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Tetraaquabis[(1-ammonio-1-phosphonoethyl)phosphonato]zinc(II) tetrahydrate

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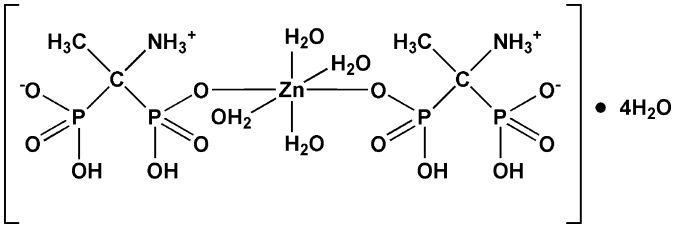
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.037; wR factor = 0.081; data-to-parameter ratio = 12.3.

The title compound, $[Zn(C_2H_8NO_6P_2)_2(H_2O)_4]\cdot 4H_2O$, was synthesized by the reaction of $ZnCl_2$ with 1-aminoethane-1,1-diyldiphosphonic acid in aqueous solution. The asymmetric unit contains one-half of the complex and two water molecules of solvation. The Zn atom occupies a special position on an inversion centre. This results in a slightly distorted octahedral coordination environment, which consists of the O atoms from two phosphonic acids and four water molecules. The crystal structure displays N—H···O and O—H···O hydrogen bonding, which creates a three-dimensional network.

Related literature

Diphosphonic acids are efficient drugs for the prevention of calcification and the inhibition of bone resorption, see: Matczak-Jon & Videnova-Adrabinska (2005). Diphosphonic acids and their metal complexes are used in the treatment of Pagets disease, osteoporosis and tumoral osteolysis, see: Szabo *et al.* (2002). For related structures, see: Li *et al.* (2006, 2007); Lin *et al.* (2007).



Experimental

Crystal data

$[Zn(C_2H_8NO_6P_2)_2(H_2O)_4]\cdot 4H_2O$
M_r = 617.57
Triclinic, $P\overline{1}$
a = 5.6712 (4) Å
b = 9.3279 (6) Å
c = 10.7009 (7) Å
α = 96.440 (3)°
β = 90.788 (3)°
γ = 102.080 (3)°
V = 549.65 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.50 mm^{-1}
T = 173 K
0.36 × 0.10 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: numerical (*SADABS*; Bruker, 2005)
T_{min} = 0.612, T_{max} = 0.945
8897 measured reflections
2244 independent reflections
1747 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.081
S = 1.00
2244 reflections
182 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O6^{i}	0.93 (4)	1.96 (4)	2.796 (4)	150 (3)
N1—H1B···O10	0.85 (4)	1.99 (4)	2.827 (4)	168 (3)
N1—H1C···O3^{i}	0.90 (4)	2.01 (4)	2.851 (3)	153 (3)
O2—H2O···O3^{ii}	0.78 (3)	1.76 (3)	2.536 (3)	172 (4)
O5—H5O···O6^{iii}	0.793 (18)	1.726 (19)	2.519 (3)	177 (4)
O7—H71···O8^{iv}	0.84 (4)	2.05 (4)	2.826 (3)	155 (3)
O7—H72···O10	0.76 (4)	2.00 (4)	2.748 (3)	168 (4)
O8—H81···O2	0.82 (4)	1.97 (4)	2.772 (3)	163 (3)
O8—H82···O9	0.86 (4)	1.79 (4)	2.646 (3)	174 (3)
O9—H91···O5^{v}	0.87 (4)	1.94 (4)	2.810 (3)	172 (3)
O9—H92···O4^{vi}	0.83 (4)	1.91 (4)	2.715 (3)	165 (4)
O10—H101···O4^{vii}	0.85 (4)	1.90 (4)	2.744 (3)	175 (3)
O10—H102···O9^{iv}	0.80 (4)	1.96 (4)	2.741 (3)	167 (4)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2201).

References

Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, M., Chen, S., Xiang, J., He, H., Yuan, L. & Sun, J. (2006). *Cryst. Growth Des.* **6**, 1250–1255.
Li, M. & Sun, J.-T. (2007). *Acta Cryst.* E**63**, m1370–m1372.
Lin, L., Zhang, T., Fan, Y., Ding, D. & Hou, H. (2007). *J. Mol. Struct.* **837**, 107–117.
Matczak-Jon, E. & Videnova-Adrabinska, V. (2005). *Coord. Chem. Rev.* **249**, 2458–2488.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Szabo, Ch. M., Martin, M. B. & Oldfield, E. (2002). *J. Med. Chem.* **45**, 2894–2903.
Westrip, S. P. (2009). *publCIF*. In preparation.

supporting information

Acta Cryst. (2009). E**65**, m459 [doi:10.1107/S1600536809010599]

Tetraaquabis[(1-ammonio-1-phosphonoethyl)phosphonato]zinc(II) tetrahydrate

A. Dudko, V. Bon, A. Kozachkova and V. Pekhnyo

S1. Comment

Organic diphosphonic acids are potentially very powerful chelating agents used in metal extractions and are tested by the pharmaceutical industry for use as efficient drugs preventing calcification and inhibiting bone resorption (Matczak-Jon *et al.*, 2005). Diphosphonic acids and their metal complexes are used in the treatment of Pagets disease, osteoporosis and tumoral osteolysis (Szabo *et al.*, 2002). The asymmetric unit of title compound contains one-half of the formula unit (Fig.1); Zn atom occupy special position at the inversion centre and creates a slightly distorted octahedral coordination environment, which consist of two phosphonic and four aqueous oxygen atoms. The coordinated diphosphonic acids residue exist as zwitterions with positive charge on NH_3 group and negative on the oxygen atom of the non-coordinated phosphonic group. The crystal structure displays N—H···O and O—H···O hydrogen bonding, which creates a three-dimensional network (Table 1, Fig.2).

S2. Experimental

10 ml of the 0.01 *M* $ZnCl_2$ aqueous solution was added to the 10 ml of 0.02 *M* water solution of 1-aminoethane-1,1-diyldiphosphonic acid. Colorless crystals of title compound were obtained after 2 weeks of slow evaporation of the resulted solution.

S3. Refinement

H atoms bonded to N and O were located in a difference map and were freely refined with U_{iso}(H) = 1.2 U_{eq} of the carrier atom. Other H atoms which bonded to C were positioned geometrically and refined using a riding model with C—H = 0.98 Å for CH_3 [U_{iso}(H) = 1.5Ueq(C)].

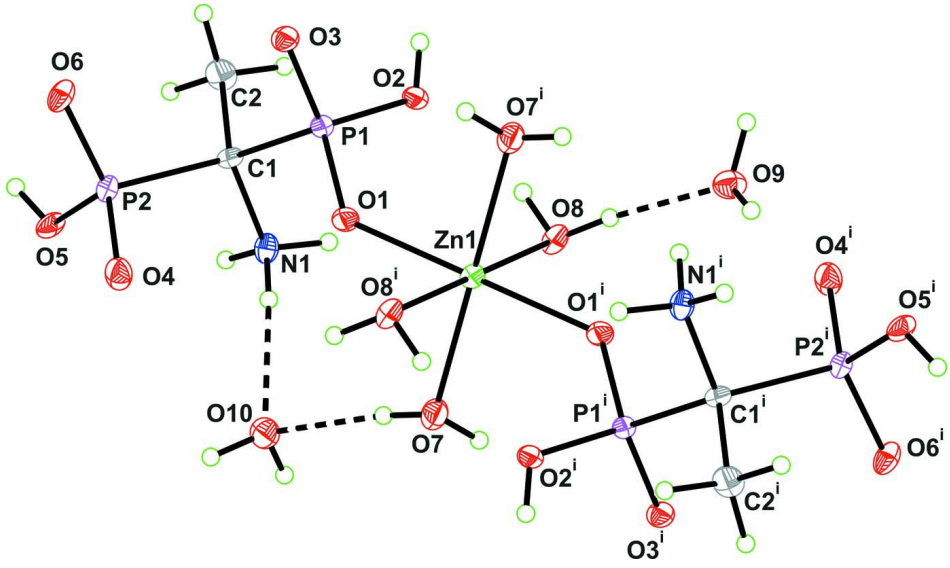


Figure 1

The title compound showing 50% probability displacement ellipsoids for the non-hydrogen atoms [Symmetry code: (i) -*x*, 1 - *y*, 1 - *z*].

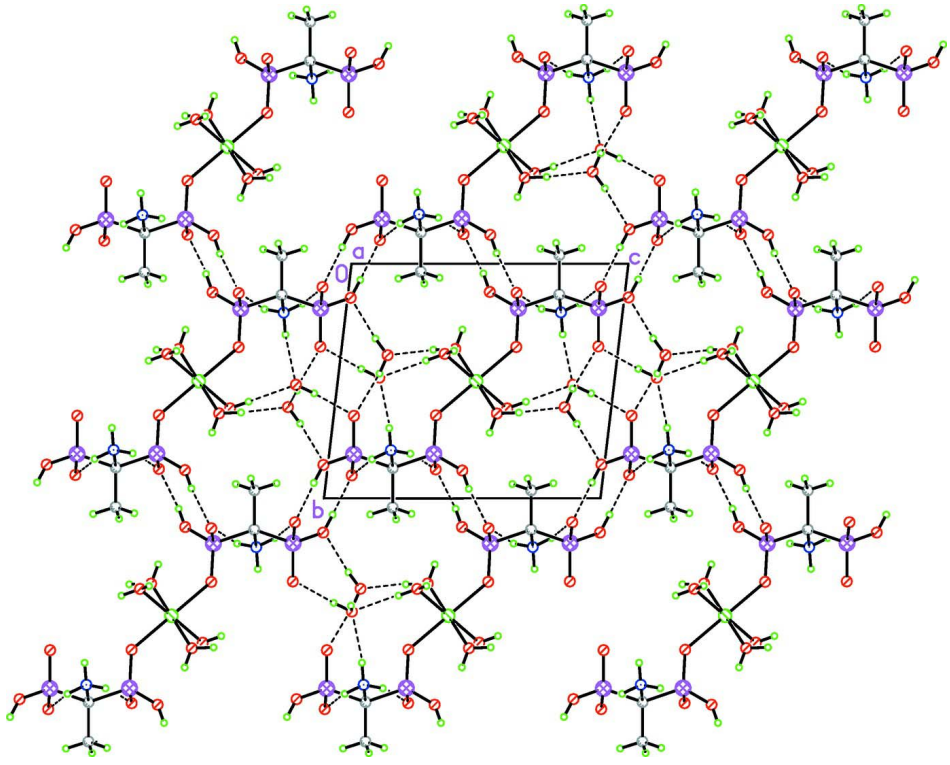


Figure 2

Crystal packing of title compound, projection along *a* axis. Dashed lines indicate hydrogen bonds.

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Crystal data

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Hall symbol: -P 1
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$b = 9.3279$ (6) Å
$c = 10.7009$ (7) Å
$\alpha = 96.440$ (3)°
$\beta = 90.788$ (3)°
$\gamma = 102.080$ (3)°
$V = 549.65$ (6) Å^3
$Z = 1$
$F(000) = 320$
$D_x = 1.866$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2105 reflections
$\theta = 2.3$–$25.9°$
$\mu = 1.50$ mm^{-1}
$T = 173$ K
Block, colourless
0.36 × 0.10 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.26 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2005)
$T_{min} = 0.612$, $T_{max} = 0.945$
8897 measured reflections
2244 independent reflections
1747 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.3°$
$h = -7\rightarrow 7$
$k = -11\rightarrow 10$
$l = -13\rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.081$
$S = 1.00$
2244 reflections
182 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.0000	0.5000	0.5000	0.01171 (16)
P1	0.02405 (14)	0.80873 (8)	0.37915 (7)	0.01033 (19)

P2	−0.00669 (14)	0.81048 (9)	0.09143 (7)	0.0116 (2)
C1	0.1808 (5)	0.8672 (3)	0.2381 (3)	0.0109 (6)
C2	0.2791 (6)	1.0348 (3)	0.2544 (3)	0.0176 (7)
H2A	0.3983	1.0614	0.3248	0.026*
H2B	0.1461	1.0855	0.2716	0.026*
H2C	0.3557	1.0644	0.1770	0.026*
N1	0.3905 (5)	0.7921 (3)	0.2240 (3)	0.0133 (6)
H1A	0.483 (6)	0.830 (4)	0.160 (3)	0.020*
H1B	0.349 (6)	0.699 (4)	0.208 (3)	0.020*
H1C	0.485 (6)	0.807 (4)	0.295 (3)	0.020*
O1	−0.0090 (4)	0.6449 (2)	0.37040 (19)	0.0135 (5)
O2	0.2165 (4)	0.8783 (2)	0.4886 (2)	0.0143 (5)
H2O	0.206 (6)	0.956 (4)	0.519 (3)	0.017*
O3	−0.1966 (4)	0.8741 (2)	0.39210 (19)	0.0139 (5)
O4	−0.0857 (4)	0.6470 (2)	0.0759 (2)	0.0181 (5)
O5	0.1793 (4)	0.8548 (2)	−0.0123 (2)	0.0148 (5)
H5O	0.182 (6)	0.931 (3)	−0.039 (3)	0.018*
O6	−0.1990 (4)	0.8997 (2)	0.0930 (2)	0.0156 (5)
O7	0.1908 (4)	0.3844 (3)	0.3764 (2)	0.0183 (5)
H71	0.319 (7)	0.371 (4)	0.408 (3)	0.022*
H72	0.204 (7)	0.413 (4)	0.312 (4)	0.022*
O8	0.3234 (4)	0.6366 (3)	0.5883 (2)	0.0152 (5)
H81	0.311 (6)	0.719 (4)	0.571 (3)	0.018*
H82	0.300 (6)	0.633 (4)	0.667 (4)	0.018*
O9	0.2666 (4)	0.6106 (3)	0.8304 (2)	0.0181 (5)
H91	0.228 (6)	0.681 (4)	0.882 (3)	0.022*
H92	0.189 (6)	0.532 (4)	0.852 (3)	0.022*
O10	0.3107 (4)	0.4849 (3)	0.1490 (2)	0.0187 (5)
H101	0.236 (6)	0.448 (4)	0.079 (4)	0.022*
H102	0.437 (7)	0.460 (4)	0.143 (3)	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0117 (3)	0.0109 (3)	0.0129 (3)	0.0029 (2)	0.0003 (2)	0.0021 (2)
P1	0.0105 (4)	0.0103 (4)	0.0105 (4)	0.0031 (3)	0.0003 (3)	0.0009 (3)
P2	0.0115 (4)	0.0125 (4)	0.0116 (4)	0.0031 (3)	−0.0009 (3)	0.0035 (3)
C1	0.0096 (15)	0.0088 (15)	0.0146 (16)	0.0030 (12)	0.0003 (12)	0.0007 (12)
C2	0.0208 (18)	0.0114 (16)	0.0183 (18)	−0.0021 (13)	0.0001 (14)	0.0017 (13)
N1	0.0105 (14)	0.0155 (15)	0.0134 (15)	0.0010 (12)	−0.0017 (11)	0.0032 (12)
O1	0.0179 (12)	0.0093 (11)	0.0133 (12)	0.0028 (9)	0.0007 (9)	0.0011 (8)
O2	0.0164 (12)	0.0141 (12)	0.0129 (12)	0.0067 (10)	−0.0032 (9)	−0.0032 (9)
O3	0.0118 (11)	0.0150 (12)	0.0154 (12)	0.0049 (9)	−0.0013 (9)	−0.0004 (9)
O4	0.0224 (13)	0.0143 (12)	0.0158 (12)	0.0001 (9)	−0.0047 (10)	0.0013 (9)
O5	0.0187 (12)	0.0118 (12)	0.0167 (12)	0.0061 (10)	0.0061 (9)	0.0080 (9)
O6	0.0113 (11)	0.0206 (12)	0.0178 (12)	0.0060 (9)	0.0024 (9)	0.0092 (9)
O7	0.0186 (13)	0.0225 (13)	0.0162 (13)	0.0090 (10)	−0.0004 (11)	0.0043 (10)
O8	0.0146 (12)	0.0139 (12)	0.0181 (13)	0.0034 (10)	−0.0017 (10)	0.0054 (10)

O9	0.0201 (13)	0.0148 (12)	0.0199 (13)	0.0042 (10)	0.0041 (10)	0.0025 (10)
O10	0.0152 (13)	0.0239 (13)	0.0176 (13)	0.0072 (11)	−0.0022 (10)	−0.0004 (10)

Geometric parameters (Å, º)

Zn1—O1	2.050 (2)	C2—H2A	0.9800
Zn1—O1^{i}	2.050 (2)	C2—H2B	0.9800
Zn1—O7^{i}	2.071 (2)	C2—H2C	0.9800
Zn1—O7	2.071 (2)	N1—H1A	0.93 (4)
Zn1—O8^{i}	2.141 (2)	N1—H1B	0.85 (4)
Zn1—O8	2.141 (2)	N1—H1C	0.90 (4)
P1—O1	1.492 (2)	O2—H2O	0.78 (3)
P1—O3	1.504 (2)	O5—H5O	0.793 (18)
P1—O2	1.575 (2)	O7—H71	0.84 (4)
P1—C1	1.839 (3)	O7—H72	0.76 (4)
P2—O4	1.486 (2)	O8—H81	0.82 (4)
P2—O6	1.503 (2)	O8—H82	0.86 (4)
P2—O5	1.571 (2)	O9—H91	0.87 (4)
P2—C1	1.846 (3)	O9—H92	0.83 (4)
C1—N1	1.502 (4)	O10—H101	0.85 (4)
C1—C2	1.535 (4)	O10—H102	0.80 (4)
O1—Zn1—O1^{i}	179.999 (1)	N1—C1—P1	107.2 (2)
O1—Zn1—O7^{i}	90.77 (9)	C2—C1—P1	110.6 (2)
O1^{i}—Zn1—O7^{i}	89.23 (9)	N1—C1—P2	106.55 (19)
O1—Zn1—O7	89.23 (9)	C2—C1—P2	110.3 (2)
O1^{i}—Zn1—O7	90.77 (9)	P1—C1—P2	113.58 (16)
O7^{i}—Zn1—O7	180.00 (11)	C1—C2—H2A	109.5
O1—Zn1—O8^{i}	88.74 (9)	C1—C2—H2B	109.5
O1^{i}—Zn1—O8^{i}	91.26 (9)	H2A—C2—H2B	109.5
O7^{i}—Zn1—O8^{i}	92.46 (9)	C1—C2—H2C	109.5
O7—Zn1—O8^{i}	87.54 (9)	H2A—C2—H2C	109.5
O1—Zn1—O8	91.27 (9)	H2B—C2—H2C	109.5
O1^{i}—Zn1—O8	88.73 (9)	C1—N1—H1A	108 (2)
O7^{i}—Zn1—O8	87.54 (9)	C1—N1—H1B	114 (2)
O7—Zn1—O8	92.46 (9)	H1A—N1—H1B	110 (3)
O8^{i}—Zn1—O8	180.0	C1—N1—H1C	113 (2)
O1—P1—O3	118.11 (12)	H1A—N1—H1C	108 (3)
O1—P1—O2	107.82 (12)	H1B—N1—H1C	104 (3)
O3—P1—O2	111.01 (12)	P1—O1—Zn1	133.80 (13)
O1—P1—C1	107.13 (13)	P1—O2—H2O	115 (3)
O3—P1—C1	108.84 (13)	P2—O5—H5O	118 (3)
O2—P1—C1	102.79 (13)	Zn1—O7—H71	113 (2)
O4—P2—O6	117.67 (13)	Zn1—O7—H72	114 (3)
O4—P2—O5	108.21 (12)	H71—O7—H72	114 (4)
O6—P2—O5	110.56 (12)	Zn1—O8—H81	101 (2)
O4—P2—C1	108.34 (13)	Zn1—O8—H82	103 (2)
O6—P2—C1	108.52 (13)	H81—O8—H82	108 (3)

O5—P2—C1	102.44 (13)	H91—O9—H92	106 (3)
N1—C1—C2	108.4 (3)	H101—O10—H102	103 (3)
O1—P1—C1—N1	−47.7 (2)	O6—P2—C1—C2	−54.5 (2)
O3—P1—C1—N1	−176.47 (18)	O5—P2—C1—C2	62.5 (2)
O2—P1—C1—N1	65.8 (2)	O4—P2—C1—P1	−58.45 (19)
O1—P1—C1—C2	−165.7 (2)	O6—P2—C1—P1	70.38 (18)
O3—P1—C1—C2	65.6 (2)	O5—P2—C1—P1	−172.68 (15)
O2—P1—C1—C2	−52.2 (2)	O3—P1—O1—Zn1	−92.94 (19)
O1—P1—C1—P2	69.67 (18)	O2—P1—O1—Zn1	33.8 (2)
O3—P1—C1—P2	−59.08 (18)	C1—P1—O1—Zn1	143.85 (17)
O2—P1—C1—P2	−176.85 (15)	O7^{i}—Zn1—O1—P1	41.88 (18)
O4—P2—C1—N1	59.3 (2)	O7—Zn1—O1—P1	−138.12 (18)
O6—P2—C1—N1	−171.88 (19)	O8^{i}—Zn1—O1—P1	134.32 (18)
O5—P2—C1—N1	−54.9 (2)	O8—Zn1—O1—P1	−45.68 (18)
O4—P2—C1—C2	176.7 (2)		

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O6^{ii}	0.93 (4)	1.96 (4)	2.796 (4)	150 (3)
N1—H1*B*···O10	0.85 (4)	1.99 (4)	2.827 (4)	168 (3)
N1—H1*C*···O3^{ii}	0.90 (4)	2.01 (4)	2.851 (3)	153 (3)
O2—H2*O*···O3^{iii}	0.78 (3)	1.76 (3)	2.536 (3)	172 (4)
O5—H5*O*···O6^{iv}	0.79 (2)	1.73 (2)	2.519 (3)	177 (4)
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O8—H82···O9	0.86 (4)	1.79 (4)	2.646 (3)	174 (3)
O9—H91···O5^{vi}	0.87 (4)	1.94 (4)	2.810 (3)	172 (3)
O9—H92···O4^{i}	0.83 (4)	1.91 (4)	2.715 (3)	165 (4)
O10—H101···O4^{vii}	0.85 (4)	1.90 (4)	2.744 (3)	175 (3)
O10—H102···O9^{v}	0.80 (4)	1.96 (4)	2.741 (3)	167 (4)

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