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

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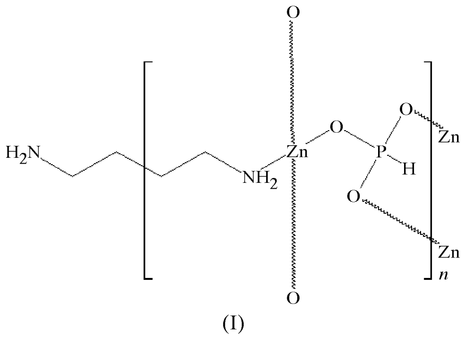
The title compound, poly[zinc(II)-μ-butane-1,4-diamine-μ-(hydrogen phosphito)] $(C_4H_{12}N_2)_{0.5}[ZnHPO_3]$, is a hybrid organic–inorganic solid built up from 1,4-diaminobutane molecules, Zn^{2+} cations (coordinated by three O atoms and one N atom) and HPO_3^{2-} hydrogen phosphite groups. The organic species bonds to the Zn atom as an unprotonated ligand, resulting in it acting as a bridge between infinite $ZnHPO_3$ layers, which propagate in (100). The complete butane-1,4-diamine species is generated from a $H_2N(CH_2)_2$– half molecule by inversion symmetry. The zincophosphite sheets contain polyhedral four- and eight-membered rings in a 4.8^2 topology.

Comment

The title compound, $[H_2N(CH_2)_4NH_2]_{0.5}[ZnHPO_3]$, (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).



(I)

Compound (I) (Fig. 1) is built up from neutral unprotonated butane-1,4-diamine $[H_2N(CH_2)_4NH_2]$ molecules, Zn^{2+} cations and HPO_3^{2-} hydrogen phosphite groups. Each complete butane-1,4-diamine entity is generated from a half-molecule $H_2N(CH_2)_2$– 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 HPO_3^{2-} groups [mean Zn—O—P = 131.3 (2)°]. The pseudo-pyramidal HPO_3^{2-} 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 ZnO_3N and 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 (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 4.8^2 sheet (O'Keeffe & Hyde, 1996).

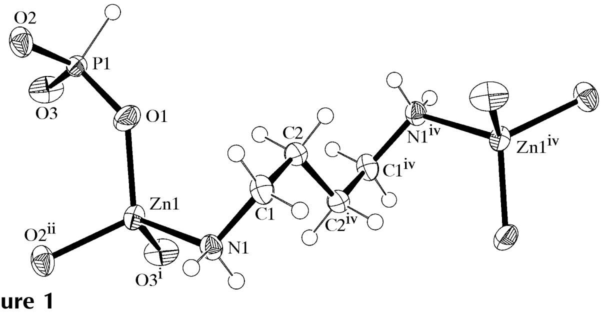


Figure 1
A view of a fragment of (I) (50% probability displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radii. Symmetry codes are as in Table 1.

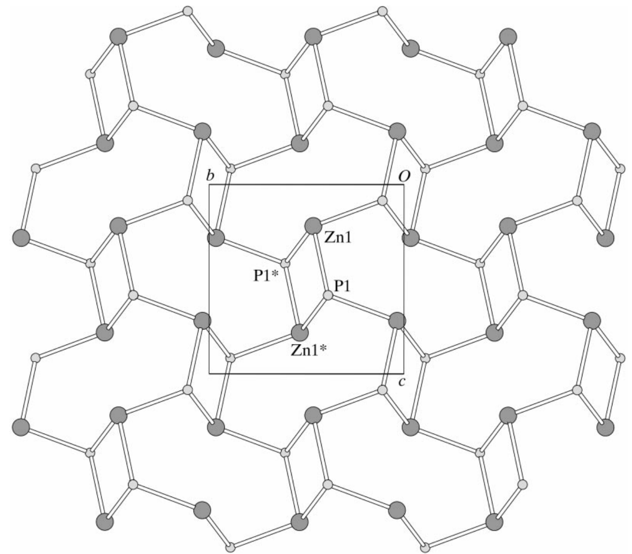


Figure 2
A view down [100] of a fragment of a $ZnHPO_3$ layer in (I), showing the topologial connectivity of the Zn (large spheres) and P (small spheres) tetrahedral nodes into 4.8^2 sheets. Atoms labelled with an asterisk (*) are at the symmetry position $(2 - x, 1 - y, 1 - z)$. The lines linking the Zn and P atoms represent Zn—O—P bridges, which are not linear (see Table 1).

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The organic species crosslink the (100) $ZnHPO_3$ 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 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 P—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 N—H···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 $[H_2N(CH_2)_2NH_2]_{0.5}[ZnHPO_3]$ (Rodgers & Harrison, 2000). Here, however, the zincophosphite 8-ring pores are highly flattened, whereas in $[H_2N(CH_2)_2NH_2]_{0.5}$-$[ZnHPO_3]$ they are far more regular.

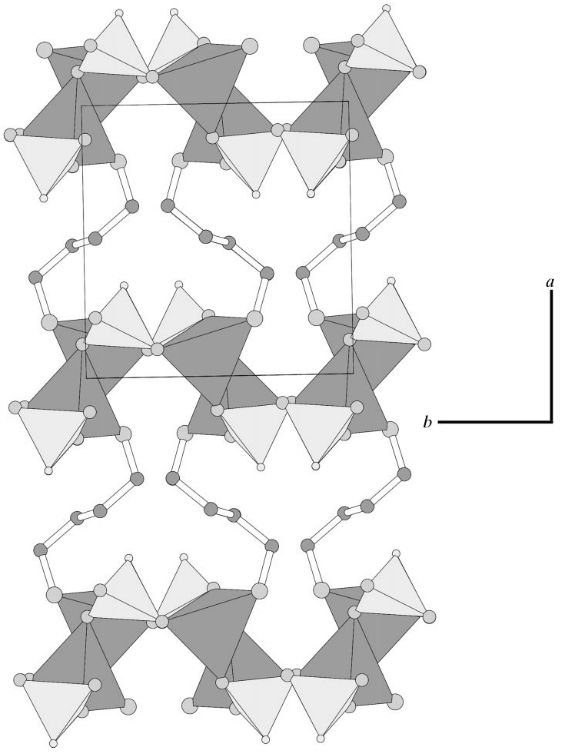

Figure 3
The unit-cell packing in (I), viewed down [001], in a polyhedral representation (ZnO_3N groups: dark shading; HPO_3 groups: light shading). All H atoms, except for atom H1, have been omitted for clarity.

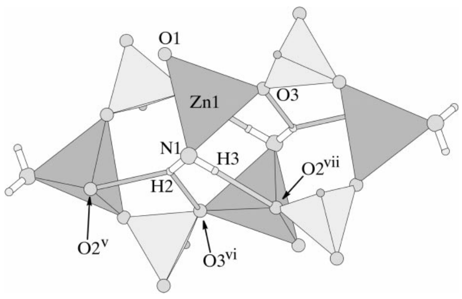

Figure 4
A polyhedral view of a fragment of a (100) $ZnHPO_3$ layer in (I), showing the N—H···O bonds associated with a flattened 8-ring window. Symmetry codes are as in Table 2.

Compound (I) complements several other 'pillared' networks built up from ZnO_3N_l (N_l = ligand amine N atom) tetrahedra and pyramidal or pseudo-pyramidal inorganic oxyanions. Both modifications of ethylenediamine zinc selenite, $[H_2N(CH_2)_2NH_2]_{0.5}[ZnSeO_3]$ (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 $H_2N(CH_2)_2NH_2$ 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 $(C_6N_2H_8)_{0.5}$-$[ZnHPO_3]$ (Kirkpatrick & Harrison, 2004) acts in a similar way to ethylenediamine in the $[H_2N(CH_2)_2NH_2]_{0.5}[ZnSeO_3]$ phases; in this case, 6^3 polyhedral sheets arise. Finally, $[H_2N(CH_2)_2NH_2]_{0.5}[ZnHPO_3]$ (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

$(C_4H_{12}N_2)_{0.5}[ZnHPO_3]$	D_x = 2.241 Mg m^{-3}
M_r = 189.43	Mo *Kα* radiation
Monoclinic, $P2_1/c$	Cell parameters from 3298 reflections
a = 8.4713 (4) Å	*θ* = 2.5–32.2°
b = 8.2489 (4) Å	*μ* = 4.57 mm^{-1}
c = 8.0805 (4) Å	*T* = 293 (2) K
β = 96.093 (1)°	Slab, colourless
V = 561.47 (5) Å^3	0.32 × 0.30 × 0.13 mm
Z = 4	

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
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.323$, $T_{\max} = 0.588$
5407 measured reflections

1964 independent reflections
1667 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 32.2°$
$h = -12 \rightarrow 12$
$k = -5 \rightarrow 12$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.049$
$S = 1.07$
1964 reflections
74 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0032 (7)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H2$\cdots$O2$^{\rm v}$	0.90	2.47	3.2107 (17)	140
N1—H2$\cdots$O3$^{\rm vi}$	0.90	2.57	3.1143 (16)	119
N1—H3$\cdots$O2$^{\rm vii}$	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 Å, N—H = 0.90 Å, C—H = 0.97 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom)].

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

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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supporting information

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Computing details

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*.

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

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M_r = 189.43
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.4713 (4) Å
b = 8.2489 (4) Å
c = 8.0805 (4) Å
β = 96.093 (1)°
V = 561.47 (5) Å^3
Z = 4
$F(000)$ = 380
D_x = 2.241 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3298 reflections
θ = 2.5–32.2°
μ = 4.57 mm^{-1}
T = 293 K
Slab, colourless
0.32 × 0.30 × 0.13 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min}$ = 0.323, $T_{\max}$ = 0.588
5407 measured reflections
1964 independent reflections
1667 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 32.2°, $\theta_{\min}$ = 2.4°
$h = -12 \rightarrow 12$
$k = -5 \rightarrow 12$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.049$
S = 1.07
1964 reflections
74 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
$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.32 e Å^{-3}
Extinction correction: *SHELXL97*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0032 (7)

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 (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Zn1	0.897600 (18)	0.46510 (2)	0.218542 (18)	0.02079 (6)
P1	0.80502 (4)	0.38978 (5)	0.58340 (4)	0.01849 (8)
H1	0.6629	0.3526	0.6249	0.022*
O1	0.77922 (14)	0.46180 (16)	0.41029 (13)	0.0341 (3)
O2	0.87536 (13)	0.51177 (15)	0.71268 (13)	0.0292 (2)
O3	0.89785 (15)	0.23256 (13)	0.58785 (15)	0.0340 (3)
N1	0.79215 (13)	0.63445 (15)	0.06227 (14)	0.0216 (2)
H2	0.8534	0.7239	0.0694	0.026*
H3	0.7898	0.5968	−0.0425	0.026*
C1	0.62758 (16)	0.68278 (19)	0.09135 (18)	0.0255 (3)
H4	0.5892	0.7625	0.0085	0.031*
H5	0.6306	0.7339	0.1998	0.031*
C2	0.51209 (16)	0.54297 (19)	0.08398 (16)	0.0243 (3)
H6	0.4102	0.5830	0.1110	0.029*
H7	0.5496	0.4645	0.1685	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02292 (9)	0.01930 (9)	0.01926 (9)	0.00246 (6)	−0.00184 (5)	−0.00111 (6)
P1	0.01839 (15)	0.02006 (17)	0.01691 (15)	−0.00126 (13)	0.00140 (11)	0.00077 (12)
O1	0.0351 (6)	0.0467 (8)	0.0206 (5)	0.0139 (5)	0.0030 (4)	0.0097 (5)
O2	0.0231 (5)	0.0312 (6)	0.0319 (6)	0.0012 (4)	−0.0032 (4)	−0.0115 (4)
O3	0.0484 (7)	0.0190 (5)	0.0363 (6)	0.0068 (5)	0.0134 (5)	0.0076 (5)
N1	0.0189 (5)	0.0203 (6)	0.0250 (5)	−0.0029 (4)	0.0001 (4)	0.0030 (5)
C1	0.0216 (6)	0.0242 (7)	0.0298 (7)	0.0025 (6)	−0.0010 (5)	−0.0025 (6)
C2	0.0195 (6)	0.0322 (8)	0.0212 (6)	−0.0025 (6)	0.0020 (4)	−0.0019 (6)

Geometric parameters (Å, º)

Zn1—O1	1.9331 (11)	N1—C1	1.4924 (18)
Zn1—O3$^{\rm i}$	1.9427 (11)	N1—H2	0.9000
Zn1—O2$^{\rm ii}$	1.9539 (11)	N1—H3	0.9000
Zn1—N1	2.0260 (12)	C1—C2	1.509 (2)
P1—O1	1.5140 (11)	C1—H4	0.9700

P1—O3	1.5152 (12)	C1—H5	0.9700
P1—O2	1.5254 (11)	C2—C2^{iv}	1.526 (3)
P1—H1	1.3200	C2—H6	0.9700
O2—Zn1^{ii}	1.9539 (11)	C2—H7	0.9700
O3—Zn1^{iii}	1.9427 (11)		

O1—Zn1—O3^{i}	117.03 (5)	Zn1—N1—H2	108.2
O1—Zn1—O2^{ii}	110.62 (5)	C1—N1—H3	108.2
O3^{i}—Zn1—O2^{ii}	100.29 (5)	Zn1—N1—H3	108.2
O1—Zn1—N1	106.10 (5)	H2—N1—H3	107.4
O3^{i}—Zn1—N1	105.41 (5)	N1—C1—C2	113.71 (12)
O2^{ii}—Zn1—N1	117.75 (5)	N1—C1—H4	108.8
O1—P1—O3	112.42 (7)	C2—C1—H4	108.8
O1—P1—O2	112.43 (7)	N1—C1—H5	108.8
O3—P1—O2	112.60 (7)	C2—C1—H5	108.8
O1—P1—H1	106.3	H4—C1—H5	107.7
O3—P1—H1	106.3	C1—C2—C2^{iv}	114.55 (15)
O2—P1—H1	106.3	C1—C2—H6	108.6
P1—O1—Zn1	135.21 (7)	C2^{iv}—C2—H6	108.6
P1—O2—Zn1^{ii}	124.08 (7)	C1—C2—H7	108.6
P1—O3—Zn1^{iii}	134.49 (7)	C2^{iv}—C2—H7	108.6
C1—N1—Zn1	116.33 (9)	H6—C2—H7	107.6
C1—N1—H2	108.2		

O3—P1—O1—Zn1	−32.09 (14)	O2—P1—O3—Zn1^{iii}	84.33 (12)
O2—P1—O1—Zn1	96.23 (12)	O1—Zn1—N1—C1	−18.17 (11)
O3^{i}—Zn1—O1—P1	75.42 (13)	O3^{i}—Zn1—N1—C1	106.60 (10)
O2^{ii}—Zn1—O1—P1	−38.56 (13)	O2^{ii}—Zn1—N1—C1	−142.64 (9)
N1—Zn1—O1—P1	−167.34 (11)	Zn1—N1—C1—C2	−57.62 (14)
O1—P1—O2—Zn1^{ii}	−93.89 (10)	N1—C1—C2—C2^{iv}	−61.9 (2)
O3—P1—O2—Zn1^{ii}	34.34 (11)	C1—C2—C2^{iv}—C1^{iv}	180.0
O1—P1—O3—Zn1^{iii}	−147.44 (10)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···O2^{v}	0.90	2.47	3.2107 (17)	140
N1—H2···O3^{vi}	0.90	2.57	3.1143 (16)	119
N1—H3···O2^{vii}	0.90	2.29	3.1501 (15)	160

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