For all determinations, data collection: *MDIF*4 (Kutoglu, 1997); cell refinement: *CRYMIS* (Kutoglu, 1995); data reduction: *PROFILE* (Naumov & Boldyreva, 1997); program used to solve structure: *SHELXS*86 (Sheldrick, 1990); program used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ENVIRON* (Naumov & Boldyreva, 1998); software used to prepare material for publication: *SHELXL*93.

The experimental study was carried out at the University of Marburg, where EVB was spending her research term as a Humboldt Fellow. The financial support of the Humboldt Foundation is gratefully acknowledged. The authors are grateful to Dr H. Sowa for providing the single crystal of $AlPO_4$, as well as for many helpful discussions and much advice, and also to Dr S. Werner for providing a sample of steel for the gasket. EVB is grateful to Dr H. Uchtmann and to Professor F. Hensel for their hospitality, helpful discussions and assistance in solving various practical problems.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1022). Services for accessing these data are described at the back of the journal.

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$(NH_4)Zn_2(PO_4)(HPO_4)$

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(Received 9 February 1998; accepted 22 April 1998)

Abstract

Ammonium dizinc phosphate hydrogenphosphate, a new ammonium zinc phosphate, consists of corrugated anionic layers of ZnO_4 and PO_4 tetrahedra, sharing vertices [d_{av}(Zn—O) = 1.948 (1), d_{av}(P—O) = 1.534 (1) Å and θ_{av}(Zn—O—P) = 136 (8)°]. Trigonally coordinated O atoms are present in these layers. Extra-layer NH_4^+ cations [d_{av}(N···O) = 2.993 (3) Å] complete the structure, which is isostructural with that of $KZn_2(PO_4)(HPO_4)$.

Comment

Zinc phosphate framework structures which complement aluminosilicate zeolite networks are currently of interest (Gier & Stucky, 1991; Harrison, Broach *et al.*, 1996; Harrison, Gier *et al.*, 1996; Bu *et al.*, 1997; Feng *et al.*, 1997). We report here the structure of $(NH_4)Zn_2(PO_4)(HPO_4)$, which is layered with respect to zinc–phosphorus–oxygen connectivity.

The Zn and P atoms both adopt tetrahedral coordination: d_{av}(Zn1—O) = 1.939 (1) Å, BVS(Zn1) = 2.13; d_{av}(Zn2—O) = 1.957 (1) Å, BVS(Zn2) = 2.03; d_{av}(P1—O) = 1.534 (1) Å, BVS(P1) = 5.01; d_{av}(P2—O) = 1.534 (1) Å, BVS(P2) = 5.02 [bond-valence-sum (BVS) values were calculated using the program *VALENCE* (Brown, 1996)]. Six of the eight unique O atoms form bicoordinate Zn—O—P bridges [θ_{av} = 136 (8)°, excluding O4]. One O atom (O4) is trigonally coordinated to Zn1, Zn2 and P2. This type of O-atom coordination leads to three-rings of tetrahedral centres (Fig. 1), and has been seen in other layered zincophosphates (Nenoff *et al.*, 1993) and three-dimensional zincophosphate networks (Harrison *et al.*, 1992; Feng *et al.*, 1997). The trigonal coordination of O4 leads to rather long Zn—O4 and P2—O4 links. However, the valence of O4 [2.07; Brown, 1996] is satisfied by this geometry. The remaining O atom (O8) forms part of a terminal P—OH bond.

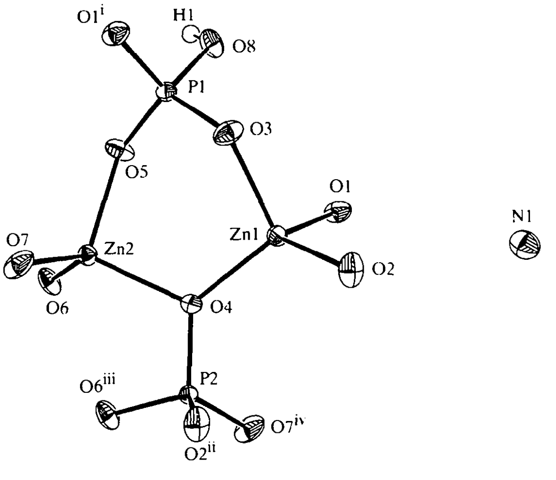

Fig. 1. Fragment of the $(NH_4)Zn_2(PO_4)(HPO_4)$ structure showing the trigonally coordinated O4 atom and the tetrahedral three-rings (50% displacement ellipsoids). Symmetry codes are as in Table 1.

The polyhedral connectivity of the tetrahedral units results in corrugated anionic layers of stoichiometry $[Zn_2(PO_4)(HPO_4)]^-$, which are arranged normal to [001]. Based on geometrical placement of H1, an intersheet hydrogen bond is present, as O8—H1···O5 [d(O···O) = 2.603 (3) Å] (Fig. 2). Zn_2O_7 'dimers' (bridging O4 atom) are present in the layers: there is no infinite connectivity of the zinc centres as seen, for example, in $Na_2Zn(OH)PO_4$ (Kabalov *et al.*, 1972) or $[NH(CH_3)_3]Zn_4(H_2O)(PO_4)_3$ (Bu *et al.*, 1996). Three-rings (two Zn and one P nodes) and four-rings (two Zn and two P nodes) arise from this tetrahedral connectivity.

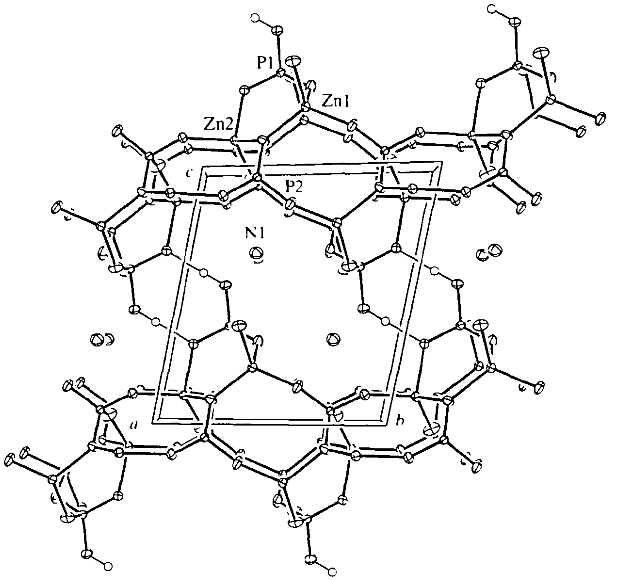

Fig. 2. View of the $(NH_4)Zn_2(PO_4)(HPO_4)$ structure down [100].

Extra-layer NH_4 cations complete the crystal structure of $(NH_4)Zn_2(PO_4)(HPO_4)$. When viewed down [100], these species occupy channel-like interstices. The hydrogen-bonding behaviour of these ammonium cations was not established in the present experiment. However, a number of N···O contacts of suitable length (d < 3.2 Å) suggest that N—H···O bonds are probably present. $(NH_4)Zn_2(PO_4)(HPO_4)$ is isostructural with $KZn_2(PO_4)(HPO_4)$ (Averbuch-Pouchot, 1979), with the ammonium and potassium cations occupying similar seven-coordinate extra-layer sites [d_{av}(N···O) = 2.993 (3) and d_{av}(K—O) = 2.878 Å], assuming a maximum contact distance of 3.4 Å in each case.

Experimental

$(NH_4)Zn_2(PO_4)(HPO_4)$ was synthesized from a mixture of ZnO (3.356 g), V_2O_5 (1.25 g), VCl_3 (1.08 g), guanidinium carbonate {$[C(NH_2)_3]CO_3$; 1.252 g}, 85% H_3PO_4 solution (8.113 g) and H_2O (10.72 ml). The reactants were sealed in a 23 ml teflon-lined hydrothermal bomb and heated to 453 K for 48 h. After slow cooling, the bomb was opened to reveal a mixture of clear crystals of $(NH_4)Zn_2(PO_4)(HPO_4)$ and unidentified green and white powders. We have not managed to prepare $(NH_4)Zn_2(PO_4)(HPO_4)$ in the absence of the vanadium oxides or from a more direct source of ammonium cations.

Crystal data

$(NH_4)Zn_2(PO_4)(HPO_4)$
$M_r = 339.75$
Triclinic
$P\bar{1}$
$a = 5.2442\ (5)$ Å
$b = 8.938\ (2)$ Å
$c = 9.731\ (2)$ Å
$\alpha = 75.01\ (2)°$
$\beta = 77.72\ (2)°$
$\gamma = 73.06\ (1)°$
$V = 416.81\ (9)$ Å^3
$Z = 2$
$D_x = 2.71$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 7.3–12.6°$
$\mu = 6.15$ mm^{-1}
$T = 298$ K
Chunk
$0.30 \times 0.20 \times 0.15$ mm
Clear

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (North *et al.*, 1968)
  $T_{min} = 0.275$, $T_{max} = 0.389$
3852 measured reflections
3007 independent reflections
3007 reflections with $I > 0$

$R_{int} = 0.03$
$\theta_{max} = 32.50°$
$h = -1 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.033$
$wR = 0.031$
$S = 1.16$
3007 reflections
120 parameters
Only H-atom *U*'s refined
Chebychev polynomial (Carruthers & Watkin, 1979) with 3 parameters 0.366, 0.0945 and 0.134

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.00$ e Å^{-3} (0.72 Å from Zn1)
$\Delta\rho_{min} = -0.77$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 32.2 (17)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Zn1—O1	1.9486 (15)	P1—O1^{i}	1.5161 (16)
Zn1—O2	1.8926 (15)	P1—O3	1.5176 (16)
Zn1—O3	1.9481 (15)	P1—O5	1.5273 (16)
Zn1—O4	1.9655 (14)	P1—O8	1.5756 (15)
Zn2—O4	2.0155 (14)	P2—O2^{ii}	1.5133 (15)
Zn2—O5	1.9829 (15)	P2—O4	1.5697 (15)
Zn2—O6	1.9223 (15)	P2—O6^{iii}	1.5387 (15)
Zn2—O7	1.9073 (16)	P2—O7^{iv}	1.5135 (16)
Zn1—O1—P1^{iv}	130.56 (9)	Zn2—O4—P2	113.49 (8)
Zn1—O2—P2^{ii}	147.99 (11)	Zn2—O5—P1	127.89 (9)
Zn1—O3—P1	128.43 (9)	Zn2—O6—P2^{iii}	134.7 (1)
Zn1—O4—Zn2	117.34 (7)	Zn2—O7—P2^{i}	144.10 (11)
Zn1—O4—P2	125.88 (9)		

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

Data collection: *P*4 *Software* (Siemens, 1995). Cell refinement: *P*4 *Software*. Data reduction: *P*4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996). Molecular graphics: *ORTEP*-3 (Farrugia, 1997). Software used to prepare material for publication: *CRYSTALS*.

The authors thank the Australian Research Council for funding.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1214). Services for accessing these data are described at the back of the journal.

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