

## 2-Hydroxypropane-1,3-diammonium bis(phosphonato)zincate(II) hemihydrate

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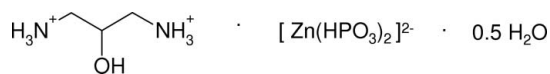
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Key indicators: single-crystal X-ray study;  $T = 120$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å; disorder in main residue;  $R$  factor = 0.028;  $wR$  factor = 0.064; data-to-parameter ratio = 15.7.

In the title compound,  $(\text{C}_3\text{H}_{12}\text{N}_2\text{O})[\text{Zn}(\text{HPO}_3)_2] \cdot 0.5\text{H}_2\text{O}$ , the inorganic macroanionic chain is built up from  $\text{ZnO}_4$  tetrahedra and  $\text{HPO}_3$  pseudo-pyramids sharing vertices. The organic dication shows positional disorder of its central  $-\text{OH}$  group in a 0.614 (7):0.386 (7) ratio. The components interact by way of  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds. The Zn atom lies on a crystallographic twofold axis and one C atom, the disordered O atoms of the  $-\text{OH}$  groups and the water O atom lie on a crystallographic mirror plane.

### Related literature

For background, see: Holtby *et al.* (2007). For other inorganic networks templated by the same cation, see: Chidambaram *et al.* (1999); Choudhury *et al.* (2000); Vaidhyanathan & Natarajan (1999).



### Experimental

#### Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2\text{O})[\text{Zn}(\text{HPO}_3)_2] \cdot 0.5\text{H}_2\text{O}$   
 $M_r = 326.48$   
 Orthorhombic,  $Pbcm$   
 $a = 8.8554$  (3) Å  
 $b = 7.8466$  (3) Å  
 $c = 16.6251$  (5) Å

$V = 1155.19$  (7) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.43$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 $0.28 \times 0.20 \times 0.10$  mm

#### Data collection

Nonius KappaCCD diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2003)  
 $T_{\min} = 0.550$ ,  $T_{\max} = 0.793$

10217 measured reflections  
 1370 independent reflections  
 1271 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.064$   
 $S = 1.12$   
 1370 reflections

87 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.45$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

Zn1—O1 <sup>i</sup>	1.9314 (17)	P1—O1	1.5197 (17)
Zn1—O2	1.9501 (16)	P1—O2	1.5264 (17)
P1—O3	1.4999 (19)		

Symmetry code: (i)  $-x, -y + 1, -z$ .

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O4A—H4A <sup>ii</sup> ···O3	0.90	2.17	3.072 (4)	179
O4B—H4B <sup>iii</sup> ···O3 <sup>ii</sup>	0.90	1.96	2.863 (5)	179
N1—H2 <sup>iii</sup> ···O2 <sup>iii</sup>	0.91	1.92	2.822 (3)	168
N1—H3 <sup>iii</sup> ···O3	0.91	1.85	2.738 (3)	166
N1—H4 <sup>iii</sup> ···O3 <sup>ii</sup>	0.91	1.85	2.763 (3)	177
O5—H5 <sup>iv</sup> ···O1 <sup>iv</sup>	0.91	1.97	2.801 (4)	150

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

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK and DENZO (Otwinowski & Minor, 1997), and SORTAV (Blessing, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2549).

### References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.  
 Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Chidambaram, D., Neeraj, S., Natarajan, S. & Rao, C. N. R. (1999). *J. Solid State Chem.* **147**, 154–169.  
 Choudhury, A., Natarajan, S. & Rao, C. N. R. (2000). *Chem. Eur. J.* **6**, 1168–1175.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Holtby, A. S., Harrison, W. T. A., Yilmaz, V. T. & Büyükgüngör, O. (2007). *Solid State Sci.* **9**, 149–154.  
 Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter, Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Vaidhyanathan, R. & Natarajan, S. (1999). *J. Mater. Chem.* **9**, 1807–1811.

**supplementary materials**

*Acta Cryst.* (2007). E63, m2779 [ doi:10.1107/S1600536807051197 ]

## 2-Hydroxypropane-1,3-diammonium bis(phosphonato)zincate(II) hemihydrate

A. S. Holtby and W. T. A. Harrison

### Comment

The title compound,  $C_3H_{12}N_2O \cdot Zn(HPO_3)_2 \cdot 0.5H_2O$ , (I), (Fig. 1) complements the growing family of templated zincophosphate networks (*e.g.* Holtby *et al.*, 2007).

The connectivity of the polyhedra in the inorganic zincophosphate component of (I) results in macroanionic chains of 4-rings propagating in [010]. The constituent  $ZnO_4$  and  $HPO_3$  units have normal geometrical parameters (Table 1), with the Zn atom lying on a crystallographic 2-fold axis. Each Zn atom therefore serves as a node for the chain with O1 and O2 serving as the linking atoms whereas P1—O3 is a terminal bond.

The complete  $[H_3NCH_2CHOHCH_2NH_3]^{2+}$  dication in (I) is generated by mirror symmetry, with C2 lying on the reflecting plane. The pendant —OH group attached to C2 is disordered over two positions, with both O atoms also occupying the reflection plane. A water molecule (site symmetry *m*) with a fractional site occupancy of 0.5 completes the structure of (I).

The unit-cell packing for (I) (Fig. 2) results in the [010] chains of stoichiometry  $[Zn(HPO_3)_2]^{2-}$  being crosslinked by the water molecule in the [001] direction, with linking O—H $\cdots$ O hydrogen bonds (Table 2) as the key structural feature. The organic cation occupies the space between the pseudo (100) layers and further consolidates the structure through O—H $\cdots$ O and also N—H $\cdots$ O hydrogen bonds.

The  $[H_3NCH_2CHOHCH_2NH_3]^{2+}$  cation has been used to template other inorganic networks including zinc phosphates (Chidambaram *et al.*, 1999), tin phosphates (Vaidhyanathan & Natarajan, 1999) and iron oxalato-phosphates (Choudhury *et al.*, 2000). It is notable that in most of these phases, the —OH group of the template shows similar positional disorder to that observed here.

### Experimental

Zinc oxide, phosphorus acid and 1,3-diamino-2-propanol were mixed in a 1:2:1:500 molar ratio with 20 ml  $H_2O$  and shaken. The mixture was placed in a sealed plastic bottle and heated to 353 K for 2 days. Upon cooling and filtration, colourless blocks of (I) were recovered.

### Refinement

The water O5 atom yielded an unreasonably large  $U_{iso}$  value when full fractional occupancy was assumed. Refining the occupancy for O5 led to a value near 1/2, which was fixed for the final cycles of refinement. Reducing the occupancy for O5 also lowered the *R* factors and led to a more plausible  $U_{iso}$  value, before anisotropic refinement was finally carried out. The —OH group of the dication is disordered over two positions in a 0.614 (7):0.386 (7) ratio (sum constrained to unity).

## supplementary materials

Upon anisotropic refinement, O4a, O4b and O5 showed elongated displacement ellipsoids. Attempts to model this situation with split-atom sites or in lower symmetry space groups were not successful. On account of the resulting short H4...H4B distance of 1.86 Å, the positions of the H atoms of the –OH groups should be regarded as less certain. However, it is notable that both H4 and H4b are involved in hydrogen bonds to the same acceptor atom.

The water H atom was located in a difference map and refined as riding in its as-found relative position with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . The other H atoms were placed in calculated positions (C—H = 0.99 Å, N—H = 0.91 Å, O—H = 0.90 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ . The –NH<sub>3</sub> group was allowed to rotate, but not to tip, to best fit the electron density.

### Figures

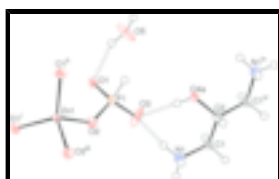


Fig. 1. View of the asymmetric unit of (I) expanded to show the complete organic dication and the Zn coordination sphere. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are drawn as spheres of arbitrary radius. Hydrogen bonds are shown as double dashed lines. Symmetry codes: (i)  $-x, 1 - y, -z$ ; (ii)  $-x, y - 1/2, z$ ; (iii)  $x, 1/2 - y, -z$ ; (iv)  $x, y, 1/2 - z$ . Only one disorder component of the organic species is shown.

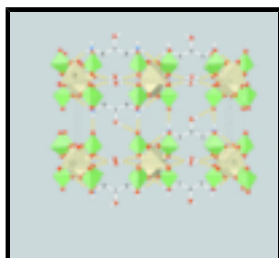


Fig. 2. Unit-cell packing for (I) viewed down [010]. ZnO<sub>4</sub> tetrahedra sand, HPO<sub>3</sub> tetrahedra green, C grey, H white, N blue, O red. The hydrogen bonds are shaded yellow.

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#### Crystal data

(C<sub>3</sub>H<sub>12</sub>N<sub>2</sub>O)[Zn(HPO<sub>3</sub>)<sub>2</sub>] $\cdot$ 0.5H<sub>2</sub>O

$M_r = 326.48$

Orthorhombic, *Pbcm*

Hall symbol: -P 2c 2b

$a = 8.8554$  (3) Å

$b = 7.8466$  (3) Å

$c = 16.6251$  (5) Å

$V = 1155.19$  (7) Å<sup>3</sup>

$Z = 4$

$F_{000} = 668$

$D_x = 1.877$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 1544 reflections

$\theta = 2.9$ – $27.5^\circ$

$\mu = 2.43$  mm<sup>-1</sup>

$T = 120$  (2) K

Block, colourless

$0.28 \times 0.20 \times 0.10$  mm

#### Data collection

Nonius KappaCCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

1370 independent reflections

1271 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$T = 120(2)$  K  $\theta_{\max} = 27.5^\circ$   
 $\omega$  and  $\varphi$  scans  $\theta_{\min} = 3.5^\circ$   
 Absorption correction: multi-scan (SADABS; Bruker, 2003)  $h = -9 \rightarrow 11$   
 $T_{\min} = 0.550$ ,  $T_{\max} = 0.793$   $k = -10 \rightarrow 8$   
 10217 measured reflections  $l = -21 \rightarrow 19$

### Refinement

Refinement on  $F^2$  Hydrogen site location: difmap and geom  
 Least-squares matrix: full H-atom parameters constrained  
 $R[F^2 > 2\sigma(F^2)] = 0.028$   $w = 1/[\sigma^2(F_o^2) + (0.0046P)^2 + 2.8213P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $wR(F^2) = 0.064$   $(\Delta/\sigma)_{\max} = 0.002$   
 $S = 1.12$   $\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$   
 1370 reflections  $\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$   
 87 parameters Extinction correction: SHELXL97 (Sheldrick, 1997),  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.0029 (6)  
 Secondary atom site location: difference Fourier map

### 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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.04498 (4)	0.2500	0.0000	0.01367 (13)	
P1	0.19574 (7)	0.55780 (8)	0.09909 (4)	0.01743 (16)	
H1	0.1771	0.4733	0.1670	0.021*	
O1	0.06921 (19)	0.6883 (2)	0.09460 (10)	0.0226 (4)	
O2	0.18811 (18)	0.4268 (2)	0.03132 (10)	0.0207 (4)	
O3	0.3492 (2)	0.6382 (3)	0.10293 (17)	0.0458 (7)	
C1	0.6993 (3)	0.5624 (3)	0.17508 (14)	0.0230 (5)	
H1A	0.6814	0.6869	0.1765	0.028*	
H1B	0.8097	0.5431	0.1735	0.028*	
C2	0.6344 (4)	0.4814 (6)	0.2500	0.0280 (9)	
H2A	0.5234	0.4971	0.2500	0.034*	0.614 (7)

## supplementary materials

H2B	0.6565	0.3578	0.2500	0.034*	0.386 (7)
O4A	0.4821 (4)	0.4546 (7)	0.2500	0.0288 (14)	0.614 (7)
H4A	0.4429	0.5079	0.2067	0.035*	0.307 (4)
O4B	0.6225 (16)	0.3254 (10)	0.2500	0.071 (5)	0.386 (7)
H4B	0.6301	0.2665	0.2038	0.085*	0.193 (4)
N1	0.6289 (2)	0.4895 (3)	0.10193 (12)	0.0197 (4)	
H2	0.6785	0.5282	0.0576	0.024*	
H3	0.5303	0.5217	0.0995	0.024*	
H4	0.6348	0.3738	0.1038	0.024*	
O5	0.0333 (10)	0.8202 (10)	0.2500	0.063 (3)	0.50
H5	0.0134	0.7591	0.2956	0.075*	0.50

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.01189 (19)	0.0156 (2)	0.0135 (2)	0.000	0.000	-0.00179 (14)
P1	0.0180 (3)	0.0157 (3)	0.0186 (3)	-0.0003 (2)	-0.0065 (2)	-0.0010 (2)
O1	0.0190 (8)	0.0317 (10)	0.0170 (8)	0.0083 (7)	-0.0034 (7)	-0.0029 (7)
O2	0.0190 (8)	0.0211 (9)	0.0219 (8)	-0.0053 (7)	0.0026 (7)	-0.0059 (7)
O3	0.0162 (9)	0.0245 (11)	0.097 (2)	0.0013 (8)	-0.0156 (11)	-0.0235 (12)
C1	0.0217 (12)	0.0284 (13)	0.0189 (12)	-0.0072 (10)	-0.0013 (10)	-0.0016 (10)
C2	0.0234 (18)	0.043 (2)	0.0173 (16)	-0.0162 (17)	0.000	0.000
O4A	0.012 (2)	0.059 (3)	0.0146 (19)	-0.0111 (19)	0.000	0.000
O4B	0.174 (13)	0.016 (4)	0.022 (4)	-0.029 (6)	0.000	0.000
N1	0.0168 (10)	0.0230 (11)	0.0195 (10)	-0.0010 (8)	0.0024 (8)	-0.0028 (8)
O5	0.113 (7)	0.062 (5)	0.013 (3)	-0.052 (5)	0.000	0.000

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Zn1—O1 <sup>i</sup>	1.9314 (17)	C2—O4B	1.229 (9)
Zn1—O1 <sup>ii</sup>	1.9314 (17)	C2—O4A	1.365 (5)
Zn1—O2	1.9501 (16)	C2—C1 <sup>iv</sup>	1.512 (3)
Zn1—O2 <sup>iii</sup>	1.9501 (16)	C2—H2A	0.9900
P1—O3	1.4999 (19)	C2—H2B	0.9900
P1—O1	1.5197 (17)	O4A—H2A	0.4951
P1—O2	1.5264 (17)	O4A—H4A	0.9023
P1—H1	1.3200	O4B—H2B	0.3939
O1—Zn1 <sup>i</sup>	1.9314 (17)	O4B—H4B	0.8991
C1—N1	1.481 (3)	N1—H2	0.9100
C1—C2	1.512 (3)	N1—H3	0.9100
C1—H1A	0.9900	N1—H4	0.9100
C1—H1B	0.9900	O5—H5	0.9142
O1 <sup>i</sup> —Zn1—O1 <sup>ii</sup>	116.86 (10)	O4A—C2—C1 <sup>iv</sup>	116.1 (2)
O1 <sup>i</sup> —Zn1—O2	112.29 (8)	O4B—C2—C1	116.8 (3)
O1 <sup>ii</sup> —Zn1—O2	107.53 (7)	O4A—C2—C1	116.1 (2)
O1 <sup>i</sup> —Zn1—O2 <sup>iii</sup>	107.53 (7)	C1 <sup>iv</sup> —C2—C1	110.9 (3)
O1 <sup>ii</sup> —Zn1—O2 <sup>iii</sup>	112.29 (8)	O4B—C2—H2A	92.2

O2—Zn1—O2 <sup>iii</sup>	98.92 (10)	C1 <sup>iv</sup> —C2—H2A	109.0
O3—P1—O1	112.76 (11)	C1—C2—H2A	109.0
O3—P1—O2	110.78 (12)	O4A—C2—H2B	92.5
O1—P1—O2	112.62 (10)	C1 <sup>iv</sup> —C2—H2B	109.7
O3—P1—H1	106.7	C1—C2—H2B	109.7
O1—P1—H1	106.7	H2A—C2—H2B	108.5
O2—P1—H1	106.7	C2—O4A—H4A	108.0
P1—O1—Zn1 <sup>i</sup>	126.51 (10)	H2A—O4A—H4A	88.4
P1—O2—Zn1	134.82 (10)	C2—O4B—H4B	120.4
N1—C1—C2	110.7 (2)	H2B—O4B—H4B	105.9
N1—C1—H1A	109.5	C1—N1—H2	109.5
C2—C1—H1A	109.5	C1—N1—H3	109.5
N1—C1—H1B	109.5	H2—N1—H3	109.5
C2—C1—H1B	109.5	C1—N1—H4	109.5
H1A—C1—H1B	108.1	H2—N1—H4	109.5
O4B—C2—O4A	76.2 (7)	H3—N1—H4	109.5
O4B—C2—C1 <sup>iv</sup>	116.8 (3)		
O3—P1—O1—Zn1 <sup>i</sup>	103.54 (17)	O1 <sup>ii</sup> —Zn1—O2—P1	-23.26 (18)
O2—P1—O1—Zn1 <sup>i</sup>	-22.74 (17)	O2 <sup>iii</sup> —Zn1—O2—P1	-140.15 (19)
O3—P1—O2—Zn1	168.39 (15)	N1—C1—C2—O4B	45.9 (8)
O1—P1—O2—Zn1	-64.28 (18)	N1—C1—C2—O4A	-41.3 (5)
O1 <sup>i</sup> —Zn1—O2—P1	106.65 (16)	N1—C1—C2—C1 <sup>iv</sup>	-176.8 (2)

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O4A—H4A...O3	0.90	2.17	3.072 (4)	179
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O5—H5...O1 <sup>iv</sup>	0.91	1.97	2.801 (4)	150

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

Fig. 1

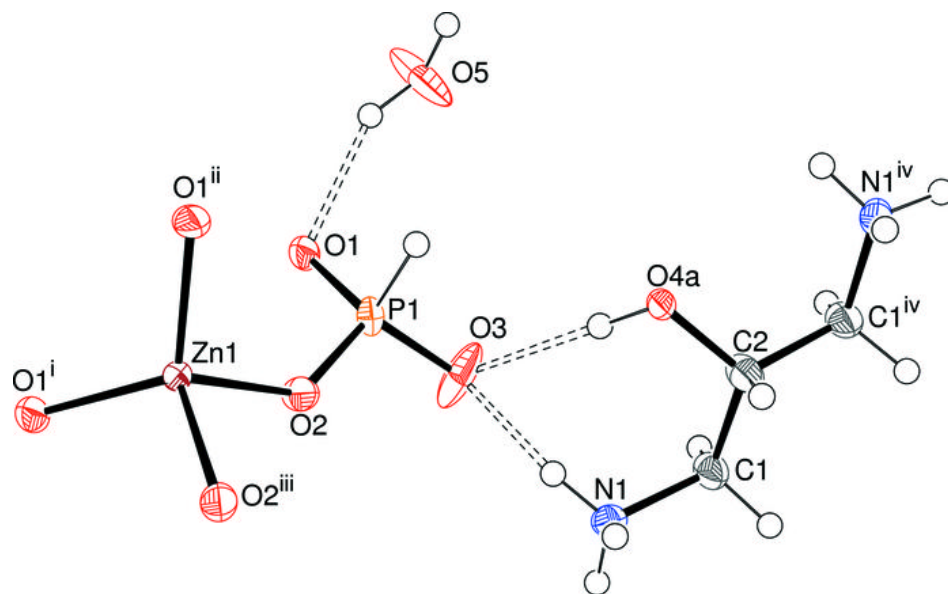




Fig. 2

