Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

The crystal structure of $(C_2H_9N_2)_2[Zn_3(HPO_3)_4]$, a three-dimensional zincophosphite framework containing 16-membered rings templated by the unsymmetrical dimethyl hydrazinium cation

Judita Katinaite and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland. *Correspondence e-mail: w.harrison@abdn.ac.uk

Received 14 April 2017
Accepted 16 April 2017

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; zinc phosphite; unsymmetrical dimethyl hydrazine; open framework.

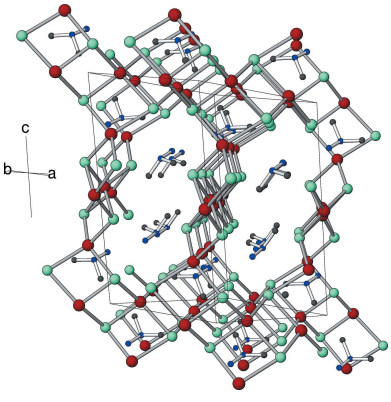
CCDC reference: 1544227

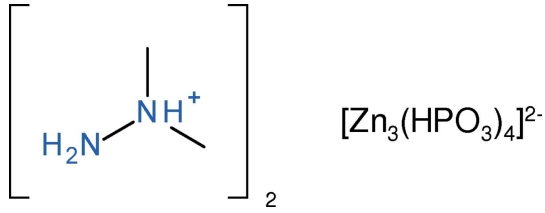
Supporting information: this article has supporting information at journals.iucr.org/e

The solution-mediated synthesis and crystal structure of 1,1-dimethylhydrazinium tetraphoshonoatotrizincate, $(C_2H_9N_2)_2[Zn_3(HPO_3)_4]$, are described. The anionic $[Zn_3(HPO_3)_4]^{2-}$ framework is built up from alternating ZnO_4 tetrahedra and HPO_3 pseudo-pyramids to generate a three-dimensional 4,3-net encapsulating the $C_2H_9N_2^+$ cations. The organic cations, which are protonated at their central N atoms, occupy pores delineated by large 16-membered polyhedral rings and interact with the framework by way of N—H···O hydrogen bonds and possible C—H···O interactions. One of the zinc ions lies on a crystallographic twofold rotation axis and all the other atoms lie on general positions. The crystal studied was found to be rotationally twinned about the [001] axis in reciprocal space in a 0.585 (5):0.415 (5) ratio.

1. Chemical context

Organically templated zinc phosphites are now a well-established family of open frameworks (e.g.: Phillips *et al.*, 2002; Luo *et al.*, 2010; Wang *et al.*, 2011; Dong *et al.*, 2015; Huang *et al.*, 2017). As part of our occasional studies in this area (Harrison & McNamee, 2010), we now describe the synthesis and structure of the title compound, (I), which represents the first example of a protonated unsymmetrical dimethyl hydrazine ($C_2H_8N_2$ or UDMH is the neutral molecule and $C_2H_9N_2^+$ is the cation) acting as a templating agent for an inorganic open framework. So far as we are aware, the only crystal structures containing $C_2H_9N_2^+$ that have been reported previously are molecular salts with different simple counterions (Katinaitė & Harrison, 2016, and references therein).





2. Structural commentary

The asymmetric unit of (I) comprises two zinc cations (Zn1 with site symmetry 2 and Zn2 on a general position), two HPO_3^{2-} hydrogen phosphite groups and one $C_2H_9N_2^+$ cation

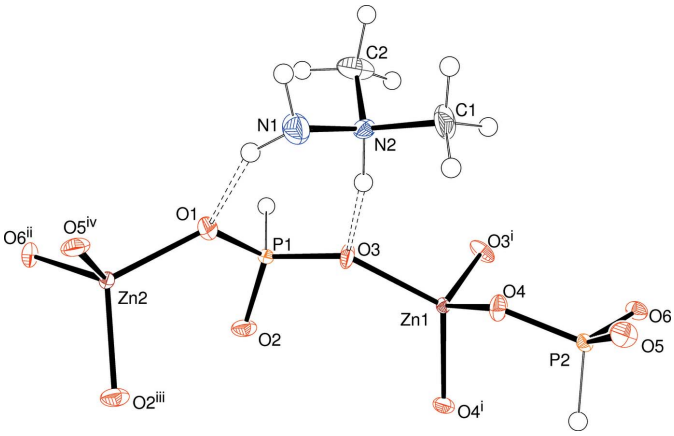


Figure 1
The asymmetric unit of (I) expanded to show the zinc coordination polyhedra (50% displacement ellipsoids). For symmetry codes, see Table 1.

(Fig. 1). Both zinc ions adopt their usual tetrahedral coordination geometries (Table 1) to four nearby O atoms with mean Zn—O separations of 1.942 and 1.945 Å for Zn1 and Zn2, respectively. The range of O—Zn—O bond angles for Zn1 of 100.0 (2)–121.0 (2)° indicates considerable distortion from the ideal tetrahedral value of 109.5°; the spread of values for Zn2 of 99.8 (2)–115.1 (2)° is somewhat smaller. Bond-valence-sum values (in valence units; Brown & Altermatt, 1985) for Zn1 and Zn2 of 2.11 and 2.09, respectively, are in adequate agreement with the expected values of 2.00.

Both phosphorus atoms in (I) display their expected HPO_3 pseudo-tetrahedral geometries with mean P—O distances (1.517 Å for P1 and 1.516 Å for P2) and O—P—O angles (112.7° for P1 and 112.6° for P2) that are consistent with previous results (Dong *et al.*, 2015). P1 deviates from its pyramid of attached O atoms by 0.418 (4) and the equivalent deviation for P2 is 0.420 (3) Å.

The structure of (I) is completed by the charge-balancing $C_2H_9N_2^+$ cation, which is protonated at the central (methylated) N2 atom, as is most commonly seen for this species

Table 1
Selected geometric parameters (Å, °).

Zn1—O4	1.938 (5)	P1—O2	1.504 (5)
Zn1—O4^{i}	1.938 (5)	P1—O1	1.515 (6)
Zn2—O5^{ii}	1.936 (6)	P1—O3	1.533 (5)
Zn2—O2^{iii}	1.943 (5)	P2—O5	1.500 (6)
Zn2—O6^{iv}	1.946 (5)	P2—O6	1.520 (5)
Zn2—O1	1.954 (6)	P2—O4	1.529 (5)
P1—O1—Zn2	128.0 (3)	P2—O4—Zn1	123.6 (3)
P1—O2—Zn2^{iii}	140.3 (3)	P2—O5—Zn2^{v}	138.4 (4)
P1—O3—Zn1	137.2 (3)	P2—O6—Zn2^{vi}	120.8 (3)

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

(Katinaitė & Harrison, 2016). The C—N and N—N bond lengths are indistinguishable and N2 deviates from the plane of N1, C1 and C2 by 0.434 (8) Å.

In the extended framework structure of (I), the zinc- and phosphorus-centred building units strictly alternate: every O atom forms a Zn—O—P bridge (mean angle = 131.4°), thus there are no 'dangling' Zn—OH_2, P═O or P—OH bonds as found in some zincophosphite frameworks (Shi *et al.*, 2004; Liu *et al.*, 2008), which is fully consistent with the 3:4 Zn:P stoichiometry of the anionic $[Zn_3(HPO_3)_4]^{2-}$ component of the structure (Harrison & McNamee, 2010). In addition, there are no Zn—N bonds (direct metal-to-template links) in (I); compare Kirkpatrick & Harrison (2004), Lin *et al.* (2004) and Harrison (2006).

The polyhedral connectivity in (I) can be broken down as follows: the Zn2, P1 and P2 polyhedra form four-ring (*i.e.*: a loop of two Zn atoms and two P atoms) chains, with the zinc

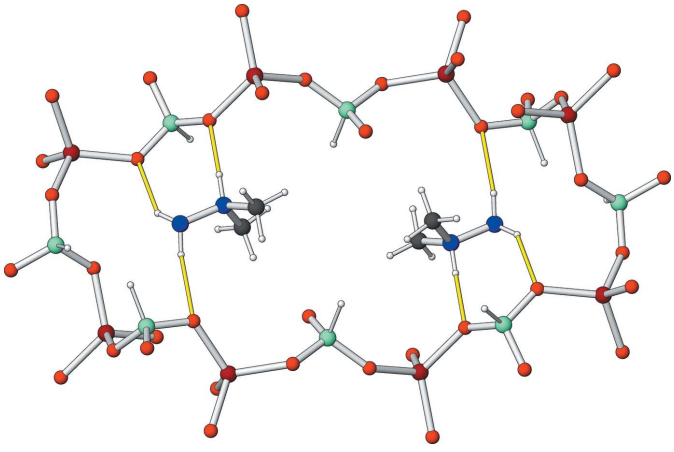


Figure 2
Fragment of (I) showing a 16-ring channel occupied side-by-side by two $C_2H_9N_2^+$ template cations.

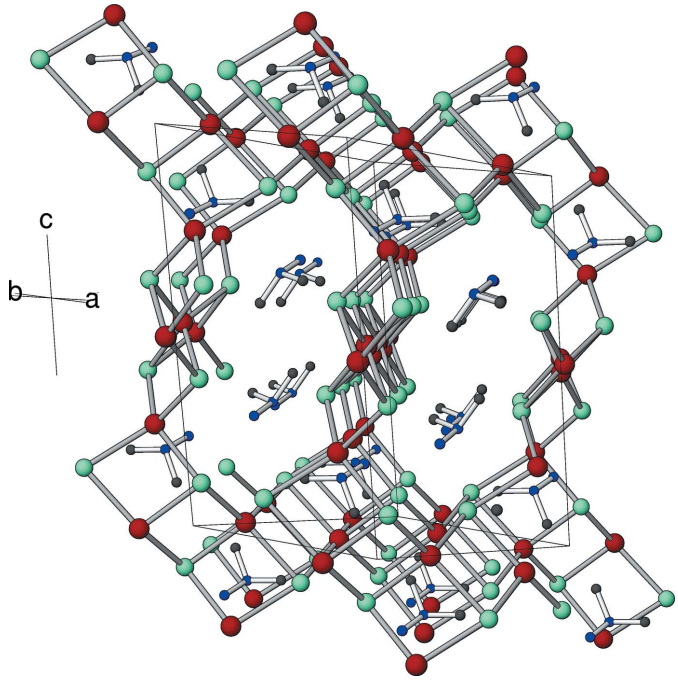


Figure 3
The unit-cell packing in (I) viewed approximately along [110] with the framework represented topologically (*i.e.* as Zn—P links).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O1	0.91	2.34	3.130 (9)	146
N1—H2N···O6^{vii}	0.91	2.35	3.133 (9)	144
N2—H3N···O3	1.00	1.79	2.762 (8)	163
C1—H1A···O1^{v}	0.98	2.50	3.474 (11)	173
C1—H1C···O5^{viii}	0.98	2.50	3.295 (11)	138
C2—H2C···O2^{ix}	0.98	2.43	3.355 (9)	157

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

atoms as the linking nodes, which propagate alternately in the [$\bar{1}$10] and [110] directions with respect to the *c*-axis direction. Atom Zn1 serves to link these criss-cross chains into a three-dimensional open framework. If the template is omitted, a *PLATON* (Spek, 2009) analysis indicates that 878 Å^3 (43.3%) of the unit cell is 'empty space' and the 'framework density' (FD) (number of Zn and P atoms per 1000 Å^3; Brunner & Meier, 1989) of (I) is 13.8. This low FD is comparable to that of the unusual open-framework MAPSO-46, which contains Mg, Al, P and Si as its tetrahedral framework atoms (Bennett & Marcus, 1988). When the template is included in the calculation, *PLATON* indicates no free space, suggesting that the template is a 'snug fit' within the inorganic framework of (I).

In the extended structure, large 16-ring pores (Figs. 2 and 3) are apparent in the framework, which alternately propagate in [$\bar{1}$10] and [110] with respect to the *c*-axis direction. Measured atom-to-atom, the 16-ring has a dimension of ~5.7 × 14.6 Å. Pairs of template cations lie roughly in the plane of the 16-rings and interact with framework oxygen atoms by way of N—H···O hydrogen bonds (Table 2). It is notable that the H···O separation for the charge-assisted N2$^+$—H3N···O3 bond is much shorter than the H···O separations for the terminal N1H$_2$ grouping. Within the asymmetric unit, an $R_2^2(7)$ loop is apparent (Fig. 1). Possible weak C—H···O interactions (Table 2) consolidate the structure.

3. Database survey

A survey of of the Cambridge Structural Database (Groom *et al.*, 2016: updated to April 2017) for organically templated zinc phosphite frameworks (those containing a Zn—O—P—H fragment) revealed 172 matches.

4. Synthesis and crystallization

Caution! UDMH is toxic, potentially carcinogenic and may form explosive mixtures with oxidizing agents: all appropriate safety precautions should be taken when handling it. Zinc oxide (1.63 g), phosphorus acid (1.64 g) and 20 ml of a 1.0 *M* aqueous UDMH solution were mixed in a 1:1:1 molar ratio in a sealed PTFE bottle and heated to 353 K for 24 h and then cooled to room temperature over a few hours. Product recovery by vacuum filtration yielded some colourless blocks of (I) accompanied by an unidentified white powder.

Table 3
Experimental details.

Crystal data	
Chemical formula	$(C_2H_9N_2)_2[Zn_3(HPO_3)_4]$
M_r	638.24
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	100
a, *b*, *c* (Å)	15.1154 (5), 8.7269 (3), 16.1675 (6)
β (°)	108.156 (1)
V (Å^3)	2026.48 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.90
Crystal size (mm)	0.19 × 0.11 × 0.05
Data collection	
Diffractometer	Rigaku Mercury CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2004)
T_{min}, T_{max}	0.527, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2273, 2273, 2169
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.068, 0.239, 1.22
No. of reflections	2273
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.51, −1.24

Computer programs: *CrysAlis PRO* (Rigaku, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *ATOMS* (Shape Software, 2005) and *publCIF* (Westrip, 2010).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The N-bound H atoms were located in difference maps, relocated to idealized locations (N—H = 0.91–1.00 Å) and refined as riding atoms. The other hydrogen atoms were placed geometrically (P—H = 1.32, C—H = 0.98 Å) and refined as riding atoms. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) or 1.5U_{eq}(methyl carrier) was applied in all cases. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The crystal chosen for data collection was found to be rotationally twinned about the [001] axis in reciprocal space in a 0.585 (5):0.415 (5) ratio.

Acknowledgements

We thank the EPSRC National Crystallography Service (University of Southampton) for the X-ray data collection.

References

Bennett, J. M. & Marcus, B. K. (1988). *Stud. Surf. Sci. Catal.* **37**, 269–279.
Brunner, G. O. & Meier, W. M. (1989). *Nature (London)*, **337**, 146–147.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Dong, Z.-J., Yan, Y., Zhang, W.-Q., Wang, Y. & Li, J.-Y. (2015). *Chem. Res. Chin. Univ.* **31**, 498–502.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Harrison, W. T. A. (2006). *Acta Cryst.* C**62**, m156–m158.
Harrison, W. T. A. & McNamee, P. M. (2010). *J. Chem. Res. (S)*, **34**, 641–642.
Huang, H.-L., Lin, H.-Y., Chen, P.-S., Lee, J.-J., Kung, H.-C. & Wang, S.-L. (2017). *Dalton Trans.* **46**, 364–368.
Katinaitė, J. & Harrison, W. T. A. (2016). *Acta Cryst.* E**72**, 1206–1210.
Kirkpatrick, A. & Harrison, W. T. A. (2004). *Solid State Sci.* **6**, 593–598.
Lin, Z.-E., Zhang, J., Zheng, S.-T. & Yang, G.-Y. (2004). *Microporous Mesoporous Mater.* **68**, 65–70.
Liu, L., Zhang, L., Wang, X., Li, G., Liu, Y. & Pang, W. (2008). *Dalton Trans.* pp. 2009–2014.
Luo, X.-C., Gong, M.-C., Chen, Y.-Q. & Lin, Z.-E. (2010). *Microporous Mesoporous Mater.* **131**, 418–422.
Phillips, M. L. F., Nenoff, T. M., Thompson, C. T. & Harrison, W. T. A. (2002). *J. Solid State Chem.* **167**, 337–343.
Rigaku (2015). *CrysAlis PRO*. Rigaku Corporation, Tokyo, Japan.
Shape Software (2005). *ATOMS*. Shape Software Inc., Kingsport, Tennessee, USA.
Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Shi, S., Qian, W., Li, G., Wang, L., Yuan, H., Xu, J., Zhu, G., Song, T. & Qiu, S. (2004). *J. Solid State Chem.* **177**, 3038–3044.
Wang, S.-D., Luo, D.-B., Luo, X.-C., Chen, Y.-Q. & Lin, Z.-E. (2011). *Solid State Sci.* **13**, 904–907.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2017). E**73**, 759-762 [https://doi.org/10.1107/S2056989017005758]

The crystal structure of $(C_2H_9N_2)_2[Zn_3(HPO_3)_4]$, a three-dimensional zincophosphite framework containing 16-membered rings templated by the unsymmetrical dimethyl hydrazinium cation

Judita Katinaitė and William T. A. Harrison

Computing details

Data collection: *CrysAlis PRO* (Rigaku, 2015); cell refinement: *CrysAlis PRO* (Rigaku, 2015); data reduction: *CrysAlis PRO* (Rigaku, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *ATOMS* (Shape Software, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2010).

1,1-Dimethylhydrazinium tetraphoshonoatotrizincate(II)

Crystal data

$(C_2H_9N_2)_2[Zn_3(HPO_3)_4]$
M_r = 638.24
Monoclinic, *C*2/*c*
a = 15.1154 (5) Å
b = 8.7269 (3) Å
c = 16.1675 (6) Å
β = 108.156 (1)°
V = 2026.48 (12) Å^3
Z = 4
F(000) = 1280
D_x = 2.092 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6272 reflections
θ = 2.6–27.6°
μ = 3.90 mm^{-1}
T = 100 K
Block, colourless
0.19 × 0.11 × 0.05 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
T_{min} = 0.527, T_{max} = 1.000
2273 measured reflections
2273 independent reflections
2169 reflections with $I > 2\sigma(I)$
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −19→18
k = −11→11
l = −11→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.239
S = 1.22
2273 reflections
127 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1587P)^2 + 13.6003P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.51 e Å^{-3}
$\Delta\rho_{min}$ = −1.24 e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (2)

Special details

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

Refinement. Refined as a 2-component twin with components rotated about (001) in reciprocal space

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.0000	0.16565 (13)	0.2500	0.0076 (4)
Zn2	0.36570 (6)	0.37073 (9)	0.48484 (5)	0.0096 (4)
P1	0.15444 (13)	0.3885 (2)	0.37817 (11)	0.0091 (5)
H1	0.1147	0.5248	0.3662	0.011*
P2	−0.01597 (13)	−0.0917 (2)	0.11747 (11)	0.0088 (5)
H2	−0.0253	−0.1970	0.1728	0.011*
O1	0.2557 (4)	0.4152 (7)	0.3858 (3)	0.0193 (12)
O2	0.1393 (5)	0.3246 (6)	0.4592 (3)	0.0180 (12)
O3	0.1081 (4)	0.2975 (7)	0.2948 (3)	0.0160 (11)
O4	0.0428 (4)	0.0362 (6)	0.1728 (3)	0.0146 (11)
O5	0.0321 (4)	−0.1690 (6)	0.0604 (4)	0.0169 (12)
O6	−0.1139 (4)	−0.0379 (6)	0.0684 (3)	0.0124 (10)
C1	0.1591 (7)	0.2877 (11)	0.0880 (5)	0.028 (2)
H1A	0.1821	0.1825	0.1002	0.043*
H1B	0.1847	0.3339	0.0452	0.043*
H1C	0.0909	0.2867	0.0649	0.043*
C2	0.1529 (8)	0.5365 (10)	0.1562 (6)	0.029 (2)
H2A	0.1818	0.5963	0.2091	0.043*
H2B	0.0852	0.5358	0.1439	0.043*
H2C	0.1683	0.5827	0.1072	0.043*
N1	0.2898 (6)	0.3663 (9)	0.2063 (5)	0.0249 (17)
H1N	0.3067	0.3880	0.2642	0.030*
H2N	0.3170	0.4346	0.1793	0.030*
N2	0.1884 (5)	0.3781 (7)	0.1691 (4)	0.0132 (13)
H3N	0.1608	0.3280	0.2110	0.016*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0064 (7)	0.0080 (6)	0.0076 (6)	0.000	0.0008 (4)	0.000
Zn2	0.0093 (6)	0.0109 (5)	0.0078 (5)	−0.0032 (3)	0.0015 (4)	0.0003 (3)
P1	0.0106 (10)	0.0085 (8)	0.0076 (8)	−0.0011 (6)	0.0021 (7)	0.0010 (6)
P2	0.0085 (9)	0.0093 (8)	0.0077 (8)	0.0008 (6)	0.0014 (7)	0.0001 (6)
O1	0.020 (3)	0.024 (3)	0.012 (2)	−0.006 (2)	0.001 (2)	0.002 (2)

O2	0.033 (3)	0.009 (2)	0.013 (2)	−0.002 (2)	0.009 (2)	0.0000 (18)
O3	0.013 (3)	0.023 (3)	0.012 (2)	−0.010 (2)	0.004 (2)	−0.006 (2)
O4	0.015 (3)	0.014 (2)	0.014 (2)	0.000 (2)	0.002 (2)	−0.006 (2)
O5	0.025 (3)	0.012 (2)	0.016 (2)	0.005 (2)	0.009 (2)	−0.0021 (19)
O6	0.008 (3)	0.016 (2)	0.013 (2)	0.000 (2)	0.0020 (19)	0.004 (2)
C1	0.039 (5)	0.024 (4)	0.015 (3)	−0.003 (4)	−0.002 (4)	−0.008 (3)
C2	0.048 (6)	0.020 (4)	0.024 (4)	0.005 (4)	0.020 (4)	0.006 (3)
N1	0.019 (4)	0.034 (4)	0.020 (3)	−0.004 (3)	0.004 (3)	0.002 (3)
N2	0.017 (4)	0.013 (3)	0.011 (3)	−0.004 (2)	0.008 (3)	−0.001 (2)

Geometric parameters (Å, º)

Zn1—O4	1.938 (5)	O2—Zn2^{iii}	1.943 (5)
Zn1—O4^{i}	1.938 (5)	O5—Zn2^{v}	1.936 (6)
Zn1—O3^{i}	1.945 (5)	O6—Zn2^{vi}	1.946 (5)
Zn1—O3	1.945 (5)	C1—N2	1.475 (9)
Zn2—O5^{ii}	1.936 (6)	C1—H1A	0.9800
Zn2—O2^{iii}	1.943 (5)	C1—H1B	0.9800
Zn2—O6^{iv}	1.946 (5)	C1—H1C	0.9800
Zn2—O1	1.954 (6)	C2—N2	1.474 (10)
P1—O2	1.504 (5)	C2—H2A	0.9800
P1—O1	1.515 (6)	C2—H2B	0.9800
P1—O3	1.533 (5)	C2—H2C	0.9800
P1—H1	1.3200	N1—N2	1.465 (10)
P2—O5	1.500 (6)	N1—H1N	0.9100
P2—O6	1.520 (5)	N1—H2N	0.9100
P2—O4	1.529 (5)	N2—H3N	1.0000
P2—H2	1.3200		
O4—Zn1—O4^{i}	108.7 (3)	P1—O3—Zn1	137.2 (3)
O4—Zn1—O3^{i}	121.0 (2)	P2—O4—Zn1	123.6 (3)
O4^{i}—Zn1—O3^{i}	100.0 (2)	P2—O5—Zn2^{v}	138.4 (4)
O4—Zn1—O3	100.0 (2)	P2—O6—Zn2^{vi}	120.8 (3)
O4^{i}—Zn1—O3	121.0 (2)	N2—C1—H1A	109.5
O3^{i}—Zn1—O3	107.4 (4)	N2—C1—H1B	109.5
O5^{ii}—Zn2—O2^{iii}	99.8 (2)	H1A—C1—H1B	109.5
O5^{ii}—Zn2—O6^{iv}	115.1 (2)	N2—C1—H1C	109.5
O2^{iii}—Zn2—O6^{iv}	110.8 (2)	H1A—C1—H1C	109.5
O5^{ii}—Zn2—O1	107.5 (3)	H1B—C1—H1C	109.5
O2^{iii}—Zn2—O1	114.1 (3)	N2—C2—H2A	109.5
O6^{iv}—Zn2—O1	109.3 (2)	N2—C2—H2B	109.5
O2—P1—O1	114.2 (3)	H2A—C2—H2B	109.5
O2—P1—O3	115.0 (3)	N2—C2—H2C	109.5
O1—P1—O3	108.9 (3)	H2A—C2—H2C	109.5
O2—P1—H1	106.0	H2B—C2—H2C	109.5
O1—P1—H1	106.0	N2—N1—H1N	109.3
O3—P1—H1	106.0	N2—N1—H2N	109.2
O5—P2—O6	113.4 (3)	H1N—N1—H2N	109.5

O5—P2—O4	112.6 (3)	N1—N2—C2	114.3 (7)
O6—P2—O4	111.9 (3)	N1—N2—C1	108.3 (6)
O5—P2—H2	106.1	C2—N2—C1	112.4 (7)
O6—P2—H2	106.1	N1—N2—H3N	107.2
O4—P2—H2	106.1	C2—N2—H3N	107.2
P1—O1—Zn2	128.0 (3)	C1—N2—H3N	107.2
P1—O2—Zn2^{iii}	140.3 (3)		
O2—P1—O1—Zn2	2.2 (6)	O5—P2—O4—Zn1	177.2 (3)
O3—P1—O1—Zn2	−127.8 (4)	O6—P2—O4—Zn1	48.1 (4)
O1—P1—O2—Zn2^{iii}	−86.8 (7)	O6—P2—O5—Zn2^{v}	110.4 (6)
O3—P1—O2—Zn2^{iii}	40.2 (8)	O4—P2—O5—Zn2^{v}	−18.0 (7)
O2—P1—O3—Zn1	28.0 (7)	O5—P2—O6—Zn2^{vi}	−68.4 (4)
O1—P1—O3—Zn1	157.6 (5)	O4—P2—O6—Zn2^{vi}	60.3 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.91	2.34	3.130 (9)	146
N1—H2*N*···O6^{vii}	0.91	2.35	3.133 (9)	144
N2—H3*N*···O3	1.00	1.79	2.762 (8)	163
C1—H1*A*···O1^{v}	0.98	2.50	3.474 (11)	173
C1—H1*C*···O5^{viii}	0.98	2.50	3.295 (11)	138
C2—H2*C*···O2^{ix}	0.98	2.43	3.355 (9)	157

Symmetry codes: (v) −*x*+1/2, *y*−1/2, −*z*+1/2; (vii) *x*+1/2, *y*+1/2, *z*; (viii) −*x*, −*y*, −*z*; (ix) *x*, −*y*+1, *z*−1/2.