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Ammonium zinc hydrogenphosphite hydrate, $(NH_4)_2Zn_5(HPO_3)_6\cdot 4H_2O$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.002 Å
R factor = 0.026
wR factor = 0.074
Data-to-parameter ratio = 26.5

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

The title compound contains HPO_3 pseudo-pyramids [d_{av}(P—O) = 1.516 (2) Å], ZnO_4 tetrahedra [d_{av}(Zn—O) = 1.939 (2) Å], and *trans*-$ZnO_2(H_2O)_4$ octahedra. These building units link together by way of Zn—O—P bridges [θ_{av} = 128.1°], resulting in a layered structure.

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Comment

Zinc (hydrogen)phosphites containing the $[HPO_3]^{2-}$ grouping have been less intensively studied than zinc phosphates. For example, in the August 2001 release of the inorganic crystal structure database (ICSD), there are 220 compounds containing Zn, P, and O, but only eight of these can be clearly identified as phosphites (Ortiz-Avila *et al.*, 1989; Shieh *et al.*, 1990; Durand *et al.*, 1992; Marcos *et al.*, 1993). In addition, we have recently reported the structure of $NaZn(H_2PO_3)_3\cdot H_2O$ (Ouarsal *et al.*, 2002).

The title compound (Fig. 1) contains ZnO_4 tetrahedra (Zn1- and Zn2-centred groups), HPO_3 pseudo-pyramids and $ZnO_2(H_2O)_4$ octahedra (Zn3). The ZnO_4 groups [d_{av}(Zn—O) = 1.939 (2) Å] both make four links to nearby P atoms which form the centres of phosphite groups. The three phosphite moieties show their typical geometries [d_{av}(P—O) = 1.516 (2) Å] and each makes three P—O—Zn links in pyramidal geometry. The fourth tetrahedral vertex is assumed to be a P—H bond (*d* = 1.32 Å), as invariably observed for phosphites (Ortiz-Avila *et al.*, 1989). The octahedral

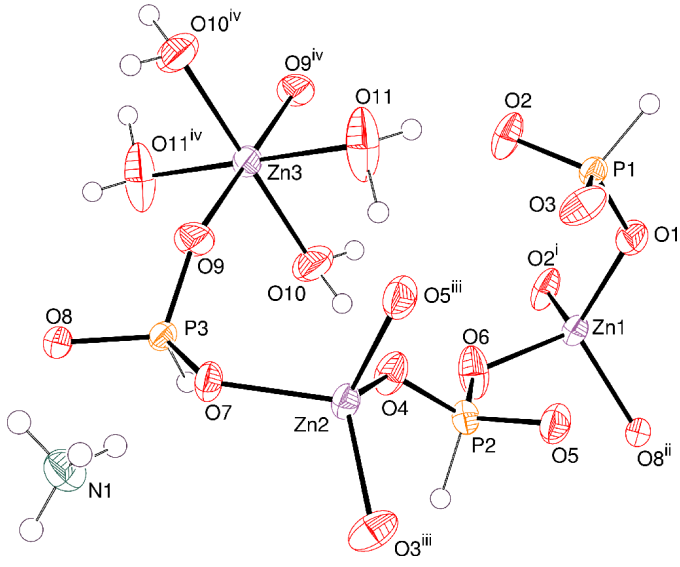

Figure 1
Fragment of $(NH_4)_2Zn_5(HPO_3)_6\cdot 4H_2O$ (50% displacement ellipsoids, arbitrary spheres for the H atoms), showing the different polyhedra. Symmetry codes are as in Table 1.

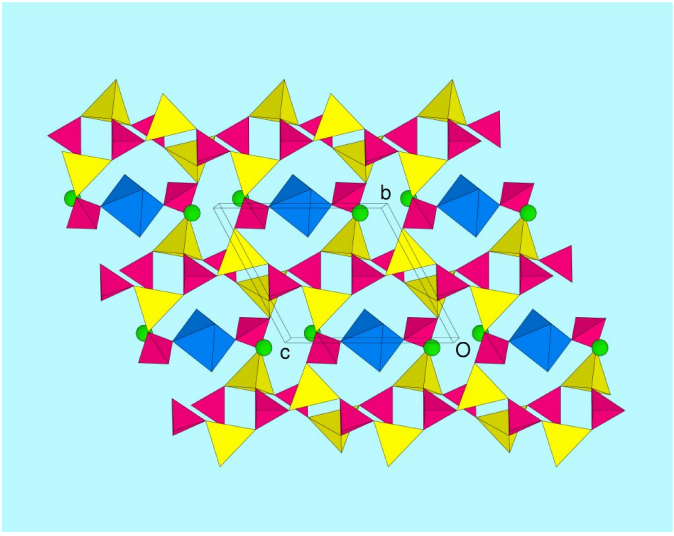

Figure 2
Packing diagram for $(NH_4)_2Zn_5(HPO_3)_6{\cdot}4H_2O$ in polyhedral representation, viewed approximately down [100]. Colour key: ZnO_4 tetrahedra yellow, HPO_3 tetrahedra red, $ZnO_2(H_2O)_4$ octahedra blue, and N atoms green.

$Zn3O_2(H_2O)_4$ group (Zn3 with site symmetry $\overline{1}$) makes two Zn—O—P links in *trans* configuration. The terminal $Zn—OH_2$ links are distinctly longer than the Zn—O(P) bonds. Of the 11 O atoms in the structure, nine (O1—O9) form bicoordinate P—O—Zn bridges [θ_{av} = 128.1°] and two (O10 and O11) are parts of water molecules. An extra-framework ammonium cation completes the structure. This species makes four N—H···O hydrogen bonds and has eight O atom neighbours within 3.5 Å [d_{av}(N···O) = 3.133 (3) Å].

The polyhedral connectivity in $(NH_4)_2Zn_5(HPO_3)_6{\cdot}4H_2O$ can be decomposed into highly contorted 4-ring (four polyhedral building blocks with nodal atoms Zn1, Zn2, P1, and P2) ladders propagating along [001]. Similar ladders have been seen in β-$C_2N_4H_4{\cdot}ZnHPO_3$ (Harrison *et al.*, 2001), although in this structure there are also ZnO_3N tetrahedra. In $(NH_4)_2Zn_5(HPO_3)_6{\cdot}4H_2O$, the ladders are crosslinked in the [010] direction by the $[HP3O_3]^{2-}$ groups to result in macroanionic sheets of stoichiometry $[Zn_2(HPO_3)_3]^{2-}$. These sheets delimit two types of holes; a squashed 8-ring associated with the ammonium cation and a bifurcated 12-ring. The octahedral Zn3 moiety bridges across the 12 ring (Fig. 2) and intra-layer $Zn—OH_2\cdots O$ hydrogen bonds result (Table 2). An edge-on view of the layers (Fig. 3) shows the sheets propagating parallel to the (100) plane. Inter-sheet bonding between the formally neutral layers is by way of N—H···O hydrogen bonds and van der Waals forces.

Experimental

The title compound arose as a by-product of our studies of amino acid templated zinc phosphites: 1.462 g L-glutamine, 0.814 g ZnO, 0.82 g H_3PO_3 and 20 ml of water were mixed and left in a polypropylene bottle at 353 K for 4 d. Product recovery was by vacuum filtration and washing with cold water.

Crystal data

$(NH_4)_2Zn_5(HPO_3)_6{\cdot}4H_2O$
M_r = 457.43
Triclinic, $P\overline{1}$
a = 7.2263 (3) Å
b = 9.7728 (4) Å
c = 10.2349 (5) Å
α = 63.409 (1)°
β = 87.162 (1)°
γ = 72.969 (1)°
V = 615.18 (5) Å^3
Z = 2
D_x = 2.469 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3972 reflections
θ = 2.5–32.4°
μ = 5.29 mm^{-1}
T = 293 (2) K
Chunky plate, colourless
0.39 × 0.28 × 0.13 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.232, T_{max} = 0.547
6425 measured reflections
4274 independent reflections
3646 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 32.5°
$h = -10 \rightarrow 9$
$k = -13 \rightarrow 14$
$l = -15 \rightarrow 15$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.074
S = 1.02
4274 reflections
161 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0101 (10)

Table 1
Selected geometric parameters (Å, °).

Zn1—O6	1.9283 (16)	Zn3—O11^{iv}	2.166 (2)
Zn1—O2^{i}	1.9325 (15)	Zn3—O11	2.166 (2)
Zn1—O1	1.9462 (17)	P1—O3	1.5050 (17)
Zn1—O8^{ii}	1.9583 (15)	P1—O2	1.5140 (16)
Zn2—O3^{iii}	1.9079 (16)	P1—O1	1.5260 (17)
Zn2—O4	1.9365 (15)	P2—O6	1.5104 (18)
Zn2—O7	1.9480 (14)	P2—O4	1.5114 (16)
Zn2—O5^{iii}	1.9529 (17)	P2—O5	1.5281 (16)
Zn3—O9^{iv}	2.0014 (14)	P3—O9	1.5079 (16)
Zn3—O9	2.0014 (14)	P3—O7	1.5197 (15)
Zn3—O10	2.1290 (19)	P3—O8	1.5219 (15)
Zn3—O10^{iv}	2.1290 (19)		
P1—O1—Zn1	127.86 (10)	P2—O6—Zn1	125.97 (10)
P1—O2—Zn1^{i}	129.28 (10)	P3—O7—Zn2	124.65 (8)
P1—O3—Zn2^{iii}	128.74 (11)	P3—O8—Zn1^{v}	119.29 (9)
P2—O4—Zn2	127.96 (10)	P3—O9—Zn3	143.17 (12)
P2—O5—Zn2^{iii}	126.35 (10)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, -z$; (iv) $1-x, -y, 1-z$; (v) $x, y-1, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H4···O8^{i}	0.95	1.96	2.904 (2)	170
N1—H5···O9^{ii}	0.80	2.23	3.035 (3)	174
N1—H6···O5^{iii}	0.87	2.00	2.865 (3)	173
N1—H7···O7	0.95	1.94	2.887 (2)	172
O10—H8···O1^{iv}	0.77	2.31	3.022 (3)	154
O10—H9···O4	0.96	2.08	3.004 (3)	162
O10—H9···O6	0.96	2.38	3.069 (3)	129
O11—H10···O2	0.81	2.00	2.742 (2)	153
O11—H11···O4	1.10	2.43	3.410 (3)	148

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $x, y-1, z$; (iv) $1-x, 1-y, 1-z$.

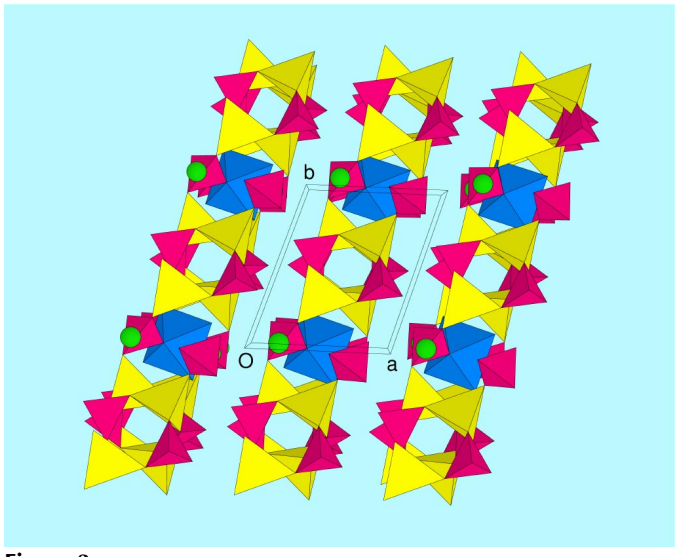

Figure 3
Packing diagram for $(NH_4)_2Zn_5(HPO_3)_6{\cdot}4H_2O$ in polyhedral representation, viewed approximately down [001]. Colour key is as in Fig. 2.

Fourier difference peaks for the water molecule H atoms were barely above background noise level and the locations of these atoms should be regarded as uncertain.

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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