Poly[ethylenediammonium di-μ4-phosphatodizincate(II)]

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In the title compound, $(C_2H_{10}N_2)[ZnPO_4]_2$, alternating ZnO_4 [Zn—O = 1.899 (5)–1.940 (6) Å] and PO_4 [P—O = 1.525 (6)–1.539 (6) Å] tetrahedra are linked through their vertices to generate a three-dimensional zeolite-like framework with perpendicular six- and eight-membered ring channels. The disordered ethylenediammonium dications are located in the eight-membered ring channels near the twofold axes. The C atom and H atoms attached to C and N are disordered over two positions in a ratio of 0.55:0.45. All atoms are located in general positions.

Related literature

The title compound has a zeolite DFT topology (Baerlocher *et al.*, 2001) and its framework is identical to those of UCSB-3 (ZnAsO and GaGeO), ACP-3 (CoAlPO) (Bu, Feng, Gier, Zhao *et al.*, 1998; Bu, Feng, Gier & Stucky, 1998) and $[Fe_{0.4}Zn_{0.6}PO_4]_2 \cdot [NH_3CH_2CH_2NH_3]$ (Zhao *et al.*, 2005). For general background, see: Davis & Lobo (1992); Cheetham *et al.* (1999); Rao *et al.* (2001).
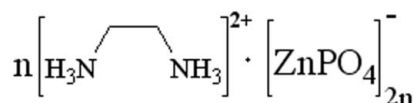
Experimental

Crystal data

$(C_2H_{10}N_2)[ZnPO_4]_2$
$M_r = 382.80$
Tetragonal, $P4_2/n$
$a = 10.3940 (8)$ Å
$c = 8.9094 (10)$ Å
$V = 962.53 (15)$ Å^3

$Z = 4$
Mo $K\alpha$ radiation
$\mu = 5.35$ mm^{-1}
$T = 293 (2)$ K
$0.12 \times 0.12 \times 0.10$ mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.566$, $T_{max} = 0.617$
(expected range = 0.538–0.586)

2819 measured reflections
841 independent reflections
616 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.128$
$S = 1.04$
841 reflections

55 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A$$\cdots$O3[i]	0.89	1.99	2.874 (6)	172
N1—H2$A$$\cdots$O2[ii]	0.89	2.12	2.924 (6)	149
N1—H3$A$$\cdots$O4	0.89	1.96	2.838 (6)	168
N1—H3$A$$\cdots$O3[iii]	0.89	2.45	2.920 (7)	113
N1—H1$B$$\cdots$O3[iii]	0.89	2.03	2.920 (7)	173
N1—H1$B$$\cdots$O4	0.89	2.32	2.838 (6)	117
N1—H2$B$$\cdots$O1[i]	0.89	2.23	3.101 (7)	168
N1—H2$B$$\cdots$O3[i]	0.89	2.40	2.874 (6)	114
N1—H3$B$$\cdots$O2[ii]	0.89	2.25	2.924 (6)	133
N1—H3$B$$\cdots$O1[ii]	0.89	2.57	3.345 (7)	146

Symmetry codes: (i) $y + \frac{1}{2}, -x + 2, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (iii) $-y + \frac{5}{2}, x, -z + \frac{1}{2}$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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supplementary materials

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J.-X. Pan and G.-Y. Yang

Comment

Organically templated metal phosphates have attracted considerable attention in recent years because of their potential applications in catalysis, ion exchange and separation (Davis & Lobo, 1992). Among these, zinc phosphates constitute an important family and compounds with zero-, one-, two- and three-dimensional architectures have been isolated (Cheetham *et al.*, 1999; Rao *et al.*, 2001). In the course of our studies of open-framework zinc phosphates, we have got the title compound with zeolite DFT topology. The asymmetric unit of compound (I) is composed of half of a diprotonated ethylenediamine cation and a $[ZnPO_4]^-$ anion (Fig. 1). The Zn and P atoms both adopt tetrahedral coordination with d_{av}(Zn—O) = 1.921 (6) Å and d_{av}(P—O) = 1.532 (6) Å. Each Zn atom makes four Zn—O—P links to nearby P atoms *via* bicoordinate O atom bridges and *vice versa*, thus a fully connected alternating three-dimensional framework arises. The compound consists of 4-, 6-, and 8-rings and its framework topology is identical to that of UCSB-3, ACP-3 (Bu, Feng, Gier, Zhao *et al.*, 1998; Bu, Feng, Gier & Stucky, 1998) and $[Fe_{0.4}Zn_{0.6}PO_4]_2 \cdot [NH_3CH_2CH_2NH_3]$ (Zhao *et al.*, 2005). The anionic $[ZnPO_4]^-$ framework encloses a system of fairly regular 8-ring (*i.e.* eight tetrahedral centres made up of four ZnO_4 and four PO_4 units) channels propagating along [001] direction (Fig. 2) (approximate atom-to-atom dimensions = 7.36 × 4.63 Å). These intersect with the 8-ring channels (dimensions ~ 7.18 × 3.56 Å) which propagate along [110] and [−110] directions (Fig. 3). The diprotonated ethylenediamine molecules are located at the center of 8-ring channels viewed along the *c* axis. Two nitrogen atoms are ordered, whereas two carbon atoms each have two possible locations, as illustrated in Fig. 1. The twofold axis (1/4, 1/4, *z*) along the *c* axis passes through ethylenediamine molecules in both orientations. The template molecules form N—H···O type hydrogen bonds with the oxygen atoms of the framework (Table 1).

Experimental

The title compound was prepared by hydrothermal synthesis from a mixture of ZnO (0.162 g, 2 mmol), diethylenetriamine (0.22 ml, 2 mmol), 85% H_3PO_4 (0.20 ml, 3 mmol) and 37% HCl (1 ml) in H_2O (3.6 ml). The mixture was sealed in a Teflon autoclave, heated at 433 K for 4 d, and cooled. The resulting product, containing colorless prismlike single crystals, was filtered, washed with distilled water, and then dried at ambient temperature (87% yield based on Zn).

Refinement

All the hydrogen atoms were positioned geometrically (the C—H and N—H bonds were fixed at 0.97 and 0.89 Å, respectively) and refined in the riding mode, with U_{iso}(H) = 1.2U_{eq}(C) and U_{iso}(H) = 1.5U_{eq}(N). The C1 atom in dication was treated as disordered between two positions with occupancies of 0.55 and 0.45, respectively. Subsequently, the H atoms attached to atoms C1 and N1 were treated as disordered too.
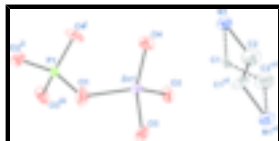
supplementary materials

Figures

Fig. 1. The asymmetric unit of the title compound with displacement ellipsoids drawn at the 40% probability level. Two orientations of diprotonated ethylenediamine are also shown. H atoms have been omitted. Symmetry codes are as in Table 1.
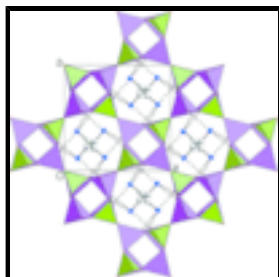

Fig. 2. Polyhedral view of the structure of the title compound along the [001] direction showing the 8-ring channels. Dotted lines indicate hydrogen-bonding interactions and H atoms have been omitted. Color code: ZnO_4 tetrahedra, magenta; PO_4 tetrahedra, green; N, blue; C, gray.
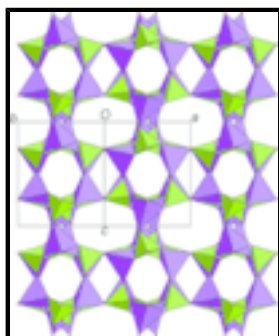

Fig. 3. Polyhedral view of the eight-ring channels along the [110] direction in the title compound. Color key is as in Fig. 2.

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Crystal data

$(C_2H_{10}N_2)[ZnPO_4]_2$	$Z = 4$
$M_r = 382.80$	$F_{000} = 760$
Tetragonal, $P4_2/n$	$D_x = 2.642$ Mg m^{-3}
$a = 10.3940\,(8)$ Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 10.3940\,(8)$ Å	Cell parameters from 36 reflections
$c = 8.9094\,(10)$ Å	$\theta = 2.8–25.0º$
$\alpha = 90º$	$\mu = 5.35$ mm^{-1}
$\beta = 90º$	$T = 293\,(2)$ K
$\gamma = 90º$	Prism, colorless
$V = 962.53\,(15)$ Å^3	$0.12 \times 0.12 \times 0.10$ mm

Data collection

Siemens SMART CCD diffractometer	841 independent reflections
Radiation source: fine-focus sealed tube	616 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.056$

$T = 293(2)$ K	$\theta_{max} = 25.0°$
φ and ω scans	$\theta_{min} = 2.8°$
Absorption correction: mulit-scan (SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 12$
$T_{min} = 0.566$, $T_{max} = 0.617$	$k = -12 \rightarrow 8$
2819 measured reflections	$l = -10 \rightarrow 6$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	H-atom parameters constrained
$wR(F^2) = 0.128$	$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 6.4771P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
841 reflections	$\Delta\rho_{max} = 0.67$ e Å^{-3}
55 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Zn1	1.11040 (8)	0.87230 (8)	0.33996 (9)	0.0193 (3)	
P1	1.11143 (19)	0.59342 (19)	0.2006 (2)	0.0180 (5)	
O1	1.0614 (7)	0.7318 (6)	0.2109 (7)	0.0461 (18)	
O2	1.0612 (6)	0.8386 (6)	0.5432 (6)	0.0293 (14)	
O3	0.9986 (6)	1.0023 (6)	0.2537 (7)	0.0354 (16)	
O4	1.2829 (5)	0.9291 (6)	0.3159 (6)	0.0369 (16)	
N1	1.3804 (7)	1.1268 (7)	0.5038 (9)	0.032 (16)	
H1A	1.4138	1.0814	0.5790	0.047*	0.45
H2A	1.4422	1.1726	0.4598	0.047*	0.45
H3A	1.3454	1.0736	0.4371	0.047*	0.45
H1B	1.4146	1.0809	0.4295	0.047*	0.55
H2B	1.3480	1.0739	0.5727	0.047*	0.55

H3B	1.4410	1.1757	0.5454	0.047*	0.55
C1	1.2800 (17)	1.2149 (16)	0.5630 (2)	0.025 (7)	0.45
H4A	1.2129	1.1654	0.6120	0.030*	0.45
H5A	1.3175	1.2725	0.6366	0.030*	0.45
C2	1.2739 (2)	1.2120 (2)	0.4420 (3)	0.051 (8)	0.55
H4B	1.3566	1.2199	0.3924	0.061*	0.55
H5B	1.2268	1.1383	0.4040	0.061*	0.55

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0177 (5)	0.0194 (6)	0.0206 (5)	0.0019 (4)	0.0008 (4)	0.0003 (4)
P1	0.0178 (11)	0.0171 (11)	0.0190 (10)	−0.0038 (8)	−0.0008 (8)	−0.0025 (8)
O1	0.067 (5)	0.028 (4)	0.044 (4)	0.007 (3)	−0.008 (3)	−0.014 (3)
O2	0.036 (4)	0.032 (3)	0.020 (3)	−0.007 (3)	0.000 (3)	−0.003 (3)
O3	0.046 (4)	0.033 (4)	0.027 (3)	0.024 (3)	−0.005 (3)	−0.004 (3)
O4	0.019 (3)	0.060 (4)	0.032 (3)	−0.009 (3)	0.008 (3)	−0.006 (3)
N1	0.026 (4)	0.030 (4)	0.039 (4)	0.006 (4)	−0.003 (3)	−0.002 (3)
C1	0.024 (11)	0.018 (12)	0.031 (15)	0.010 (8)	−0.016 (8)	−0.016 (7)
C2	0.048 (15)	0.052 (17)	0.053 (18)	0.006 (10)	0.001 (10)	−0.002 (10)

Geometric parameters (Å, °)

Zn1—O4	1.900 (6)	N1—H2A	0.8900
Zn1—O2	1.914 (6)	N1—H3A	0.8900
Zn1—O1	1.927 (6)	N1—H1B	0.8900
Zn1—O3	1.941 (6)	N1—H2B	0.8900
P1—O4^i	1.522 (6)	N1—H3B	0.8900
P1—O2^{ii}	1.532 (6)	C1—C1^{vi}	0.9599
P1—O1	1.532 (7)	C1—C2	1.0803
P1—O3^{iii}	1.538 (6)	C1—C2^{vi}	1.4329
O2—P1^{iv}	1.532 (6)	C1—H4A	0.9700
O3—P1^v	1.538 (6)	C1—H5A	0.9700
O4—P1^i	1.522 (6)	C2—C2^{vi}	0.9332
N1—C1	1.4852	C2—C1^{vi}	1.4329
N1—C2	1.5208	C2—H4B	0.9700
N1—H1A	0.8900	C2—H5B	0.9700
O4—Zn1—O2	114.6 (2)	C1—N1—H3B	89.8
O4—Zn1—O1	114.7 (3)	C2—N1—H3B	109.5
O2—Zn1—O1	110.8 (3)	H1A—N1—H3B	73.3
O4—Zn1—O3	107.7 (3)	H2A—N1—H3B	50.8
O2—Zn1—O3	110.0 (3)	H3A—N1—H3B	157.3
O1—Zn1—O3	97.7 (3)	H1B—N1—H3B	109.5
O4^i—P1—O2^{ii}	109.8 (3)	H2B—N1—H3B	109.5
O4^i—P1—O1	110.4 (4)	C1^{vi}—C1—C2	89.0
O2^{ii}—P1—O1	112.0 (4)	C1^{vi}—C1—C2^{vi}	48.9

O4^{i}—P1—O3^{iii}	104.9 (4)	C2—C1—C2^{vi}	40.6
O2^{ii}—P1—O3^{iii}	110.9 (3)	C1^{vi}—C1—N1	157.7
O1—P1—O3^{iii}	108.5 (4)	C2—C1—N1	70.7
P1—O1—Zn1	131.1 (4)	C2^{vi}—C1—N1	109.5
P1^{iv}—O2—Zn1	138.2 (4)	C1^{vi}—C1—H4A	86.3
P1^{v}—O3—Zn1	141.3 (4)	C2—C1—H4A	113.1
P1^{i}—O4—Zn1	135.2 (4)	C2^{vi}—C1—H4A	109.8
C1—N1—C2	42.1	N1—C1—H4A	109.8
C1—N1—H1A	109.5	C1^{vi}—C1—H5A	78.0
C2—N1—H1A	149.9	C2—C1—H5A	135.7
C1—N1—H2A	109.5	C2^{vi}—C1—H5A	109.8
C2—N1—H2A	93.1	N1—C1—H5A	109.8
H1A—N1—H2A	109.5	H4A—C1—H5A	108.2
C1—N1—H3A	109.5	C2^{vi}—C2—C1	90.4
C2—N1—H3A	79.8	C2^{vi}—C2—C1^{vi}	48.9
H1A—N1—H3A	109.5	C1—C2—C1^{vi}	42.0
H2A—N1—H3A	109.5	C2^{vi}—C2—N1	151.7
C1—N1—H1B	151.1	C1—C2—N1	67.2
C2—N1—H1B	109.5	C1^{vi}—C2—N1	108.7
H1A—N1—H1B	96.9	C2^{vi}—C2—H4B	113.6
H2A—N1—H1B	70.8	C1—C2—H4B	113.6
H3A—N1—H1B	48.2	C1^{vi}—C2—H4B	130.1
C1—N1—H2B	82.5	N1—C2—H4B	64.5
C2—N1—H2B	109.5	C2^{vi}—C2—H5B	113.6
H1A—N1—H2B	45.7	C1—C2—H5B	113.6
H2A—N1—H2B	155.1	C1^{vi}—C2—H5B	118.9
H3A—N1—H2B	85.5	N1—C2—H5B	91.9
H1B—N1—H2B	109.5	H4B—C2—H5B	110.8

Symmetry codes: (i) −x+5/2, −y+3/2, z; (ii) −y+2, x−1/2, z−1/2; (iii) y, −x+3/2, −z+1/2; (iv) y+1/2, −x+2, z+1/2; (v) −y+3/2, x, −z+1/2; (vi) −x+5/2, −y+5/2, z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
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Fig. 1

Fig. 2

Fig. 3