

Hexagonal ammonium zinc
phosphate, $(\text{NH}_4)\text{ZnPO}_4$, at 10 KWilliam T. A. Harrison,^{a*} Alexandre N. Sobolev^b and
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The title compound, $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$, is built up from a three-dimensional network of ZnO_4 and PO_4 tetrahedra [$d_{\text{av}}(\text{Zn}-\text{O}) = 1.9400(7) \text{ \AA}$ and $d_{\text{av}}(\text{P}-\text{O}) = 1.5396(7) \text{ \AA}$], fused together *via* $\text{Zn}-\text{O}-\text{P}$ links [$\theta_{\text{av}} = 133.47(4)^\circ$]. An undistorted linear $\text{Zn}-\text{O}-\text{P}$ bond occurs (all three atoms lie on a threefold axis). Extra-framework NH_4^+ cations, which interact with the $[\text{ZnPO}_4]^-$ framework by hydrogen bonds, complete the crystal structure.

Comment

$M\text{ZnPO}_4$ phases (M is a univalent cation) built up from a three-dimensional framework of vertex-sharing ZnO_4 and PO_4 tetrahedra are of interest for their physical properties (Blum *et al.*, 1986), their phase transition behaviour (Kahlenberg, 1998; Hammond *et al.*, 1998), and their structural relationship to polymorphs of silica and aluminosilicate zeolites (Harrison, 2000). Here, we describe the low-temperature (10 K) structure of the hexagonal form (Averbuch-Pouchot & Durif, 1968) of ammonium zinc phosphate, $(\text{NH}_4)\text{ZnPO}_4$. We have named this phase $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$ in order to distinguish it from monoclinic $(\text{NH}_4)\text{ZnPO}_4\text{-ABW}$ (Bu *et al.*, 1997).

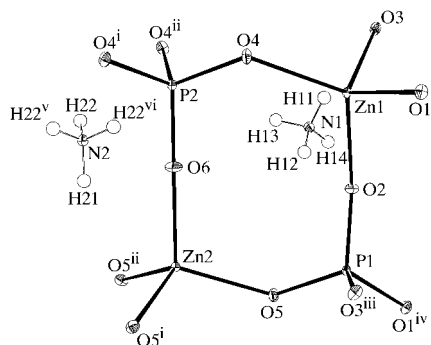


Figure 1

Fragment of the $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$ structure (50% displacement ellipsoids). [Symmetry codes: (i) $1 - x + y, 1 - x, z$; (ii) $1 - y, x - y, z$; (iii) $1 + x - y, x, -\frac{1}{2} + z$; (iv) $y, 1 - x + y, -\frac{1}{2} + z$; (v) $-x + y, -x, z$; (vi) $-y, x - y, z$.]

There are 12 framework (two Zn, two P and eight O) and eight extra-framework (two N and six H) atoms in this structure. The geometrical parameters for the ZnO_4 and PO_4 tetrahedra [$d_{\text{av}}(\text{Zn}-\text{O}) = 1.9400(7) \text{ \AA}$ and $d_{\text{av}}(\text{P}-\text{O}) = 1.5396(7) \text{ \AA}$] are typical (Bu *et al.*, 1997). The linkage of these moieties by $\text{Zn}-\text{O}-\text{P}$ bonds results in a strictly alternating array of Zn and P tetrahedral nodes, with an average $\text{Zn}-\text{O}-\text{P}$ bond angle of $133.47(4)^\circ$, excluding the linear $\text{Zn2}-\text{O6}-\text{P2}$ bond.

The framework structure of $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$ is built up from infinite sheets of tetrahedral six-rings arrayed normal to $[0001]$ (Fig. 2). Topologically, this linkage pattern of Zn and P atoms *via* O-atom bridges may be described as layers of simple 6^3 hexagonal nets (Hyde & O'Keeffe, 1996). The fourth Zn—O or P—O vertex points approximately either up (*U*) or down (*D*) with respect to the $[0001]$ direction. Using the up/down classification (Liebau, 1985), two types of six-ring may be identified as *UDUDUD* and *UUUDDD*. In this structure, there are three *UUUDDD* rings for every *UDUDUD* ring in any $[0001]$ sheet.

The extra-framework ammonium cations occupy the $[0001]$ channels and interact with the $[\text{ZnPO}_4]^-$ framework by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). N1 occupies the *UUUDDD* channels and makes four $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to framework oxygen species. N2 occupies the *UDUDUD* channels and makes three equivalent hydrogen bonds as $\text{N2}-\text{H22}\cdots\text{O1}$. The $\text{N2}-\text{H21}$ moiety, which occupies the threefold axis does not participate in any hydrogen bond; all these bonds point the same way in this polar crystal structure. Framework atoms O1–O5 act as hydrogen-bond acceptors, with only O6 not involved in these guest-framework interactions.

$(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$ is isostructural with $(\text{NH}_4)\text{CoPO}_4$ (Feng *et al.*, 1997) and $\alpha\text{-AgZnPO}_4$ (Hammond *et al.*, 1998). As noted recently (Hammond *et al.*, 1998; Harrison, 2000), the $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$ structure is not isostructural with hexagonal nepheline types, such as $\beta\text{-(Na}_{3/4}\text{K}_{1/4})\text{AlGeO}_4$

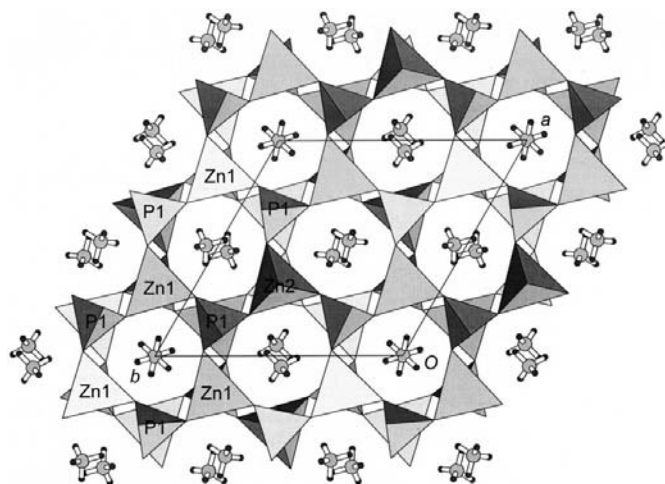


Figure 2

Polyhedral view down $[0001]$ of $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$, with selected tetrahedra labelled to show a *UDUDUD* six-ring centred at $x = 0, y = 1$, and a *UUUDDD* six-ring at $x = \frac{1}{2}, y = 1$. The N1 ammonium cations occupy the *UUUDDD* channels and the N2 ammonium cations occupy the *UDUDUD* channels.

(Hammond & Barbier, 1998), which have the same space group and similar lattice parameters to $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$. The nepheline types contain just one topologically distinct six-ring (type *UDUDUD*), as adopted by the tridymite form of SiO_2 .

A notable feature of the $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$ structure is the symmetry constrained linear Zn2-O6-P2 bond. At 10 K, there is negligible anisotropy in the thermal motion of O6, which has a ratio of longest-to-shortest ellipsoid axes, U_3/U_1 , of 3.11, compared to an average of 2.53 for the other five O atoms. Conversely, in $\alpha\text{-AgZnPO}_4$ (Hammond *et al.*, 1998), the equivalent linear Zn-O-P bond is disordered over three equivalent positions about the threefold axis [resulting Zn-O-P bond angle = $165.8(4)^\circ$]. It was suggested that Ag-O bonding may play a role in promoting this situation, whereas for $(\text{NH}_4)\text{ZnPO}_4\text{-HEX}$, the linear Zn-O6-P bond is the only one not involved in interactions with the ammonium cation.

Experimental

A mixture of N_2H_4 (2.35 g, 73 mmol), zinc acetate (2.20 g, 10 mmol), 85% H_3PO_4 (4.6 g, 40 mmol) and water (9.08 g, 500 mmol) was placed in a plastic bottle (initial pH = 6.5) and heated to 343 K for 14 d. Numerous bicapped hexagonal rods (maximum size 1 mm) of the title compound were recovered by vacuum filtration and drying in air. Elemental analyses (found: N 7.85, 2.22%; calculated: 7.86, H 2.24%) were consistent with the crystal structure.

Crystal data

$(\text{NH}_4)\text{ZnPO}_4$	Mo $K\alpha$ radiation
$M_r = 178.38$	Cell parameters from 20 reflections
Hexagonal, $P6_3$	$\theta = 13.3\text{--}13.7^\circ$
$a = 10.702(2) \text{ \AA}$	$\mu = 5.95 \text{ mm}^{-1}$
$c = 8.703(2) \text{ \AA}$	$T = 10(2) \text{ K}$
$V = 863.2(3) \text{ \AA}^3$	Hexagonal prism, colourless
$Z = 8$	$0.20 \times 0.20 \times 0.20 \text{ mm}$
$D_x = 2.745 \text{ Mg m}^{-3}$	

Data collection

Huber diffractometer	$R_{\text{int}} = 0.026$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 37.6^\circ$
Absorption correction: analytical (<i>ABSORB</i> ; Hall <i>et al.</i> , 1995)	$h = 0 \rightarrow 18$
$T_{\text{min}} = 0.824$, $T_{\text{max}} = 0.952$	$k = -18 \rightarrow 15$
9471 measured reflections	$l = -14 \rightarrow 14$
3049 independent reflections	3 standard reflections
3026 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.003$
$R[F^2 > 2\sigma(F^2)] = 0.013$	$\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$
$wR(F^2) = 0.031$	$\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$
$S = 1.15$	Extinction correction: <i>SHELXL97</i>
3049 reflections	(Sheldrick, 1997)
109 parameters	Extinction coefficient: 0.0329 (5)
All H-atom parameters refined	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 0.062P]$	Flack parameter: 0.000 (5)
where $P = (F_o^2 + 2F_c^2)/3$	

All H atoms were located from difference maps and their atomic coordinates and isotropic displacement factors were freely refined.

Table 1

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

Zn1—O4	1.9399 (7)	P1—O2	1.5398 (7)
Zn1—O1	1.9406 (8)	P1—O3 ⁱⁱⁱ	1.5423 (7)
Zn1—O2	1.9494 (7)	P1—O1 ^{iv}	1.5423 (7)
Zn1—O3	1.9577 (7)	P1—O5	1.5451 (7)
Zn2—O6	1.8953 (12)	P2—O6	1.5081 (13)
Zn2—O5 ⁱ	1.9455 (7)	P2—O4 ⁱ	1.5465 (7)
Zn2—O5 ⁱⁱ	1.9455 (7)	P2—O4	1.5465 (7)
Zn2—O5	1.9455 (7)	P2—O4 ⁱⁱⁱ	1.5465 (7)
P1 ^v —O1—Zn1	131.77 (4)	P2—O4—Zn1	130.37 (4)
P1—O2—Zn1	142.46 (4)	P1—O5—Zn2	129.17 (4)
P1 ^{vi} —O3—Zn1	133.60 (4)	P2—O6—Zn2	180.0

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

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H11 \cdots O5 ⁱ	0.83 (3)	1.97 (2)	2.7843 (13)	165 (2)
N1—H12 \cdots O4 ⁱⁱ	0.84 (3)	1.98 (3)	2.8018 (14)	169 (3)
N1—H13 \cdots O2 ⁱⁱⁱ	0.864 (17)	2.070 (17)	2.8553 (12)	150.7 (19)
N1—H14 \cdots O3 ^{iv}	0.89 (2)	1.90 (2)	2.7702 (14)	166 (2)
N2—H22 \cdots O1 ⁱⁱⁱ	0.85 (2)	2.10 (2)	2.8670 (15)	150.3 (17)

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

Data collection: local routines; cell refinement: local routines; data reduction: local routines; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1138). Services for accessing these data are described at the back of the journal.

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