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Synthesis and structure of poly[(μ_3-hydrogen phosphato)(pyridine)zinc(II)]

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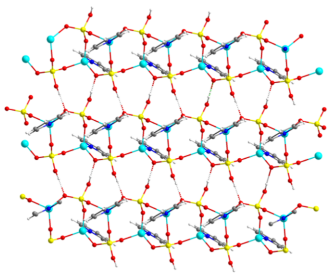
The title compound, $[Zn(HPO_4)(C_5H_5N)]_n$ or $pyZn(HPO_4)$ (**1**), was prepared from the solvothermal reaction of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]ZnCl_4$ and H_3PO_4 in a mixture of pyridine and water. It displays an infinite ladder structure built of alternately arranged ZnO_3N and $PO_3(OH)$ tetrahedra, linked O—H⋯O hydrogen bonds into supramolecular sheets. C—H⋯O interactions between CH groups of the pyridine rings and phosphate groups connect the sheets into a three-dimensional framework structure.

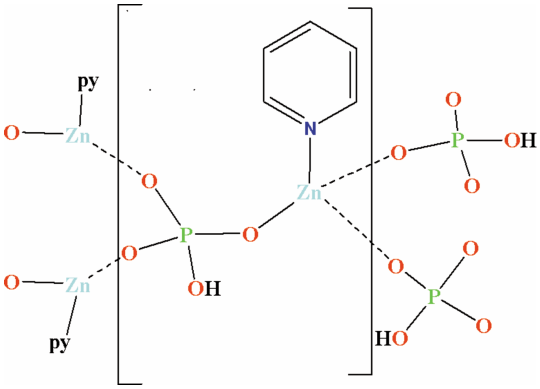
1. Chemical context

Divalent metal phosphates such as hydroxylapatite $[Ca_5(PO_4)_3(OH)]$, the main component of human bones, play an essential role in body structure. Zinc phosphates are extensively involved in bone development, dental materials, environmentally friendly anticorrosive and antirust pigments and industrial additives. They exhibit a vast structural diversity including cluster, chain, layer and open-framework structures (Mao *et al.*, 2020; Amghouz *et al.*, 2014; Chen *et al.*, 2007; Lin *et al.*, 2003*b*, 2007; Yang *et al.*, 2009; Choudhury *et al.*, 2000; Rayes *et al.*, 2001). A number of $LZn(H_xPO_4)$ where Zn^{2+} is datively coordinated to Lewis basic ligands [x = 0–2; L = Cl^- (Chen *et al.*, 2007; Rayes *et al.*, 2001); NH_3 (Amghouz *et al.*, 2014); 5-(4-pyridyl)tetrazolate) (Yang *et al.*, 2009); 1,10-phenanthroline (Lin *et al.*, 2003*a*); 4,4 -dimethyl-2,2-dipyridyl, 5,5-dimethyl-2,2-dipyridly (Lin *et al.*, 2007) 1,2-dimethylimidazole (Mao *et al.*, 2020); 4*H*-1,2,4-triazole-κN^1 (Aitenneite *et al.*, 2012); $CaZn_2Fe(PO_4)_3$ (Khmiyas *et al.*, 2016)] to form discrete or one-dimensional ladder structures. Herein, a new family member of zinc phosphates datively coordinated by an aromatic pyridine ligand, namely $pyZn(HPO_4)$ (**1**), is reported including its synthesis, isolation and single-crystal structural characterization.



2. Structural commentary

As illustrated in Fig. 1, the asymmetric unit of the title compound, $[pyZn(HPO_4)]_n$, contains one Zn^{2+} cation, one $(HPO_4)^{2-}$ anion and an pyridine ligand. The Zn^{2+} cation is coordinated by three O atoms from three phosphate ligands and the Lewis basic N atom from the pyridine ligand in a quite regular tetrahedral geometry with bond angles in the range 110.2 (1)–116.6 (1)°. Each phosphate anion is connected to three Zn^{2+} cations with the strict alternation of ZnO_3N tetrahedra and HPO_4 tetrahedra giving rise to an extended ladder structure (Fig. 2) characteristic of $Zn_2P_2O_4$ eightmembered rings. The Zn—O bonds range from 1.911 (2) to 1.941 (3) Å, similar to the reported values, but at 2.043 (3) Å the Zn—N bond is markedly longer than those for example in Zn-mmim [1,2-dimethylimidazole, 1.988 (2) Å; Mao *et al.* 2020)], indicative of weaker Zn–py bonding. The P—O bond lengths fall in the range 1.505 (3)–1.579 (3) Å, similar to those [1.508 (2)–1.587 (2) Å] in mmimZnHPO$_4$ (Mao *et al.* 2020) with the longest P—O bond being assigned to the P—OH group.



3. Supramolecular features

Fig. 3 illustrates the hydrogen-bonded sheet of **1** (numerical details of the hydrogen bonds are given in Table 1). The short OH···O separation of 2.647 (3) Å and almost linear O—H···O angle [168 (4)°] indicate the significant hydrogen bonding interactions between the ladders. The hydrogen bonding network are characteristic of the P$_2$ZnO$_5$H$_2$ ten-membered ring as demonstrated in Fig. 3. The pyridine ligands are almost perpendicular to the hydrogen binding layers. There are significant interactions between the hydrogen-bonded sheets through C—H···O—P interactions (Table 1), which lead to the formation of three-dimensional supramolecular framework as shown in Fig. 4.

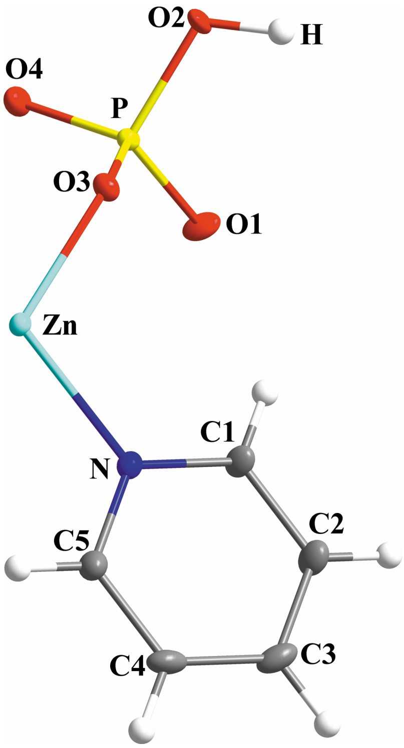


Figure 1
The asymmetric unit of **1** with 50% probability displacement ellipsoids.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H···O3^{i}	0.94 (4)	1.73 (4)	2.647 (3)	168 (4)
C1—H1···O1^{ii}	0.98 (4)	2.58 (4)	3.452 (5)	149 (3)
C3—H3···O3^{iii}	0.96 (2)	2.61 (3)	3.465 (5)	148 (3)
C4—H4···O4^{iv}	0.95 (4)	2.49 (4)	3.354 (5)	152 (3)

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

4. Database survey

A Cambridge Structural Database online search (July 17, 2025; Groom *et al.*, 2016) for the [(μ_3-hydrogenphosphato)(pyridine)zinc] unit yielded no hits, indicating that no zinc phosphates coordinated by pyridine ligands have been

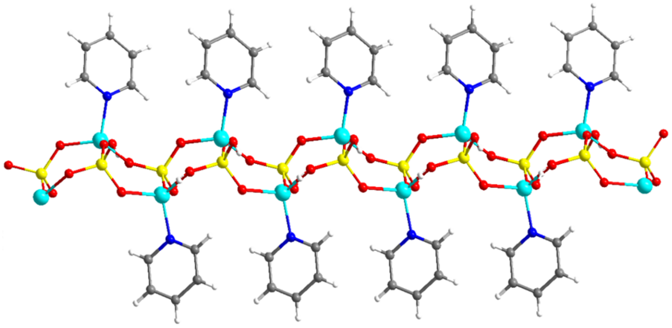


Figure 2
One-dimensional ladder structure of **1**.

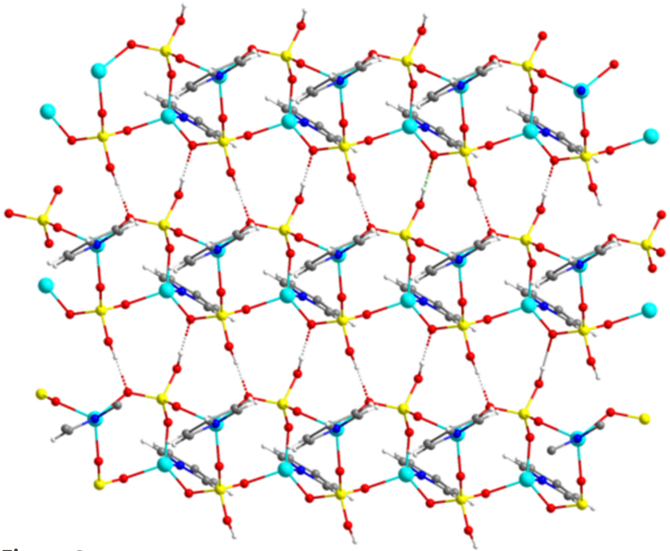


Figure 3
Two-dimensional hydrogen-bonded structure of **1**.

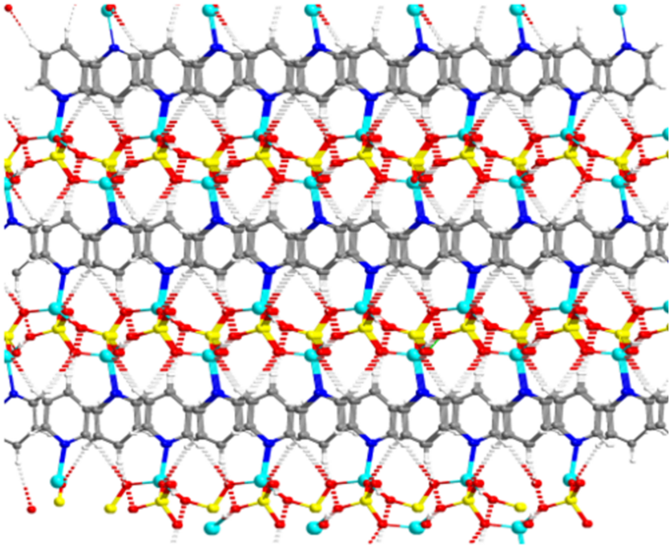


Figure 4
Three-dimensional hydrogen-bonded framework of **1**.

reported. A search for zinc phosphates datively coordinated by N-donor ligands revealed several species containing NH_3 (Amghouz *et al.*, 2014); 5-(4-pyridyl)tetrazolate) (Yang *et al.*, 2009); 1,10-phenanthroline (Lin *et al.*, 2003*a*); 4,4-dimethyl-2,2-dipyridyl, 5,5-dimethyl-2,2-dipyridyl (Lin *et al.*, 2007) 1,2-dimethylimidazole (Mao *et al.*, 2020); 4H-1,2,4-triazole-kN^1 (Aitenneite *et al.*, 2012).

5. Synthesis and crystallization

$[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]ZnCl_4\cdot 8H_2O$ (0.1 g, 0.1 mmol) (Xu *et al.*, 2018, 2025) was added to a mixture of H_3PO_4 (85%, 0.3 ml), pyridine (py, 6 ml) and water (4 ml). The resulting mixture was sealed in a 25 ml Teflon-lined steel autoclave and heated at 393 K for three days. The reactor was cooled to room temperature at a rate of 4 K h^{-1} to produce colourless crystals of pyZn(HPO_4) (**1**), differing from the previous synthetic methodology of zinc phosphates wherein zinc sources were from zinc oxides or zinc salts such as $Zn(O_2CCH_3)_2$. The synthesis is shown in Fig. 5. Notably, the solvothermal reactions using zinc oxides or zinc salts instead of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]ZnCl_4$ failed to produce pyZn(HPO_4) (**1**), indicative of some role of the dianionic group $ZnCl_4^{2-}$ as zinc source.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Zn(HPO_4)(C_5H_5N)]$
M_r	240.45
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	150
a, *b*, *c* (Å)	7.7394 (3), 5.3806 (2), 9.0929 (4)
β (°)	91.246 (2)
V (Å^3)	378.56 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.42
Crystal size (mm)	0.21 × 0.15 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.789, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	2993, 1489, 1467
R_{int}	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.066, 0.87
No. of reflections	1489
No. of parameters	134
No. of restraints	7
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.42
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.051 (19)

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*) and *DIAMOND* (Brandenburg, 2005).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal studied was refined as an inversion twin.

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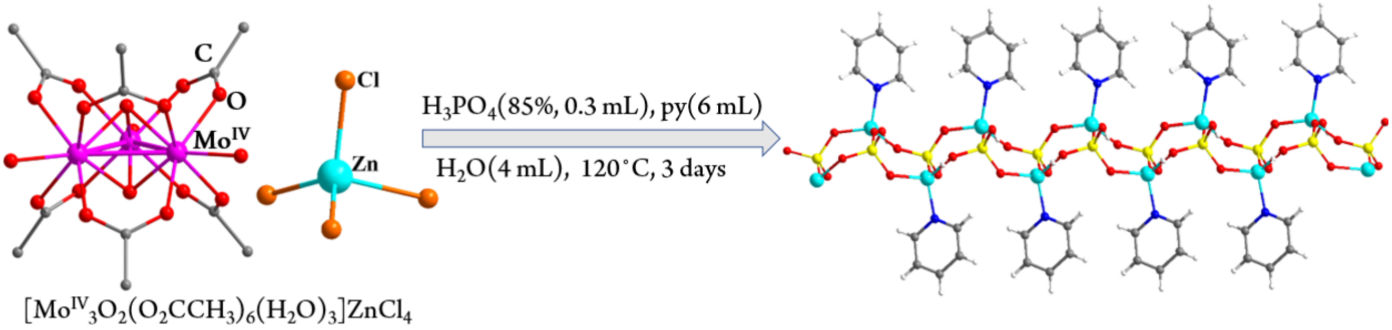

Figure 5
Solvothermal synthesis of **1**.

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supporting information

Acta Cryst. (2025). E**81**, 1040-1043 [https://doi.org/10.1107/S2056989025008308]

Synthesis and structure of poly[(μ_3-hydrogen phosphato)(pyridine)zinc(II)]

Liming Huang, Fochang Luo, Qingshi Wang, Xian Xu and Zhifeng Pan

Computing details

Poly[(μ_3-hydrogen phosphato)(pyridine)zinc(II)]

Crystal data

[Zn(HPO$_4$)(C$_5$H$_5$N)]
M_r = 240.45
Monoclinic, $P2_1$
a = 7.7394 (3) Å
b = 5.3806 (2) Å
c = 9.0929 (4) Å
β = 91.246 (2)°
V = 378.56 (3) Å^3
Z = 2
$F(000)$ = 240
D_x = 2.109 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2993 reflections
θ = 3.5–27.5°
μ = 3.42 mm^{-1}
T = 150 K
Plate, white
0.21 × 0.15 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{\min}$ = 0.789, $T_{\max}$ = 1.000
2993 measured reflections
1489 independent reflections
1467 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.032
$\theta_{\max}$ = 27.5°, $\theta_{\min}$ = 3.5°
$h = -10 \rightarrow 10$
$k = -6 \rightarrow 6$
$l = -10 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.066
S = 0.87
1489 reflections
134 parameters
7 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.051 (19)

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 an inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Zn	0.84495 (4)	0.37175 (6)	0.86294 (3)	0.00820 (15)
P	0.75242 (9)	0.8661 (2)	1.02007 (8)	0.00782 (19)
O1	0.7596 (4)	0.7061 (6)	0.8821 (3)	0.0141 (5)
O2	0.5993 (3)	0.7752 (6)	1.1188 (3)	0.0133 (5)
H	0.496 (5)	0.724 (13)	1.073 (5)	0.041 (17)*
O3	0.7118 (3)	1.1366 (5)	0.9761 (3)	0.0105 (5)
O4	0.9091 (3)	0.8453 (7)	1.1202 (3)	0.0150 (6)
N	0.7918 (4)	0.3106 (6)	0.6448 (3)	0.0108 (7)
C1	0.6998 (5)	0.1149 (8)	0.5928 (4)	0.0134 (7)
H1	0.670 (5)	−0.016 (7)	0.662 (4)	0.010 (12)*
C2	0.6540 (5)	0.0929 (8)	0.4445 (4)	0.0178 (8)
H2	0.589 (7)	−0.050 (8)	0.416 (5)	0.035 (15)*
C3	0.7034 (6)	0.2769 (8)	0.3478 (4)	0.0176 (8)
H3	0.667 (5)	0.283 (9)	0.246 (3)	0.014 (12)*
C4	0.8002 (5)	0.4766 (8)	0.4008 (4)	0.0172 (8)
H4	0.831 (6)	0.623 (7)	0.349 (5)	0.021 (14)*
C5	0.8404 (5)	0.4859 (8)	0.5486 (4)	0.0150 (8)
H5	0.894 (6)	0.623 (7)	0.594 (5)	0.017 (12)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.0081 (2)	0.0080 (2)	0.0085 (2)	0.00058 (18)	−0.00045 (13)	−0.00030 (19)
P	0.0070 (3)	0.0077 (4)	0.0087 (4)	0.0005 (5)	0.0001 (3)	0.0012 (5)
O1	0.0213 (13)	0.0094 (12)	0.0117 (13)	0.0050 (11)	0.0012 (10)	−0.0018 (11)
O2	0.0093 (12)	0.0185 (13)	0.0121 (12)	−0.0043 (11)	0.0003 (9)	0.0040 (11)
O3	0.0098 (11)	0.0081 (12)	0.0136 (12)	0.0004 (10)	0.0014 (9)	0.0000 (10)
O4	0.0091 (10)	0.0213 (16)	0.0144 (11)	−0.0005 (12)	−0.0015 (8)	0.0032 (13)
N	0.0100 (13)	0.0109 (17)	0.0116 (14)	0.0011 (10)	−0.0009 (10)	−0.0007 (11)
C1	0.0172 (18)	0.0097 (16)	0.0132 (17)	−0.0017 (15)	−0.0011 (14)	−0.0020 (14)
C2	0.023 (2)	0.016 (2)	0.0146 (18)	−0.0008 (15)	−0.0040 (16)	−0.0034 (16)
C3	0.022 (2)	0.0205 (18)	0.0107 (17)	0.0075 (16)	0.0001 (15)	−0.0025 (15)
C4	0.0170 (19)	0.020 (2)	0.0145 (17)	0.0021 (16)	0.0037 (15)	0.0030 (16)
C5	0.0152 (19)	0.015 (2)	0.0149 (18)	−0.0035 (15)	0.0010 (15)	−0.0021 (16)

Geometric parameters (Å, º)

Zn—O4$^{\rm i}$	1.911 (2)	N—C1	1.351 (5)
Zn—O1	1.926 (3)	C1—C2	1.392 (5)
Zn—O3$^{\rm ii}$	1.941 (3)	C1—H1	0.97 (2)
Zn—N	2.043 (3)	C2—C3	1.383 (6)
P—O4	1.505 (3)	C2—H2	0.95 (3)
P—O1	1.523 (3)	C3—C4	1.390 (6)
P—O3	1.540 (3)	C3—H3	0.96 (2)
P—O2	1.579 (3)	C4—C5	1.374 (6)

O2—H	0.93 (3)	C4—H4	0.95 (3)
N—C5	1.345 (5)	C5—H5	0.94 (2)
O4^{i}—Zn—O1	113.89 (14)	C5—N—Zn	117.7 (3)
O4^{i}—Zn—O3^{ii}	116.63 (13)	C1—N—Zn	124.0 (3)
O1—Zn—O3^{ii}	111.95 (11)	N—C1—C2	121.8 (4)
O4^{i}—Zn—N	104.18 (11)	N—C1—H1	118 (3)
O1—Zn—N	100.16 (12)	C2—C1—H1	120 (3)
O3^{ii}—Zn—N	108.16 (12)	C3—C2—C1	119.1 (4)
O4—P—O1	114.37 (17)	C3—C2—H2	124 (3)
O4—P—O3	112.61 (19)	C1—C2—H2	117 (3)
O1—P—O3	109.36 (16)	C2—C3—C4	119.2 (4)
O4—P—O2	103.77 (15)	C2—C3—H3	124 (3)
O1—P—O2	109.52 (18)	C4—C3—H3	117 (3)
O3—P—O2	106.80 (16)	C5—C4—C3	118.4 (4)
P—O1—Zn	128.43 (18)	C5—C4—H4	114 (3)
P—O2—H	119 (3)	C3—C4—H4	128 (3)
P—O3—Zn^{iii}	130.24 (16)	N—C5—C4	123.4 (4)
P—O4—Zn^{iv}	146.21 (16)	N—C5—H5	113 (3)
C5—N—C1	118.1 (3)	C4—C5—H5	123 (3)
O4—P—O1—Zn	40.3 (3)	C5—N—C1—C2	−0.5 (5)
O3—P—O1—Zn	167.62 (19)	Zn—N—C1—C2	174.2 (3)
O2—P—O1—Zn	−75.7 (2)	N—C1—C2—C3	−0.3 (6)
O4—P—O3—Zn^{iii}	64.0 (2)	C1—C2—C3—C4	1.2 (6)
O1—P—O3—Zn^{iii}	−64.4 (3)	C2—C3—C4—C5	−1.3 (6)
O2—P—O3—Zn^{iii}	177.22 (19)	C1—N—C5—C4	0.5 (6)
O1—P—O4—Zn^{iv}	55.2 (5)	Zn—N—C5—C4	−174.6 (3)
O3—P—O4—Zn^{iv}	−70.5 (4)	C3—C4—C5—N	0.4 (6)
O2—P—O4—Zn^{iv}	174.4 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H···O3^{v}	0.94 (4)	1.73 (4)	2.647 (3)	168 (4)
C1—H1···O1^{ii}	0.98 (4)	2.58 (4)	3.452 (5)	149 (3)
C3—H3···O3^{vi}	0.96 (2)	2.61 (3)	3.465 (5)	148 (3)
C4—H4···O4^{vii}	0.95 (4)	2.49 (4)	3.354 (5)	152 (3)

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