{i}	0.95	1.65	2.5970 (17)	170
N10—H10A···N3	0.86	2.18	3.030 (2)	168
N10—H10B···O4^{i}	0.86	2.25	2.863 (2)	128
N11—H11A···O6	0.86	2.06	2.8702 (19)	156
N11—H11B···O5^{iv}	0.86	2.13	2.923 (2)	154
N12—H12A···N1^{iv}	0.86	2.16	3.006 (2)	168
N12—H12B···O7^{i}	0.86	2.38	3.0951 (19)	141
O4—H41···O1^{v}	0.76 (3)	2.07 (3)	2.824 (2)	169 (3)
O4—H42···O6	0.85 (2)	2.02 (3)	2.864 (2)	171 (3)
O5—H51···O3^{vi}	0.84 (3)	1.91 (3)	2.739 (2)	169 (2)
O5—H52···O7	0.88 (3)	2.05 (3)	2.903 (2)	163 (2)
O6—H61···O7^{vii}	0.78 (2)	2.11 (2)	2.873 (2)	168 (3)
O6—H62···O2	0.89 (3)	1.82 (3)	2.691 (2)	166 (2)
O7—H71···O1	0.91 (2)	1.91 (2)	2.8046 (19)	169 (2)
O7—H72···O2^{viii}	0.85 (3)	1.83 (3)	2.6743 (19)	171 (2)

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

The melaminium N—H and phosphite P—H H atoms were refined as riding [U_{iso}(H) = 1.2U_{eq} of the attached atom]. The positions of the water molecule H atoms were refined freely, with U_{iso}(H) fixed at 1.5U_{eq}(O).

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 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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