

Butane-1,4-diamine zinc(II) hydrogen phosphite

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Received 25 August 2004

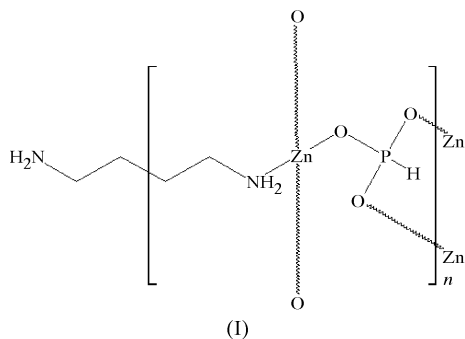
Accepted 4 October 2004

Online 11 November 2004

The title compound, poly[zinc(II)- μ -butane-1,4-diamine- μ -(hydrogen phosphito)] ($C_4H_{12}N_2$)_{0.5}[ZnHPO₃], is a hybrid organic–inorganic solid built up from 1,4-diaminobutane molecules, Zn²⁺ cations (coordinated by three O atoms and one N atom) and HPO₃²⁻ hydrogen phosphite groups. The organic species bonds to the Zn atom as an unprotonated ligand, resulting in it acting as a bridge between infinite ZnHPO₃ layers, which propagate in (100). The complete butane-1,4-diamine species is generated from a H₂N(CH₂)₂-half molecule by inversion symmetry. The zincophosphite sheets contain polyhedral four- and eight-membered rings in a 4.8² topology.

Comment

The title compound, [H₂N(CH₂)₄NH₂]_{0.5}[ZnHPO₃], (I), is another example of the rapidly expanding family of organically templated zinc hydrogen phosphite (ZnHPO) networks (Kirkpatrick & Harrison, 2004, and references therein; Fu *et al.*, 2004) and is the first reported ZnHPO compound to incorporate butane-1,4-diamine as the organic species. Compound (I) was prepared in single-crystal form by a typical mild-condition solution-mediated reaction (Cheetham *et al.*, 1999).



Compound (I) (Fig. 1) is built up from neutral unprotonated butane-1,4-diamine [H₂N(CH₂)₄NH₂] molecules, Zn²⁺ cations and HPO₃²⁻ hydrogen phosphite groups. Each complete butane-1,4-diamine entity is generated from a half-molecule

H₂N(CH₂)₂-fragment by inversion symmetry (Table 1). The N atom makes a ligand-like bond to the Zn atom by formal donation of its lone pair of electrons, as seen in related systems (Rodgers & Harrison, 2000). The tetrahedral zinc coordination is completed by three O atoms [mean Zn–O = 1.943 (2) Å], all of which form bridges to nearby HPO₃²⁻ groups [mean Zn–O–P = 131.3 (2)°]. The pseudo-pyramidal HPO₃²⁻ moiety has typical geometrical parameters, with a mean P–O distance of 1.518 (2) Å and a mean O–P–O angle of 112.48 (9)° (Kirkpatrick & Harrison, 2004). Its three O atoms all make bridges to nearby zinc cations. As usual, the P–H moiety does not interact with any nearby chemical species.

The polyhedral building units in (I) thus consist of ZnO₃N and HPO₃ tetrahedra, linked by way of the O atoms. These units form sheets, built up from strictly alternating Zn- and P-centred moieties, which propagate in the (100) plane. Every tetrahedral node (*i.e.* the Zn and P atoms) participates in one four-membered ring (generated by inversion symmetry) and two eight-membered rings (Fig. 2), and this topology is classed as a 4.8² sheet (O’Keeffe & Hyde, 1996).

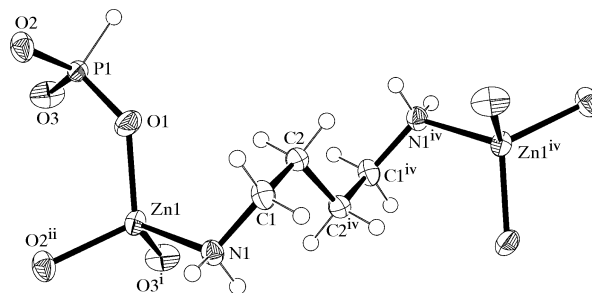


Figure 1
 A view of a fragment of (I) (50% probability displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radii. Symmetry codes are as in Table 1.

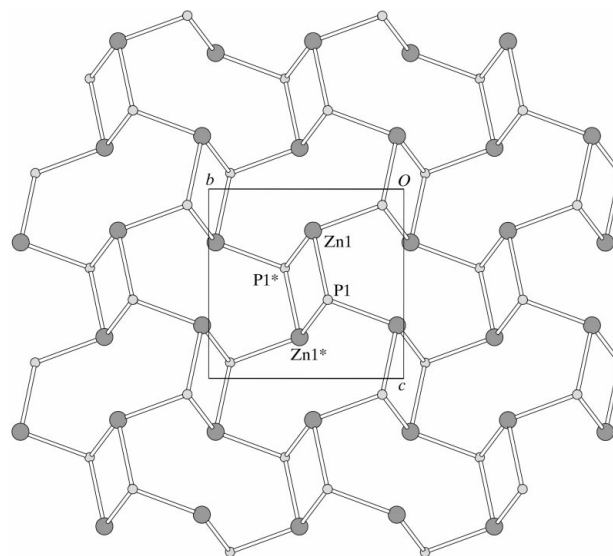


Figure 2
 A view down [100] of a fragment of a ZnHPO₃ layer in (I), showing the topological connectivity of the Zn (large spheres) and P (small spheres) tetrahedral nodes into 4.8² sheets. Atoms labelled with an asterisk (*) are at the symmetry position (2 – x, 1 – y, 1 – z). The lines linking the Zn and P atoms represent Zn–O–P bridges, which are not linear (see Table 1).

The organic species crosslink the (100) ZnHPO_3 sheets in a $\text{Zn}-b-\text{Zn}$ (b is the organic bridge) fashion, as shown in Fig. 3, resulting in a hybrid 'pillared' structure in which the inorganic and organic components alternate along [100]. In principle, this arrangement represents a novel kind of microporosity, with the channels bounded by both inorganic and organic surfaces. However, in (I), the presence of the $\text{P}-\text{H}$ bond protruding into the channel region and the highly twisted conformation of the 1,4-diaminobutane moiety mean that there is no possibility of ingress by other chemical species. Finally, the butane-1,4-diamine NH_2 groups in (I) participate in $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2), of which one (*via* H3) is simple and one (*via* H2) is bifurcated (Fig. 4). These hydrogen bonds appear to help to anchor the organic moiety to an eight-membered ring window in the zinc hydrogen phosphite layer, in a similar way to the behaviour of ethylenediamine in $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5}[\text{ZnHPO}_3]$ (Rodgers &

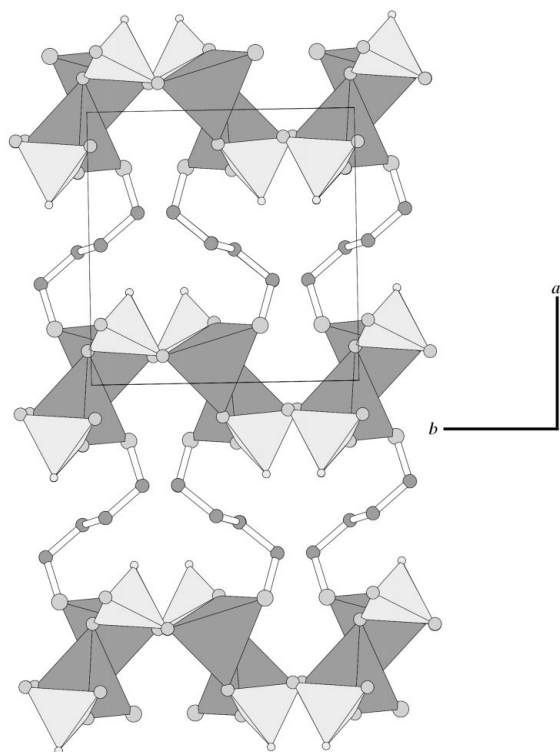


Figure 3
The unit-cell packing in (I), viewed down [001], in a polyhedral representation (ZnO_3N groups: dark shading; HPO_3 groups: light shading). All H atoms, except for atom H1, have been omitted for clarity.

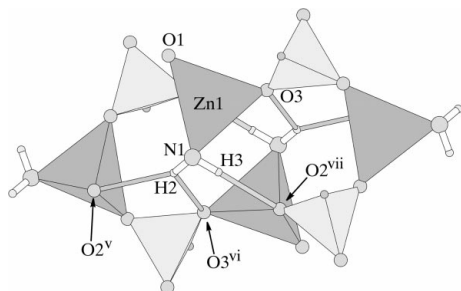


Figure 4
A polyhedral view of a fragment of a (100) ZnHPO_3 layer in (I), showing the $\text{N}-\text{H}\cdots\text{O}$ bonds associated with a flattened 8-ring window. Symmetry codes are as in Table 2.

Harrison, 2000). Here, however, the zincophosphate 8-ring pores are highly flattened, whereas in $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5}[\text{ZnHPO}_3]$ they are far more regular.

Compound (I) complements several other 'pillared' networks built up from ZnO_3N_1 (N_1 = ligand amine N atom) tetrahedra and pyramidal or pseudo-pyramidal inorganic oxyanions. Both modifications of ethylenediamine zinc selenite, $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5}[\text{ZnSeO}_3]$ (Choudhury *et al.*, 2002; Millange *et al.*, 2004), contain sheets of ZnO_3N and SeO_3 groups fused into a three-dimensional network by the ethylenediamine moieties bonding to the Zn atom from each end of the $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ species. The first of these (Choudhury *et al.*, 2002) is based on 6^3 inorganic sheets (each nodal atom participates in three six-membered rings), whereas the second (Millange *et al.*, 2004) is based on 4.8^2 sheets, as seen here for (I). The 1,4-diaminobenzene template in $(\text{C}_6\text{N}_2\text{H}_8)_{0.5}[\text{ZnHPO}_3]$ (Kirkpatrick & Harrison, 2004) acts in a similar way to ethylenediamine in the $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5}[\text{ZnSeO}_3]$ phases; in this case, 6^3 polyhedral sheets arise. Finally, $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5}[\text{ZnHPO}_3]$ (Rodgers & Harrison, 2000) has a novel structure based on 4.8^2 sheets in which two independent networks form an interpenetrating array akin to coordination polymers.

Experimental

Zinc oxide, phosphorus acid (H_3PO_3) and butane-1,4-diamine in a 1:2:2 molar ratio were shaken in distilled water (25 ml) in a 60 ml HDPE bottle for a few minutes until a white slurry formed. The bottle was then placed in an oven at 353 K for 2 d. The solid product was filtered off hot by suction filtration using a Buchner funnel and rinsed with water and acetone, resulting in intergrown block-like crystals of (I). An *ATOMS* (Shape Software, 1999) simulation of the X-ray powder pattern of (I), based on the single-crystal structure described here, was in excellent agreement with the measured data, indicating phase purity.

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_2)_{0.5}[\text{ZnHPO}_3]$
 $M_r = 189.43$
 Monoclinic, $P2_1/c$
 $a = 8.4713$ (4) Å
 $b = 8.2489$ (4) Å
 $c = 8.0805$ (4) Å
 $\beta = 96.093$ (1)°
 $V = 561.47$ (5) Å³
 $Z = 4$

$D_x = 2.241$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3298 reflections
 $\theta = 2.5\text{--}32.2^\circ$
 $\mu = 4.57$ mm⁻¹
 $T = 293$ (2) K
 Slab, colourless
 $0.32 \times 0.30 \times 0.13$ mm

Table 1

Selected geometric parameters (Å, °).

Zn1—O1	1.9331 (11)	P1—O1	1.5140 (11)
Zn1—O3 ⁱ	1.9427 (11)	P1—O3	1.5152 (12)
Zn1—O2 ⁱⁱ	1.9539 (11)	P1—O2	1.5254 (11)
Zn1—N1	2.0260 (12)		
P1—O1—Zn1	135.21 (7)	P1—O3—Zn1 ⁱⁱⁱ	134.49 (7)
P1—O2—Zn1 ⁱⁱ	124.08 (7)	C1—N1—Zn1	116.33 (9)
Zn1—N1—C1—C2	−57.62 (14)	C1—C2—C2 ^{iv} —C1 ^{iv}	180.0
N1—C1—C2—C2 ^{iv}	−61.9 (2)		

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

Data collection

Bruker SMART 1000 CCD diffractometer	1964 independent reflections
ω scans	1667 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.017$
$T_{\text{min}} = 0.323$, $T_{\text{max}} = 0.588$	$\theta_{\text{max}} = 32.2^\circ$
5407 measured reflections	$h = -12 \rightarrow 12$
	$k = -5 \rightarrow 12$
	$l = -12 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.019$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.049$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
1964 reflections	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
74 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0032 (7)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H2 \cdots O2^v$	0.90	2.47	3.2107 (17)	140
$N1-H2 \cdots O3^{vi}$	0.90	2.57	3.1143 (16)	119
$N1-H3 \cdots O2^{iii}$	0.90	2.29	3.1501 (15)	160

Symmetry codes: (v) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (vi) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $x, y, z - 1$.

All H atoms were placed in idealized positions and refined as riding on their carrier atoms [$P-H = 1.32 \text{ \AA}$, $N-H = 0.90 \text{ \AA}$, $C-H = 0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$].

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and ATOMS (Shape Software, 1999); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1100). Services for accessing these data are described at the back of the journal.

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