

**$\beta$ -[H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>0.5</sub>[ZnHPO<sub>3</sub>], a second modification of ethylenediamine zinc hydrogen phosphite**

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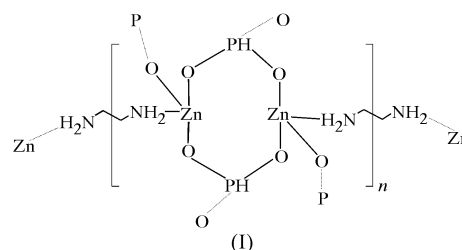
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The title compound, poly[dizinc(II)- $\mu$ -ethylenediamine-di- $\mu$ -(hydrogen phosphito)],  $\beta$ -[H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>0.5</sub>[ZnHPO<sub>3</sub>] or [Zn<sub>2</sub>(HPO<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)]<sub>n</sub>, is a hybrid organic/inorganic solid built up from ethylenediamine molecules (which lie about inversion centres), Zn<sup>2+</sup> cations (coordinated by three O atoms and one N atom) and HPO<sub>3</sub><sup>2-</sup> hydrogen phosphite groups. The organic species bond to the Zn atom as unprotonated ligands, acting as bridges between infinite ZnHPO<sub>3</sub> layers that propagate as very buckled (001) sheets. The zincophosphite sheets contain polyhedral four- and eight-membered rings in a 4.8<sup>2</sup> topology.  $\beta$ -[H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>0.5</sub>·ZnHPO<sub>3</sub> complements the previously described  $\alpha$  modification of the same stoichiometry [Rodgers & Harrison (2000). *Chem. Commun.* pp. 2385–2386].

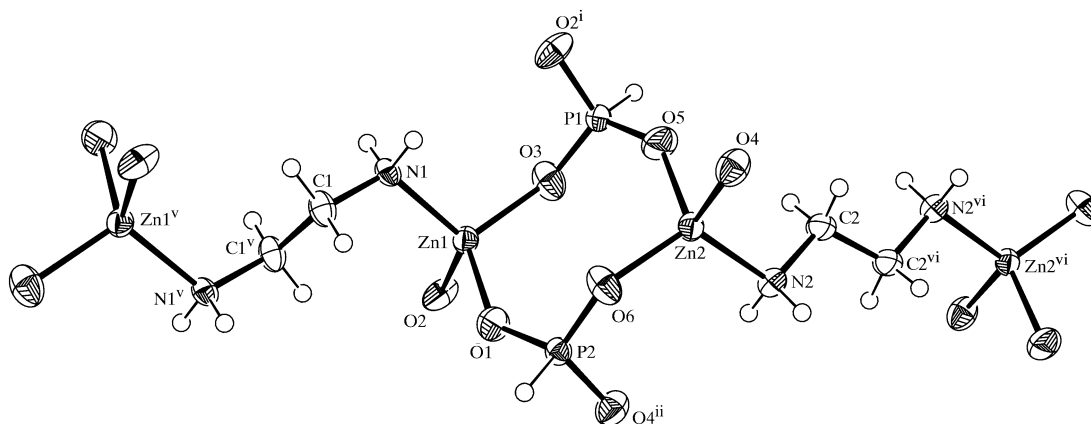
**Comment**

Among the myriad variety of organically templated inorganic networks (Cheetham *et al.*, 1999), a small but distinctive family contains tetrahedral ZnO<sub>3</sub>N and pyramidal SeO<sub>3</sub> or pseudo-

pyramidal HPO<sub>3</sub> building blocks. The inorganic moieties share vertices, as Zn–O–Se or Zn–O–P bonds, thereby forming an infinite sheet. The linear-chain diamine organic species bonds directly to zinc as a ligand *via* each N atom, thus acting as a ‘pillar’ between the inorganic sheets. Both modifications of ethylenediamine zinc selenite, [H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>0.5</sub>·ZnSeO<sub>3</sub> (Choudhury *et al.*, 2002; Millange *et al.*, 2004), contain such sheets of ZnO<sub>3</sub>N and SeO<sub>3</sub> groups, fused into a three-dimensional network by the ethylenediamine moieties bonding to the Zn atoms *via* each NH<sub>2</sub> group. These modifications differ in the topological connectivity (O’Keeffe & Hyde, 1996) of the Zn and Se nodal atoms; the first (Choudhury *et al.*, 2002) is based on 6<sup>3</sup> inorganic sheets (each nodal atom participates in three six-membered rings), whereas the second (Millange *et al.*, 2004) contains 4.8<sup>2</sup> sheets. The 1,4-diaminobenzene template in [C<sub>6</sub>N<sub>2</sub>H<sub>8</sub>]<sub>0.5</sub>[ZnHPO<sub>3</sub>] (Kirkpatrick & Harrison, 2004) acts in a similar way to ethylenediamine in the zinc selenite phases; in this case, 6<sup>3</sup> polyhedral sheets built up from ZnO<sub>3</sub>N and HPO<sub>3</sub> units arise. Conversely, in [H<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]<sub>0.5</sub>[ZnHPO<sub>3</sub>] (Ritchie & Harrison, 2004), 4.8<sup>2</sup> polyhedral sheets arise from the ZnO<sub>3</sub>N and HPO<sub>3</sub> units. Finally, [H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>0.5</sub>[ZnHPO<sub>3</sub>] (Rodgers & Harrison, 2000; hereafter known as the  $\alpha$  modification of this stoichiometry) has a novel structure based on 4.8<sup>2</sup> sheets in which two independent networks form an interpenetrating array akin to some coordination polymers.



We describe here the title compound, (I), which crystallizes as a second,  $\beta$ , modification of [H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>0.5</sub>[ZnHPO<sub>3</sub>]. Compound (I) (Fig. 1) is built up from neutral unprotonated ethylenediamine [H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> or C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>] molecules, Zn<sup>2+</sup>

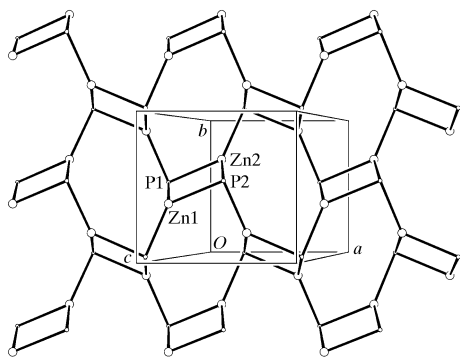
**Figure 1**

A view of a fragment of (I), showing the different conformations of the N1 and N2 ethylenediamine species. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. The symmetry codes are as given in Table 1.

cations and  $\text{HPO}_3^{2-}$  hydrogen phosphite groups. Each complete ethylenediamine entity is generated from a half-molecule  $\text{H}_2\text{NCH}_2-$  fragment by inversion symmetry. However, these entities differ significantly in their conformations (Table 1); in the N1-containing molecule, atoms Zn1 and C1<sup>v</sup> (see Table 1 for symmetry code) are *gauche*, whereas in the N2-containing molecule, the equivalent pair of atoms, Zn2 and C2<sup>vi</sup>, are close to *anti*. Both the N atoms of each  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$  molecule make ligand-like bonds to zinc by formal donation of their lone pair of electrons, as observed for the related systems (Rodgers & Harrison, 2000; Kirkpatrick & Harrison, 2004) noted above. The tetrahedral zinc coordination is completed by three O atoms [mean Zn–O = 1.931 (10) Å], each of which form bridges to P atoms of nearby  $\text{HPO}_3^{2-}$  groups [mean Zn–O–P = 135.1 (6)°]. The pseudopyramidal  $\text{HPO}_3^{2-}$  moieties have typical (Kirkpatrick & Harrison, 2004) geometric parameters, with a mean P–O distance of 1.513 (10) Å and a mean O–P–O angle of 112.9 (7)°. Both distinct  $\text{HPO}_3^{2-}$  groups form bridges to three nearby zinc cations. As usual, the PH moieties do not interact with any nearby chemical species.

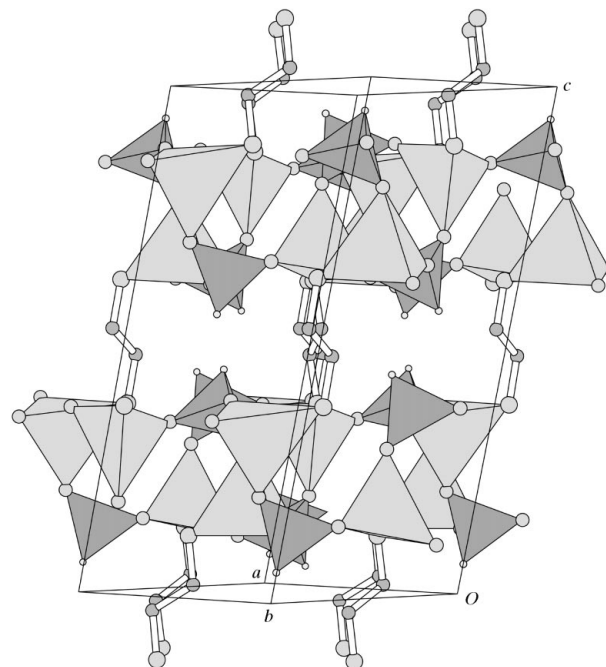
The polyhedral building units in (I) thus consist of  $\text{ZnO}_3\text{N}$  and  $\text{HPO}_3$  tetrahedra, linked by way of the O atoms. These units form sheets, built up from strictly alternating Zn- and P-centred moieties, which propagate in the (001) plane. Every tetrahedral node (*i.e.* the Zn and P atoms) participates in one four-atom loop (composed of the asymmetric unit atoms) and two eight-atom loops (Fig. 2), thus generating a  $4.8^2$  sheet topology (O’Keeffe & Hyde, 1996).

The organic species crosslink the (001)  $\text{ZnHPO}_3$  sheets in a Zn–b–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 of the structure alternate along [001]. In principle, this arrangement represents an unusual kind of microporosity, with the channels bounded by both inorganic and organic surfaces. However, in (I), unlike the case of organically pillared zirconyl phosphates (Alberti *et al.*, 1999), the presence of the P–H bond protruding into the channel region and the steric bulk of the ethylenediamine moieties



**Figure 2**

A view of a fragment of a  $\text{ZnHPO}_3$  layer in (I), showing the topological connectivity of the Zn (large spheres) and P (small spheres) tetrahedral nodes into  $4.8^2$  sheets. The lines linking the Zn and P nodes represent Zn–O–P bridges, which are not linear (see Table 1).



**Figure 3**

The unit-cell packing in (I), in a polyhedral representation ( $\text{ZnO}_3\text{N}$  groups: light shading;  $\text{HPO}_3$  groups: dark shading; ethylenediamine molecules in ball-and-stick representation). All H atoms, except the hydrogen phosphite H1 and H2 species, have been omitted for clarity.

means that there is no possibility of ingress by other chemical species. Finally, the ethylenediamine  $-\text{NH}_2$  groups in (I) participate in N–H...O hydrogen bonds (Table 2), all of which are close to linear (mean H–H...O = 172°). 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  $\alpha\text{-}[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5}[\text{ZnHPO}_3]$  (Rodgers & Harrison, 2000). However, the zincophosphite eight-membered ring pores in (I) are distinctly flattened, whereas in  $\alpha\text{-}[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5}[\text{ZnHPO}_3]$  they are far more regular. The recently reported ethylenediammonium zinc hydrogen phosphite  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3][\text{Zn}_2(\text{HPO}_3)_3]$  (Lin *et al.*, 2004) is a more conventional templated network (Cheetham *et al.*, 1999), in which the organic species is protonated and interacts with the inorganic component by way of N–H...O hydrogen bonds. Interestingly, a  $4.8^2$  network topology is formed by the  $[\text{Zn}_2(\text{HPO}_3)_3]^{2-}$  sheets.

## Experimental

A mixture of zinc oxide (3.00 g), phosphorus acid ( $\text{H}_3\text{PO}_3$ , 2.02 g) and ethylenediamine (1.48 g) (molar ratio 2:3:2) was shaken in distilled water (20 ml) in a 60 ml HDPE (high-density polyethylene) bottle for a few minutes, resulting in the formation of a white slurry. The bottle was then placed in an oven at 353 K for 2 d. The solid product was filtered by suction filtration using a Buchner funnel and rinsed with water and acetone, resulting in intergrown fans of needle- and blade-like crystals of (I) accompanied by some undissolved zinc oxide.

Crystal data

[Zn<sub>2</sub>(HPO<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)]  
*M<sub>r</sub>* = 350.80  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 8.3609 (4) Å  
*b* = 7.9369 (4) Å  
*c* = 15.8259 (7) Å  
 $\beta$  = 104.689 (1)°  
*V* = 1015.88 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 2.294 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5099 reflections  
 $\theta$  = 2.5–27.4°  
 $\mu$  = 5.04 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Slab, colourless  
 0.33 × 0.30 × 0.11 mm

Data collection

Bruker SMART 1000 CCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)  
*T<sub>min</sub>* = 0.287, *T<sub>max</sub>* = 0.607  
 7093 measured reflections  
 2309 independent reflections  
 2075 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.031  
 $\theta_{\text{max}}$  = 27.5°  
*h* = -10 → 8  
*k* = -9 → 10  
*l* = -20 → 20

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.064  
*wR* (*F*<sup>2</sup>) = 0.171  
 $S$  = 1.28  
 2309 reflections  
 128 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0155P)^2 + 26.0795P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.23 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.01 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0028 (5)

Table 1

Selected geometric parameters (Å, °).

|                           |            |                            |            |
|---------------------------|------------|----------------------------|------------|
| Zn1—O1                    | 1.929 (8)  | Zn2—N2                     | 2.021 (8)  |
| Zn1—O3                    | 1.932 (8)  | P1—O5                      | 1.497 (8)  |
| Zn1—O2                    | 1.932 (8)  | P1—O3                      | 1.518 (9)  |
| Zn1—N1                    | 2.016 (8)  | P1—O2 <sup>i</sup>         | 1.519 (7)  |
| Zn2—O6                    | 1.923 (7)  | P2—O6                      | 1.511 (8)  |
| Zn2—O5                    | 1.934 (8)  | P2—O1                      | 1.513 (8)  |
| Zn2—O4                    | 1.938 (8)  | P2—O4 <sup>ii</sup>        | 1.519 (8)  |
| P2—O1—Zn1                 | 141.0 (5)  | P2 <sup>iv</sup> —O4—Zn2   | 133.3 (5)  |
| P1 <sup>iii</sup> —O2—Zn1 | 128.8 (5)  | P1—O5—Zn2                  | 143.6 (6)  |
| P1—O3—Zn1                 | 134.9 (5)  | P2—O6—Zn2                  | 128.9 (5)  |
| Zn1—N1—C1—C1 <sup>v</sup> | -64.8 (13) | Zn2—N2—C2—C2 <sup>vi</sup> | 170.1 (11) |

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

Several crystals of (I) were examined, and the diffraction quality was rather poor in all cases, with some peaks showing signs of being ‘smeared’ or split. All H atoms were placed in idealized locations and refined as riding on their carrier atoms (P—H = 1.32 Å, N—H = 0.90 Å and C—H = 0.97 Å). For all H atoms, the constraint *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(carrier atom) was applied. The maximum difference peak is 1.22 Å from atom H2A.

Table 2

Hydrogen-bonding geometry (Å, °).

| <i>D</i> —H... <i>A</i>    | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1A...O3 <sup>i</sup>   | 0.90        | 2.20          | 3.099 (11)            | 173                     |
| N1—H1B...O4 <sup>iii</sup> | 0.90        | 2.10          | 2.984 (11)            | 167                     |
| N2—H2A...O2 <sup>iv</sup>  | 0.90        | 2.11          | 2.995 (11)            | 170                     |
| N2—H2B...O6 <sup>ii</sup>  | 0.90        | 2.14          | 3.038 (12)            | 177                     |

Symmetry codes: (i)  $-x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (iii)  $-x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (iv)  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ .

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1223). Services for accessing these data are described at the back of the journal.

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