Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$, an organically templated zincophosphate analogue of the aluminosilicate zeolite edingtonite

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Received 14 May 2001
Accepted 17 May 2001
Online 22 May 2001

Key indicators

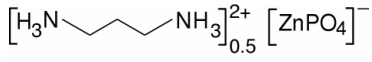
Single-crystal X-ray study
T = 298 K
Mean σ(P–O) = 0.010 Å
Some non-H atoms missing
R factor = 0.085
wR factor = 0.222
Data-to-parameter ratio = 28.3

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

Hydrothermally prepared propane-1,3-diammonium bis(zinc phosphate), $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$ is an analogue of the aluminosilicate zeolite edingtonite. A three-dimensional network of vertex-sharing ZnO_4 and PO_4 tetrahedra [d_{av}(Zn—O) = 1.945 (9) Å, d_{av}(P—O) = 1.513 (10) Å and θ_{av}(Zn—O—P) = 134 (5)°] encapsulate the highly disordered propane-1,3-diammonium cations in a three-dimensional 8-ring channel system.

Comment

The Zn and P atoms both adopt tetrahedral coordination (Fig. 1) with d_{av}(Zn—O) = 1.945 (9) Å and d_{av}(P—O) = 1.513 (10) Å. Each Zn atom makes four Zn—O—P links to nearby P atoms *via* bicoordinate O atom bridges [θ_{av} = 134 (5)°] and *vice versa*, thus a fully connected alternating three-dimensional framework arises. Zn1 and P1 occupy special positions with $\bar{4}$ symmetry. The distinctive 4=1 secondary building unit (SBU) (Meier & Olson, 1992), as found in the family of fibrous aluminosilicate zeolites (Breck, 1974), arises from this connectivity. In turn, these 4=1 SBUs self assemble into infinite fib columns (Smith, 1988). Cross-linking of the fib columns (Fig. 2) *via* Zn2—O4—P2 bonds results in an infinite zincophosphate network.



(I)

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 [110] (Fig. 3) and [$\bar{1}\bar{1}$0] (approximate atom-to-atom dimensions = 6.71 × 6.71 Å). These intersect with channels formed from significantly squashed 8-rings (dimensions ∼ 5.17 × 8.83 Å) which propagate along [001] (Fig. 4).

A topological analysis of the zincophosphate framework of $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$ (ZnPO–EDI) with KRIBER (Grosse Kunstleve & Bialek, 1995) indicated that the title compound, (I), has the same tetrahedral connectivity as that found in the zeolite edingtonite family, exemplified by the type material $BaAl_2Si_3O_{10}\cdot 4H_2O$ (Taylor & Jackson, 1933; Kvick & Smith, 1983). An important difference arises in terms of the 1:1 Zn:P ordering in $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$ *versus* the 3:2 Si:Al ordering in the aluminosilicate phase. This results in a unit-cell doubling in the c direction for the title compound which is precisely the situation predicted by Alberti & Gottardi (1975) in their analysis of the various theoretical

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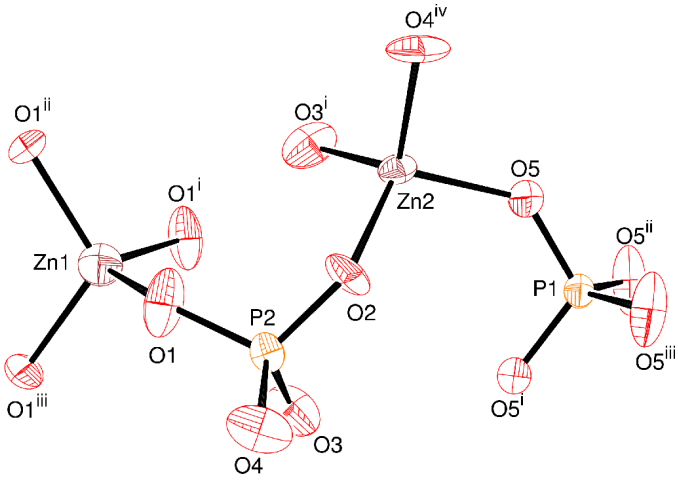

Figure 1
Fragment of $[H_3N(CH_2)_3NH_3]_{0.5}ZnPO_4$ (50% displacement ellipsoids). Symmetry codes as in Table 1.

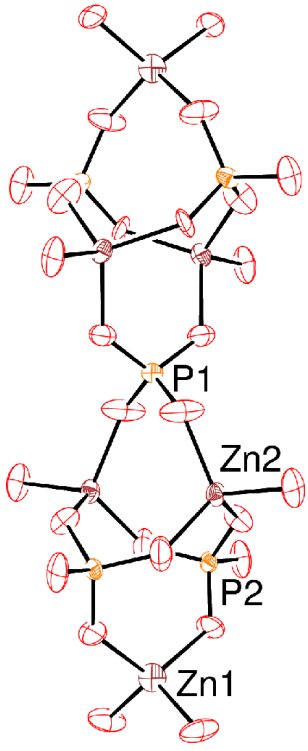

Figure 2
Fragment of $[H_3N(CH_2)_3NH_3]_{0.5}ZnPO_4$ (50% displacement ellipsoids) showing the connectivity of the ZnO_4 and PO_4 groups into a fib column of 4=1 SBUs.

possibilities for connecting adjacent columns of 4=1 SBUs into three-dimensional networks.

A *CALC SOLV* analysis with *PLATON* (Spek, 1990) indicated that the amount of void space encapsulated by the zincophosphate framework in the title compound is 508.5 Å^3, or 38.6% of the unit cell volume. Location and definite identification of the extra-framework organic species within these regions was problematical, hence a *SQUEEZE* analysis was carried out (Spek, 1998). This degree of disorder makes it

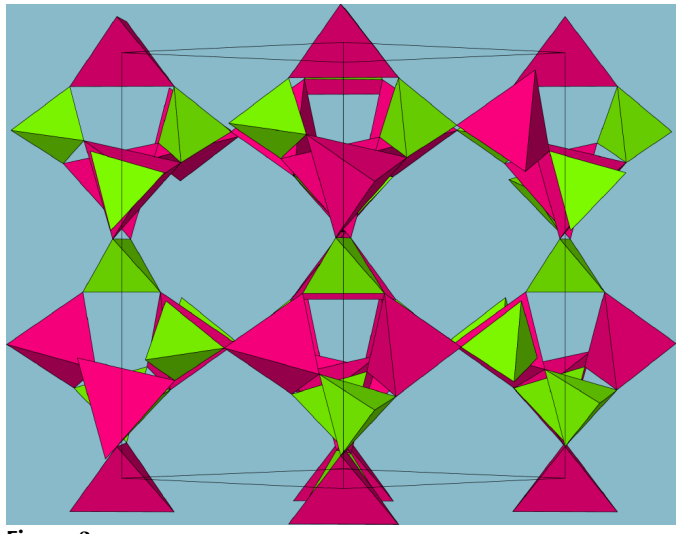

Figure 3
View down [110] for $[H_3N(CH_2)_3NH_3]_{0.5}ZnPO_4$ showing the polyhedral connectivity of the ZnO_4 (magenta) and PO_4 (lime green) moieties, resulting in 8-ring channels.

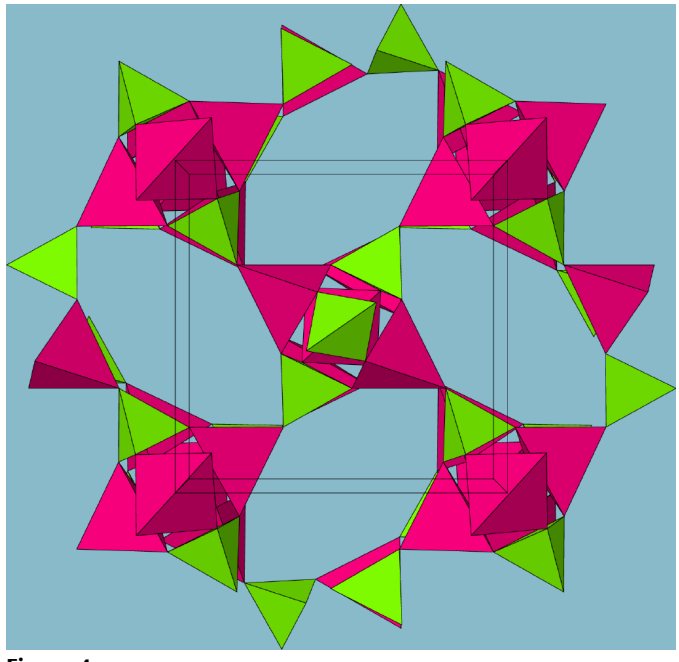

Figure 4
Polyhedral view down [001] for $[H_3N(CH_2)_3NH_3]_{0.5}ZnPO_4$ (colour key as for Fig. 3). Note the squashed 8-ring channels.

impossible to speculate about the role of N—H···O hydrogen bonds in establishing or stabilizing this structure (Harrison, 2001). Similar problems of template disorder were encountered by Feng *et al.* (1997) in their studies of thomsonite-type cobalt-containing zeolite analogues. Severe template disorder also occurs in thomsonite-type $[H_3NCH_2CH(NH_3)CH_3]_{0.5}[ZnPO_4]$ (Ng & Harrison, 2001), where the templating species is propane-1,2-diammonium.

$[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$ complements the phase known as ZP-4, or $KZnPO_4{\cdot}0.8H_2O$, described recently by Broach *et al.* (1999). ZP-4 also crystallizes as an edingtonite type, thus the unusual situation of the same framework type being

templated by either an organic cation or rubidium cations plus water molecules occurs (Cheetham *et al.*, 1999). A somewhat similar situation occurs for for the $M_3Zn_4O(XO_4)\cdot nH_2O$ (M = alkali metal with n = 4–6 or M = methylammonium cations with n = 0; X = P or As) family of phases (Harrison *et al.*, 1999).

Experimental

First, 0.5 g P_2O_5 was dissolved in 10 ml water (this reaction is vigorous) contained in a 23-ml teflon pot. Then, 0.285 g ZnO, 0.444 g oxalic acid dihydrate, and 0.522 g 1,3-diaminopropane were added sequentially. The unstirred vessel was sealed and placed in an oven at 423 K for three days. Upon removal from the oven and cooling over several hours, the resulting solids were recovered by suction filtration and rinsing with acetone, resulting in a mixture of several crystal morphologies, including poorly formed rods of the title compound, well faceted gem-like blocks of gismondine-type $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$ (Neeraj & Natarajan, 2000; Harrison, 2001), and unidentified white powder. As yet, preparation of pure edingtonite-type $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$ has proved impossible; in the absence of oxalic acid, it has not been synthesized at all.

Crystal data

$0.5C_3H_{12}N_2\cdot ZnPO_4$	Mo $K\alpha$ radiation
M_r = 198.42	Cell parameters from 3235 reflections
Tetragonal, $P\bar{4}2_1c$	θ = 1.6–27.6°
a = 9.9015 (12) Å	μ = 4.86 mm^{-1}
c = 13.4199 (16) Å	T = 298 K
V = 1315.7 (3) Å^3	Rod, colourless
Z = 10	0.45 × 0.04 × 0.04 mm
D_x = 2.024 Mg m^{-3}	

Data collection

Bruker SMART1000 CCD diffractometer	1620 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.098
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	θ_{max} = 30.0°
T_{min} = 0.840, T_{max} = 0.928	$h = -13 \rightarrow 13$
10 634 measured reflections	$k = -6 \rightarrow 13$
1923 independent reflections	$l = -18 \rightarrow 18$
	Intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1153P)^2 + 13.2499P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.085	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.222	$\Delta\rho_{max}$ = 2.66 e Å^{-3}
S = 1.10	$\Delta\rho_{min}$ = −2.55 e Å^{-3}
1923 reflections	Absolute structure: Flack (1983)
68 parameters	Flack parameter = 0.00 (9)
H atoms not located	

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.948 (8)	P1—O5^{v}	1.505 (10)
Zn1—O1^{i}	1.948 (8)	P1—O5^{vi}	1.505 (10)
Zn1—O1^{ii}	1.948 (8)	P1—O5^{i}	1.505 (10)
Zn1—O1^{iii}	1.948 (8)	P1—O5	1.505 (10)
Zn2—O3^{i}	1.923 (10)	P2—O4	1.504 (8)
Zn2—O4^{iv}	1.926 (7)	P2—O2	1.509 (8)
Zn2—O5	1.957 (10)	P2—O3	1.523 (9)
Zn2—O2	1.961 (7)	P2—O1	1.549 (9)
P2—O1—Zn1	133.5 (6)	P2—O4—Zn2^{vii}	142.8 (6)
P2—O2—Zn2	130.5 (5)	P1—O5—Zn2	132.4 (6)
P2—O3—Zn2^{i}	130.9 (6)		

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

In an effort to improve the poor fit, various models involving symmetry reduction to orthorhombic (space group $P2_12_12$) and/or (pseudo)merohedral twinning about [001] were tried. These failed to result in any significant improvement. Refinement with *SHELXL* using *TWIN*/*BASF* instructions indicated merohedral (enantiomeric) twinning in a 0.81 (6):0.19 (6) ratio in the individual crystal studied. A number of electron density maxima were found in the channel system, and tentatively assigned with C-atom scattering factors. This procedure lowered the crystallographic residuals by several percent, but the apparent geometry of the resulting fragments cannot be correlated with any reasonable conformation of the 1,3-diammonium propane template. Using SQUEEZE (Spek, 1998) reduced the $R(F)$ residual from 0.13 to 0.09, suggesting that the disorder of the extra-framework species is at least in part responsible for the high residuals. The calculated number of 152 'void electrons' per unit cell is tolerably close to the 210 template electrons required to correspond to the proposed formulation of $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$. However, a situation of template decomposition to ammonium cations, which serve to template the channels, and other products, cannot be ruled out based on the present evidence. The largest difference peak not associated with the channel regions is 1.72 Å from Zn1, the deepest difference hole is 0.37 Å from Zn1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SMART*; 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) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL*97.

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