

catena-Poly[oxidanium [tris(μ -[amino(iminio)-methyl]phosphonato)zincate(II)]]

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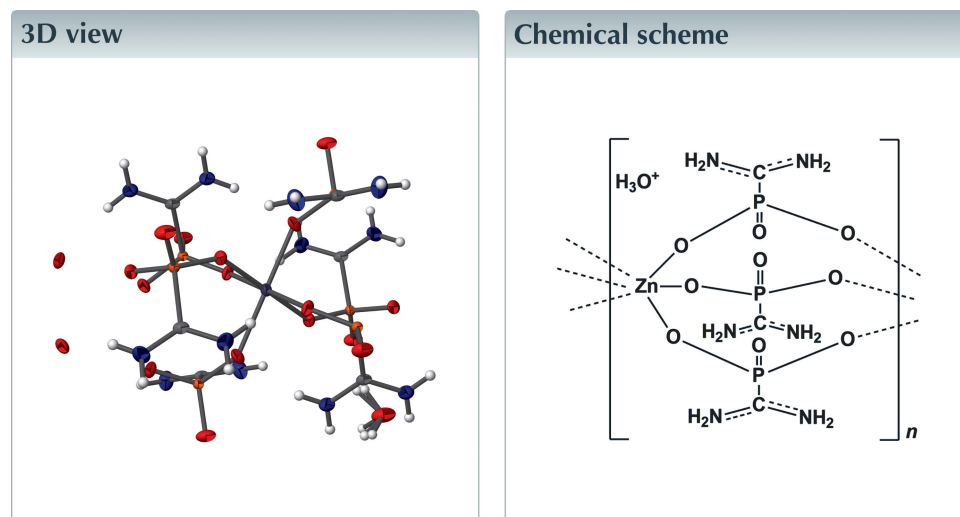
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Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the anionic zinc–[amino(iminio)methyl]phosphonate one-dimensional coordination polymer, Zn-AIMP, is reported; the negative charge is balanced by an oxidanium cation (H_3O^+) to give the composition $\{(\text{H}_3\text{O})[\text{Zn}(\text{CH}_4\text{N}_2\text{PO}_3)_3]\}_n$. The building unit of the coordination polymer comprises a divalent Zn^{2+} cation (site symmetry $\bar{3}$.) and three [amino(iminio)methyl]phosphonate mono-anionic ligands (point group symmetry m). The AIMP ligand exists in a zwitterionic form with a total charge -1 as the phosphonate is fully deprotonated ($-\text{PO}_3^{2-}$), while the amino(iminio)methyl moiety is protonated ($\text{H}_2\text{N}-\text{C}-\text{NH}_2^+$).



Structure description

The chemistry of phosphonic acids was initiated by the need for hydrolysis-resistant replacements for polyphosphates. Synthetic access to a variety of phosphonic acid structures is possible through several well-established routes (Sevrain *et al.*, 2017). To the inorganic chemist, phosphonic acids are a valuable synthetic tool as versatile ligands for generating a plethora of metal phosphonate compounds that present diverse structural architectures, from molecular complexes, to chains and layers, to framework structures (Clearfield & Demadis, 2012). Herein, we report a new Zn^{II} phosphonate one-dimensional anionic coordination polymer that contains the ligand [amino(iminio)methyl]phosphonate ($\{[\text{Zn}(\text{CH}_4\text{N}_2\text{PO}_3)_3]\}_n$, Zn-AIMP) and an oxidanium (H_3O^+) cation. The ligand AIMP was generated *in situ* during the synthesis by the decomposition of the hexaethyl 1,3,5-triazine-2,4,6-triyltris(phosphonate) ester upon dealkylation with trimethylbromosilane.

The crystal structure of amino(iminio)methyl]phosphonate (obtained by decomposition of the ester hexaethyl 1,3,5-triazine-2,4,6-triyltris(phosphonate) *via* acid hydrolysis

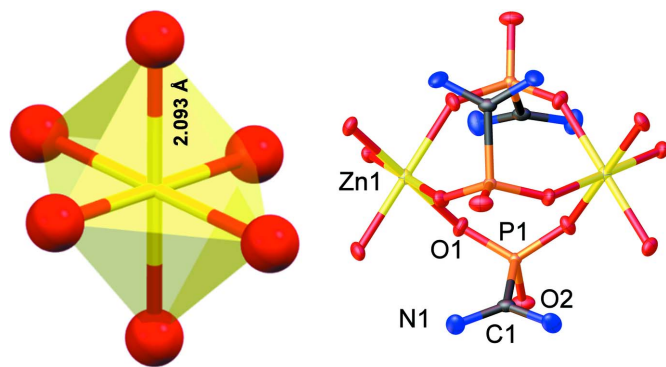


Figure 1
 (left) The octahedral environment of the Zn^{2+} cation. (right) The bridging AIMP^- ligands with numbering scheme (H atoms and the disordered oxidanium cation are omitted for clarity). Displacement ellipsoids are shown at the 50% probability level. Colour codes: Zn yellow, P orange, O red, C black, N blue.

and subsequent heating at 373 K) has been reported in the literature (Yang *et al.*, 2010). Interestingly, the sulfonate analogue of AIMP, aminoiminomethanesulfonic acid $(\text{NH}_2)_2\text{CSO}_3$ has been reported, and its crystal structure shows that this is also a zwitterion (Makarov *et al.*, 1999). Our dealkylation approach of the hexaethyl 1,3,5-triazine-2,4,6-triyltris(phosphonate) ester to yield the acid under mild conditions and with the use of trimethylbromosilane did not lead to the desired (1,3,5-triazine-2,4,6-triyl)tris(phosphonic acid) product, but to AIMP.

AIMP exists as a zwitterion in acidic solutions and it is neutral. However, at the pH of the reaction with Zn^{II} , its second phosphonic acid group is deprotonated, thus generating the AIMP anion. The $\text{Zn}:\text{AIMP}$ molar ratio in Zn-AIMP is 1:3. Upon careful examination, the +2 charge of Zn^{II} is offset by three mono-anionic AIMP ligands, offering a total charge of -3 . In the absence of any other cations in solution, the excess -1 charge per building unit is balanced by an oxidanium cation that is generated by protonation of water (from the solvent). Zn-AIMP is a one-dimensional coordination polymer, its chains extending parallel to the c axis. The

Table 1
 Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1-H1A}\cdots\text{O2}^{\text{i}}$	0.86	2.19	2.925 (3)	143
$\text{N1-H1B}\cdots\text{O1}^{\text{ii}}$	0.86	2.16	2.926 (3)	147
$\text{O3-H3}\cdots\text{O2}$	0.98	1.59	2.520 (3)	155

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

Zn^{2+} cation has a slightly distorted octahedral geometry, as illustrated in Fig. 1, coordinated exclusively by six phosphonate oxygen atoms from six different AIMP ligands. The $\text{Zn}-\text{O}$ distance is 2.0927 (16) \AA , which falls in the expected $\text{Zn}-\text{O}(\text{phosphonate})$ range (Colodrero *et al.*, 2010). Each AIMP ligand bridges two neighbouring Zn^{2+} cations, Fig. 1.

The phosphonate group in the AIMP ligand is fully deprotonated, while the $\text{N}-\text{C}-\text{N}$ moiety is protonated, hence each N atom bears two H atoms. From symmetry, the $\text{C1}-\text{N1}$ bonds are equivalent, with the bond length at 1.310 (3) \AA being intermediate between those of a single and a double bond. The $\text{C}-\text{N}$ bond length is comparable to that found in 'free' AIMP [1.299 (5) \AA and 1.314 (5) \AA ; Yang *et al.*, 2010].

The $\text{P}-\text{O}$ bond lengths are 1.4957 (15) \AA (coordinating) and 1.527 (2) \AA (non-coordinating). It is reasonable to assume that the -2 charge on the phosphonate group is delocalized over all three O atoms. However, the $\text{P1}-\text{O2}$ bond (non-coordinating) is substantially longer than the $\text{P1}-\text{O1}$ bond (coordinating) and this can be rationalized by the formation of hydrogen bonds between O2 with two $\text{N}-\text{H}$ moieties and the oxidanium cation (see below). The packing of the chains in Zn-AIMP along the b - and c -axis directions is shown in Fig. 2 (left and middle). The linear chains (intra-chain $\text{Zn}-\text{Zn}-\text{Zn}$ angle = 180°) are packed parallel to the c axis. The oxidanium cation sits close to the non-coordinating $\text{P}-\text{O}$ moiety of the chain and close to the $\text{N}-\text{C}-\text{N}$ moiety of the neighbouring chain. The arrangement of the oxidanium cations (viewed down the c axis) is better described as staggered triangles that are ~ 4.75 \AA apart, see Fig. 2 (right).

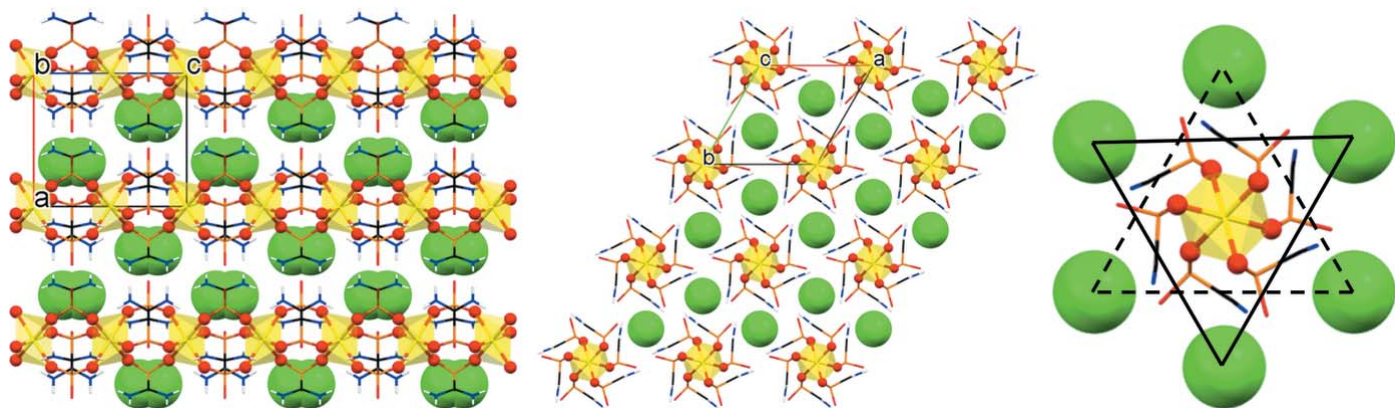


Figure 2
 Packing of Zn-AIMP along the b axis (left) and along the c axis (middle). Arrangement of the H_3O^+ staggered triangles (right). The disordered H_3O^+ cations are shown as exaggerated green spheres. Colour coding is the same as in Fig. 1.

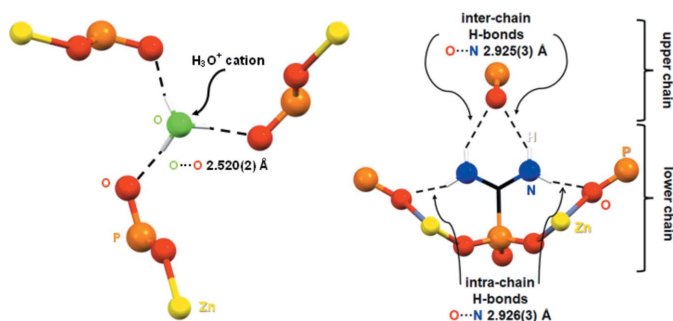


Figure 3 Hydrogen-bonding schemes in the structure of Zn-AIMP. (left) Hydrogen bonds between the disordered H₃O⁺ cation and three non-coordinated O atoms from three different phosphonate groups. (right) Intra-chain and inter-chain hydrogen bonds of the [H₂N-C-NH₂]⁺ moiety with phosphonate O atoms.

The presence of several hydrogen-bond donors and acceptors in the structure creates hydrogen-bonding schemes that deserve some discussion, see Fig. 3. First, the H₃O⁺ cation is located between the chains and utilizes all its H atoms to form three strong hydrogen bonds with three different non-coordinating phosphonate O atoms originating from three neighbouring chains [O...O distance = 2.520(3) Å, O3-H3...O2 angle = 155°, see Table 1 for symmetry codes]. Presumably, the H₃O⁺ cations fill the intra-chain void space and stabilize the packing of the one-dimensional chains. It is noted the oxidanium-O3 atom, which is statistically disordered (see *Refinement*), does not form a close interaction along the threefold axis it resides upon of less than 3.6 Å. In addition, the chains further interact *via* hydrogen bonds that include the cationic [H₂N-C-NH₂]⁺ moiety. Specifically, there are two intra-chain hydrogen bonds with Zn-coordinating phosphonate O atoms [N...O distance = 2.926(3) Å, N1-H1B-O2 angle = 147°] and two inter-chain hydrogen bonds with the non-coordinating phosphonate oxygen from a neighboring chain [N...O distance = 2.925(3) Å, N1-H1A-O1 angle = 143°].

Synthesis and crystallization

Reagents and materials All starting materials were obtained from commercial sources and used without further purification. Ion-exchange column-deionized (DI) water was used for all syntheses. The starting reagents triethyl phosphite (98%), cyanuric chloride (98%) and zinc nitrate hexahydrate were from Alfa Aesar. The solvents petroleum ether, acetonitrile, methanol and nitric acid (70%) were from Scharlau. Trimethylbromosilane was from Flurochem.

Syntheses of [amino(iminio)methyl]phosphonate (AIMP). AIMP was synthesized from the dealkylation of the hexaethyl ester of 1,3,5-triazine-2,4,6-triyltris(phosphonate). The latter was synthesized based on the synthetic procedure reported in the literature (Morrison, 1957) with modifications (Maxim *et al.*, 2010). Yield: 0.916 g, 92%. The 'as synthesized' solid ester (pure by NMR) was then dealkylated using trimethylbromosilane, as follows. In a dry vial the ester (0.490 g, 1.0 mmol) and trimethylbromosilane (1044 μL, 8.0 mmol) were dissolved in

Table 2 Experimental details.

Crystal data	(H ₃ O)[Zn(CH ₄ N ₂ PO ₃) ₃]
Chemical formula	453.49
<i>M_r</i>	Hexagonal, <i>P</i> 6 ₃ / <i>m</i>
Crystal system, space group	298
Temperature (K)	9.5157 (15), 9.4946 (8)
<i>a</i> , <i>c</i> (Å)	744.5 (2)
<i>V</i> (Å ³)	2
<i>Z</i>	Ag <i>K</i> α, λ = 0.56086 Å
Radiation type	1.06
μ (mm ⁻¹)	0.12 × 0.11 × 0.09
Crystal size (mm)	
Data collection	Bruker D8 Venture
Diffractometer	Multi-scan (<i>SADABS</i> ; Bruker, 2019)
Absorption correction	0.684, 0.745
<i>T</i> _{min} , <i>T</i> _{max}	6814, 608, 534
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	0.062
<i>R</i> _{int}	0.649
(sin θ/λ) _{max} (Å ⁻¹)	
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.027, 0.072, 1.13
No. of reflections	608
No. of parameters	43
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.28, -0.50

Computer programs: *APEX3* and *SAINTE* (Bruker, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

acetonitrile (10 ml). The solution was stirred for 24 h, and the colour changed from faint orange to dark orange. Then the homogenous orange solution was left to stand at ambient temperature to allow evaporation of the solvent, yielding an orange oil. Methanol (10 ml) was added to remove the trimethylsilyl group from the phosphonate moiety (as its methoxy ester), and the mixture was stirred for 1 h to allow precipitation of the desired AIMP product (Yield: 0.598 g, 60%). ¹³C NMR (75.5 MHz, DMSO-*d*⁶) δ 169.71 (*d*). ³¹P NMR (121.5 MHz, DMSO-*d*⁶) δ 2.85.

Synthesis of {(H₃O)[Zn(CH₄N₂PO₃)₃]}_{*n*} (Zn-AIMP). The synthesis of Zn-AIMP was performed at ambient temperature. Specifically, AIMP (0.016 g, 0.071 mmol); an excess was used, as it was found to give a product with better crystallinity) was dissolved in DI water (7 ml), Zn(NO₃)₂·6H₂O (0.005 g, 0.017 mmol, dissolved in 1 ml DI water) was added, and the pH was adjusted to ~3.5 using nitric acid. After 30 days a crystalline precipitate appeared, which was isolated by filtration and rinsed with a small amount of water (Yield: 0.001 g, 13%). The crystal used for measurement was handled under inert conditions, being manipulated while immersed in a perfluoropolyether protecting oil, and was mounted on a MiTeGen Micromount[™].

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The oxygen atom of the H₃O⁺

cation falls on a threefold axis and is disordered with respect to a mirror plane over two half-occupied O-atom positions. No further constraints were necessary to model the disorder.

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full crystallographic data

IUCrData (2022). 7, x220247 [https://doi.org/10.1107/S2414314622002474]

catena-Poly[oxidanium [tris{ μ -[amino(iminio)methyl]phosphonato}zincate(II)]

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catena-Poly[oxidanium [tris{ μ -[amino(iminio)methyl]phosphonato}zincate(II)]

Crystal data

(H₃O)[Zn(CH₄N₂PO)₃]

$M_r = 453.49$

Hexagonal, $P6_3/m$

$a = 9.5157$ (15) Å

$c = 9.4946$ (8) Å

$V = 744.5$ (2) Å³

$Z = 2$

$F(000) = 460$

$D_x = 2.023$ Mg m⁻³

Ag $K\alpha$ radiation, $\lambda = 0.56086$ Å

Cell parameters from 1652 reflections

$\theta = 3.4$ – 21.3°

$\mu = 1.06$ mm⁻¹

$T = 298$ K

Prism, colourless

$0.12 \times 0.11 \times 0.09$ mm

Data collection

Bruker D8 Venture

diffractometer

Radiation source: high brilliance microfocus

sealed tube

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 201)

$T_{\min} = 0.684$, $T_{\max} = 0.745$

6814 measured reflections

608 independent reflections

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

$R_{\text{int}} = 0.062$

$\theta_{\max} = 21.3^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 10$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.072$

$S = 1.13$

608 reflections

43 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.6811P]$

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

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

$\Delta\rho_{\max} = 0.28$ e Å⁻³

$\Delta\rho_{\min} = -0.50$ e Å⁻³

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. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 or 1.5 times those of the respective carrier atom.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.000000	0.000000	-0.500000	0.01420 (19)	
P1	-0.00820 (9)	0.24927 (9)	-0.750000	0.0108 (2)	
O2	-0.0548 (3)	0.3813 (3)	-0.750000	0.0223 (5)	
O1	-0.05380 (19)	0.1544 (2)	-0.61573 (16)	0.0187 (4)	
N1	0.2927 (3)	0.4198 (3)	-0.6296 (2)	0.0256 (5)	
H1A	0.395890	0.485001	-0.628272	0.031*	
H1B	0.239885	0.386350	-0.551784	0.031*	
C1	0.2161 (4)	0.3713 (4)	-0.750000	0.0148 (6)	
O3	-0.333333	0.333333	-0.8104 (8)	0.0351 (16)	0.5
H3	-0.238480	0.340450	-0.762355	0.15 (4)*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0155 (2)	0.0155 (2)	0.0115 (3)	0.00776 (12)	0.000	0.000
P1	0.0106 (4)	0.0102 (4)	0.0112 (4)	0.0049 (3)	0.000	0.000
O2	0.0176 (12)	0.0148 (12)	0.0367 (14)	0.0096 (10)	0.000	0.000
O1	0.0184 (8)	0.0226 (9)	0.0144 (8)	0.0099 (7)	0.0019 (6)	0.0064 (6)
N1	0.0158 (10)	0.0259 (11)	0.0232 (11)	0.0015 (9)	-0.0035 (8)	0.0017 (8)
C1	0.0121 (14)	0.0104 (14)	0.0220 (15)	0.0057 (12)	0.000	0.000
O3	0.0222 (19)	0.0222 (19)	0.061 (4)	0.0111 (10)	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Zn1—O1 ⁱ	2.0927 (16)	P1—O1	1.4957 (15)
Zn1—O1 ⁱⁱ	2.0927 (16)	P1—C1	1.851 (3)
Zn1—O1 ⁱⁱⁱ	2.0927 (16)	N1—H1A	0.8600
Zn1—O1	2.0927 (16)	N1—H1B	0.8600
Zn1—O1 ^{iv}	2.0927 (16)	N1—C1	1.310 (3)
Zn1—O1 ^v	2.0927 (16)	O3—O3 ^{vii}	1.147 (15)
P1—O2	1.527 (2)	O3—H3	0.9830
P1—O1 ^{vi}	1.4957 (15)		
O1 ⁱ —Zn1—O1	85.04 (6)	O2—P1—C1	101.65 (14)
O1 ^{iv} —Zn1—O1 ⁱⁱⁱ	85.04 (6)	O1 ^{vi} —P1—O2	112.38 (8)
O1 ^{iv} —Zn1—O1 ⁱⁱ	94.96 (6)	O1—P1—O2	112.38 (8)
O1 ⁱ —Zn1—O1 ^{iv}	180.0	O1 ^{vi} —P1—O1	116.94 (14)
O1 ⁱ —Zn1—O1 ⁱⁱ	85.04 (6)	O1 ^{vi} —P1—C1	105.92 (8)
O1—Zn1—O1 ^{iv}	94.96 (6)	O1—P1—C1	105.92 (8)
O1—Zn1—O1 ⁱⁱⁱ	180.0	P1—O1—Zn1	140.57 (10)
O1 ⁱ —Zn1—O1 ^v	94.96 (6)	H1A—N1—H1B	120.0
O1 ^v —Zn1—O1 ⁱⁱⁱ	94.96 (6)	C1—N1—H1A	120.0
O1—Zn1—O1 ^v	85.04 (6)	C1—N1—H1B	120.0
O1—Zn1—O1 ⁱⁱ	94.96 (6)	N1—C1—P1	119.02 (15)
O1 ^{iv} —Zn1—O1 ^v	85.04 (6)	N1 ^{vi} —C1—P1	119.02 (15)

O1 ^v —Zn1—O1 ⁱⁱ	180.0	N1—C1—N1 ^{vi}	121.6 (3)
O1 ⁱ —Zn1—O1 ⁱⁱⁱ	94.96 (6)	O3 ^{vii} —O3—H3	62.3
O1 ⁱⁱⁱ —Zn1—O1 ⁱⁱ	85.04 (6)		
O2—P1—O1—Zn1	-161.51 (15)	O1—P1—C1—N1 ^{vi}	155.6 (2)
O2—P1—C1—N1	86.8 (2)	O1 ^{vi} —P1—C1—N1 ^{vi}	30.8 (3)
O2—P1—C1—N1 ^{vi}	-86.8 (2)	O1—P1—C1—N1	-30.8 (3)
O1 ^{vi} —P1—O1—Zn1	66.3 (2)	C1—P1—O1—Zn1	-51.35 (19)
O1 ^{vi} —P1—C1—N1	-155.6 (2)		

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

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 O2 ^{viii}	0.86	2.19	2.925 (3)	143
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Symmetry codes: (i) $y, -x+y, -z-1$; (viii) $-y+1, x-y+1, z$.