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Ammonium zinc phosphate, $(NH_4)Zn(HPO_4)(H_2PO_4)$

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(P–O) = 0.002 Å
R factor = 0.031
wR factor = 0.075
Data-to-parameter ratio = 20.7

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

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Ammonium zinc phosphate, $(NH_4)Zn(HPO_4)(H_2PO_4)$, is built up from infinite 4-ring chains of vertex-sharing ZnO_4 and $(H/H_2)PO_4$ tetrahedra [d_{av}(Zn—O) = 1.943 (2) Å and d_{av}(P—O) = 1.534 (2) Å] crosslinked by ammonium cations. The intrachain O—H···O hydrogen bond appears to be essentially symmetric [d(O···O) = 2.442 (3) Å].

Comment

The title compound complements the known ammonium zinc phosphates $(NH_4)Zn(HPO_4)(H_2PO_4)\cdot H_2O$ (Boudjada *et al.*, 1980), $(NH_4)Zn_2(PO_4)(HPO_4)$ (Bircsak & Harrison, 1998), $(NH_4)ZnPO_4$–ABW (Bu *et al.*, 1997) and $(NH_4)ZnPO_4$–HEX (Xu *et al.*, 1998). The first two phases are layered with respect to the connectivity of the tetrahedral ZnO_4/PO_4 building units whereas the latter two are three-dimensional and resemble related aluminosilicate zeolites (Harrison, 2000).

In the title compound (Fig. 1), ZnO_4 and PO_4 tetrahedral building blocks [d_{av}(Zn—O) = 1.943 (2) Å and d_{av}(P—O) = 1.534 (2) Å] assemble into infinite chains which propagate along [001] (Fig. 2). The chains are built up from polyhedral 4-rings with the zinc centres serving to fuse the 4-rings into chains, which results in the 1:2 Zn:P ratio. Similar zincophosphate 4-ring chains have been seen in $RbZn(HPO_4)(H_2PO_4)\cdot H_2O$ (Harrison *et al.*, 1997) and $N_2C_6H_{14}\cdot Zn(HPO_4)_2\cdot H_2O$ (Chavez *et al.*, 1999). In $(NH_4)Zn(HPO_4)(H_2PO_4)$, four O atoms serve as Zn—O—P links (θ_{av} = 128.5°) and four are terminal to P. Assuming the presence of ammonium cations rather than unprecendented neutral ammonia,

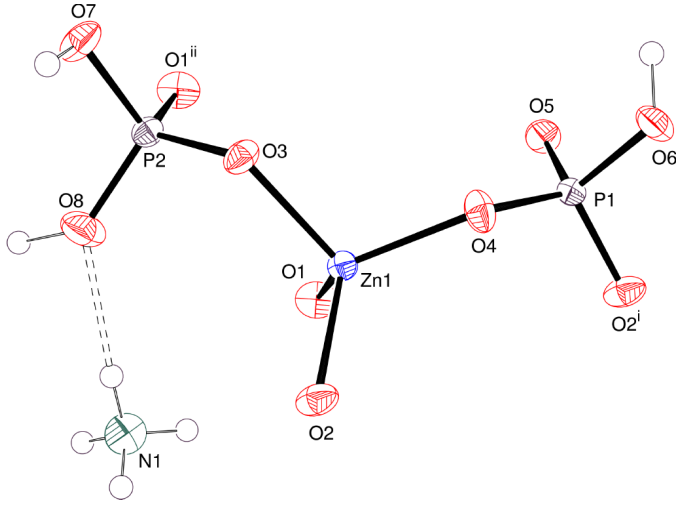

Figure 1
Fragment of $(NH_4)Zn(HPO_4)(H_2PO_4)$ shown with 50% probability displacement ellipsoids. The symmetry codes are as in Table 1. The N1—H4···O8 hydrogen bond is indicated by a dashed line.

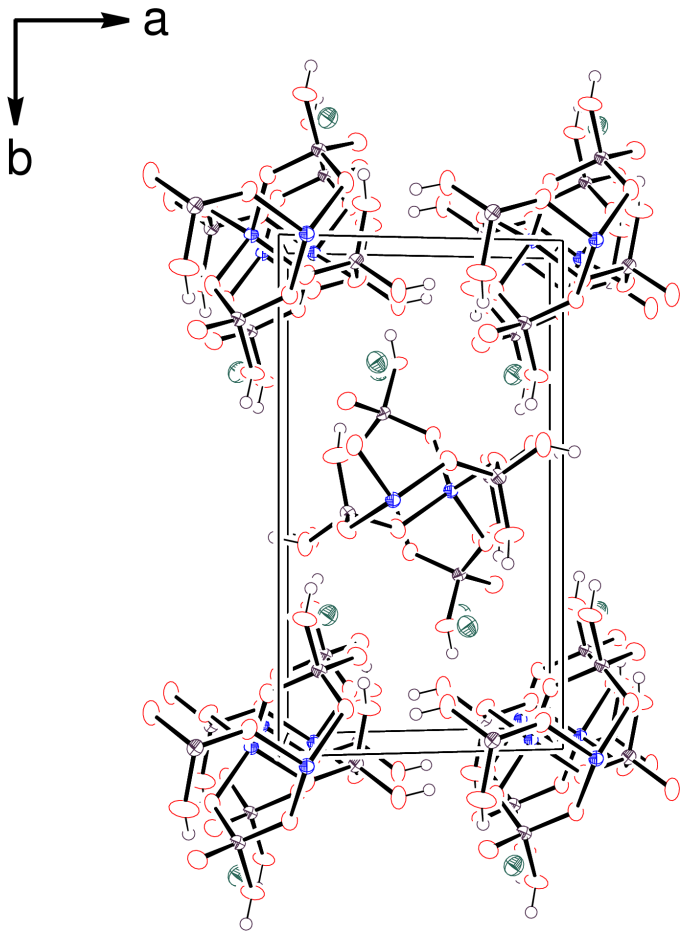

Figure 2
Packing diagram for $(NH_4)Zn(HPO_4)(H_2PO_4)$ viewed down [001] (50% displacement ellipsoids; ammonium H atoms have been omitted for clarity; atom colours are as in Fig. 1).

three H atoms are required for charge balancing. The structures of similar phases (Harrison *et al.*, 1997; Bircsak & Harrison, 1998) indicate that they are almost certainly associated with terminal P—O bonds. In $(NH_4)Zn(HPO_4)(H_2PO_4)$, two of these are well defined and the P1—O6 and P2—O7 bonds show their expected P—O bond lengths (Lightfoot & Masson, 1996). Both P1—O6—H6 and P2—O7—H7 partake in inter-chain hydrogen bonds (Table 2). The O6—H6···O3 interaction links adjacent chains along [010], and the O7—H7···O2 bond performs a similar function along [100]. The location of the third H atom is considerably less certain. The largest difference map feature corresponded to a region roughly half way betweeen O8 and $O5^{i}$ [symmetry code: (i) $1-x, 1-y, -z$]. Inclusion of a riding H atom at this point marginally lowered the crystallographic residuals. If the H atom is really located here, this intra-chain hydrogen bond (Fig. 3) is essentially symmetric (Fillaux *et al.*, 1999), although there are no symmetry constraints. However, further investigation, perhaps using neutron diffraction (Wilson, 2001) would be necessary to confirm this site.

The ammonium cation appears to participate in two strong well defined hydrogen bonds (*via* atoms H3 and H4) and two weaker bifurcated linkages involving H1 and H2. These N—H···O bonds serve to link the anionic $[Zn(HPO_4(H_2PO_4]^-$ chains into a three-dimensional array.

Experimental

The title compound was prepared hydrothermally from a mixture of H_3PO_4, ZnO, NH_4OH and TiO_2. It appears that titania must be present for $(NH_4)Zn(HPO_4)(H_2PO_4)$ to form, although its role is unknown.

Crystal data

$(NH_4)Zn(HPO_4)(H_2PO_4)$
$M_r = 276.38$
Monoclinic, $P2_1/n$
$a = 7.6801$ (19) Å
$b = 13.235$ (3) Å
$c = 8.0780$ (16) Å
$\beta = 107.690$ (16)°
$V = 782.3$ (3) Å^3
$Z = 4$
$D_x = 2.347$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.4$–12.8°
$\mu = 3.56$ mm^{-1}
$T = 298$ (2) K
Lump, colourless
0.40 × 0.35 × 0.35 mm

Data collection

Bruker *P*4 diffractometer
θ–2θ scans
Absorption correction: ψ scan (*XEMP*; Bruker, 1997)
$T_{min} = 0.395$, $T_{max} = 0.530$
2957 measured reflections
2280 independent reflections
1911 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 30.0°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 18$
$l = -11 \rightarrow 11$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.075$
$S = 1.07$
2280 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.6283P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0051 (9)

Table 1
Selected geometric parameters (Å, °).

Zn1—O4	1.9298 (19)	P1—O2^{i}	1.535 (2)
Zn1—O1	1.9307 (19)	P1—O6	1.5720 (19)
Zn1—O2	1.9484 (19)	P2—O1^{ii}	1.510 (2)
Zn1—O3	1.9620 (18)	P2—O3	1.5251 (18)
P1—O4	1.514 (2)	P2—O8	1.529 (2)
P1—O5	1.5240 (19)	P2—O7	1.564 (2)
O4—Zn1—O1	119.18 (9)	O2^{i}—P1—O6	106.43 (12)
O4—Zn1—O2	109.19 (9)	O1^{ii}—P2—O3	113.04 (12)
O1—Zn1—O2	103.70 (9)	O1^{ii}—P2—O8	112.73 (13)
O4—Zn1—O3	105.57 (8)	O3—P2—O8	108.00 (11)
O1—Zn1—O3	108.96 (8)	O1^{ii}—P2—O7	104.37 (11)
O2—Zn1—O3	110.14 (8)	O3—P2—O7	108.22 (11)
O4—P1—O5	114.18 (11)	O8—P2—O7	110.37 (13)
O4—P1—O2^{i}	110.62 (11)	P2^{ii}—O1—Zn1	133.91 (13)
O5—P1—O2^{i}	110.56 (11)	P1^{i}—O2—Zn1	122.89 (11)
O4—P1—O6	106.05 (12)	P2—O3—Zn1	124.07 (11)
O5—P1—O6	108.60 (11)	P1—O4—Zn1	132.90 (12)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5^{i}	0.90	2.44	2.971 (3)	118
N1—H1···O1	0.90	2.51	3.192 (3)	133
N1—H2···O4^{ii}	0.90	2.18	3.014 (3)	154
N1—H2···O6^{iii}	0.90	2.56	2.978 (3)	109
N1—H3···O7^{iv}	0.90	2.01	2.907 (3)	176
N1—H4···O8	0.90	2.02	2.901 (3)	167
O6—H6···O3^{v}	0.95	1.74	2.603 (3)	150
O7—H7···O2^{vi}	0.95	1.73	2.603 (3)	151
O8—H8···O5^{vii}	1.15	1.30	2.442 (3)	175

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

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; 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.

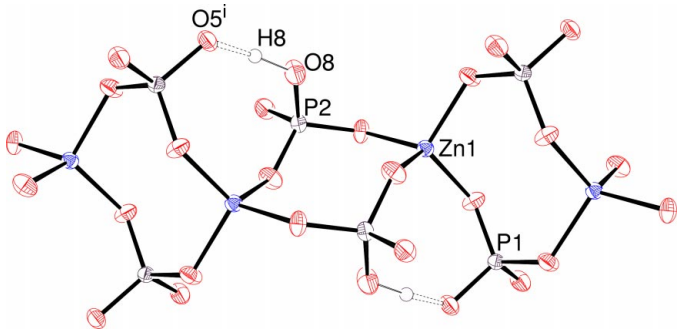

Figure 3
Side-on view of a zincophosphate tetrahedral chain in $(NH_4)Zn(HPO_4)(H_2PO_4)$ showing the proposed O8—H8···O5 intra-chain hydrogen bond as a dashed line [50% displacement ellipsoids; symmetry code: (i) $1-x, 1-y, -z$].

References

Bircsak, Z. & Harrison, W. T. A. (1998). *Acta Cryst.* C**54**, 1383–1385.
Boudjada, A., Tranqui, D. & Guitel, J. C. (1980). *Acta Cryst.* B**36**, 1176–1178.
Bruker (1997). *XSCANS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bu, X., Feng, P., Gier, T. E. & Stucky, G. D. (1997). *Zeolites*, **19**, 200–208.
Chavez, A., Nenoff, T. M., Hannooman, L. & Harrison, W. T. A. (1999). *J. Solid State Chem.* **147**, 585–591.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565–565.
Fillaux, F., Leygue, N., Tomkinson, J., Cousson, A. & Paulus, W. (1999). *Chem. Phys.* **244**, 387–403.
Harrison, W. T. A. (2000). *Z. Kristallogr.* **215**, 288–292.
Harrison, W. T. A., Bircsak, Z. & Hannooman, L. (1997). *J. Solid State Chem.* **134**, 148–157.
Lightfoot, P. & Masson, D. (1996). *Acta Cryst.* C**52**, 1077–1080.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Wilson, C. C. (2001). *Acta Cryst.* B**57**, 435–439.
Xu, J., Yuan, H., Shi, S., Sun, J., Song, T., Feng, S., Xu, R., Bu, W., Mao, Y., Ye, L. & Fan, Y. (1998). *Gaodeng Xuexiao Huaxue Xuebao*, **19**, 1707–1710.