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$[H_3N(CH_2)_2NH_3]_{0.5}[BePO_4]$, a beryllophosphate analogue of aluminosilicate zeolite gismondine

William T. A. Harrison

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

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Hydrothermally prepared ethylenediammonium beryllophosphate, $(C_2H_{10}N_2)_{0.5}[BePO_4]$, is an analogue of aluminosilicate zeolite gismondine. A three-dimensional network of vertex-sharing BeO_4 and PO_4 tetrahedra [$d_{av}(Be-O)$ = 1.618 (3) Å, $d_{av}(P-O)$ = 1.5246 (14) Å and $\theta_{av}(Be-O-P)$ = 139.8°] encapsulates the disordered ethylenediammonium cations in an eight-ring channel system.

Comment

Both beryllium and phosphorus adopt tetrahedral coordination [$d_{av}(Be-O)$ = 1.618 (3) Å and $d_{av}(P-O)$ = 1.5246 (14) Å] with typical geometrical parameters (Harrison, 2001*a*). Be1 makes four links to nearby P1 atoms *via* bicoordinate O-atom bridges (θ_{av} = 139.8°) and *vice versa*, thus a fully connected three-dimensional tetrahedral framework arises. Perfect 1:1 alternation of the Be and P species occurs.

The anionic $[BePO_4]^-$ framework encloses fairly regular eight-ring (*i.e.* eight tetrahedral centres made up of four BeO_4 and four PO_4 units) channels propagating along [100] and [001], with atom-to-atom dimensions of 5.42 × 5.42 Å and 5.62 × 5.62 Å, respectively. Conversely, there are no channels apparent in the [010] direction. A topological analysis with the program *KRIBER* (Grosse Kunstleve & Bialek, 1995) indicated that the title compound (Figs. 1 and 2) has the same tetrahedral connectivity as the zeolite gismondine family, as exemplified by the type material $Ca(AlSiO_4)_2\cdot 4H_2O$ (Vezzalini *et al.*, 1993).

A *CALC SOLV* analysis with *PLATON* (Spek, 1990) indicated that the amount of void space encapsulated by the framework in $[H_3N(CH_2)_2NH_3]_{0.5}[BePO_4]$ is 295.7 Å^3, or 35.5% of the unit-cell volume. However, when the extra framework species are included, there is no 'solvent-accessible' volume, indicating that the channels are essentially filled by the organic cations.

To achieve charge balance, we assume that the extra-framework organic species is doubly protonated, as the ethylenediammonium cation. Geometrical placement of H atoms resulted in a situation where all six N—H bonds are involved in N—H···O interactions, with one of the hydrogen bonds being bifurcated (Table 2). This situation is similar to that seen in other organically templated beryllophosphate frameworks (Harrison, 2001*a*), although the present results should not be regarded as definitive in this aspect due to the substantial template disorder.

$[H_3N(CH_2)_2NH_3]_{0.5}[BePO_4]$ complements several other non-aluminosilicate gismondine analogues that have been characterized recently, including the cobaltophosphate CoPO–GIS, or $[H_3N(CH_2)_2NH_3]_{0.5}[CoPO_4]$ (Yuan *et al.*, 2000), and the zincophosphate ZnPO–GIS, or $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$ (Neeraj & Natarajan, 2000; Harrison, 2001*b*), as well as novel GIS frameworks containing three distinct tetrahedral atom types [Al/Co/P (Feng *et al.*, 1997), Zn/Ga/P (Chippindale *et al.*, 1998) and Zn/B/P (Kneip *et al.*, 1999)]. Interestingly, in CoPO–GIS, which crystallizes in the same space group as $[H_3N(CH_2)_2NH_3]_{0.5}[BePO_4]$, the same template cation occupies a different location in the channels and is completely ordered. A *CALC SOLV* analysis showed that some 302.4 Å^3 of free space, essentially the same value as that for the title compound, is available to the template in CoPO–GIS. Conversely, for ZnPO–GIS, well

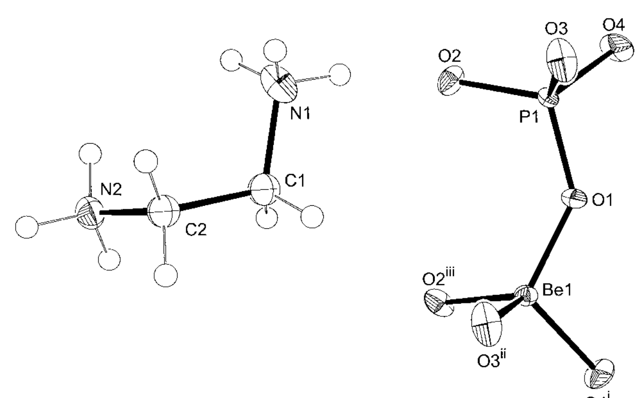

Figure 1
A fragment of $[H_3N(CH_2)_2NH_3]_{0.5}[BePO_4]$ with 50% probability displacement ellipsoids. Symmetry codes are as in Table 1.

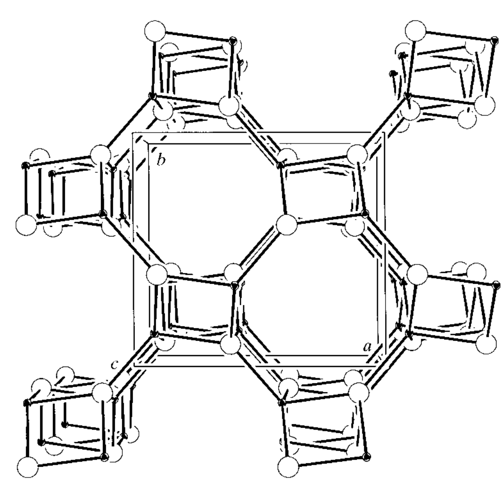

Figure 2
View down [001] of $[H_3N(CH_2)_2NH_3]_{0.5}[BePO_4]$, showing the topological connectivity between the Be (small shaded circles) and P (large open circles) tetrahedral nodes, resulting in an infinite framework of four- and eight-rings.

ordered 1,3-propanediammonium cations template the $[ZnPO_4]^-$ framework, suggesting that a bulkier template molecule is appropriate for the zincophosphate phase. This is supported by the fact that in each unit cell of $[H_3N(CH_2)_3NH_3]_{0.5}[ZnPO_4]$, a pore volume of 395.7 Å^3 {some 100 Å^3 more than the equivalent value for $[H_3N(CH_2)_2NH_3]_{0.5}[BePO_4]$} is available to the extra-framework species. However, this simple approach takes no account of the shape (or preferred conformation) of the template, nor its hydrogen-bonding capability.

Experimental

Ethylenediamine (en; 0.3 g), BeO (0.125 g) and P_2O_5 (1.065 g) were dissolved in water (10 ml). This mixture (en:Be:P ratio $\simeq$ 1:1:3) was heated to 423 K for 3 d in a 23 ml capacity sealed Teflon-lined hydrothermal bomb. After cooling the bomb to ambient temperature over 2–3 h, a small yield of perfectly faceted prismatic rods of the title compound was recovered by vacuum filtration and washing with water. Unidentified white powder products arise from 1:1:2 or 1:1:4 en:Be:P starting ratios under the same hydrothermal conditions. Caution! Beryllium compounds are highly toxic. Take all appropriate safety precautions, especially to avoid dust contamination.

Crystal data

$(C_2H_{10}N_2)_{0.5}[BePO_4]$
$M_r = 135.04$
Monoclinic, $I2/a$
$a = 9.6165$ (7) Å
$b = 9.0032$ (7) Å
$c = 9.6231$ (7) Å
$\beta = 90.951$ (2)°
$V = 833.05$ (11) Å^3
$Z = 8$
$D_x = 2.153$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1618 reflections
$\theta = 3.0$–$30.0°$
$\mu = 0.56$ mm^{-1}
$T = 298$ K
Rod, colourless
0.40 × 0.06 × 0.05 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.912$, $T_{max} = 0.974$
3583 measured reflections
1227 independent reflections
1001 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 30.0°$
$h = -13 \rightarrow 10$
$k = -11 \rightarrow 12$
$l = -13 \rightarrow 13$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.093$
$S = 1.02$
1227 reflections
81 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Be1—O1	1.600 (3)	P1—O3	1.5267 (13)
Be1—O4^{i}	1.613 (3)	P1—O1	1.5273 (15)
Be1—O3^{ii}	1.625 (3)	N1—C1	1.492 (5)
Be1—O2^{iii}	1.632 (3)	N2—C2	1.491 (5)
P1—O4	1.5216 (15)	C1—C2	1.496 (5)
P1—O2	1.5226 (14)		
O1—Be1—O4^{i}	109.56 (16)	O2—P1—O3	109.09 (8)
O1—Be1—O3^{ii}	113.72 (16)	O4—P1—O1	105.58 (8)
O4^{i}—Be1—O3^{ii}	103.98 (15)	O2—P1—O1	112.06 (8)
O1—Be1—O2^{iii}	113.48 (16)	O3—P1—O1	110.72 (9)
O4^{i}—Be1—O2^{iii}	111.25 (16)	P1—O1—Be1	137.59 (13)
O3^{ii}—Be1—O2^{iii}	104.38 (15)	P1—O2—Be1^{iii}	134.33 (13)
O4—P1—O2	113.37 (9)	P1—O3—Be1^{ii}	141.57 (13)
O4—P1—O3	105.81 (8)	P1—O4—Be1^{iv}	145.86 (14)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.95	1.99	2.928 (4)	167
N1—H2···O3^{i}	0.95	1.89	2.831 (4)	173
N1—H3···O4^{ii}	0.95	2.34	3.203 (4)	152
N2—H4···O1^{iii}	0.95	2.03	2.942 (4)	161
N2—H5···O4^{ii}	0.94	2.14	2.978 (4)	148
N2—H6···O3^{iv}	0.95	2.38	3.112 (4)	134
N2—H6···O1^{ii}	0.95	2.57	3.143 (4)	119

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

A handful of very weak reflections, possibly corresponding to a $2a \times 2b \times 2c$ supercell, were observed, but no convincing models could be established in the larger cell. The site occupancies of the disordered N and C atoms were varied and refined to 0.5 within experimental error and were fixed at this value for the final cycles of least-squares refinement. H atoms were treated as riding with C—H = 0.93–0.96 Å and N—H = 0.94–0.95 Å

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1154). Services for accessing these data are described at the back of the journal.

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