

**$\beta$ -[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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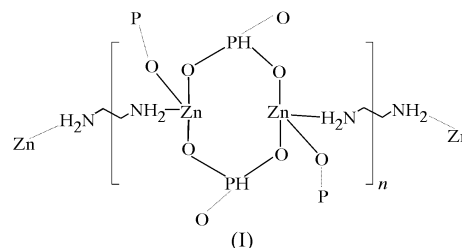
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The title compound, poly[dizinc(II)- $\mu$ -ethylenediamine-di- $\mu$ -(hydrogen phosphito)],  $\beta$ -[H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>0.5</sub>[ZnHPO<sub>3</sub>] or [Zn<sub>2</sub>(HPO<sub>3</sub>)<sub>2</sub>(C<sub>2</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].

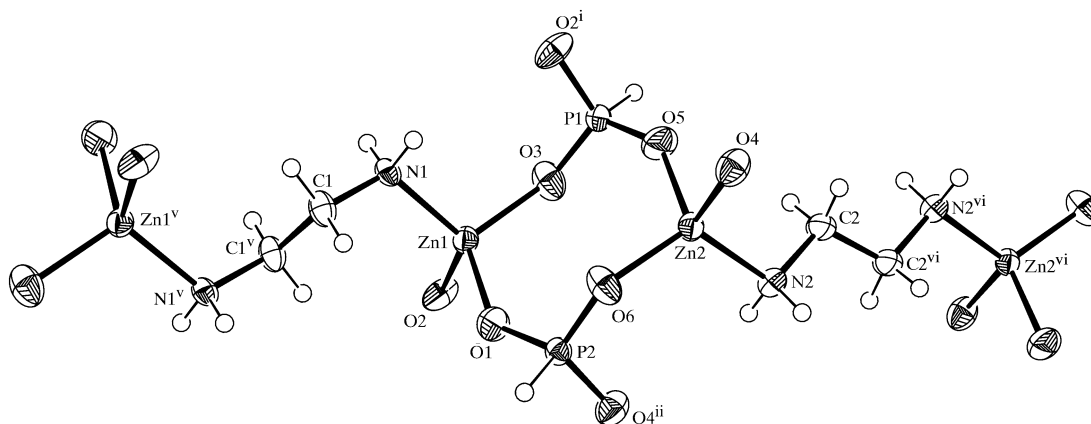
**Comment**

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>

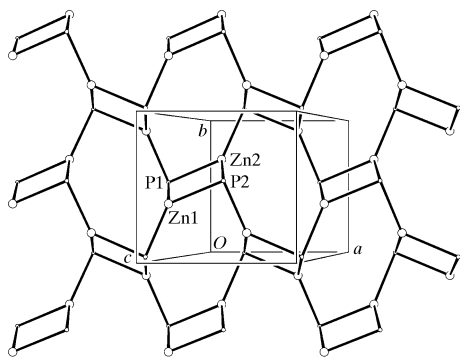
**Figure 1**

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.

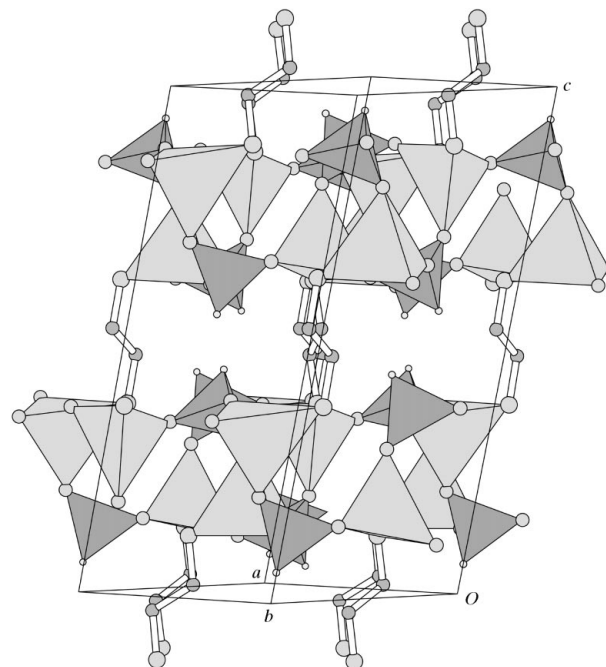
The polyhedral building units in (I) thus consist of  $\text{ZnO}_3\text{N}$  and  $\text{HPO}_3$  tetrahedra, linked by way of the O atoms. These units form sheets, built up from strictly alternating Zn- and P-centred moieties, which propagate in the (001) plane. Every tetrahedral node (*i.e.* the Zn 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*.

The authors thank Jillian Johnstone for experimental assistance.

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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## supporting information

*Acta Cryst.* (2004). C60, m637–m639 [doi:10.1107/S0108270104027039]

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### Computing details

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*.

### poly[dizinc(II)- $\mu$ -ethylenediamine-di- $\mu$ -(hydrogen phosphito)]

#### 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>)]

$M_r = 350.80$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.3609$  (4) Å

$b = 7.9369$  (4) Å

$c = 15.8259$  (7) Å

$\beta = 104.689$  (1)°

$V = 1015.88$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 696$

$D_x = 2.294$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5099 reflections

$\theta = 2.5$ – $27.4$ °

$\mu = 5.04$  mm<sup>-1</sup>

$T = 293$  K

Slab, colourless

$0.33 \times 0.30 \times 0.11$  mm

#### Data collection

Bruker SMART 1000 CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 1999)

$T_{\min} = 0.287$ ,  $T_{\max} = 0.607$

7093 measured reflections

2309 independent reflections

2075 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 2.5$ °

$h = -10 \rightarrow 8$

$k = -9 \rightarrow 10$

$l = -20 \rightarrow 20$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.064$

$wR(F^2) = 0.171$

$S = 1.28$

2309 reflections

128 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0155P)^2 + 26.0795P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 1.23 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.01 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97*,  
 $F_c^* = kF_c [1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0028 (5)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.11474 (14)	0.38756 (15)	0.83143 (7)	0.0235 (3)
Zn2	0.38904 (14)	0.68996 (14)	0.68286 (7)	0.0230 (3)
P1	0.0169 (3)	0.5316 (3)	0.63692 (16)	0.0213 (5)
H1	−0.0418	0.4539	0.5617	0.026*
P2	0.4857 (3)	0.5427 (3)	0.87062 (16)	0.0220 (5)
H2	0.5634	0.6090	0.9464	0.026*
O1	0.3405 (9)	0.4468 (13)	0.8874 (6)	0.045 (2)
O2	0.1208 (9)	0.1473 (9)	0.8516 (6)	0.0372 (19)
O3	0.0580 (11)	0.3934 (11)	0.7053 (5)	0.0409 (19)
O4	0.3895 (10)	0.9280 (10)	0.6555 (5)	0.0359 (18)
O5	0.1630 (9)	0.6304 (12)	0.6262 (6)	0.043 (2)
O6	0.4385 (11)	0.6892 (10)	0.8084 (5)	0.0370 (18)
N1	−0.0377 (10)	0.5380 (10)	0.8779 (5)	0.0222 (16)
H1A	−0.0448	0.6370	0.8494	0.027*
H1B	−0.1390	0.4912	0.8632	0.027*
C1	0.0031 (14)	0.5758 (13)	0.9738 (6)	0.029 (2)
H1C	0.1130	0.6244	0.9916	0.034*
H1D	−0.0746	0.6583	0.9850	0.034*
N2	0.5245 (10)	0.5470 (11)	0.6212 (5)	0.0238 (17)
H2A	0.6267	0.5907	0.6302	0.029*
H2B	0.5338	0.4421	0.6435	0.029*
C2	0.4463 (12)	0.5392 (15)	0.5258 (6)	0.031 (2)
H2C	0.4180	0.6526	0.5044	0.037*
H2D	0.3444	0.4753	0.5163	0.037*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0245 (6)	0.0229 (6)	0.0247 (6)	0.0007 (5)	0.0091 (4)	0.0014 (4)
Zn2	0.0252 (6)	0.0221 (6)	0.0235 (6)	0.0007 (4)	0.0094 (4)	0.0005 (4)
P1	0.0228 (11)	0.0203 (12)	0.0212 (11)	−0.0004 (10)	0.0063 (9)	−0.0021 (9)
P2	0.0232 (12)	0.0227 (12)	0.0202 (11)	−0.0003 (10)	0.0057 (9)	−0.0020 (9)

O1	0.027 (4)	0.064 (6)	0.044 (5)	-0.007 (4)	0.010 (3)	0.016 (4)
O2	0.028 (4)	0.021 (4)	0.068 (6)	0.001 (3)	0.021 (4)	0.008 (4)
O3	0.062 (5)	0.033 (4)	0.029 (4)	0.002 (4)	0.014 (4)	-0.005 (3)
O4	0.034 (4)	0.030 (4)	0.048 (5)	-0.002 (3)	0.017 (3)	-0.002 (4)
O5	0.025 (4)	0.049 (5)	0.055 (5)	-0.004 (4)	0.010 (4)	0.011 (4)
O6	0.062 (5)	0.025 (4)	0.024 (4)	0.007 (4)	0.012 (4)	-0.003 (3)
N1	0.029 (4)	0.018 (4)	0.021 (4)	0.000 (3)	0.007 (3)	0.005 (3)
C1	0.042 (6)	0.023 (5)	0.024 (5)	-0.003 (4)	0.013 (4)	-0.002 (4)
N2	0.023 (4)	0.023 (4)	0.027 (4)	-0.001 (3)	0.007 (3)	-0.005 (3)
C2	0.026 (5)	0.042 (6)	0.023 (5)	0.007 (5)	0.004 (4)	0.000 (4)

*Geometric parameters (Å, °)*

Zn1—O1	1.929 (8)	P2—H2	1.3200
Zn1—O3	1.932 (8)	O2—P1 <sup>iii</sup>	1.519 (7)
Zn1—O2	1.932 (8)	O4—P2 <sup>iv</sup>	1.519 (8)
Zn1—N1	2.016 (8)	N1—C1	1.499 (12)
Zn2—O6	1.923 (7)	N1—H1A	0.9000
Zn2—O5	1.934 (8)	N1—H1B	0.9000
Zn2—O4	1.938 (8)	C1—C1 <sup>v</sup>	1.469 (19)
Zn2—N2	2.021 (8)	C1—H1C	0.9700
P1—O5	1.497 (8)	C1—H1D	0.9700
P1—O3	1.518 (9)	N2—C2	1.486 (12)
P1—O2 <sup>i</sup>	1.519 (7)	N2—H2A	0.9000
P1—H1	1.3200	N2—H2B	0.9000
P2—O6	1.511 (8)	C2—C2 <sup>vi</sup>	1.494 (19)
P2—O1	1.513 (8)	C2—H2C	0.9700
P2—O4 <sup>ii</sup>	1.519 (8)	C2—H2D	0.9700
O1—Zn1—O3	115.1 (4)	P2 <sup>iv</sup> —O4—Zn2	133.3 (5)
O1—Zn1—O2	100.5 (4)	P1—O5—Zn2	143.6 (6)
O3—Zn1—O2	100.6 (4)	P2—O6—Zn2	128.9 (5)
O1—Zn1—N1	108.9 (4)	C1—N1—Zn1	119.0 (6)
O3—Zn1—N1	110.5 (3)	C1—N1—H1A	107.6
O2—Zn1—N1	121.1 (3)	Zn1—N1—H1A	107.6
O6—Zn2—O5	114.0 (4)	C1—N1—H1B	107.6
O6—Zn2—O4	102.8 (3)	Zn1—N1—H1B	107.6
O5—Zn2—O4	101.1 (4)	H1A—N1—H1B	107.0
O6—Zn2—N2	119.8 (3)	C1 <sup>v</sup> —C1—N1	112.1 (10)
O5—Zn2—N2	103.9 (4)	C1 <sup>v</sup> —C1—H1C	109.2
O4—Zn2—N2	114.0 (3)	N1—C1—H1C	109.2
O5—P1—O3	114.6 (5)	C1 <sup>v</sup> —C1—H1D	109.2
O5—P1—O2 <sup>i</sup>	111.2 (5)	N1—C1—H1D	109.2
O3—P1—O2 <sup>i</sup>	113.1 (5)	H1C—C1—H1D	107.9
O5—P1—H1	105.7	C2—N2—Zn2	111.0 (6)
O3—P1—H1	105.7	C2—N2—H2A	109.4
O2 <sup>i</sup> —P1—H1	105.7	Zn2—N2—H2A	109.4
O6—P2—O1	114.4 (5)	C2—N2—H2B	109.4

O6—P2—O4 <sup>ii</sup>	111.6 (5)	Zn2—N2—H2B	109.4
O1—P2—O4 <sup>ii</sup>	112.5 (5)	H2A—N2—H2B	108.0
O6—P2—H2	105.8	N2—C2—C2 <sup>vi</sup>	113.7 (10)
O1—P2—H2	105.8	N2—C2—H2C	108.8
O4 <sup>ii</sup> —P2—H2	105.8	C2 <sup>vi</sup> —C2—H2C	108.8
P2—O1—Zn1	141.0 (5)	N2—C2—H2D	108.8
P1 <sup>iii</sup> —O2—Zn1	128.8 (5)	C2 <sup>vi</sup> —C2—H2D	108.8
P1—O3—Zn1	134.9 (5)	H2C—C2—H2D	107.7
O6—P2—O1—Zn1	29.8 (12)	O2 <sup>i</sup> —P1—O5—Zn2	109.7 (10)
O4 <sup>ii</sup> —P2—O1—Zn1	-98.9 (10)	O6—Zn2—O5—P1	-28.0 (11)
O3—Zn1—O1—P2	22.6 (12)	O4—Zn2—O5—P1	-137.5 (10)
O2—Zn1—O1—P2	129.7 (10)	N2—Zn2—O5—P1	104.1 (10)
N1—Zn1—O1—P2	-102.1 (10)	O1—P2—O6—Zn2	-86.1 (8)
O1—Zn1—O2—P1 <sup>iii</sup>	149.6 (7)	O4 <sup>ii</sup> —P2—O6—Zn2	43.2 (8)
O3—Zn1—O2—P1 <sup>iii</sup>	-92.1 (7)	O5—Zn2—O6—P2	83.7 (8)
N1—Zn1—O2—P1 <sup>iii</sup>	29.9 (9)	O4—Zn2—O6—P2	-167.9 (7)
O5—P1—O3—Zn1	75.9 (9)	N2—Zn2—O6—P2	-40.3 (8)
O2 <sup>i</sup> —P1—O3—Zn1	-53.1 (9)	O1—Zn1—N1—C1	-41.9 (7)
O1—Zn1—O3—P1	-78.3 (9)	O3—Zn1—N1—C1	-169.3 (7)
O2—Zn1—O3—P1	174.6 (8)	O2—Zn1—N1—C1	73.7 (8)
N1—Zn1—O3—P1	45.5 (9)	Zn1—N1—C1—C1 <sup>v</sup>	-64.8 (13)
O6—Zn2—O4—P2 <sup>iv</sup>	102.1 (7)	O6—Zn2—N2—C2	168.8 (7)
O5—Zn2—O4—P2 <sup>iv</sup>	-139.9 (7)	O5—Zn2—N2—C2	40.1 (8)
N2—Zn2—O4—P2 <sup>iv</sup>	-29.1 (8)	O4—Zn2—N2—C2	-69.0 (8)
O3—P1—O5—Zn2	-20.1 (12)	Zn2—N2—C2—C2 <sup>vi</sup>	170.1 (11)

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

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

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

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