

Poly[(μ_3 -hydrogenphosphato)(4*H*-1,2,4-triazole- κ N¹)zinc]

Hafid Aitenneite,^{a*} Abdeslam El Bouari,^a Said Sebti,^b Mohamed Saadi,^c Lahcen El Ammari^d and Karim Adil^e

^aLaboratoire de Chimie des Matériaux Solides, Faculté des Sciences Ben M'sik Casablanca, Morocco, ^bLaboratoire de Chimie Organique Catalyse et Environnement, Faculté des Sciences Ben M'sik Casablanca, Morocco, ^cLaboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Université Mohammed V-Agdal, Avenue Ibn Batouta, BP 1014, Rabat, Morocco, ^dLaboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Université Mohammed V-Agdal, Avenue Ibn Batouta, BP 1014, Rabat, Morocco, and ^eLUNAM Université, Université du Maine, CNRS UMR 6283, Institut des Molécules et Matériaux du Mans, Avenue Olivier Messiaen, 72085 Le Mans CEDEX 9, France

Correspondence e-mail: h_aitenneite@yahoo.com

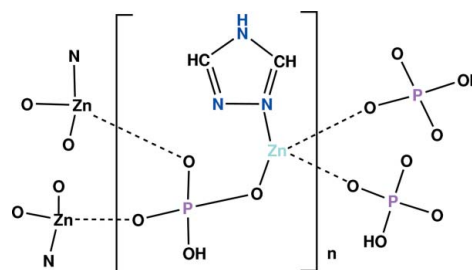
Received 22 October 2012; accepted 24 October 2012

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{N}-\text{C}) = 0.002$ Å; R factor = 0.021; wR factor = 0.051; data-to-parameter ratio = 33.2.

The asymmetric unit of the title compound, $[\text{Zn}(\text{HPO}_4)(\text{C}_2\text{H}_3\text{N}_3)]_n$, contains one Zn^{2+} cation, one $(\text{HPO}_4)^{2-}$ anion and a 1,2,4 triazole ligand. The Zn^{2+} cation is coordinated in a quite regular tetrahedral geometry by O atoms from three phosphate groups and a tertiary N atom from the triazole ring. Each phosphate anion is connected to three Zn^{II} cations, leading to a series of corrugated organic–inorganic layers parallel to the ac plane. The overall structure involves stacking of complex hybrid organic–inorganic layers along the b axis. Cohesion in the crystal is ensured by an infinite three-dimensional network of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the phosphate groups and the triazole ligands.

Related literature

For background to potential applications of similar compounds, see: Horcajada *et al.* (2012); Li *et al.* (2012); Wang *et al.* (2012); Yoon *et al.* (2012). For hybrid compounds with zinc phosphates, see: Umeyama *et al.* (2012); Horike *et al.* (2012). For phosphonate, carboxylate and azolate compounds, see: Stock & Biswas (2012). For bond-valence analysis, see: Brown & Altermatt (1985).



Experimental

Crystal data

$[\text{Zn}(\text{HPO}_4)(\text{C}_2\text{H}_3\text{N}_3)]$
 $M_r = 230.42$
 Orthorhombic, $Pca2_1$
 $a = 8.5467$ (13) Å
 $b = 8.4344$ (12) Å
 $c = 8.9674$ (13) Å

$V = 646.43$ (16) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 4.01$ mm⁻¹
 $T = 296$ K
 $0.24 \times 0.18 \times 0.12$ mm

Data collection

Bruker X8 APEXII diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1999)
 $T_{\text{min}} = 0.511$, $T_{\text{max}} = 0.638$

8746 measured reflections
 3318 independent reflections
 3207 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.051$
 $S = 1.04$
 3318 reflections
 100 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.40$ e Å⁻³
 Absolute structure: Flack (1983),
 1184 Friedel pairs
 Flack parameter: 0.020 (6)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3}\cdots\text{O2}^{\text{i}}$	0.86	1.99	2.8427 (15)	175
$\text{O4}-\text{H4}\cdots\text{O1}^{\text{ii}}$	0.82	1.80	2.5978 (12)	164

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5276).

References

- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.

- Bruker (2005). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Horcajada, P., Gref, R., Baati, T., Allan, P. K., Maurin, G., Couvreur, P., Férey, G., Morris, R. E. & Serre, C. (2012). *Chem. Rev.* **112**, 1232–1268.
- Horike, S., Umeyama, D., Inukai, M., Itakura, T. & Kitagawa, S. (2012). *J. Am. Chem. Soc.* **134**, 7612–7615.
- Li, J.-R., Sculley, J. & Zhou, H.-C. (2012). *Chem. Rev.* **112**, 869–932.
- Sheldrick, G. M. (1999). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stock, N. & Biswas, S. (2012). *Chem. Rev.* **112**, 933–969.
- Umeyama, D., Horike, S., Inukai, M., Itakura, T. & Kitagawa, S. (2012). *J. Am. Chem. Soc.* **134**, 12780–12785.
- Wang, C., Zhang, T. & Lin, W. (2012). *Chem. Rev.* **112**, 1084–1104.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yoon, M., Srirambalaji, R. & Kim, K. (2012). *Chem. Rev.* **112**, 1196–1231.

supporting information

Acta Cryst. (2012). E68, m1426–m1427 [doi:10.1107/S1600536812044182]

Poly[(μ_3 -hydrogenphosphato)(4*H*-1,2,4-triazole- κ N¹)zinc]

Hafid Aitenneite, Abdeslam El Bouari, Said Sebti, Mohamed Saadi, Lahcen El Ammari and Karim Adil

S1. Comment

Research into organic-inorganic hybrid materials has been an active area in recent years because of their potential applications in catalysis (Yoon *et al.*, 2012), drug-delivery (Horcajada *et al.*, 2012), enantio-selective separation (Li *et al.*, 2012) and non-linear optical materials (Wang *et al.*, 2012). A variety of new solids have been discovered with fascinating structural architectures ranging from clusters, chains and layers to porous frameworks using phosphonates, carboxylates and/or azolates (Stock & Biswas, 2012). In this paper, we report the hydrothermal synthesis and crystal structure of a new inorganic–organic hybrid compound based on a zinc cation coordinated by three hydrogenphosphate anions and a 1,2,4-triazole ligand.

The three-dimensional structure of [(TAZ)Zn(HPO₄)]_n (HTAZ = 1,2,4 triazole) consists of infinite complex zinc-hydrogenphosphate layers. Each zinc cation is tetrahedrally coordinated by three O atoms belonging to three crystallographic equivalent phosphate groups and one azote from triazole ring (Fig.1). Zn–O distances range from 1.9172 (9) to 1.9635 (9) Å, and the Zn1–N1 distance is 1.988 (1) Å (see Table 1). The PO₄ tetrahedron is reasonably regular with the P–O distances and O–P–O angles varying between 1.5031 (9) and 1.5730 (9) Å and 104.95 (6)° and 113.91 (6)° respectively. These values are in a good agreement with those typically observed in other phosphate based compounds (Umeyama *et al.*, 2012; Horike, *et al.*, 2012).

A three dimensional view of the crystal structure of the title compound is displayed on Fig.2. The structure can be described as the stacking of corrugated inorganic-organic layers parallel to (010) resulting from the connexion of vertex of PO₄ groups with ZnO₃N tetrahedra (Fig.2).

Bond valence sum calculations (Brown & Altermatt, 1985) for Zn²⁺ and P⁵⁺ ions are as expected, *viz.* 2.05 and 5.02 valence units, respectively. The values of the bond valence sums calculated for the oxygen atoms show low values for O4 when the contribution of H atom is not considered (*i.e.* 1.13 valence units). Hence this O atom is associated with a proton and is involved in O4–H4···O1 hydrogen bonding. The crystal structure cohesion is ensured by an infinite three-dimensional network of N3–H3···O2 and O4–H4···O1 hydrogen bonds between the phosphate groups and the triazole ligands (Table 1 and Fig.2).

S2. Experimental

All chemicals purchased were of reagent grade and were used without further purification. The title compound was synthesized in a hydrothermal system. A mixture of H₃PO₄ 85% (0.25 ml), zinc (II) nitrate hexahydrate Zn(NO₃)₂·6H₂O (0.189 g), 1,2,4-triazole (0.138 g) and water (5 ml) was placed in a Parr acid digestion bomb and heated at 393 K for 48 h. The reaction vessel was allowed to cool to room temperature. Colourless crystals of (C₂H₃N₃)ZnHPO₄ were filtered off, washed with distilled water, dried in a desiccator at room temperature and manually selected for the structural determination and other characterization. The results of elemental analysis of crystals are: Zn, 28.62; P, 13.50; O, 28.02;

N, 18.40; C, 10.52 and H, 0.88%.

S3. Refinement

The highest peak and the deepest hole in the final Fourier map are at 0.92 Å and 0.72 Å, from N1 and Zn1 respectively. H atoms were located in a difference map and treated as riding with C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (aromatic) and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ (hydroxide). The space group is not centrosymmetric and the polar axis restraint is generated automatically by the *SHELXL* program. The 1184 Friedel opposite reflections were not merged.

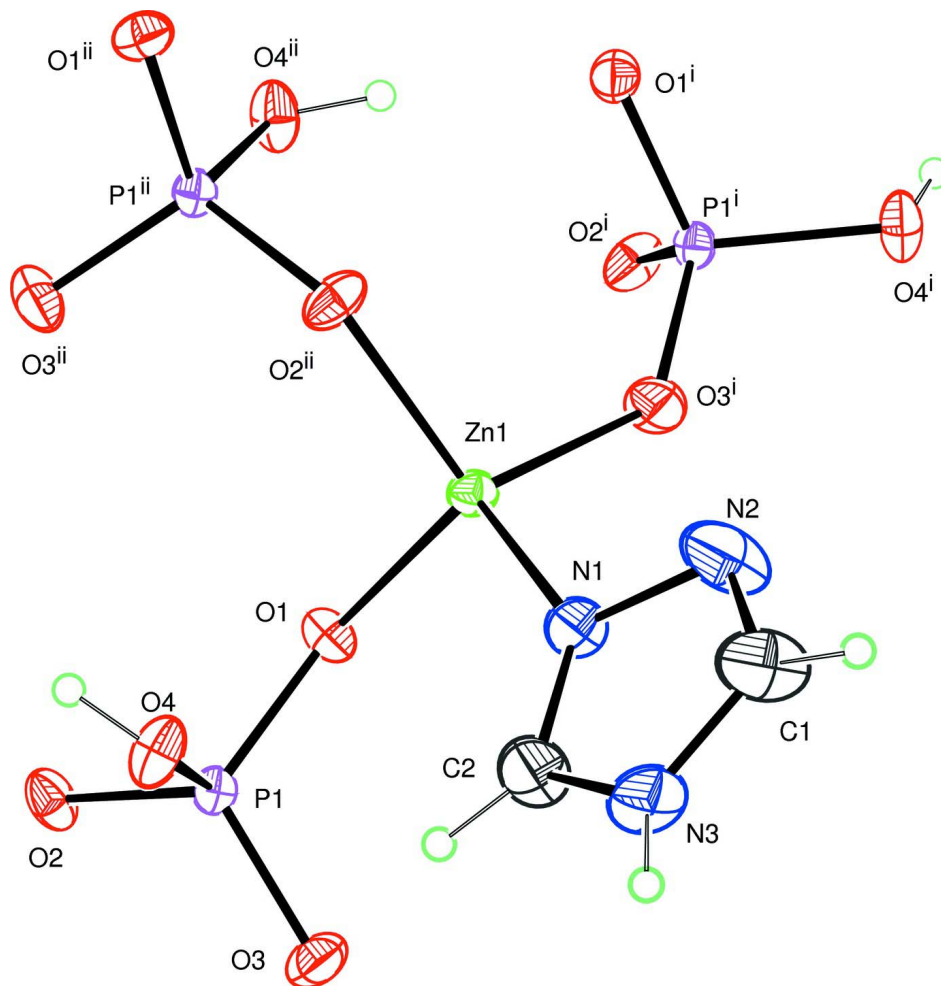
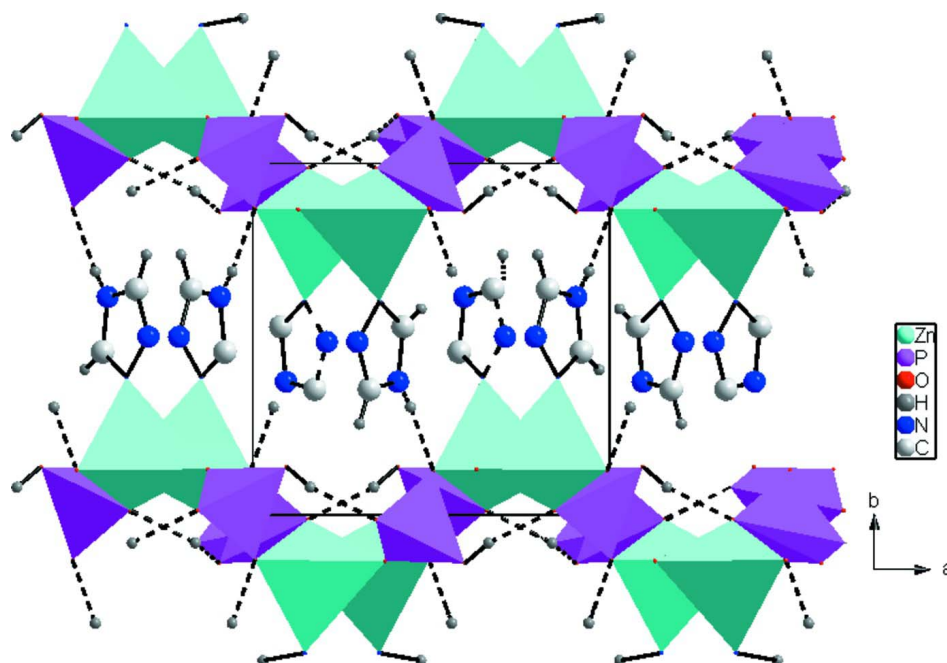


Figure 1

A view of the structure of the title compound showing the coordination environment of the Zn and P atoms. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-x + 3/2, y, z + 1/2$; (ii) $-x + 2, -y, z + 1/2$; (iii) $-x + 2, -y, z - 1/2$; (iv) $-x + 3/2, y, z - 1/2$.

**Figure 2**

A three dimensional view of the $(\text{C}_2\text{H}_3\text{N}_3)\text{ZnHPO}_4$ framework structure showing a stacking of the inorganic and organic layers. The PO_4 tetrahedron is shown in pink and the ZnO_3N tetrahedron is blue green. Hydrogen bonds are drawn as dashed lines.

Poly[(μ_3 -hydrogenphosphato)(4*H*-1,2,4-triazole- κN^1)zinc]

Crystal data

$[\text{Zn}(\text{HPO}_4)(\text{C}_2\text{H}_3\text{N}_3)]$

$M_r = 230.42$

Orthorhombic, $Pca2_1$

Hall symbol: $P\ 2c\ -2ac$

$a = 8.5467\ (13)\ \text{\AA}$

$b = 8.4344\ (12)\ \text{\AA}$

$c = 8.9674\ (13)\ \text{\AA}$

$V = 646.43\ (16)\ \text{\AA}^3$

$Z = 4$

$F(000) = 456$

$D_x = 2.368\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3318 reflections

$\theta = 4.1\text{--}40.2^\circ$

$\mu = 4.01\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colourless

$0.24 \times 0.18 \times 0.12\ \text{mm}$

Data collection

Bruker X8 APEXII

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1999)

$T_{\min} = 0.511$, $T_{\max} = 0.638$

8746 measured reflections

3318 independent reflections

3207 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 40.2^\circ$, $\theta_{\min} = 4.1^\circ$

$h = -14 \rightarrow 15$

$k = -13 \rightarrow 15$

$l = -16 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.051$
 $S = 1.04$
 3318 reflections
 100 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0181P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.40 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 1184 Friedel
 pairs
 Absolute structure parameter: 0.020 (6)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.832301 (12)	0.167666 (13)	0.51177 (2)	0.01245 (3)
P1	0.94990 (3)	0.03491 (3)	0.21240 (3)	0.01101 (4)
O1	0.84382 (9)	0.01275 (12)	0.34886 (10)	0.01568 (14)
O2	1.00560 (10)	-0.12805 (10)	0.16133 (10)	0.01765 (14)
O3	0.87260 (11)	0.13060 (13)	0.09170 (11)	0.02070 (16)
O4	1.09420 (9)	0.13727 (12)	0.26275 (11)	0.01867 (15)
H4	1.1612	0.0792	0.2988	0.028*
N1	0.85494 (13)	0.39236 (14)	0.44809 (12)	0.01976 (17)
N2	0.7928 (2)	0.50750 (18)	0.54065 (17)	0.0380 (3)
N3	0.90713 (16)	0.62060 (15)	0.35052 (15)	0.0269 (2)
H3	0.9420	0.6926	0.2913	0.032*
C1	0.8267 (2)	0.6419 (2)	0.4777 (2)	0.0356 (4)
H1	0.7988	0.7405	0.5158	0.043*
C2	0.9214 (2)	0.46424 (18)	0.33568 (19)	0.0295 (3)
H2	0.9715	0.4136	0.2568	0.035*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01506 (5)	0.00996 (5)	0.01234 (5)	-0.00078 (3)	-0.00004 (4)	0.00108 (4)
P1	0.01043 (8)	0.00993 (9)	0.01266 (9)	-0.00027 (7)	-0.00016 (8)	-0.00024 (8)
O1	0.0150 (3)	0.0176 (4)	0.0145 (3)	-0.0025 (2)	0.0026 (2)	-0.0032 (3)
O2	0.0218 (3)	0.0103 (3)	0.0209 (3)	-0.0001 (3)	0.0082 (3)	-0.0016 (3)

O3	0.0171 (3)	0.0248 (4)	0.0202 (4)	0.0019 (3)	-0.0041 (3)	0.0069 (3)
O4	0.0130 (3)	0.0132 (3)	0.0298 (4)	-0.0019 (2)	-0.0056 (3)	0.0002 (3)
N1	0.0269 (4)	0.0113 (4)	0.0212 (4)	0.0000 (3)	0.0032 (3)	0.0026 (3)
N2	0.0693 (10)	0.0169 (5)	0.0279 (7)	0.0023 (6)	0.0179 (6)	0.0004 (4)
N3	0.0365 (6)	0.0144 (4)	0.0299 (5)	-0.0042 (4)	0.0016 (5)	0.0081 (4)
C1	0.0667 (13)	0.0122 (5)	0.0279 (7)	-0.0014 (6)	0.0031 (6)	-0.0021 (5)
C2	0.0412 (7)	0.0161 (5)	0.0312 (7)	0.0034 (5)	0.0128 (5)	0.0091 (5)

Geometric parameters (Å, °)

Zn1—O3 ⁱ	1.9179 (9)	O4—H4	0.8200
Zn1—O2 ⁱⁱ	1.9570 (8)	N1—C2	1.3064 (18)
Zn1—O1	1.9624 (9)	N1—N2	1.3836 (19)
Zn1—N1	1.9888 (11)	N2—C1	1.299 (2)
P1—O3	1.5031 (10)	N3—C2	1.331 (2)
P1—O2	1.5250 (9)	N3—C1	1.343 (2)
P1—O1	1.5345 (9)	N3—H3	0.8600
P1—O4	1.5717 (9)	C1—H1	0.9300
O2—Zn1 ⁱⁱⁱ	1.9570 (8)	C2—H2	0.9300
O3—Zn1 ^{iv}	1.9179 (9)		
O3 ⁱ —Zn1—O2 ⁱⁱ	111.25 (4)	P1—O4—H4	109.5
O3 ⁱ —Zn1—O1	102.44 (4)	C2—N1—N2	107.71 (12)
O2 ⁱⁱ —Zn1—O1	111.16 (4)	C2—N1—Zn1	134.92 (11)
O3 ⁱ —Zn1—N1	110.58 (5)	N2—N1—Zn1	117.34 (9)
O2 ⁱⁱ —Zn1—N1	106.89 (4)	C1—N2—N1	105.42 (14)
O1—Zn1—N1	114.58 (5)	C2—N3—C1	105.33 (13)
O3—P1—O2	113.89 (6)	C2—N3—H3	127.3
O3—P1—O1	112.33 (5)	C1—N3—H3	127.3
O2—P1—O1	108.30 (5)	N2—C1—N3	111.50 (16)
O3—P1—O4	104.89 (6)	N2—C1—H1	124.3
O2—P1—O4	109.66 (5)	N3—C1—H1	124.3
O1—P1—O4	107.55 (5)	N1—C2—N3	110.04 (14)
P1—O1—Zn1	122.83 (5)	N1—C2—H2	125.0
P1—O2—Zn1 ⁱⁱⁱ	125.50 (5)	N3—C2—H2	125.0
P1—O3—Zn1 ^{iv}	139.29 (6)		

Symmetry codes: (i) $-x+3/2, y, z+1/2$; (ii) $-x+2, -y, z+1/2$; (iii) $-x+2, -y, z-1/2$; (iv) $-x+3/2, y, z-1/2$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N3—H3 \cdots O2 ^v	0.86	1.99	2.8427 (15)	175
O4—H4 \cdots O1 ^{vi}	0.82	1.80	2.5978 (12)	164

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