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$(C_4H_{12}N_2)[Zn_2(PO_4)(HPO_4)(H_2PO_4)]$, a layered zinc phosphate with intercalated *N*-methylpropane-1,3-diaminium cations

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.009 Å
R factor = 0.028
wR factor = 0.086
Data-to-parameter ratio = 14.5

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

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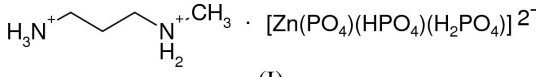
The title compound, *catena*-poly[[*N*-methylpropane-1,3-diaminium [μ-phosphato-(μ-hydrogen phosphato)(μ-dihydrogen phosphato)dizincate(II)]], $\{(C_4H_{14}N_2)[Zn_2(PO_4)(HPO_4)(H_2PO_4)]\}_n$, consists of macroanionic $[Zn_2(PO_4)(HPO_4)(H_2PO_4)]^{2-}$ layers and intercalated $(C_4H_{12}N_2)^{2+}$ cations. The layers are built up from ZnO_4 and $PO_4/HPO_4/H_2PO_4$ tetrahedra that result in small channels of approximate diameter 3.7 Å within the layers. Framework-to-framework O—H···O and template-to-framework N—H···O hydrogen bonds are important in stabilizing the structure.

Comment

Zinc phosphates have become an important class of open-framework materials due to their large structural variety and capability of forming chain, layer and framework structures (Rao *et al.*, 2001; Natarajan, 2002; Norquist & O'Hare, 2004). Generally, these solids have been synthesized through a synthetic route requiring hydrothermal conditions and the presence of organic amines which act as templates.



(I)

The title compound, (I) (Fig. 1), has been obtained in the presence of a 3-methylaminopropylamine (MPA) template. In the asymmetric unit of (I), there are two crystallographically distinct Zn atoms and three P atoms, all of them being tetrahedrally coordinated. The Zn—O distances (Table 1) are in the range 1.911 (3)–1.965 (4) Å, in accordance with literature values (Harrison, 2001; Guo *et al.*, 2005). All of the P—O distances that lie in the range 1.499 (4)–1.547 (3) Å correspond to P—O—Zn bridges, whereas those in the 1.560 (4)–

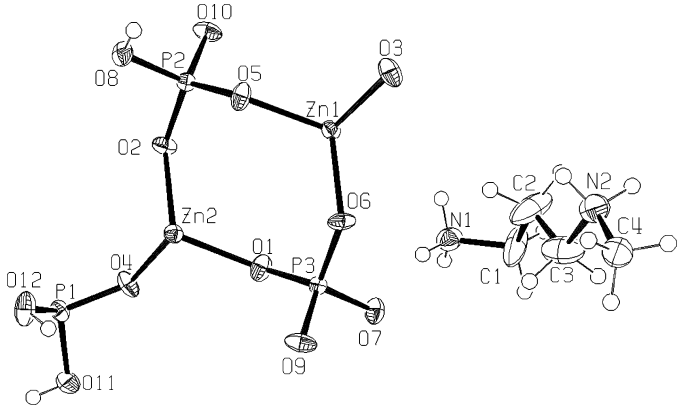


Figure 1
The asymmetric unit of (I), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

1.566 (4) Å range were assigned to the terminal P—OH groups (Guo *et al.*, 2005). In addition, P3—O7 is an unprotonated terminal bond with a length of 1.545 (4) Å, which is greater than the typical P═O distance. The P3—O7 bond may be lengthened because O7 accepts a short strong hydrogen bond (Table 2) from an O8—H8 grouping in an adjacent layer. Overall, this results in the presence of phosphate, hydrogen phosphate and dihydrogen phosphate groups in (I). The four-membered rings (*i.e.* four tetrahedral centres), as primary building units of the structure of (I), are formed by a link of the —Zn1—O6—P3—O1—Zn2—O2—P2—O5— atoms. Neighbouring rings are connected by two oxygen bridges (P3—O9—Zn1 and Zn2—O10—P2). Such a ring connection gives rise to a channel of about 3.7 Å diameter. Adjacent columns are linked into a layer by the Zn1—O3—P1—O4—Zn2 bridges. The negative charge of the zinc phosphate layers is compensated by diprotonated diamine molecules, which lie between the layers parallel to the ring channels. The protonated diamine molecules interact with the zinc phosphate layers through N—H···O hydrogen bonds (Table 2) with N···O separations from 2.823 (6) to 3.089 (5) Å. The interlayer O—H···O hydrogen bonds result in O···O separations ranging from 2.480 (5) to 2.580 (5) Å.

Very recently a similar zinc phosphate structure was reported by Jensen *et al.* (2005). The use of a different organic amine, namely *N*,*N*′-dimethylethylendiamine, in that synthesis led to a structure with very similar unit-cell dimensions and the same inorganic zinc phosphate layers, but a different arrangement of organic cations and consequently a higher structural symmetry (space group *P*2/*n*).

Experimental

A mixture having a relative molar composition of $Zn(OAc)_2$:5.5H_3PO_4:2MPA:100H_2O, where $Zn(OAc)_2$ is zinc acetate dihydrate (Aldrich) and MPA is a 98% 3-methylaminopropylamine solution (Fluka) was prepared by successive additions of phosphoric acid and MPA to a solution of zinc acetate in water with vigorous stirring. Crystallization, which was performed hydrothermally at 437 K for 2 d, gave parallelepiped-shaped crystals of (I).

Crystal data

$(C_4H_{14}N_2)[Zn_2(PO_4)(HPO_4)(H_2PO_4)]$
M_r = 508.85
Monoclinic, *Pn*
a = 11.8920 (2) Å
b = 5.1318 (1) Å
c = 12.3063 (2) Å
β = 98.125 (1)°
V = 743.48 (2) Å^3
Z = 2
D_x = 2.273 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1860 reflections
θ = 2.6–27.5°
μ = 3.61 mm^{-1}
T = 295 (2) K
Prism, colourless
0.2 × 0.2 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.490, T_{max} = 0.835
3295 measured reflections
3108 independent reflections
3029 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.5°
h = −15 → 15
k = −6 → 6
l = −15 → 15

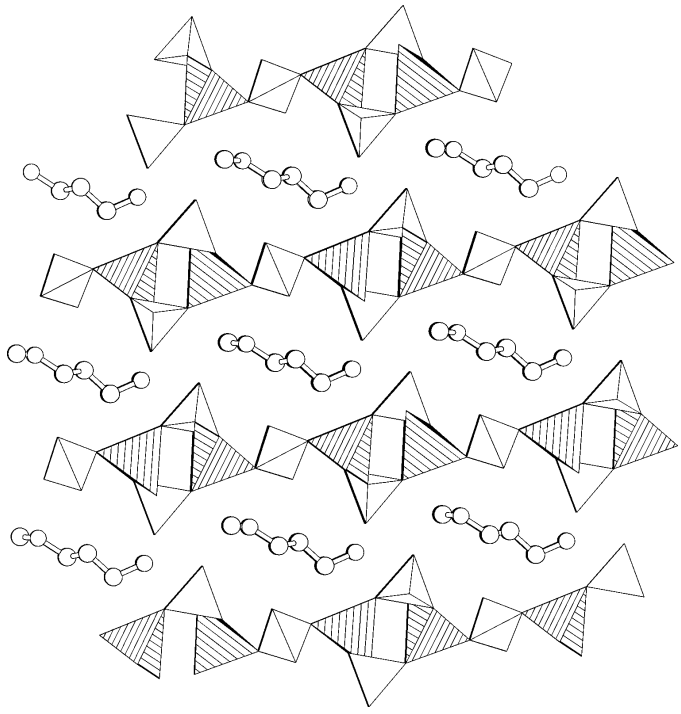


Figure 2
Polyhedral view of (I), showing zinc–phosphate layers (ZnO_4 tetrahedra indicated by hatching) and intercalated *N*-methylpropane-1,3-diaminium molecules.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.087
S = 1.19
3108 reflections
214 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.3227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.93 e Å^{-3}
Absolute structure: Flack (1983), 1399 Friedel pairs
Flack parameter: 0.44 (1)

Table 1
Selected geometric parameters (Å, °).

Zn1—O9^{i}	1.911 (3)	P1—O12	1.560 (4)
Zn1—O5	1.927 (4)	P1—O11	1.566 (4)
Zn1—O3	1.946 (3)	P2—O10	1.522 (3)
Zn1—O6	1.960 (3)	P2—O5	1.525 (3)
Zn2—O1	1.926 (4)	P2—O2	1.547 (3)
Zn2—O10^{ii}	1.928 (3)	P2—O8	1.563 (4)
Zn2—O4	1.963 (3)	P3—O1	1.517 (4)
Zn2—O2	1.965 (3)	P3—O9	1.525 (3)
P1—O3^{iii}	1.499 (4)	P3—O6	1.540 (4)
P1—O4	1.518 (3)	P3—O7	1.545 (4)

P3—O1—Zn2	131.9 (2)	P3—O9—Zn1^{ii}	133.9 (2)
P2—O2—Zn2	121.39 (19)	P2—O10—Zn2^{i}	132.3 (2)
P1^{iv}—O3—Zn1	136.9 (3)	N1—C1—C2	112.8 (5)
P1—O4—Zn2	130.0 (2)	C3—C2—C1	112.8 (5)
P2—O5—Zn1	130.9 (2)	C2—C3—N2	113.1 (5)
P3—O6—Zn1	124.30 (18)	C4—N2—C3	113.5 (4)
P2—O8—H8	109.5		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8···O7^{v}	0.82	1.66	2.480 (5)	176
O11—H11···O6^{vi}	0.82	1.76	2.567 (5)	169
O12—H12···O2^{ii}	0.82	1.77	2.580 (5)	167
N1—H1A···O7^{vii}	0.89	1.96	2.823 (6)	164
N1—H1B···O10^{viii}	0.89	2.25	3.085 (5)	155
N2—H2D···O4^{iv}	0.90	2.08	2.938 (5)	159

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

The possible centrosymmetric space group $P2/n$ was not selected for the refinement because it causes statistical disorder of the non-symmetric *N*-methylpropane-1,3-diaminium molecules and poorer *R* factors. We emphasize again that the space group $P2/n$ was determined in a recently published structure refinement of a similar zinc phosphate, where a symmetric organic molecule, *viz*. $CH_3NHCH_2CH_2NHCH_3$, was used in the synthesis (Jensen *et al.*, 2005). H atoms were included at calculated positions (C—H = 0.96–0.97 Å, N—H = 0.89–0.90 Å and O—H = 0.82 Å) and modelled as riding on their attached O, C or N atoms. The value of the Flack parameter indicates an inversion twin.

Data collection: *COLLECT* (Hooft, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997) and *ATOMS* (Dowty, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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