



# Consistent zincophosphate 4-ring 'ladder' chain structural motif with isomeric ligands

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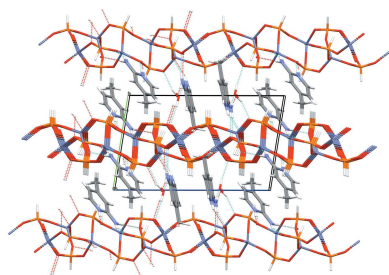
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The syntheses and crystal structures of four hydrothermally prepared organo-zinc phosphites, *viz.* poly[[2-amino-3-methylpyridine)- $\mu_3$ -phosphonato-zinc] hemihydrate],  $[\{Zn(HPO_3)(C_6H_8N_2)\} \cdot 0.5H_2O]_n$ , (I), poly[2-amino-4-methylpyridine)- $\mu_3$ -phosphonato-zinc],  $[Zn(HPO_3)(C_6H_8N_2)]_n$ , (II), poly[2-amino-5-methylpyridine)- $\mu_3$ -phosphonato-zinc],  $[Zn(HPO_3)(C_6H_8N_2)]_n$ , (III), and poly[bis(2-amino-4-methylpyridinium) [tetra- $\mu_3$ -phosphonato-trizinc] monohydrate],  $\{(C_6H_9N_2)_2[Zn_3(HPO_3)_4] \cdot H_2O\}_n$ , (IV), are described. Compounds (I)–(III) are constructed from vertex-sharing  $ZnO_3N$  tetrahedra (the organic molecule acting as a ligand) and  $HPO_3$  pseudo pyramids in a 1:1 ratio to generate the same *motif* of infinite 4-ring 'ladder' chains propagating in the [010], [101] and [100] directions, respectively, whereas (IV) consists of (010) layers of vertex-sharing  $ZnO_4$  and  $HPO_3$  units in a 3:4 ratio with the protonated organic molecule acting as a template. When an excess of HCl is used in the synthesis, the simple hydrated molecular salt, bis(2-amino-3-methylpyridinium) tetrachlorozincate monohydrate,  $(C_6H_8N_2)_2[ZnCl_4] \cdot H_2O$ , (V), arises. Compounds (I)–(V) feature extensive networks of hydrogen bonds, both classical (N–H $\cdots$ O, N–H $\cdots$ Cl, O–H $\cdots$ O) and non-classical (C–H $\cdots$ O, C–H $\cdots$ Cl) in nature, which help to consolidate the extended structures.

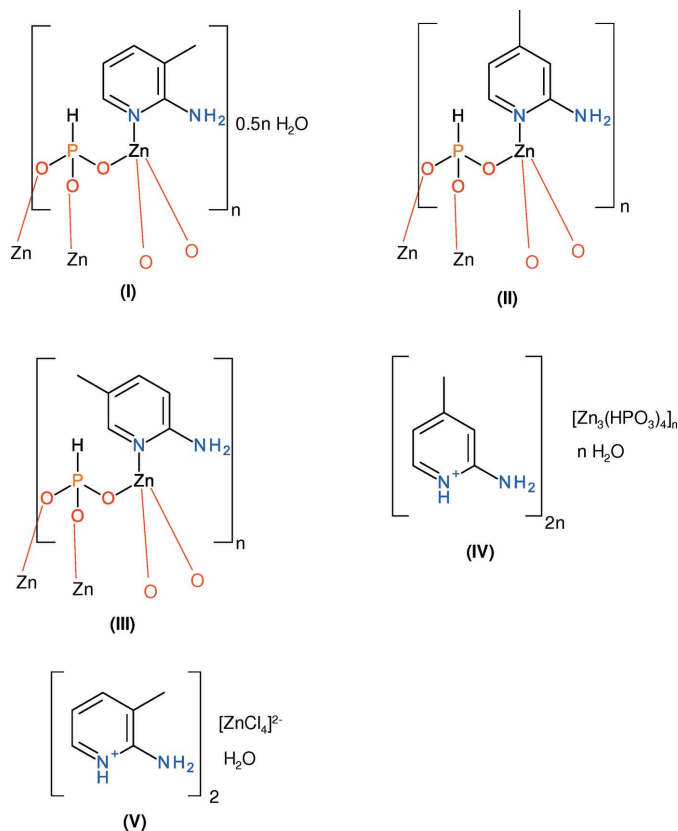
## 1. Chemical context

Since the first report (Harrison *et al.*, 2001) of zincophosphate ( $ZnPO$ ) networks built up from vertex-sharing  $ZnO_4$  or  $ZnO_3N$  and  $HPO_3$  building units templated or ligated by organic species, this family has grown to include well over 200 structures in the Cambridge Structural Database (CSD; Groom *et al.*, 2016). Recent papers have described a  $ZnPO$  templated by a chiral amino acid, which displays non-linear optical behaviour (Mao *et al.*, 2021) and a mixed-ligand  $ZnPO$  with promising gas sorption properties (Chen *et al.*, 2022). As well as their potential applications,  $ZnPO$ s are of ongoing academic interest in terms of the challenge of designing rational and reproducible syntheses and the elucidation of the systematics of their crystal chemistry, for example, the effect of the Zn:P ratio, different polyhedral connectivities, hydrogen bonding and the 'dual role' (bonded ligand or protonated guest) of the organic template on the structure (Holmes *et al.*, 2018).

In a continuation of our ongoing studies of these systems (Katinaitė & Harrison, 2017; Holmes *et al.*, 2018), we now describe the hydrothermal syntheses and crystal structures of four organo-zinc phosphites featuring isomeric ligands, *viz.*: poly[[2-amino-3-methylpyridine)- $\mu_3$ -phosphonato-zinc]

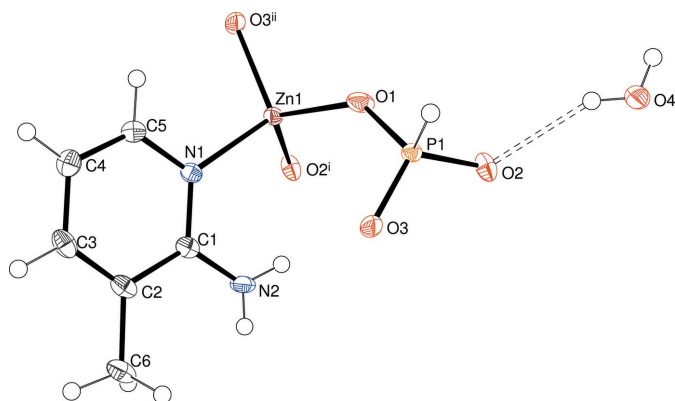


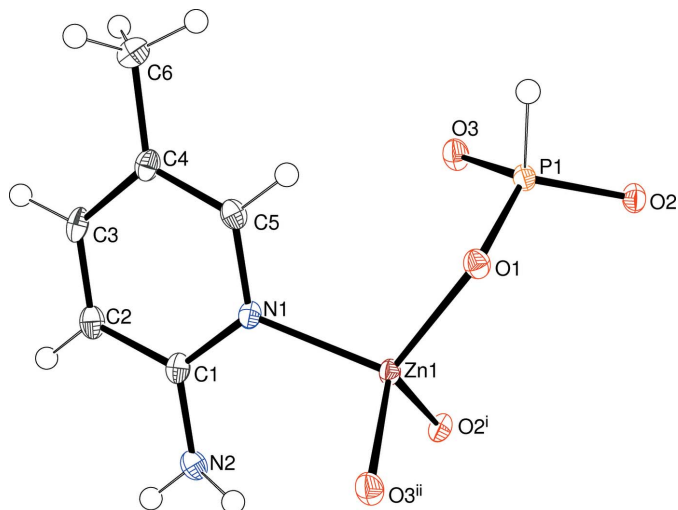
hemihydrate],  $\{[\text{Zn}(\text{HPO}_3)(\text{C}_6\text{H}_8\text{N}_2)] \cdot 0.5\text{H}_2\text{O}\}_n$ , (I), poly[(2-amino-4-methylpyridine)- $\mu_3$ -phosphonato-zinc],  $[\text{Zn}(\text{HPO}_3)(\text{C}_6\text{H}_8\text{N}_2)]_n$ , (II), poly[(2-amino-5-methylpyridine)- $\mu_3$ -phosphonato-zinc],  $[\text{Zn}(\text{HPO}_3)(\text{C}_6\text{H}_8\text{N}_2)]_n$ , (III), and poly[bis(2-amino-4-methylpyridinium) [tetra- $\mu_3$ -phosphonato-trizinc] monohydrate],  $\{(\text{C}_6\text{H}_9\text{N}_2)_2[\text{Zn}_3(\text{HPO}_3)_4] \cdot \text{H}_2\text{O}\}_n$ , (IV). The simple molecular salt bis(2-amino-3-methylpyridinium) tetrachlorozincate monohydrate,  $(\text{C}_6\text{H}_8\text{N}_2)_2 \cdot \text{ZnCl}_4 \cdot \text{H}_2\text{O}$  (V), is also described.



## 2. Structural commentary

The asymmetric unit of (I) (Fig. 1), which crystallizes in the monoclinic space group  $C2/c$ , consists of a  $\text{Zn}^{2+}$  ion, a  $[\text{HPO}_3]^{2-}$  hydrogen phosphite anion, a  $\text{C}_6\text{H}_7\text{N}_2$  2-amino-3-methylpyridine molecule and a water molecule, the O atom of the last species lying on a crystallographic twofold axis. The zinc coordination polyhedron is a  $\text{ZnO}_3\text{N}$  tetrahedron, *i.e.*, the organic species is acting as a ligand bonding to the metal ion from its pyridine nitrogen atom and the  $\text{Zn}-\text{O}$  bonds (mean = 1.940 Å) are notably shorter than the  $\text{Zn1}-\text{N1}$  [2.0262 (14) Å] link, as previously observed for related compounds (Holmes *et al.*, 2018). The spread of bond angles about the metal ion [minimum = 104.23 (5)° for  $\text{O2}-\text{Zn1}-\text{N1}$ , maximum = 113.89 (6)° for  $\text{O1}-\text{Zn1}-\text{N1}$ ] indicates a slight degree of distortion with  $\tau_4' = 0.974$  (Okuniewski *et al.*, 2015). The  $[\text{HPO}_3]^{2-}$  group adopts its usual tetrahedral (including the H atom) or pseudo-pyramidal (excluding H) geometry and the mean  $\text{P}-\text{O}$  separation is 1.522 Å with the  $\text{O}-\text{P}-\text{O}$  bond angles tightly clustered in the range 111.98 (7)–113.57 (7)°; the

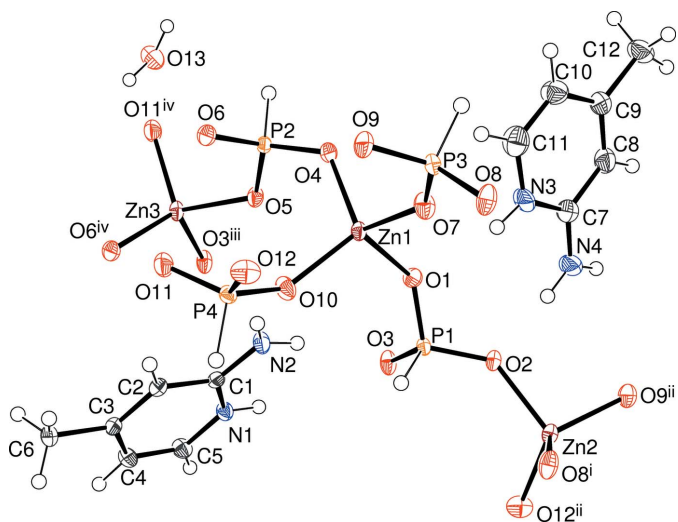




**Figure 3**  
The asymmetric unit of (III) expanded to show the complete zinc-atom coordination sphere showing 50% displacement ellipsoids. Symmetry codes: (i)  $\frac{1}{2} + x, \frac{3}{2} - y, -z$ ; (ii)  $1 + x, y, z$ .

121.28 (5)° and 0.91, respectively; mean P1–O = 1.525 Å; spread of O–P1–O bond angles = 110.64 (6)–113.78 (6)°; P1 displacement from its attached O atoms = 0.4278 (7) Å; comparable data for P2 = 1.520 Å, 111.44 (6)–113.14 (7)° and –0.4269 (8) Å, respectively. All six O atoms are bridging between Zn and P atoms with a mean bond angle of 131.3° [range = 123.26 (6)–144.09 (8)°]. The extended structure of (II) is discussed below.

Compound (III) crystallizes in the orthorhombic space group  $P2_12_12_1$  with a well-defined absolute structure and its asymmetric unit (Fig. 3) consists of a  $Zn^{2+}$  ion, a  $[HPO_3]^{2-}$  hydrogen phosphite anion and a  $C_6H_7N_2$  2-amino-5-methylpyridine molecule bonded to the metal ion from its pyridine N atom. Once again, the constituent polyhedra are  $ZnO_3N$

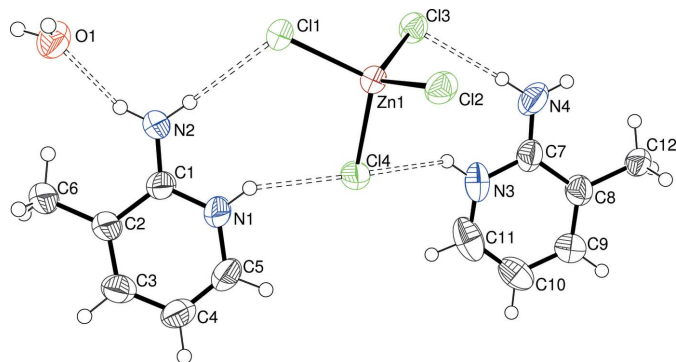


**Figure 4**  
The asymmetric unit of (IV) expanded to show the complete zinc-atom coordination sphere showing 50% displacement ellipsoids. Symmetry codes: (i)  $-x, 1 - y, 1 - z$ ; (ii)  $x - 1, y, z$ ; (iii)  $-x, 1 - y, -z$ ; (iv)  $1 - x, 1 - y, -z$ .

tetrahedra [mean Zn–O = 1.941 Å, minimum and maximum bond angles = 105.19 (9) and 115.09 (8)°, respectively,  $\tau_4' = 0.96$ ] and  $[HPO_3]^{2-}$  units [mean P–O = 1.522 Å, minimum and maximum O–P–O = 110.43 (11) and 113.86 (12)°, respectively, deviation of P1 from O1/O2/O3 = 0.4237 (14) Å]. The three O atoms bridge adjacent zinc and phosphorus atoms with a mean Zn–O–P bond angle of 126.7°. For the extended structure of (III), see below.

In (IV), which crystallizes in the triclinic space group  $P\bar{1}$ , the expanded asymmetric unit (Fig. 4) reveals different constituent polyhedra of three distinct  $ZnO_4$  tetrahedra and four  $[HPO_3]^{2-}$  pseudo pyramids as well as two protonated 2-amino-4-methylpyridinium cations, which therefore act as templates rather than ligands; a water molecule of crystallization (O13) completes the structure. Geometrical data for the zinc polyhedra are as follows: mean Zn1–O = 1.941 Å, spread of bond angles = 100.42 (8)–122.18 (9)°,  $\tau_4' = 0.90$ ; equivalent data for Zn2: 1.936 Å, 98.33 (8)–115.30 (9)° and 0.98, respectively; equivalent data for Zn3: 1.945 Å, 99.70 (8)–117.10 (8)° and 0.96, respectively. The four  $[HPO_3]^{2-}$  anions adopt their normal geometries: mean P1–O = 1.519 Å, minimum and maximum O–P1–O = 111.00 (11) and 112.70 (11)°, respectively, deviation of P1 from its attached O atoms = 0.4498 (13) Å; equivalent data for P2: 1.522 Å, 110.08 (10)°, 115.33 (11)° and –0.4122 (12) Å, respectively; equivalent data for P3: 1.516 Å, 110.19 (11)°, 114.49 (12)° and –0.4123 (13) Å, respectively; equivalent data for P4: 1.516 Å, 112.68 (12)°, 114.13 (12)° and 0.3903 (13) Å, respectively. The twelve unique O atoms all bridge Zn and P atoms (mean bond angle = 134.9, minimum = 125.40 (11), maximum = 146.90 (13), spread = 21.5°). For the extended structure of (IV), see below.

Compound (V) is a simple molecular salt (Fig. 5), which crystallizes in the triclinic space group  $P\bar{1}$ : its asymmetric unit consists of two 2-amino-3-methylpyridinium  $C_6H_8N_2^+$  cations protonated at their pyridine N atoms, a  $[ZnCl_4]^{2-}$  anion and a water molecule of crystallisation. The tetrachlorozincate ion has a mean Zn–Cl separation of 2.2704 Å [range = 2.2536 (13)–2.2867 (13) Å] and smallest and largest Cl–Zn–Cl bond angles of 104.48 (5) and 113.75 (5)°, respectively. The synthetic intent here was to lower the pH with HCl and establish if a dihydrogen phosphite ( $H_2PO_3^-$ ) anion containing a terminal P–OH moiety could be incorporated



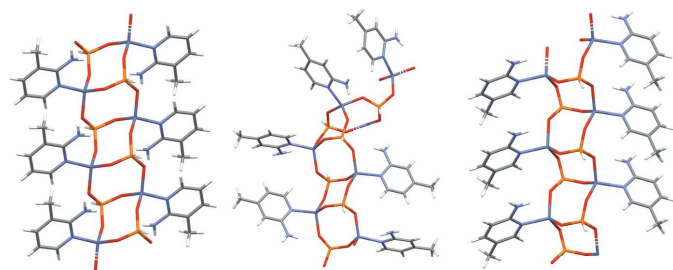
**Figure 5**  
The asymmetric unit of (V) showing 50% displacement ellipsoids. Hydrogen bonds are indicated by double-dashed lines.

into the structure (Lin *et al.*, 2003) but the presence of excess chloride ions has led to a completely different and unwanted molecular salt containing the tetrachlorozincate complex ion, which has been reported many times before, with over 1000 matches in the CSD.

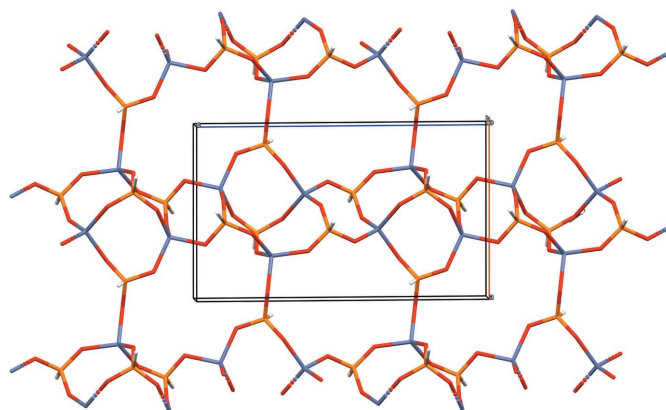
### 3. Supramolecular features

In the extended structure of (I), the constituent  $\text{ZnO}_3\text{N}$  and  $\text{HPO}_3$  polyhedra are linked by  $\text{Zn—O—P}$  bonds into [010] polyhedral 4-ring (two Zn and two P nodes) 'ladder' chains in which the zinc and phosphorus nodes strictly alternate (Fig. 6): the chains are built up by inversion symmetry at the centres of every 4-ring, as well as, of course, translation symmetry in the  $b$ -axis direction. Given that the Zn atom forms three bonds (*via* O atoms) to adjacent P atoms (and a fourth bond to the organic species) and that the P atom forms three links to zinc atoms (and a fourth P—H vertex), the 1:1 Zn:P stoichiometry is to be expected and hence no charge compensating, protonated template is needed. In (II), ladder chains similar to those seen in (I) arise in the extended structure (Fig. 6) although they are more contorted: because  $Z' = 2$ , every other 4-ring is generated by inversion symmetry and translation in the [101] direction leads to the extended array. In (III), the 4-ring ladder motif is again apparent (Fig. 6), although in this case, the combination of a  $2_1$  screw-axis parallel to the chain and  $a$ -translation symmetry generates the infinite [100] chains. In each structure, the organic molecules are pendant to the chains (Fig. 6).

The extended structure of (IV) (Fig. 7) is quite different to those of (I)–(III) and features (010) sheets of  $\text{ZnO}_4$  and  $\text{HPO}_3$  polyhedra sharing corners. One way to visualize this rather complex arrangement (although this does not necessarily imply that the synthesis proceeds in such a step-by-step fashion) is in terms of contorted chains of 4-rings featuring atoms Zn1, Zn2, Zn3, P2, P3 and P4 as the nodes propagating in the [001] direction. One out of every three 4-rings in a chain is generated by inversion symmetry. These chains are cross-linked in the  $a$ -axis direction by the P1-centred hydrogen phosphite groups to form the (010) layers, which encapsulate 8-ring voids built up from four Zn and four P nodes although there is no suggestion of 'zeolitic' porosity. So far as stoichiometry is concerned, in this case the zinc nodes forming



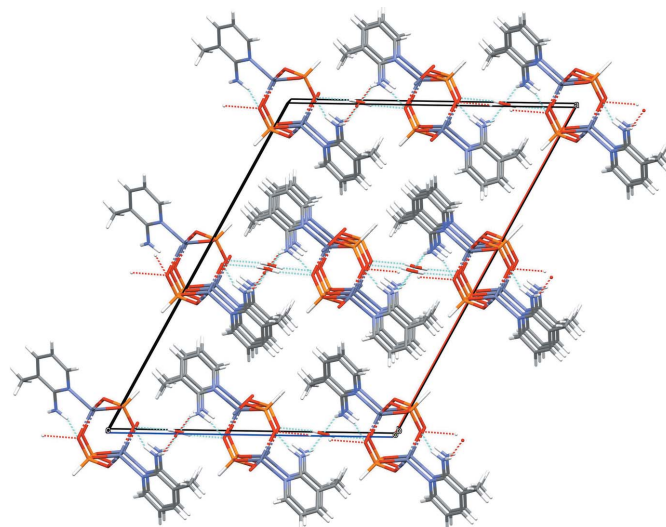
**Figure 6**  
Comparison of the zincophosphate 4-ring ladder chains in the extended structures of (I) (left), (II) (centre) and (III) (right).



**Figure 7**  
Part of an infinite (010) layer of vertex sharing  $\text{ZnO}_4$  and  $\text{HPO}_3$  moieties in the extended structure of (IV) viewed down [010].

four bonds (*via* all their O atoms) to nearby phosphorus atoms and the P nodes forming three bonds to Zn atoms leads to the 3:4 ratio of zinc and phosphorus, which is the proportion most commonly seen in this family of phases (*e.g.*, Phillips *et al.*, 2002; Lin *et al.*, 2009). In this case, the inorganic component bears a charge of  $-2$  per  $[\text{Zn}_3(\text{HPO}_3)_4]$  unit, hence the two protonated template molecules. The template cations and water molecules of crystallisation occupy the inter-layer regions.

Various classical ( $\text{N—H}\cdots\text{O}$ ,  $\text{N—H}\cdots\text{Cl}$  and  $\text{O—H}\cdots\text{O}$ ) and non-classical ( $\text{C—H}\cdots\text{O}$  and  $\text{C—H}\cdots\text{Cl}$ ) hydrogen bonds occur in these structures. As is normal, the hydrogen phosphite P—H unit does not participate in hydrogen bonding (Katinaitė & Harrison, 2017). In (I), the water molecule of crystallization, which lies on a crystallographic twofold axis, appears to play an important role in consolidating the extended structure by accepting two  $\text{N—H}\cdots\text{O}$  hydrogen bonds (Table 1) and donating two  $\text{O—H}\cdots\text{O}$  hydrogen bonds to cross-link the [001] chains into (100) layers (Fig. 8). The



**Figure 8**  
The unit-cell packing in (I) viewed down [001]. Hydrogen bonds are shown as dashed lines.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H1 <i>N</i> ...O4 <sup>i</sup>	0.78 (2)	2.19 (2)	2.919 (2)	157 (2)
N2—H2 <i>N</i> ...O2 <sup>ii</sup>	0.84 (2)	2.54 (2)	3.098 (2)	124.8 (18)
O4—H1 <i>O</i> ...O2	0.79 (2)	2.199 (19)	2.9165 (15)	152 (2)

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

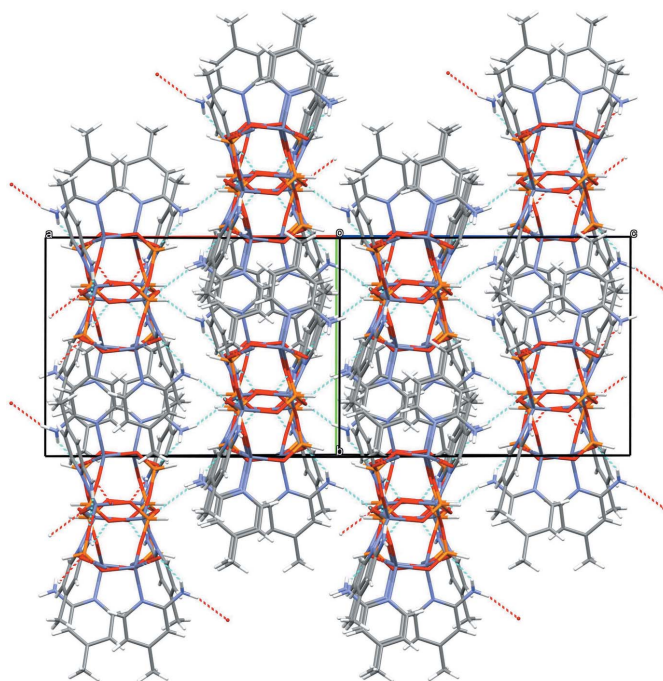
**Table 2**  
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H1 <i>N</i> ...O3 <sup>i</sup>	0.79 (2)	2.35 (2)	2.9056 (19)	128 (2)
N2—H2 <i>N</i> ...O6 <sup>ii</sup>	0.82 (2)	2.13 (2)	2.900 (2)	155 (2)
N4—H3 <i>N</i> ...O1 <sup>iii</sup>	0.88 (2)	2.18 (2)	3.0310 (18)	163.7 (18)
N4—H4 <i>N</i> ...O5 <sup>iv</sup>	0.83 (2)	2.39 (2)	3.1555 (19)	154.3 (18)
C5—H5...O2	0.95	2.57	3.315 (2)	136
C8—H8...O1 <sup>iii</sup>	0.95	2.65	3.405 (2)	137
C11—H11...O4	0.95	2.51	3.105 (2)	120

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $-x + 1, y, -z + \frac{3}{2}$ .

other hydrogen bond arising from the amine group is an intra-chain N—H...O link. There are no aromatic  $\pi$ – $\pi$  stacking interactions in (I), the shortest centroid–centroid separation being some 5.04 Å.

In (II), the N—H...O hydrogen bonds arising from the amine groups are a mix of intra- (*via* H2*N* and H4*N*) and inter-chain (*via* H1*N* and H3*N*) links, with the latter serving to cross-link the [101] chains into a three-dimensional network (Table 2; Fig. 9). The aromatic rings are interdigitated and this is reflected in the shortest centroid–centroid separation of



**Figure 9**  
The unit-cell packing in (II) viewed down [101]. Hydrogen bonds are shown as dashed lines.

**Table 3**  
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2 <i>B</i> ...O2 <sup>i</sup>	0.79 (4)	2.35 (4)	3.111 (3)	162 (3)
C2—H2...O1 <sup>ii</sup>	0.95	2.55	3.212 (3)	127

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

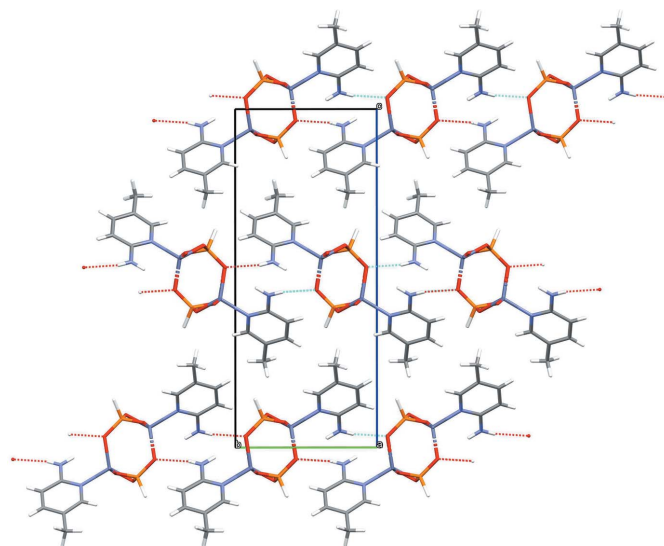
**Table 4**  
Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1 <i>A</i> ...O5 <sup>i</sup>	0.88	1.97	2.833 (3)	166
N2—H2 <i>N</i> ...O3	0.85 (4)	2.05 (4)	2.853 (3)	157 (3)
N2—H3 <i>N</i> ...O10	0.85 (4)	2.16 (4)	2.961 (3)	156 (3)
N3—H4 <i>N</i> ...O1	0.83 (4)	2.07 (4)	2.873 (3)	163 (4)
N4—H5 <i>N</i> ...O13 <sup>ii</sup>	0.93 (4)	1.95 (4)	2.871 (4)	177 (4)
N4—H6 <i>N</i> ...O2	0.88 (4)	2.05 (4)	2.918 (3)	167 (4)
O13—H1 <i>O</i> ...O12 <sup>iii</sup>	0.98	2.05	3.028 (3)	175
O13—H2 <i>O</i> ...O4 <sup>iv</sup>	0.96	2.05	2.952 (3)	157
C5—H5...O4 <sup>i</sup>	0.95	2.64	3.370 (3)	134
C8—H8...O8 <sup>v</sup>	0.95	2.48	3.350 (4)	152
C11—H11...O7	0.95	2.47	3.199 (4)	133
C11—H11...O13 <sup>iv</sup>	0.95	2.59	3.281 (4)	130

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

3.8234 (17) Å. In the extended structure of (III) (Fig. 10), the single N1—H2*B*...O2 bond (Table 3) cross-links the [100] chains into (001) sheets. The other hydrogen atom (H2*A*) of the amine grouping does not participate in a hydrogen bond, the closest acceptor O atom being some 2.77 Å distant. There are no significant  $\pi$ – $\pi$  stacking interactions in (III) [shortest centroid–centroid separation = 5.149 (2) Å].

In (IV), numerous hydrogen bonds are observed (Table 4, Fig. 11). The water molecule cross-links adjacent (010) layers *via* two O—H...O hydrogen bonds. The N—H...O hydrogen bonds originating from the protonated pyridine N atoms and



**Figure 10**  
The unit-cell packing in (III) viewed down [100]. Hydrogen bonds are shown as dashed lines.

**Table 5**  
Hydrogen-bond geometry (Å, °) for (V).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 $\cdots$ Cl4	0.88	2.35	3.134 (5)	148
N2–H2A $\cdots$ Cl1	0.88	2.54	3.375 (4)	158
N2–H2B $\cdots$ O1	0.88	2.03	2.838 (5)	152
N3–H3A $\cdots$ Cl4	0.88	2.66	3.306 (4)	132
N4–H4A $\cdots$ Cl3	0.88	2.40	3.268 (4)	170
N4–H4B $\cdots$ Cl2 <sup>i</sup>	0.88	2.51	3.333 (5)	155
O1–H1O $\cdots$ Cl3 <sup>ii</sup>	0.88	2.95	3.669 (4)	141
O1–H1O $\cdots$ Cl4 <sup>ii</sup>	0.88	2.98	3.675 (4)	138
O1–H2O $\cdots$ Cl1 <sup>iii</sup>	0.88	2.45	3.302 (4)	162
C10–H10 $\cdots$ Cl3 <sup>iv</sup>	0.95	2.92	3.696 (5)	140

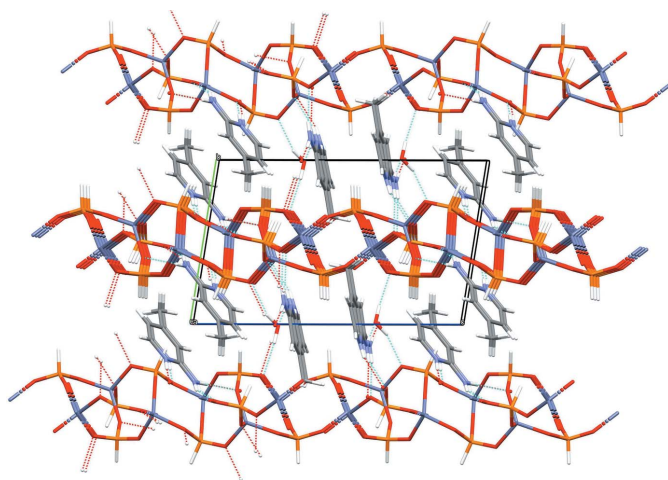
Symmetry codes: (i)  $-x+1, -y+1, -z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $x, y-1, z$ .

the  $-\text{NH}_2$  groups of the organic species all link to the same sheet for each template cation, *i.e.*, there are no inter-sheet hydrogen bonds associated with the templates. Significant aromatic  $\pi$ – $\pi$  stacking interactions occur between centrosymmetric pairs of each template cation, as indicated by the centroid–centroid separation of 3.6167 (15) Å (slippage = 1.196 Å) for the C1 species and 3.4695 (17) Å (0.146 Å) for the C7 cation.

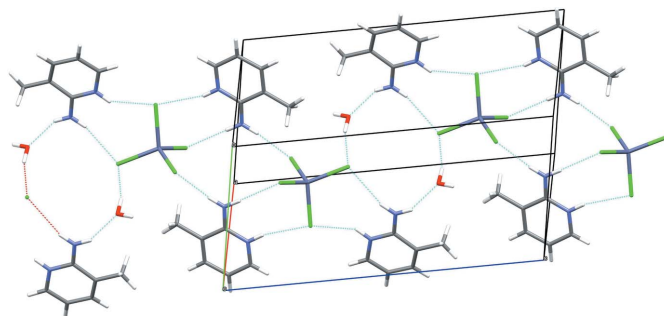
In the extended structure of (V), the hydrogen-bond scheme is completely different (Table 5) and the component cations, anions and water molecules are linked by  $\text{N}-\text{H}\cdots\text{Cl}$ ,  $\text{N}-\text{H}\cdots\text{O}_w$  ( $w$  = water) and  $\text{O}-\text{H}\cdots\text{Cl}$  interactions to generate [001] chains; within these chains, centrosymmetric assemblages of two  $\text{C}_6\text{H}_8\text{N}_2^+$  cations, two  $[\text{ZnCl}_4]^{2-}$  anions and two water molecules are apparent (Fig. 12).

#### 4. Database survey

A survey of the Cambridge Structural Database (Groom *et al.*, 2016; updated to February 2023) revealed 213 crystal structures containing zinc cations and hydrogenphosphite anions ( $\text{Zn}-\text{O}-\text{P}-\text{H}$  fragment) of which 53 contain a ligated



**Figure 11**  
The unit-cell packing in (IV) viewed down [100]. Hydrogen bonds are shown as dashed lines.



**Figure 12**  
The unit-cell packing in (V) viewed approximately down  $[10\bar{1}]$ . Hydrogen bonds are shown as dashed lines.

organic molecule ( $\text{Zn}-\text{N}$  bond). The only phase that bears a close chemical similarity to the structures described here is  $[\text{C}_5\text{H}_6\text{N}_2\text{Zn}(\text{HPO}_3)]_n$ , *catena*- $[(\mu_3\text{-hydrogenphosphito})(2\text{-aminopyridine})\text{zinc}]$  (CSD refcode LUZYUO) (Liang *et al.*, 2003), in which the  $\text{ZnO}_3\text{N}$  and  $\text{HPO}_3$  polyhedra assemble into (100) layers of 4- and 8-rings.

The fact that the N-bonded zinc ions and  $\text{HPO}_3$  units in (I), (II) and (III) self assemble to form the same 4-ring ladder chain with different isomeric pyridine-based ligands suggests that it is a reasonably robust structural feature. However, it is not a particularly common *motif* in the wider ZnPO phase space: two other examples with very different ligating molecules to those in (I)–(III) are  $[\text{C}_4\text{H}_8\text{N}_2\text{O}_3\text{Zn}(\text{HPO}_3)]_n$  ( $\text{C}_4\text{H}_8\text{N}_2\text{O}_3$  = L-asparagine) (Gordon & Harrison, 2004) and  $[\text{C}_3\text{H}_7\text{NO}_2\text{Zn}(\text{HPO}_3)]_n$  ( $\text{C}_3\text{H}_7\text{NO}_2$  = racemic DL-alanine) (Mao *et al.*, 2021); it is notable that these amino acids both bond to the zinc atom *via* one of their carboxylate O atoms rather than the pyridine N atoms in (I)–(III).

Compound (II), in which the  $\text{C}_6\text{H}_8\text{N}_2$  organic molecule acts as a ligand (a  $\text{Zn}-\text{N}$  bond and a 1:1 Zn:P ratio) and (IV), in which the same organic species acts as a protonated  $\text{C}_6\text{H}_9\text{N}_2^+$  template ( $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds and a 3:4 Zn:P ratio) arose from similar syntheses, with the only difference being the source of zinc ions (zinc oxide and zinc acetate, respectively). Assuming that hydrothermal synthesis is not just an impenetrable ‘black box’ (Ursu *et al.*, 2022), we may speculate that the acetate synthesis occurred at a lower pH, perhaps with some buffering action between acetic acid formed *in situ* and acetate ions, to allow for the protonation of the template.

#### 5. Synthesis and crystallization

Compound (I) was prepared by mixing 0.77 g of ZnO, 0.76 g of  $\text{H}_3\text{PO}_3$  and 1.14 g of 2-amino-3-methylpyridine (Zn:P:template ratio  $\approx 1:1:1$ ), which were placed in a 50 ml polypropylene bottle with 20 ml of water and shaken well to result in a white slurry. The bottle was placed in an 353 K oven for 24 h and then removed and allowed to cool to room temperature. The solids were recovered by vacuum filtration to result in a mass of needle-like transparent crystals. IR:  $2383\text{ cm}^{-1}$  (P–H stretch). Increasing the heating time to one

**Table 6**  
Experimental details.

	(I)	(II)	(III)	(IV)	(V)
Crystal data					
Chemical formula	[Zn(HPO <sub>3</sub> )(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> )]·0.5H <sub>2</sub> O	[Zn(HPO <sub>3</sub> )(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> )]	[Zn(HPO <sub>3</sub> )(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> )]	(C <sub>6</sub> H <sub>9</sub> N <sub>2</sub> ) <sub>2</sub> ·[Zn <sub>3</sub> (HPO <sub>3</sub> ) <sub>4</sub> ]·H <sub>2</sub> O	(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> [ZnCl <sub>4</sub> ]·H <sub>2</sub> O
<i>M<sub>r</sub></i>	525.00	253.49	253.49	752.34	443.49
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>	Orthorhombic, <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	93	93	93	93	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.282 (6), 5.1926 (1), 17.738 (5)	22.873 (6), 12.307 (3), 16.633 (4)	5.1487 (9), 8.5316 (19), 20.371 (5)	9.03805 (13), 9.36837 (13), 15.0207 (2)	6.9541 (8), 8.7092 (9), 16.293 (3)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 117.974 (4), 90	90, 128.954 (5), 90	90, 90, 90	81.0313 (1), 88.0646 (1), 80.0782 (1)	83.239 (11), 80.167 (10), 72.049 (9)
<i>V</i> (Å <sup>3</sup> )	1893.9 (7)	3641.1 (16)	894.8 (3)	1237.46 (3)	922.7 (2)
<i>Z</i>	4	16	4	2	2
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Cu <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.75	2.85	2.90	6.49	1.92
Crystal size (mm)	0.20 × 0.02 × 0.02	0.10 × 0.03 × 0.03	0.15 × 0.05 × 0.03	0.10 × 0.10 × 0.10	0.15 × 0.05 × 0.05
Data collection					
Diffractometer	Rigaku Pilatus 200K CCD	Rigaku Pilatus 200K CCD	Rigaku Pilatus 200K CCD	Rigaku Pilatus 200K CCD	AFC10: Fixed Chi 2 circle CCD
Absorption correction	Multi-scan <i>CrystalClear</i> (Rigaku, 2015)	Multi-scan <i>CrystalClear</i> (Rigaku, 2015)	Multi-scan <i>CrystalClear</i> (Rigaku, 2015)	Multi-scan <i>CrystalClear</i> (Rigaku, 2015)	Multi-scan
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.535, 1.000	0.783, 1.000	0.505, 1.000	0.744, 1.000	0.851, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	22221, 1729, 1644	50824, 3308, 3177	13254, 1630, 1599	11869, 4842, 4831	28291, 3383, 3172
<i>R</i> <sub>int</sub>	0.045	0.033	0.067	0.012	0.039
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.602	0.602	0.602	0.628	0.603
Refinement					
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.017, 0.048, 1.04	0.017, 0.049, 1.05	0.021, 0.051, 1.01	0.031, 0.085, 1.10	0.047, 0.111, 1.08
No. of reflections	1729	3308	1630	4842	3383
No. of parameters	133	249	125	343	203
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.27, -0.31	0.30, -0.40	0.59, -0.42	1.25, -0.67	1.10, -1.02
Absolute structure	–	–	Parsons <i>et al.</i> , 2013	–	–
Absolute structure parameter	–	–	0.011 (6)	–	–

Computer programs: *CrystalClear* (Rigaku, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

week led to the same product, with a slight improvement in crystallinity, as indicated by sharper peaks in its IR spectrum and X-ray powder diffraction pattern.

Compound (II) was prepared from 0.75 g of ZnO, 0.81 g of H<sub>3</sub>PO<sub>3</sub> and 1.10 g of 2-amino-4-methylpyridine (Zn:P:template ratio  $\approx$  1:1:1); otherwise following the same procedure as for (I). A mass of blocky transparent crystals was recovered. IR: 2394, 2382 cm<sup>-1</sup> (P–H stretch). Two peaks may arise because of the two different P–H groups in the asymmetric unit (Ma *et al.*, 2007).

To prepare compound (III), 2.20 g of Zn(OAc)<sub>2</sub>, 0.86 g of H<sub>3</sub>PO<sub>3</sub> and 1.09 g of 2-amino-5-methylpyridine (Zn:P:template ratio  $\approx$  1:1:1) and 20 ml of water were placed in a 50 ml polypropylene bottle and heated to 353 K for three days. Upon cooling, the product consisted of a mass of colourless blocks. IR: 2406 cm<sup>-1</sup> (P–H stretch).

Compound (IV) started from a mixture of 2.02 g Zn(OAc)<sub>2</sub>, 0.77 g of H<sub>3</sub>PO<sub>3</sub> and 1.03 g of 2-amino-4-methylpyridine (Zn:P:template ratio  $\approx$  1:1:1) and 20 ml of water. These components were placed in a 50-ml polypropylene bottle and heated to 353 K for 24 h. Upon cooling, the product consisted of a mass of colourless blocks. IR: 3000–3600 (broad) (O–H stretch), 2391, 2381 cm<sup>-1</sup> (P–H stretch). The same product arises if the mixture is heated for one week.

Compound (V) was prepared from the same reagents as (I) and the same synthesis procedure but with the addition of 10 ml of 1 M HCl.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. Most of the O- and N-bound H

atoms were located in difference maps and their positions were freely refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N or O})$ . The phosphite H atoms were geometrically placed ( $\text{P}-\text{H} = 1.32 \text{ \AA}$ ) and refined as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{P})$ . All the C-bound H atoms were located geometrically ( $\text{C}-\text{H} = 0.95\text{--}0.98 \text{ \AA}$ ) and refined as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. Two peaks greater than  $1 \text{ e \AA}^{-3}$  were found in the final difference map for (IV) in the vicinity of the C7 cation but they did not correspond to a plausible chemical feature. The data quality for (V) was notably poorer than for the other four crystals.

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## supporting information

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## Consistent zincophosphite 4-ring 'ladder' chain structural motif with isomeric ligands

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### Computing details

For all structures, data collection: *CrystalClear* (Rigaku, 2015); cell refinement: *CrystalClear* (Rigaku, 2015); data reduction: *CrystalClear* (Rigaku, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008). Program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015) for (I), (II), (III), (IV); *SHELXL-2018/3* (Sheldrick, 2015) for (V). For all structures, molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Poly[[2-amino-3-methylpyridine)- $\mu_3$ -phosphonato-zinc] hemihydrate] (I)

#### Crystal data

[Zn(HPO<sub>3</sub>)(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)]·0.5H<sub>2</sub>O

$M_r = 525.00$

Monoclinic, *C2/c*

$a = 23.282$  (6) Å

$b = 5.1926$  (1) Å

$c = 17.738$  (5) Å

$\beta = 117.974$  (4)°

$V = 1893.9$  (7) Å<sup>3</sup>

$Z = 4$

$F(000) = 1064$

$D_x = 1.841$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2870 reflections

$\theta = 2.6$ – $27.4$ °

$\mu = 2.75$  mm<sup>-1</sup>

$T = 93$  K

Plate, colourless

$0.20 \times 0.02 \times 0.02$  mm

#### Data collection

Rigaku Pilatus 200K CCD  
diffractometer

$\omega$  scans

Absorption correction: multi-scan  
*CrystalClear* (Rigaku, 2015)

$T_{\min} = 0.535$ ,  $T_{\max} = 1.000$

22221 measured reflections

1729 independent reflections

1644 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 25.3$ °,  $\theta_{\min} = 2.0$ °

$h = -28 \rightarrow 28$

$k = -6 \rightarrow 6$

$l = -21 \rightarrow 21$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.048$

$S = 1.04$

1729 reflections

133 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 2.3217P]$

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

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

$\Delta\rho_{\max} = 0.27$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.31$  e Å<sup>-3</sup>

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.57140 (2)	0.80209 (4)	0.58868 (2)	0.01314 (8)
P1	0.57761 (2)	0.29299 (8)	0.49128 (3)	0.01281 (11)
H1	0.623752	0.252550	0.469333	0.015*
O1	0.57635 (6)	0.5813 (2)	0.50423 (8)	0.0230 (3)
O2	0.51441 (6)	0.1968 (2)	0.41659 (7)	0.0201 (3)
O3	0.59745 (6)	0.1434 (2)	0.57337 (7)	0.0202 (3)
C1	0.62119 (8)	0.5143 (3)	0.75510 (10)	0.0155 (3)
C2	0.66659 (8)	0.4595 (3)	0.84181 (10)	0.0178 (4)
C3	0.72325 (8)	0.6005 (4)	0.87796 (10)	0.0210 (4)
H3	0.754671	0.567006	0.935325	0.025*
C4	0.73559 (8)	0.7932 (4)	0.83177 (11)	0.0198 (4)
H4	0.774780	0.890002	0.856994	0.024*
C5	0.68950 (8)	0.8368 (3)	0.74957 (11)	0.0167 (3)
H5	0.697186	0.967793	0.717992	0.020*
C6	0.65085 (10)	0.2538 (4)	0.88920 (12)	0.0232 (4)
H6A	0.609698	0.295572	0.888912	0.035*
H6B	0.685707	0.245000	0.948255	0.035*
H6C	0.646912	0.087146	0.861266	0.035*
N1	0.63290 (7)	0.7007 (3)	0.71073 (9)	0.0146 (3)
N2	0.56459 (7)	0.3842 (3)	0.71611 (10)	0.0198 (3)
H1N	0.5571 (10)	0.268 (4)	0.7377 (14)	0.024*
H2N	0.5404 (10)	0.394 (4)	0.6633 (13)	0.024*
O4	0.500000	0.0486 (4)	0.250000	0.0216 (4)
H1O	0.5071 (11)	0.136 (4)	0.2897 (12)	0.026*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.01503 (12)	0.01152 (13)	0.01196 (12)	0.00098 (7)	0.00558 (9)	0.00153 (7)
P1	0.0145 (2)	0.0111 (2)	0.0136 (2)	0.00076 (16)	0.00731 (18)	0.00110 (15)
O1	0.0414 (8)	0.0122 (7)	0.0254 (6)	0.0024 (6)	0.0239 (6)	0.0024 (5)
O2	0.0155 (6)	0.0297 (8)	0.0135 (6)	0.0022 (5)	0.0056 (5)	-0.0024 (5)
O3	0.0264 (7)	0.0123 (6)	0.0157 (6)	-0.0028 (5)	0.0047 (5)	0.0016 (5)
C1	0.0194 (8)	0.0134 (8)	0.0171 (8)	0.0051 (7)	0.0112 (7)	0.0015 (7)
C2	0.0227 (8)	0.0166 (9)	0.0168 (8)	0.0083 (7)	0.0116 (7)	0.0041 (7)
C3	0.0200 (9)	0.0248 (10)	0.0147 (8)	0.0086 (8)	0.0053 (7)	0.0037 (7)
C4	0.0149 (8)	0.0211 (10)	0.0216 (9)	0.0014 (7)	0.0072 (7)	-0.0008 (7)
C5	0.0162 (8)	0.0160 (9)	0.0196 (8)	0.0016 (7)	0.0100 (7)	0.0018 (7)
C6	0.0305 (10)	0.0227 (10)	0.0192 (9)	0.0071 (8)	0.0141 (8)	0.0073 (7)

N1	0.0149 (7)	0.0145 (8)	0.0142 (7)	0.0019 (5)	0.0067 (6)	0.0023 (5)
N2	0.0213 (8)	0.0189 (8)	0.0189 (7)	-0.0026 (7)	0.0093 (6)	0.0067 (7)
O4	0.0314 (10)	0.0168 (10)	0.0210 (9)	0.000	0.0161 (8)	0.000

*Geometric parameters (Å, °)*

Zn1—O1	1.9324 (12)	C3—C4	1.405 (3)
Zn1—O3 <sup>i</sup>	1.9333 (13)	C3—H3	0.9500
Zn1—O2 <sup>ii</sup>	1.9557 (13)	C4—C5	1.364 (2)
Zn1—N1	2.0262 (14)	C4—H4	0.9500
P1—O1	1.5167 (13)	C5—N1	1.363 (2)
P1—O3	1.5183 (12)	C5—H5	0.9500
P1—O2	1.5301 (13)	C6—H6A	0.9800
P1—H1	1.3200	C6—H6B	0.9800
C1—N2	1.348 (2)	C6—H6C	0.9800
C1—N1	1.353 (2)	N2—H1N	0.78 (2)
C1—C2	1.428 (2)	N2—H2N	0.84 (2)
C2—C3	1.376 (3)	O4—H1O	0.79 (2)
C2—C6	1.507 (2)	O4—H1O <sup>iii</sup>	0.79 (2)
O1—Zn1—O3 <sup>i</sup>	107.36 (5)	C2—C3—H3	119.3
O1—Zn1—O2 <sup>ii</sup>	113.32 (5)	C4—C3—H3	119.3
O3 <sup>i</sup> —Zn1—O2 <sup>ii</sup>	111.79 (5)	C5—C4—C3	117.90 (16)
O1—Zn1—N1	113.89 (6)	C5—C4—H4	121.1
O3 <sup>i</sup> —Zn1—N1	106.10 (5)	C3—C4—H4	121.1
O2 <sup>ii</sup> —Zn1—N1	104.23 (5)	N1—C5—C4	122.92 (16)
O1—P1—O3	112.24 (7)	N1—C5—H5	118.5
O1—P1—O2	111.98 (7)	C4—C5—H5	118.5
O3—P1—O2	113.57 (7)	C2—C6—H6A	109.5
O1—P1—H1	106.1	C2—C6—H6B	109.5
O3—P1—H1	106.1	H6A—C6—H6B	109.5
O2—P1—H1	106.1	C2—C6—H6C	109.5
P1—O1—Zn1	135.67 (7)	H6A—C6—H6C	109.5
P1—O2—Zn1 <sup>ii</sup>	125.89 (7)	H6B—C6—H6C	109.5
P1—O3—Zn1 <sup>iv</sup>	129.00 (7)	C1—N1—C5	119.16 (14)
N2—C1—N1	118.38 (15)	C1—N1—Zn1	124.96 (11)
N2—C1—C2	120.29 (15)	C5—N1—Zn1	115.87 (11)
N1—C1—C2	121.32 (15)	C1—N2—H1N	121.9 (16)
C3—C2—C1	117.33 (15)	C1—N2—H2N	121.7 (14)
C3—C2—C6	123.23 (15)	H1N—N2—H2N	114 (2)
C1—C2—C6	119.44 (16)	H1O—O4—H1O <sup>iii</sup>	109 (3)
C2—C3—C4	121.36 (15)		
O3—P1—O1—Zn1	-19.79 (15)	C1—C2—C3—C4	0.8 (3)
O2—P1—O1—Zn1	109.32 (12)	C6—C2—C3—C4	-179.11 (16)
O1—P1—O2—Zn1 <sup>ii</sup>	-65.88 (11)	C2—C3—C4—C5	0.0 (3)
O3—P1—O2—Zn1 <sup>ii</sup>	62.53 (11)	C3—C4—C5—N1	-0.6 (3)
O1—P1—O3—Zn1 <sup>iv</sup>	148.87 (9)	N2—C1—N1—C5	179.08 (15)

O2—P1—O3—Zn1 <sup>iv</sup>	20.58 (12)	C2—C1—N1—C5	0.6 (2)
N2—C1—C2—C3	-179.58 (16)	N2—C1—N1—Zn1	0.1 (2)
N1—C1—C2—C3	-1.1 (2)	C2—C1—N1—Zn1	-178.42 (11)
N2—C1—C2—C6	0.3 (2)	C4—C5—N1—C1	0.3 (2)
N1—C1—C2—C6	178.77 (15)	C4—C5—N1—Zn1	179.41 (13)

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

#### Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1N $\cdots$ O4 <sup>v</sup>	0.78 (2)	2.19 (2)	2.919 (2)	157 (2)
N2—H2N $\cdots$ O2 <sup>ii</sup>	0.84 (2)	2.54 (2)	3.098 (2)	124.8 (18)
O4—H1O $\cdots$ O2	0.79 (2)	2.199 (19)	2.9165 (15)	152 (2)

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

#### Poly[(2-amino-4-methylpyridine)- $\mu_3$ -phosphonato-zinc] (II)

##### Crystal data

[Zn(HPO<sub>3</sub>)(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)]

$M_r = 253.49$

Monoclinic,  $C2/c$

$a = 22.873$  (6) Å

$b = 12.307$  (3) Å

$c = 16.633$  (4) Å

$\beta = 128.954$  (5)°

$V = 3641.1$  (16) Å<sup>3</sup>

$Z = 16$

$F(000) = 2048$

$D_x = 1.850$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5932 reflections

$\theta = 2.0$ – $27.4$ °

$\mu = 2.85$  mm<sup>-1</sup>

$T = 93$  K

Rod, colourless

$0.10 \times 0.03 \times 0.03$  mm

##### Data collection

Rigaku Pilatus 200K CCD

diffractometer

$\omega$  scans

Absorption correction: multi-scan

CrystalClear (Rigaku, 2015)

$T_{\min} = 0.783$ ,  $T_{\max} = 1.000$

50824 measured reflections

3308 independent reflections

3177 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 25.3$ °,  $\theta_{\min} = 2.0$ °

$h = -27 \rightarrow 27$

$k = -14 \rightarrow 14$

$l = -19 \rightarrow 19$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.049$

$S = 1.05$

3308 reflections

249 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 3.9697P]$

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

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.30$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.40$  e Å<sup>-3</sup>

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.13481 (2)	0.28075 (2)	0.46631 (2)	0.01035 (6)
Zn2	0.38505 (2)	0.50195 (2)	0.68663 (2)	0.01038 (7)
P1	0.30317 (2)	0.28259 (3)	0.65170 (3)	0.01005 (9)
H1	0.342771	0.281106	0.753047	0.012*
P2	0.46680 (2)	0.44040 (3)	0.59502 (3)	0.01048 (9)
H2	0.443210	0.462953	0.501255	0.013*
O1	0.22394 (6)	0.24425 (9)	0.60565 (8)	0.0126 (2)
O2	0.30176 (6)	0.40043 (9)	0.62249 (8)	0.0142 (2)
O3	0.34276 (6)	0.20612 (9)	0.62797 (8)	0.0133 (2)
O4	0.42559 (6)	0.51766 (9)	0.61527 (9)	0.0151 (2)
O5	0.55137 (6)	0.45868 (9)	0.66790 (8)	0.0141 (2)
O6	0.44751 (6)	0.32169 (9)	0.59323 (9)	0.0192 (3)
C1	0.02104 (9)	0.45553 (13)	0.39669 (12)	0.0139 (3)
C2	-0.00238 (9)	0.56244 (13)	0.39473 (12)	0.0159 (3)
H2A	-0.051858	0.585125	0.338516	0.019*
C3	0.04591 (9)	0.63392 (13)	0.47361 (12)	0.0145 (3)
C4	0.11895 (9)	0.59656 (13)	0.55592 (12)	0.0144 (3)
H4	0.153296	0.642415	0.613212	0.017*
C5	0.13951 (9)	0.49351 (12)	0.55196 (12)	0.0127 (3)
H5	0.189116	0.470022	0.606940	0.015*
C6	0.02238 (10)	0.74823 (14)	0.47273 (14)	0.0213 (4)
H6A	0.063327	0.785428	0.536348	0.032*
H6B	-0.022360	0.746660	0.468422	0.032*
H6C	0.010814	0.787141	0.412832	0.032*
N1	0.09243 (7)	0.42276 (10)	0.47310 (10)	0.0120 (3)
N2	-0.02674 (9)	0.38312 (13)	0.32253 (12)	0.0209 (3)
H1N	-0.0668 (13)	0.4006 (18)	0.2726 (17)	0.025*
H2N	-0.0154 (12)	0.318 (2)	0.3279 (16)	0.025*
C7	0.32300 (8)	0.68978 (13)	0.72502 (11)	0.0113 (3)
C8	0.29315 (9)	0.79476 (12)	0.70867 (12)	0.0127 (3)
H8	0.272479	0.816001	0.741065	0.015*
C9	0.29372 (8)	0.86715 (13)	0.64575 (12)	0.0133 (3)
C10	0.32631 (9)	0.83349 (13)	0.60142 (13)	0.0168 (3)
H10	0.329589	0.881946	0.559930	0.020*
C11	0.35344 (10)	0.72937 (13)	0.61886 (13)	0.0160 (3)
H11	0.374707	0.706960	0.587550	0.019*
C12	0.26058 (10)	0.97887 (14)	0.62570 (14)	0.0187 (3)
H12A	0.274259	1.022946	0.590688	0.028*
H12B	0.280148	1.013133	0.691512	0.028*

H12C	0.205714	0.973379	0.581816	0.028*
N3	0.35144 (7)	0.65672 (10)	0.67863 (10)	0.0118 (3)
N4	0.32235 (8)	0.61703 (11)	0.78641 (11)	0.0151 (3)
H3N	0.3081 (11)	0.6407 (16)	0.8213 (15)	0.018*
H4N	0.3543 (12)	0.5680 (17)	0.8129 (15)	0.018*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.01047 (10)	0.00892 (10)	0.01329 (11)	−0.00061 (6)	0.00826 (9)	−0.00141 (6)
Zn2	0.01062 (11)	0.00830 (11)	0.01323 (11)	0.00089 (6)	0.00799 (9)	0.00035 (6)
P1	0.01020 (19)	0.0102 (2)	0.01011 (19)	0.00065 (14)	0.00655 (16)	0.00054 (14)
P2	0.01040 (19)	0.01063 (19)	0.01165 (19)	−0.00079 (14)	0.00753 (16)	−0.00177 (14)
O1	0.0124 (5)	0.0130 (5)	0.0136 (5)	0.0002 (4)	0.0087 (5)	0.0015 (4)
O2	0.0123 (5)	0.0115 (5)	0.0169 (5)	−0.0004 (4)	0.0082 (5)	0.0003 (4)
O3	0.0137 (5)	0.0138 (5)	0.0145 (5)	0.0029 (4)	0.0099 (5)	0.0022 (4)
O4	0.0182 (6)	0.0132 (5)	0.0200 (6)	0.0030 (5)	0.0150 (5)	0.0016 (4)
O5	0.0129 (5)	0.0150 (6)	0.0149 (5)	−0.0029 (4)	0.0089 (5)	−0.0027 (4)
O6	0.0164 (6)	0.0125 (6)	0.0312 (7)	−0.0044 (5)	0.0163 (5)	−0.0061 (5)
C1	0.0135 (7)	0.0160 (8)	0.0144 (7)	0.0000 (6)	0.0098 (7)	−0.0005 (6)
C2	0.0134 (8)	0.0175 (8)	0.0161 (8)	0.0046 (6)	0.0090 (7)	0.0034 (6)
C3	0.0186 (8)	0.0139 (8)	0.0184 (8)	0.0023 (6)	0.0152 (7)	0.0018 (6)
C4	0.0161 (8)	0.0139 (8)	0.0151 (8)	−0.0029 (6)	0.0107 (7)	−0.0036 (6)
C5	0.0099 (7)	0.0149 (8)	0.0126 (8)	−0.0004 (6)	0.0067 (7)	−0.0004 (6)
C6	0.0254 (9)	0.0146 (8)	0.0282 (10)	0.0050 (7)	0.0189 (8)	0.0013 (7)
N1	0.0117 (6)	0.0112 (6)	0.0142 (6)	−0.0001 (5)	0.0087 (6)	−0.0011 (5)
N2	0.0125 (7)	0.0188 (8)	0.0192 (8)	0.0004 (6)	0.0042 (6)	−0.0051 (6)
C7	0.0090 (7)	0.0122 (7)	0.0106 (7)	−0.0013 (6)	0.0052 (6)	−0.0011 (6)
C8	0.0128 (7)	0.0120 (7)	0.0146 (8)	0.0004 (6)	0.0093 (7)	−0.0015 (6)
C9	0.0125 (7)	0.0106 (7)	0.0145 (8)	−0.0010 (6)	0.0074 (6)	−0.0012 (6)
C10	0.0232 (8)	0.0124 (8)	0.0208 (8)	0.0018 (7)	0.0167 (7)	0.0037 (6)
C11	0.0213 (8)	0.0144 (8)	0.0200 (8)	0.0016 (6)	0.0167 (7)	0.0016 (6)
C12	0.0234 (9)	0.0121 (8)	0.0235 (9)	0.0043 (7)	0.0161 (8)	0.0023 (7)
N3	0.0130 (6)	0.0098 (6)	0.0139 (6)	0.0008 (5)	0.0092 (5)	0.0004 (5)
N4	0.0216 (7)	0.0120 (7)	0.0185 (7)	0.0043 (6)	0.0159 (6)	0.0037 (6)

*Geometric parameters (Å, °)*

Zn1—O3 <sup>i</sup>	1.9391 (12)	C4—H4	0.9500
Zn1—O6 <sup>i</sup>	1.9419 (12)	C5—N1	1.365 (2)
Zn1—O1	1.9463 (11)	C5—H5	0.9500
Zn1—N1	2.0358 (13)	C6—H6A	0.9800
Zn2—O4	1.9210 (12)	C6—H6B	0.9800
Zn2—O2	1.9423 (11)	C6—H6C	0.9800
Zn2—O5 <sup>ii</sup>	1.9567 (12)	N2—H1N	0.79 (2)
Zn2—N3	2.0269 (14)	N2—H2N	0.82 (2)
P1—O3	1.5202 (11)	C7—N3	1.347 (2)
P1—O2	1.5234 (12)	C7—N4	1.365 (2)

P1—O1	1.5324 (12)	C7—C8	1.406 (2)
P1—H1	1.3200	C8—C9	1.381 (2)
P2—O4	1.5182 (12)	C8—H8	0.9500
P2—O6	1.5209 (12)	C9—C10	1.401 (2)
P2—O5	1.5211 (12)	C9—C12	1.503 (2)
P2—H2	1.3200	C10—C11	1.373 (2)
C1—N2	1.347 (2)	C10—H10	0.9500
C1—N1	1.355 (2)	C11—N3	1.359 (2)
C1—C2	1.413 (2)	C11—H11	0.9500
C2—C3	1.376 (2)	C12—H12A	0.9800
C2—H2A	0.9500	C12—H12B	0.9800
C3—C4	1.415 (2)	C12—H12C	0.9800
C3—C6	1.503 (2)	N4—H3N	0.88 (2)
C4—C5	1.368 (2)	N4—H4N	0.83 (2)
O3 <sup>i</sup> —Zn1—O6 <sup>i</sup>	107.84 (5)	N1—C5—C4	123.38 (15)
O3 <sup>i</sup> —Zn1—O1	111.75 (5)	N1—C5—H5	118.3
O6 <sup>i</sup> —Zn1—O1	114.29 (5)	C4—C5—H5	118.3
O3 <sup>i</sup> —Zn1—N1	110.52 (5)	C3—C6—H6A	109.5
O6 <sup>i</sup> —Zn1—N1	104.06 (5)	C3—C6—H6B	109.5
O1—Zn1—N1	108.11 (5)	H6A—C6—H6B	109.5
O4—Zn2—O2	114.40 (5)	C3—C6—H6C	109.5
O4—Zn2—O5 <sup>ii</sup>	121.28 (5)	H6A—C6—H6C	109.5
O2—Zn2—O5 <sup>ii</sup>	102.36 (5)	H6B—C6—H6C	109.5
O4—Zn2—N3	100.10 (5)	C1—N1—C5	117.98 (13)
O2—Zn2—N3	111.58 (5)	C1—N1—Zn1	122.59 (11)
O5 <sup>ii</sup> —Zn2—N3	107.05 (5)	C5—N1—Zn1	119.05 (10)
O3—P1—O2	113.78 (6)	C1—N2—H1N	121.4 (16)
O3—P1—O1	112.94 (7)	C1—N2—H2N	121.4 (15)
O2—P1—O1	110.64 (6)	H1N—N2—H2N	117 (2)
O3—P1—H1	106.3	N3—C7—N4	117.81 (14)
O2—P1—H1	106.3	N3—C7—C8	121.16 (14)
O1—P1—H1	106.3	N4—C7—C8	121.02 (14)
O4—P2—O6	113.14 (7)	C9—C8—C7	120.32 (14)
O4—P2—O5	112.73 (7)	C9—C8—H8	119.8
O6—P2—O5	111.44 (6)	C7—C8—H8	119.8
O4—P2—H2	106.3	C8—C9—C10	118.03 (14)
O6—P2—H2	106.3	C8—C9—C12	120.98 (14)
O5—P2—H2	106.3	C10—C9—C12	120.99 (14)
P1—O1—Zn1	123.26 (6)	C11—C10—C9	118.96 (15)
P1—O2—Zn2	128.34 (7)	C11—C10—H10	120.5
P1—O3—Zn1 <sup>i</sup>	131.45 (7)	C9—C10—H10	120.5
P2—O4—Zn2	133.02 (7)	N3—C11—C10	123.37 (15)
P2—O5—Zn2 <sup>ii</sup>	127.58 (7)	N3—C11—H11	118.3
P2—O6—Zn1 <sup>i</sup>	144.09 (8)	C10—C11—H11	118.3
N2—C1—N1	117.88 (15)	C9—C12—H12A	109.5
N2—C1—C2	121.14 (15)	C9—C12—H12B	109.5
N1—C1—C2	120.97 (14)	H12A—C12—H12B	109.5

C3—C2—C1	120.52 (15)	C9—C12—H12C	109.5
C3—C2—H2A	119.7	H12A—C12—H12C	109.5
C1—C2—H2A	119.7	H12B—C12—H12C	109.5
C2—C3—C4	117.82 (15)	C7—N3—C11	118.08 (14)
C2—C3—C6	121.41 (15)	C7—N3—Zn2	123.09 (10)
C4—C3—C6	120.77 (15)	C11—N3—Zn2	118.72 (11)
C5—C4—C3	119.16 (14)	C7—N4—H3N	117.5 (13)
C5—C4—H4	120.4	C7—N4—H4N	117.1 (14)
C3—C4—H4	120.4	H3N—N4—H4N	117.4 (19)
O3—P1—O1—Zn1	-87.69 (9)	N2—C1—N1—C5	-175.71 (14)
O2—P1—O1—Zn1	41.16 (9)	C2—C1—N1—C5	4.6 (2)
O3—P1—O2—Zn2	-69.80 (10)	N2—C1—N1—Zn1	11.4 (2)
O1—P1—O2—Zn2	161.80 (7)	C2—C1—N1—Zn1	-168.38 (11)
O2—P1—O3—Zn1 <sup>i</sup>	-20.85 (11)	C4—C5—N1—C1	-2.1 (2)
O1—P1—O3—Zn1 <sup>i</sup>	106.36 (9)	C4—C5—N1—Zn1	171.05 (12)
O6—P2—O4—Zn2	26.92 (12)	N3—C7—C8—C9	-1.2 (2)
O5—P2—O4—Zn2	-100.68 (10)	N4—C7—C8—C9	-179.53 (15)
O4—P2—O5—Zn2 <sup>ii</sup>	35.10 (11)	C7—C8—C9—C10	-1.5 (2)
O6—P2—O5—Zn2 <sup>ii</sup>	-93.38 (9)	C7—C8—C9—C12	178.71 (14)
O4—P2—O6—Zn1 <sup>i</sup>	51.37 (15)	C8—C9—C10—C11	2.5 (2)
O5—P2—O6—Zn1 <sup>i</sup>	179.64 (11)	C12—C9—C10—C11	-177.66 (15)
N2—C1—C2—C3	176.82 (15)	C9—C10—C11—N3	-1.0 (3)
N1—C1—C2—C3	-3.5 (2)	N4—C7—N3—C11	-178.87 (14)
C1—C2—C3—C4	-0.2 (2)	C8—C7—N3—C11	2.8 (2)
C1—C2—C3—C6	179.55 (15)	N4—C7—N3—Zn2	5.08 (19)
C2—C3—C4—C5	2.6 (2)	C8—C7—N3—Zn2	-173.28 (11)
C6—C3—C4—C5	-177.19 (15)	C10—C11—N3—C7	-1.7 (2)
C3—C4—C5—N1	-1.5 (2)	C10—C11—N3—Zn2	174.54 (13)

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

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1N $\cdots$ O3 <sup>iii</sup>	0.79 (2)	2.35 (2)	2.9056 (19)	128 (2)
N2—H2N $\cdots$ O6 <sup>i</sup>	0.82 (2)	2.13 (2)	2.900 (2)	155 (2)
N4—H3N $\cdots$ O1 <sup>iv</sup>	0.88 (2)	2.18 (2)	3.0310 (18)	163.7 (18)
N4—H4N $\cdots$ O5 <sup>ii</sup>	0.83 (2)	2.39 (2)	3.1555 (19)	154.3 (18)
C5—H5 $\cdots$ O2	0.95	2.57	3.315 (2)	136
C8—H8 $\cdots$ O1 <sup>iv</sup>	0.95	2.65	3.405 (2)	137
C11—H11 $\cdots$ O4	0.95	2.51	3.105 (2)	120

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



Poly[(2-amino-5-methylpyridine)- $\mu_3$ -phosphonato-zinc] (III)

## Crystal data

[Zn(HPO<sub>3</sub>)(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)] $M_r = 253.49$ Orthorhombic,  $P2_12_12_1$  $a = 5.1487$  (9) Å $b = 8.5316$  (19) Å $c = 20.371$  (5) Å $V = 894.8$  (3) Å<sup>3</sup> $Z = 4$  $F(000) = 512$  $D_x = 1.882$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3214 reflections

 $\theta = 2.6$ – $27.5^\circ$  $\mu = 2.90$  mm<sup>-1</sup> $T = 93$  K

Prism, colourless

 $0.15 \times 0.05 \times 0.03$  mm

## Data collection

Rigaku Pilatus 200K CCD  
diffractometer $\omega$  scans

Absorption correction: multi-scan

CrystalClear (Rigaku, 2015)

 $T_{\min} = 0.505$ ,  $T_{\max} = 1.000$ 

13254 measured reflections

1630 independent reflections

1599 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.067$  $\theta_{\max} = 25.3^\circ$ ,  $\theta_{\min} = 2.6^\circ$  $h = -6 \rightarrow 6$  $k = -10 \rightarrow 10$  $l = -23 \rightarrow 24$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.021$  $wR(F^2) = 0.051$  $S = 1.01$ 

1630 reflections

125 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.0724P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.59$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.41$  e Å<sup>-3</sup>Absolute structure: Parsons *et al.*, 2013

Absolute structure parameter: 0.011 (6)

## 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.72989 (7)	0.60753 (3)	0.06019 (2)	0.01077 (13)
P1	0.23596 (17)	0.80347 (7)	0.08606 (3)	0.01135 (19)
H1	0.143314	0.860290	0.141598	0.014*
O1	0.5244 (4)	0.7749 (2)	0.09764 (10)	0.0133 (5)
O2	0.1793 (4)	0.9268 (2)	0.03353 (10)	0.0133 (4)
O3	0.0960 (4)	0.6496 (2)	0.07460 (10)	0.0163 (5)
C1	0.7698 (7)	0.2687 (3)	0.09670 (13)	0.0125 (6)
C2	0.6882 (6)	0.1306 (3)	0.12868 (15)	0.0159 (7)
H2	0.762594	0.032284	0.117423	0.019*
C3	0.5011 (7)	0.1398 (3)	0.17599 (15)	0.0152 (6)

H3	0.447008	0.046999	0.197875	0.018*
C4	0.3865 (6)	0.2842 (3)	0.19301 (14)	0.0141 (6)
C5	0.4702 (6)	0.4120 (3)	0.15785 (14)	0.0136 (6)
H5	0.393376	0.510660	0.167355	0.016*
C6	0.1796 (6)	0.2972 (3)	0.24478 (15)	0.0181 (7)
H6A	0.040112	0.222380	0.235356	0.027*
H6B	0.108871	0.403897	0.244860	0.027*
H6C	0.254815	0.274000	0.287887	0.027*
N1	0.6561 (5)	0.4067 (3)	0.11026 (11)	0.0116 (5)
N2	0.9566 (5)	0.2636 (3)	0.04934 (13)	0.0168 (6)
H2A	1.056 (7)	0.350 (4)	0.0429 (17)	0.020*
H2B	1.045 (7)	0.189 (5)	0.0452 (17)	0.020*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.01207 (19)	0.0079 (2)	0.0123 (2)	-0.00022 (13)	-0.00027 (14)	0.00120 (10)
P1	0.0124 (4)	0.0098 (3)	0.0119 (4)	0.0014 (3)	-0.0003 (3)	0.0005 (3)
O1	0.0133 (11)	0.0114 (9)	0.0152 (11)	-0.0001 (9)	-0.0013 (9)	-0.0003 (8)
O2	0.0180 (11)	0.0108 (9)	0.0111 (10)	0.0021 (8)	-0.0004 (9)	0.0009 (8)
O3	0.0123 (11)	0.0137 (10)	0.0228 (11)	-0.0010 (8)	-0.0035 (10)	0.0024 (8)
C1	0.0160 (16)	0.0131 (12)	0.0085 (14)	-0.0009 (13)	-0.0046 (14)	-0.0004 (10)
C2	0.0206 (17)	0.0096 (13)	0.0175 (16)	0.0003 (12)	-0.0030 (14)	-0.0005 (11)
C3	0.0218 (15)	0.0101 (13)	0.0139 (15)	-0.0035 (12)	-0.0042 (13)	0.0033 (11)
C4	0.0159 (15)	0.0137 (14)	0.0128 (16)	-0.0024 (12)	-0.0036 (14)	0.0018 (11)
C5	0.0149 (15)	0.0108 (13)	0.0152 (16)	0.0008 (13)	-0.0022 (12)	-0.0020 (12)
C6	0.0184 (16)	0.0204 (15)	0.0156 (17)	-0.0026 (13)	0.0016 (13)	0.0014 (12)
N1	0.0151 (13)	0.0097 (10)	0.0101 (12)	0.0003 (10)	-0.0004 (10)	0.0006 (9)
N2	0.0190 (15)	0.0110 (13)	0.0205 (15)	0.0040 (11)	0.0026 (12)	-0.0010 (11)

*Geometric parameters (Å, °)*

Zn1—O1	1.9343 (19)	C2—H2	0.9500
Zn1—O3 <sup>i</sup>	1.941 (2)	C3—C4	1.409 (4)
Zn1—O2 <sup>ii</sup>	1.949 (2)	C3—H3	0.9500
Zn1—N1	2.030 (2)	C4—C5	1.374 (4)
P1—O3	1.515 (2)	C4—C6	1.503 (4)
P1—O1	1.523 (2)	C5—N1	1.363 (4)
P1—O2	1.529 (2)	C5—H5	0.9500
P1—H1	1.3200	C6—H6A	0.9800
C1—N1	1.344 (3)	C6—H6B	0.9800
C1—N2	1.363 (4)	C6—H6C	0.9800
C1—C2	1.411 (4)	N2—H2A	0.90 (4)
C2—C3	1.365 (5)	N2—H2B	0.79 (4)
O1—Zn1—O3 <sup>i</sup>	109.56 (9)	C2—C3—C4	121.3 (3)
O1—Zn1—O2 <sup>ii</sup>	115.09 (8)	C2—C3—H3	119.4
O3 <sup>i</sup> —Zn1—O2 <sup>ii</sup>	107.80 (9)	C4—C3—H3	119.4

O1—Zn1—N1	108.82 (9)	C5—C4—C3	115.8 (3)
O3 <sup>i</sup> —Zn1—N1	105.19 (9)	C5—C4—C6	121.9 (3)
O2 <sup>ii</sup> —Zn1—N1	109.90 (8)	C3—C4—C6	122.3 (3)
O3—P1—O1	110.43 (11)	N1—C5—C4	124.4 (3)
O3—P1—O2	113.41 (12)	N1—C5—H5	117.8
O1—P1—O2	113.86 (12)	C4—C5—H5	117.8
O3—P1—H1	106.2	C4—C6—H6A	109.5
O1—P1—H1	106.2	C4—C6—H6B	109.5
O2—P1—H1	106.2	H6A—C6—H6B	109.5
P1—O1—Zn1	126.17 (12)	C4—C6—H6C	109.5
P1—O2—Zn1 <sup>iii</sup>	123.84 (11)	H6A—C6—H6C	109.5
P1—O3—Zn1 <sup>iv</sup>	130.19 (13)	H6B—C6—H6C	109.5
N1—C1—N2	118.8 (2)	C1—N1—C5	118.8 (2)
N1—C1—C2	120.5 (3)	C1—N1—Zn1	123.69 (19)
N2—C1—C2	120.7 (2)	C5—N1—Zn1	117.45 (18)
C3—C2—C1	119.2 (3)	C1—N2—H2A	118 (2)
C3—C2—H2	120.4	C1—N2—H2B	121 (3)
C1—C2—H2	120.4	H2A—N2—H2B	108 (3)
O3—P1—O1—Zn1	31.32 (19)	C2—C3—C4—C6	179.8 (3)
O2—P1—O1—Zn1	-97.61 (15)	C3—C4—C5—N1	-1.6 (4)
O3—P1—O2—Zn1 <sup>iii</sup>	-54.86 (18)	C6—C4—C5—N1	-179.7 (3)
O1—P1—O2—Zn1 <sup>iii</sup>	72.54 (16)	N2—C1—N1—C5	-179.7 (3)
O1—P1—O3—Zn1 <sup>iv</sup>	177.67 (14)	C2—C1—N1—C5	3.4 (4)
O2—P1—O3—Zn1 <sup>iv</sup>	-53.2 (2)	N2—C1—N1—Zn1	4.0 (4)
N1—C1—C2—C3	-3.3 (5)	C2—C1—N1—Zn1	-172.9 (2)
N2—C1—C2—C3	179.9 (3)	C4—C5—N1—C1	-0.9 (4)
C1—C2—C3—C4	0.6 (5)	C4—C5—N1—Zn1	175.6 (2)
C2—C3—C4—C5	1.7 (5)		

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2B $\cdots$ O2 <sup>v</sup>	0.79 (4)	2.35 (4)	3.111 (3)	162 (3)
C2—H2 $\cdots$ O1 <sup>vi</sup>	0.95	2.55	3.212 (3)	127

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

#### Poly[bis(2-amino-4-methylpyridinium) [tetra- $\mu_3$ -phosphonato-trizinc] monohydrate] (IV)

##### Crystal data

$(C_6H_9N_2)_2[Zn_3(HPO_3)_4]\cdot H_2O$

$M_r = 752.34$

Triclinic,  $P\bar{1}$

$a = 9.03805$  (13)  $\text{\AA}$

$b = 9.36837$  (13)  $\text{\AA}$

$c = 15.0207$  (2)  $\text{\AA}$

$\alpha = 81.0313$  (1) $^\circ$

$\beta = 88.0646$  (1) $^\circ$

$\gamma = 80.0782$  (1) $^\circ$

$V = 1237.46$  (3)  $\text{\AA}^3$

$Z = 2$

$F(000) = 756$

$D_x = 2.019$   $\text{Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$   $\text{\AA}$

Cell parameters from 10623 reflections

$\theta = 5.7\text{--}75.3^\circ$

$\mu = 6.49 \text{ mm}^{-1}$   
 $T = 93 \text{ K}$

Prism, colourless  
 $0.10 \times 0.10 \times 0.10 \text{ mm}$

*Data collection*

Rigaku Pilatus 200K CCD  
 diffractometer  
 Radiation source: fine-focus sealed X-ray tube  
 Graphite monochromator  
 $\omega$  scans  
 Absorption correction: multi-scan  
 CrystalClear (Rigaku, 2015)  
 $T_{\min} = 0.744$ ,  $T_{\max} = 1.000$

11869 measured reflections  
 4842 independent reflections  
 4831 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.012$   
 $\theta_{\max} = 75.4^\circ$ ,  $\theta_{\min} = 3.0^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -11 \rightarrow 11$   
 $l = -18 \rightarrow 18$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.085$   
 $S = 1.10$   
 4842 reflections  
 343 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods  
 Hydrogen site location: mixed

H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 2.3807P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.25 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{Å}^{-3}$   
 Extinction correction: SHELXL-2018/3  
 (Sheldrick 2015),  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0053 (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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{Å}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.24743 (4)	0.40103 (4)	0.26283 (2)	0.01319 (11)
Zn2	-0.39686 (4)	0.53650 (4)	0.37317 (2)	0.01450 (11)
Zn3	0.36057 (4)	0.44962 (4)	-0.08606 (2)	0.01489 (11)
P1	-0.11180 (7)	0.49421 (7)	0.23815 (4)	0.01223 (14)
H1	-0.085208	0.618572	0.259906	0.015*
O1	0.0349 (2)	0.3858 (2)	0.24886 (13)	0.0181 (4)
O2	-0.2305 (2)	0.4425 (2)	0.30286 (13)	0.0194 (4)
O3	-0.1634 (2)	0.5258 (2)	0.14074 (12)	0.0198 (4)
P2	0.43840 (7)	0.28650 (7)	0.10450 (4)	0.01276 (14)
H2	0.489858	0.157007	0.080888	0.015*
O4	0.3711 (2)	0.2551 (2)	0.19875 (12)	0.0175 (4)
O5	0.3142 (2)	0.3593 (2)	0.03697 (12)	0.0172 (4)
O6	0.5709 (2)	0.3653 (2)	0.09860 (13)	0.0196 (4)
P3	0.39182 (7)	0.30396 (7)	0.46061 (4)	0.01410 (15)
H3	0.431225	0.160024	0.476842	0.017*
O7	0.2721 (2)	0.3341 (2)	0.38856 (12)	0.0223 (4)
O8	0.3247 (2)	0.3488 (2)	0.54810 (12)	0.0219 (4)

O9	0.5344 (2)	0.3632 (2)	0.43166 (14)	0.0248 (4)
P4	0.38437 (7)	0.69938 (7)	0.20856 (4)	0.01361 (15)
H4	0.303842	0.832430	0.198557	0.016*
O10	0.2702 (2)	0.5969 (2)	0.20914 (14)	0.0220 (4)
O11	0.4872 (2)	0.6985 (2)	0.12705 (13)	0.0237 (4)
O12	0.4649 (2)	0.6836 (2)	0.29693 (13)	0.0240 (4)
C1	0.0589 (3)	0.7635 (3)	-0.01704 (17)	0.0150 (5)
C2	0.1635 (3)	0.8612 (3)	-0.03501 (17)	0.0162 (5)
H2A	0.251603	0.845508	0.000413	0.019*
C3	0.1385 (3)	0.9781 (3)	-0.10321 (18)	0.0171 (5)
C4	0.0059 (3)	0.9998 (3)	-0.15470 (18)	0.0205 (5)
H4A	-0.014596	1.081128	-0.201535	0.025*
C5	-0.0916 (3)	0.9041 (3)	-0.13684 (18)	0.0199 (5)
H5	-0.179518	0.917499	-0.172217	0.024*
C6	0.2478 (3)	1.0834 (3)	-0.1230 (2)	0.0228 (6)
H6A	0.193054	1.184235	-0.129661	0.034*
H6B	0.302513	1.067140	-0.178991	0.034*
H6C	0.319166	1.067367	-0.073283	0.034*
N1	-0.0650 (2)	0.7888 (2)	-0.06862 (15)	0.0170 (4)
H1A	-0.130665	0.728796	-0.057878	0.020*
N2	0.0770 (3)	0.6485 (3)	0.04803 (16)	0.0198 (5)
H2N	0.008 (4)	0.598 (4)	0.063 (2)	0.024*
H3N	0.152 (4)	0.637 (4)	0.083 (3)	0.024*
C7	-0.1126 (4)	0.0499 (3)	0.3638 (2)	0.0293 (6)
C8	-0.0951 (4)	-0.1046 (3)	0.3921 (2)	0.0298 (7)
H8	-0.178225	-0.153971	0.391019	0.036*
C9	0.0422 (4)	-0.1811 (3)	0.4206 (2)	0.0269 (6)
C10	0.1682 (4)	-0.1098 (4)	0.4158 (2)	0.0312 (7)
H10	0.264069	-0.162712	0.434784	0.037*
C11	0.1501 (4)	0.0345 (4)	0.3839 (2)	0.0357 (7)
H11	0.235379	0.082043	0.376766	0.043*
C12	0.0592 (4)	-0.3416 (3)	0.4520 (2)	0.0320 (7)
H12A	0.094069	-0.363281	0.514548	0.048*
H12B	0.132633	-0.393645	0.413711	0.048*
H12C	-0.037868	-0.373520	0.448605	0.048*
N3	0.0130 (3)	0.1129 (3)	0.3619 (2)	0.0287 (6)
H4N	0.011 (5)	0.199 (5)	0.338 (3)	0.034*
N4	-0.2409 (3)	0.1292 (3)	0.3372 (2)	0.0290 (6)
H5N	-0.321 (5)	0.081 (5)	0.333 (3)	0.035*
H6N	-0.249 (5)	0.225 (5)	0.321 (3)	0.035*
O13	0.4957 (3)	0.0103 (2)	-0.32132 (16)	0.0327 (5)
H1O	0.511797	0.109711	-0.317211	0.039*
H2O	0.552497	-0.056389	-0.275011	0.039*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.01172 (17)	0.01579 (18)	0.01205 (17)	-0.00462 (13)	-0.00061 (12)	0.00056 (12)

Zn2	0.01256 (18)	0.01957 (19)	0.01204 (17)	-0.00494 (13)	0.00048 (12)	-0.00209 (13)
Zn3	0.01393 (18)	0.01878 (19)	0.01254 (17)	-0.00717 (13)	-0.00082 (12)	0.00086 (13)
P1	0.0117 (3)	0.0135 (3)	0.0114 (3)	-0.0041 (2)	-0.0004 (2)	0.0008 (2)
O1	0.0112 (8)	0.0185 (9)	0.0246 (9)	-0.0046 (7)	-0.0014 (7)	-0.0009 (7)
O2	0.0194 (9)	0.0190 (9)	0.0189 (9)	-0.0047 (7)	0.0076 (7)	-0.0003 (7)
O3	0.0169 (9)	0.0286 (10)	0.0140 (9)	-0.0101 (8)	-0.0033 (7)	0.0039 (7)
P2	0.0117 (3)	0.0135 (3)	0.0128 (3)	-0.0031 (2)	0.0008 (2)	-0.0003 (2)
O4	0.0191 (9)	0.0186 (9)	0.0130 (8)	-0.0021 (7)	0.0018 (7)	0.0016 (7)
O5	0.0139 (8)	0.0230 (9)	0.0137 (8)	-0.0048 (7)	-0.0006 (7)	0.0018 (7)
O6	0.0141 (9)	0.0189 (9)	0.0264 (10)	-0.0062 (7)	-0.0004 (7)	-0.0012 (7)
P3	0.0157 (3)	0.0147 (3)	0.0121 (3)	-0.0053 (2)	0.0006 (2)	0.0002 (2)
O7	0.0250 (10)	0.0290 (10)	0.0132 (9)	-0.0081 (8)	-0.0028 (7)	0.0005 (7)
O8	0.0223 (10)	0.0330 (11)	0.0144 (9)	-0.0137 (8)	0.0026 (7)	-0.0065 (8)
O9	0.0196 (10)	0.0237 (10)	0.0314 (11)	-0.0089 (8)	0.0077 (8)	-0.0005 (8)
P4	0.0127 (3)	0.0129 (3)	0.0149 (3)	-0.0027 (2)	-0.0015 (2)	-0.0002 (2)
O10	0.0180 (9)	0.0197 (10)	0.0285 (10)	-0.0089 (8)	-0.0042 (8)	0.0031 (8)
O11	0.0281 (10)	0.0206 (10)	0.0220 (10)	-0.0060 (8)	0.0082 (8)	-0.0013 (8)
O12	0.0259 (10)	0.0257 (10)	0.0202 (10)	0.0003 (8)	-0.0084 (8)	-0.0062 (8)
C1	0.0140 (11)	0.0154 (12)	0.0148 (11)	-0.0006 (9)	0.0019 (9)	-0.0026 (9)
C2	0.0130 (11)	0.0180 (12)	0.0177 (12)	-0.0025 (10)	0.0006 (9)	-0.0031 (10)
C3	0.0159 (12)	0.0154 (12)	0.0200 (12)	-0.0032 (10)	0.0049 (10)	-0.0034 (10)
C4	0.0234 (14)	0.0173 (13)	0.0189 (12)	-0.0024 (11)	-0.0004 (10)	0.0021 (10)
C5	0.0186 (13)	0.0200 (13)	0.0201 (13)	-0.0027 (10)	-0.0053 (10)	0.0002 (10)
C6	0.0184 (13)	0.0176 (13)	0.0320 (15)	-0.0065 (11)	0.0049 (11)	0.0002 (11)
N1	0.0153 (10)	0.0165 (11)	0.0196 (11)	-0.0053 (8)	-0.0007 (8)	-0.0007 (8)
N2	0.0174 (11)	0.0223 (12)	0.0190 (11)	-0.0069 (9)	-0.0011 (9)	0.0038 (9)
C7	0.0239 (15)	0.0257 (15)	0.0362 (17)	-0.0043 (12)	0.0044 (12)	0.0008 (12)
C8	0.0315 (16)	0.0264 (15)	0.0319 (16)	-0.0093 (13)	0.0069 (13)	-0.0021 (12)
C9	0.0274 (15)	0.0214 (14)	0.0311 (15)	-0.0061 (12)	0.0042 (12)	-0.0005 (11)
C10	0.0245 (15)	0.0275 (16)	0.0416 (18)	-0.0047 (12)	-0.0027 (13)	-0.0046 (13)
C11	0.0346 (18)	0.0373 (18)	0.0385 (18)	-0.0144 (15)	0.0015 (14)	-0.0074 (14)
C12	0.0360 (17)	0.0199 (15)	0.0385 (17)	-0.0029 (13)	-0.0012 (14)	-0.0008 (12)
N3	0.0274 (13)	0.0162 (12)	0.0421 (15)	-0.0099 (10)	0.0027 (11)	0.0031 (11)
N4	0.0247 (13)	0.0191 (13)	0.0415 (15)	-0.0042 (10)	0.0023 (11)	0.0010 (11)
O13	0.0342 (12)	0.0281 (11)	0.0355 (12)	-0.0088 (10)	-0.0085 (10)	0.0016 (9)

*Geometric parameters (Å, °)*

Zn1—O7	1.9028 (19)	C2—H2A	0.9500
Zn1—O10	1.9283 (19)	C3—C4	1.416 (4)
Zn1—O4	1.9637 (19)	C3—C6	1.504 (4)
Zn1—O1	1.9710 (18)	C4—C5	1.354 (4)
Zn2—O9 <sup>i</sup>	1.913 (2)	C4—H4A	0.9500
Zn2—O8 <sup>ii</sup>	1.9154 (19)	C5—N1	1.363 (3)
Zn2—O12 <sup>i</sup>	1.945 (2)	C5—H5	0.9500
Zn2—O2	1.9690 (19)	C6—H6A	0.9800
Zn3—O6 <sup>iii</sup>	1.9202 (19)	C6—H6B	0.9800
Zn3—O11 <sup>iii</sup>	1.936 (2)	C6—H6C	0.9800

Zn3—O3 <sup>iv</sup>	1.9499 (18)	N1—H1A	0.8800
Zn3—O5	1.9720 (18)	N2—H2N	0.85 (4)
P1—O2	1.5142 (18)	N2—H3N	0.85 (4)
P1—O3	1.5196 (18)	C7—N4	1.304 (4)
P1—O1	1.5217 (19)	C7—N3	1.364 (4)
P1—H1	1.3200	C7—C8	1.426 (4)
P2—O6	1.5043 (19)	C8—C9	1.368 (5)
P2—O4	1.5279 (18)	C8—H8	0.9500
P2—O5	1.5333 (18)	C9—C10	1.411 (4)
P2—H2	1.3200	C9—C12	1.486 (4)
P3—O9	1.514 (2)	C10—C11	1.346 (5)
P3—O7	1.517 (2)	C10—H10	0.9500
P3—O8	1.5172 (19)	C11—N3	1.350 (4)
P3—H3	1.3200	C11—H11	0.9500
P4—O12	1.5103 (19)	C12—H12A	0.9800
P4—O11	1.512 (2)	C12—H12B	0.9800
P4—O10	1.5247 (19)	C12—H12C	0.9800
P4—H4	1.3200	N3—H4N	0.83 (4)
C1—N2	1.329 (3)	N4—H5N	0.93 (4)
C1—N1	1.349 (3)	N4—H6N	0.88 (4)
C1—C2	1.417 (4)	O13—H1O	0.9780
C2—C3	1.372 (4)	O13—H2O	0.9570
O7—Zn1—O10	122.18 (9)	N2—C1—C2	123.2 (2)
O7—Zn1—O4	107.57 (8)	N1—C1—C2	118.3 (2)
O10—Zn1—O4	110.71 (8)	C3—C2—C1	120.4 (2)
O7—Zn1—O1	100.42 (8)	C3—C2—H2A	119.8
O10—Zn1—O1	106.69 (8)	C1—C2—H2A	119.8
O4—Zn1—O1	108.12 (8)	C2—C3—C4	118.8 (2)
O9 <sup>i</sup> —Zn2—O8 <sup>ii</sup>	115.30 (9)	C2—C3—C6	121.2 (2)
O9 <sup>i</sup> —Zn2—O12 <sup>i</sup>	118.93 (9)	C4—C3—C6	120.0 (2)
O8 <sup>ii</sup> —Zn2—O12 <sup>i</sup>	102.04 (9)	C5—C4—C3	119.7 (2)
O9 <sup>i</sup> —Zn2—O2	98.33 (8)	C5—C4—H4A	120.2
O8 <sup>ii</sup> —Zn2—O2	110.78 (8)	C3—C4—H4A	120.2
O12 <sup>i</sup> —Zn2—O2	111.74 (8)	C4—C5—N1	120.7 (2)
O6 <sup>iii</sup> —Zn3—O11 <sup>iii</sup>	110.85 (8)	C4—C5—H5	119.7
O6 <sup>iii</sup> —Zn3—O3 <sup>iv</sup>	110.21 (8)	N1—C5—H5	119.7
O11 <sup>iii</sup> —Zn3—O3 <sup>iv</sup>	115.57 (9)	C3—C6—H6A	109.5
O6 <sup>iii</sup> —Zn3—O5	117.10 (8)	C3—C6—H6B	109.5
O11 <sup>iii</sup> —Zn3—O5	103.07 (8)	H6A—C6—H6B	109.5
O3 <sup>iv</sup> —Zn3—O5	99.70 (8)	C3—C6—H6C	109.5
O2—P1—O3	112.70 (11)	H6A—C6—H6C	109.5
O2—P1—O1	111.00 (11)	H6B—C6—H6C	109.5
O3—P1—O1	111.15 (11)	C1—N1—C5	122.1 (2)
O2—P1—H1	107.2	C1—N1—H1A	118.9
O3—P1—H1	107.2	C5—N1—H1A	118.9
O1—P1—H1	107.2	C1—N2—H2N	122 (2)
P1—O1—Zn1	135.03 (12)	C1—N2—H3N	118 (2)

P1—O2—Zn2	135.93 (12)	H2N—N2—H3N	119 (3)
P1—O3—Zn3 <sup>iv</sup>	132.51 (12)	N4—C7—N3	120.2 (3)
O6—P2—O4	115.33 (11)	N4—C7—C8	122.4 (3)
O6—P2—O5	113.41 (11)	N3—C7—C8	117.3 (3)
O4—P2—O5	110.08 (10)	C9—C8—C7	119.6 (3)
O6—P2—H2	105.7	C9—C8—H8	120.2
O4—P2—H2	105.7	C7—C8—H8	120.2
O5—P2—H2	105.7	C8—C9—C10	120.2 (3)
P2—O4—Zn1	125.40 (11)	C8—C9—C12	119.5 (3)
P2—O5—Zn3	121.78 (11)	C10—C9—C12	120.2 (3)
P2—O6—Zn3 <sup>iii</sup>	146.90 (13)	C11—C10—C9	118.8 (3)
O9—P3—O7	114.49 (12)	C11—C10—H10	120.6
O9—P3—O8	113.97 (12)	C9—C10—H10	120.6
O7—P3—O8	110.19 (11)	C10—C11—N3	121.3 (3)
O9—P3—H3	105.8	C10—C11—H11	119.4
O7—P3—H3	105.8	N3—C11—H11	119.4
O8—P3—H3	105.8	C9—C12—H12A	109.5
P3—O7—Zn1	140.37 (13)	C9—C12—H12B	109.5
P3—O8—Zn2 <sup>ii</sup>	129.47 (12)	H12A—C12—H12B	109.5
P3—O9—Zn2 <sup>v</sup>	141.65 (14)	C9—C12—H12C	109.5
O12—P4—O11	114.13 (12)	H12A—C12—H12C	109.5
O12—P4—O10	114.03 (12)	H12B—C12—H12C	109.5
O11—P4—O10	112.68 (12)	C11—N3—C7	122.5 (3)
O12—P4—H4	104.9	C11—N3—H4N	116 (3)
O11—P4—H4	104.9	C7—N3—H4N	121 (3)
O10—P4—H4	104.9	C7—N4—H5N	118 (3)
P4—O10—Zn1	138.13 (12)	C7—N4—H6N	121 (3)
P4—O11—Zn3 <sup>iii</sup>	133.31 (12)	H5N—N4—H6N	122 (4)
P4—O12—Zn2 <sup>v</sup>	138.52 (13)	H1O—O13—H2O	108.6
N2—C1—N1	118.5 (2)		
O2—P1—O1—Zn1	-131.13 (16)	O11—P4—O12—Zn2 <sup>v</sup>	-67.0 (2)
O3—P1—O1—Zn1	102.59 (17)	O10—P4—O12—Zn2 <sup>v</sup>	64.4 (2)
O3—P1—O2—Zn2	-89.87 (19)	N2—C1—C2—C3	180.0 (2)
O1—P1—O2—Zn2	144.71 (16)	N1—C1—C2—C3	0.1 (4)
O2—P1—O3—Zn3 <sup>iv</sup>	14.2 (2)	C1—C2—C3—C4	0.4 (4)
O1—P1—O3—Zn3 <sup>iv</sup>	139.51 (15)	C1—C2—C3—C6	179.7 (2)
O6—P2—O4—Zn1	74.23 (16)	C2—C3—C4—C5	-1.1 (4)
O5—P2—O4—Zn1	-55.63 (16)	C6—C3—C4—C5	179.6 (3)
O6—P2—O5—Zn3	37.41 (16)	C3—C4—C5—N1	1.3 (4)
O4—P2—O5—Zn3	168.29 (11)	N2—C1—N1—C5	-179.8 (2)
O4—P2—O6—Zn3 <sup>iii</sup>	-85.7 (2)	C2—C1—N1—C5	0.1 (4)
O5—P2—O6—Zn3 <sup>iii</sup>	42.5 (3)	C4—C5—N1—C1	-0.8 (4)
O9—P3—O7—Zn1	12.1 (3)	N4—C7—C8—C9	-179.0 (3)
O8—P3—O7—Zn1	142.09 (19)	N3—C7—C8—C9	3.7 (5)
O9—P3—O8—Zn2 <sup>ii</sup>	-1.7 (2)	C7—C8—C9—C10	-4.7 (5)
O7—P3—O8—Zn2 <sup>ii</sup>	-132.07 (16)	C7—C8—C9—C12	178.6 (3)
O7—P3—O9—Zn2 <sup>v</sup>	47.6 (3)	C8—C9—C10—C11	0.9 (5)



O8—P3—O9—Zn2 <sup>v</sup>	−80.5 (2)	C12—C9—C10—C11	177.5 (3)
O12—P4—O10—Zn1	−34.6 (2)	C9—C10—C11—N3	4.1 (5)
O11—P4—O10—Zn1	97.6 (2)	C10—C11—N3—C7	−5.2 (5)
O12—P4—O11—Zn3 <sup>iii</sup>	66.5 (2)	N4—C7—N3—C11	−176.2 (3)
O10—P4—O11—Zn3 <sup>iii</sup>	−65.6 (2)	C8—C7—N3—C11	1.2 (5)

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ O5 <sup>iv</sup>	0.88	1.97	2.833 (3)	166
N2—H2N $\cdots$ O3	0.85 (4)	2.05 (4)	2.853 (3)	157 (3)
N2—H3N $\cdots$ O10	0.85 (4)	2.16 (4)	2.961 (3)	156 (3)
N3—H4N $\cdots$ O1	0.83 (4)	2.07 (4)	2.873 (3)	163 (4)
N4—H5N $\cdots$ O13 <sup>vi</sup>	0.93 (4)	1.95 (4)	2.871 (4)	177 (4)
N4—H6N $\cdots$ O2	0.88 (4)	2.05 (4)	2.918 (3)	167 (4)
O13—H1O $\cdots$ O12 <sup>iii</sup>	0.98	2.05	3.028 (3)	175
O13—H2O $\cdots$ O4 <sup>vii</sup>	0.96	2.05	2.952 (3)	157
C5—H5 $\cdots$ O4 <sup>iv</sup>	0.95	2.64	3.370 (3)	134
C8—H8 $\cdots$ O8 <sup>viii</sup>	0.95	2.48	3.350 (4)	152
C11—H11 $\cdots$ O7	0.95	2.47	3.199 (4)	133
C11—H11 $\cdots$ O13 <sup>vii</sup>	0.95	2.59	3.281 (4)	130

Symmetry codes: (iii)  $-x+1, -y+1, -z$ ; (iv)  $-x, -y+1, -z$ ; (vi)  $-x, -y, -z$ ; (vii)  $-x+1, -y, -z$ ; (viii)  $-x, -y, -z+1$ .

(V)

Crystal data

$(C_6H_9N_2)_2[ZnCl_4]\cdot H_2O$

$M_r = 443.49$

Triclinic,  $P\bar{1}$

$a = 6.9541$  (8) Å

$b = 8.7092$  (9) Å

$c = 16.293$  (3) Å

$\alpha = 83.239$  (11)°

$\beta = 80.167$  (10)°

$\gamma = 72.049$  (9)°

$V = 922.7$  (2) Å<sup>3</sup>

$Z = 2$

$F(000) = 452$

$D_x = 1.596$  Mg m<sup>−3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3331 reflections

$\theta = 2.5$ – $27.4$ °

$\mu = 1.92$  mm<sup>−1</sup>

$T = 173$  K

Prism, colourless

$0.15 \times 0.05 \times 0.05$  mm

Data collection

AFC10: Fixed Chi 2 circle CCD  
diffractometer

Radiation source: Rotating Anode

Confocal monochromator

$\omega$  scans

Absorption correction: multi-scan

$T_{\min} = 0.851$ ,  $T_{\max} = 1.000$

28291 measured reflections

3383 independent reflections

3172 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 25.4$ °,  $\theta_{\min} = 2.5$ °

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -19 \rightarrow 19$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.111$   
 $S = 1.08$   
 3383 reflections  
 203 parameters  
 0 restraints

Primary atom site location: structure-invariant  
 direct methods  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 3.4309P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.10 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.01 \text{ e } \text{\AA}^{-3}$

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1889 (9)	0.1476 (6)	0.5224 (3)	0.0600 (15)
C2	0.1527 (15)	0.0459 (7)	0.5969 (4)	0.104 (3)
C3	0.2121 (8)	-0.1169 (6)	0.5878 (3)	0.0520 (12)
H3	0.211403	-0.188177	0.636650	0.062*
C4	0.2731 (8)	-0.1829 (6)	0.5112 (3)	0.0531 (12)
H4	0.310133	-0.296598	0.507457	0.064*
C5	0.2788 (17)	-0.0840 (8)	0.4429 (4)	0.126 (4)
H5	0.303249	-0.124879	0.389331	0.151*
C6	0.0868 (10)	0.1186 (7)	0.6779 (3)	0.0651 (16)
H6A	-0.036542	0.210386	0.674726	0.098*
H6B	0.195698	0.156258	0.691792	0.098*
H6C	0.057412	0.037620	0.721293	0.098*
N1	0.2493 (9)	0.0780 (6)	0.4499 (3)	0.0705 (15)
H1	0.271393	0.138646	0.404236	0.085*
N2	0.1632 (6)	0.3024 (5)	0.5236 (2)	0.0475 (10)
H2A	0.185700	0.360039	0.476852	0.057*
H2B	0.123470	0.349100	0.571202	0.057*
C7	0.2567 (8)	0.2446 (6)	-0.0094 (3)	0.0501 (12)
C8	0.3081 (8)	0.1491 (6)	-0.0793 (3)	0.0496 (12)
C9	0.2983 (7)	-0.0075 (6)	-0.0664 (3)	0.0461 (11)
H9	0.329701	-0.071870	-0.112816	0.055*
C10	0.2439 (8)	-0.0740 (7)	0.0125 (4)	0.0584 (14)
H10	0.242538	-0.183511	0.020582	0.070*
C11	0.1918 (9)	0.0225 (9)	0.0790 (4)	0.0737 (19)
H11	0.148649	-0.018341	0.133404	0.088*
C12	0.3736 (8)	0.2208 (6)	-0.1633 (3)	0.0449 (11)
H12A	0.483628	0.266937	-0.159640	0.067*
H12B	0.257460	0.306089	-0.182129	0.067*
H12C	0.422840	0.136364	-0.203087	0.067*

N3	0.2029 (7)	0.1758 (6)	0.0657 (3)	0.0631 (12)
H3A	0.172986	0.234488	0.109125	0.076*
N4	0.2588 (7)	0.3949 (5)	-0.0157 (3)	0.0602 (12)
H4A	0.225239	0.450402	0.029029	0.072*
H4B	0.293896	0.440766	-0.064693	0.072*
Zn1	0.40814 (8)	0.39971 (6)	0.23744 (3)	0.03752 (16)
Cl1	0.37981 (18)	0.50225 (14)	0.36231 (7)	0.0428 (3)
Cl2	0.73745 (17)	0.33366 (14)	0.17781 (8)	0.0471 (3)
Cl3	0.19082 (18)	0.57548 (14)	0.15631 (7)	0.0460 (3)
Cl4	0.2998 (2)	0.17366 (15)	0.25763 (7)	0.0508 (3)
O1	0.1386 (6)	0.5035 (5)	0.6524 (2)	0.0587 (9)
H1O	0.053464	0.539417	0.697263	0.07 (2)*
H2O	0.256463	0.514917	0.659163	0.10 (2)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.084 (4)	0.041 (3)	0.049 (3)	-0.024 (3)	0.024 (3)	-0.010 (2)
C2	0.198 (9)	0.042 (3)	0.049 (3)	-0.031 (4)	0.044 (4)	-0.006 (3)
C3	0.055 (3)	0.039 (3)	0.060 (3)	-0.015 (2)	-0.002 (2)	0.001 (2)
C4	0.054 (3)	0.040 (3)	0.062 (3)	-0.012 (2)	0.001 (2)	-0.014 (2)
C5	0.244 (12)	0.059 (4)	0.060 (4)	-0.060 (6)	0.062 (6)	-0.029 (3)
C6	0.095 (4)	0.045 (3)	0.044 (3)	-0.018 (3)	0.014 (3)	-0.002 (2)
N1	0.113 (4)	0.052 (3)	0.043 (2)	-0.038 (3)	0.028 (3)	-0.013 (2)
N2	0.063 (3)	0.040 (2)	0.037 (2)	-0.0188 (19)	0.0038 (18)	-0.0008 (16)
C7	0.056 (3)	0.058 (3)	0.035 (2)	-0.014 (2)	-0.005 (2)	-0.008 (2)
C8	0.059 (3)	0.053 (3)	0.039 (3)	-0.019 (2)	-0.007 (2)	-0.003 (2)
C9	0.038 (2)	0.048 (3)	0.054 (3)	-0.011 (2)	-0.014 (2)	-0.002 (2)
C10	0.051 (3)	0.063 (3)	0.067 (4)	-0.027 (3)	-0.018 (3)	0.016 (3)
C11	0.051 (3)	0.112 (6)	0.056 (4)	-0.031 (3)	-0.008 (3)	0.022 (4)
C12	0.055 (3)	0.043 (3)	0.035 (2)	-0.011 (2)	-0.005 (2)	-0.0054 (19)
N3	0.070 (3)	0.086 (4)	0.033 (2)	-0.024 (3)	-0.001 (2)	-0.005 (2)
N4	0.075 (3)	0.056 (3)	0.046 (2)	-0.010 (2)	-0.008 (2)	-0.018 (2)
Zn1	0.0406 (3)	0.0372 (3)	0.0340 (3)	-0.0110 (2)	-0.0026 (2)	-0.0052 (2)
Cl1	0.0489 (6)	0.0443 (6)	0.0345 (5)	-0.0129 (5)	-0.0017 (4)	-0.0090 (4)
Cl2	0.0406 (6)	0.0446 (6)	0.0526 (7)	-0.0090 (5)	0.0021 (5)	-0.0114 (5)
Cl3	0.0487 (6)	0.0458 (6)	0.0403 (6)	-0.0067 (5)	-0.0105 (5)	-0.0042 (5)
Cl4	0.0696 (8)	0.0456 (6)	0.0439 (6)	-0.0282 (6)	-0.0045 (5)	-0.0039 (5)
O1	0.061 (2)	0.070 (2)	0.053 (2)	-0.030 (2)	-0.0003 (18)	-0.0173 (18)

*Geometric parameters (Å, °)*

C1—N2	1.306 (6)	C8—C9	1.376 (7)
C1—N1	1.335 (7)	C8—C12	1.494 (6)
C1—C2	1.450 (7)	C9—C10	1.387 (7)
C2—C3	1.368 (7)	C9—H9	0.9500
C2—C6	1.472 (8)	C10—C11	1.380 (9)
C3—C4	1.380 (7)	C10—H10	0.9500

C3—H3	0.9500	C11—N3	1.351 (8)
C4—C5	1.328 (9)	C11—H11	0.9500
C4—H4	0.9500	C12—H12A	0.9800
C5—N1	1.377 (8)	C12—H12B	0.9800
C5—H5	0.9500	C12—H12C	0.9800
C6—H6A	0.9800	N3—H3A	0.8800
C6—H6B	0.9800	N4—H4A	0.8800
C6—H6C	0.9800	N4—H4B	0.8800
N1—H1	0.8800	Zn1—Cl2	2.2536 (13)
N2—H2A	0.8800	Zn1—Cl3	2.2704 (13)
N2—H2B	0.8800	Zn1—Cl1	2.2710 (12)
C7—N4	1.305 (7)	Zn1—Cl4	2.2867 (13)
C7—N3	1.344 (6)	O1—H1O	0.8802
C7—C8	1.420 (7)	O1—H2O	0.8817
N2—C1—N1	119.5 (5)	C9—C8—C12	122.6 (4)
N2—C1—C2	122.9 (5)	C7—C8—C12	119.1 (4)
N1—C1—C2	117.6 (5)	C8—C9—C10	121.8 (5)
C3—C2—C1	116.2 (5)	C8—C9—H9	119.1
C3—C2—C6	124.1 (5)	C10—C9—H9	119.1
C1—C2—C6	119.0 (5)	C11—C10—C9	118.5 (5)
C2—C3—C4	123.3 (5)	C11—C10—H10	120.7
C2—C3—H3	118.4	C9—C10—H10	120.7
C4—C3—H3	118.4	N3—C11—C10	119.1 (5)
C5—C4—C3	118.6 (5)	N3—C11—H11	120.5
C5—C4—H4	120.7	C10—C11—H11	120.5
C3—C4—H4	120.7	C8—C12—H12A	109.5
C4—C5—N1	119.8 (6)	C8—C12—H12B	109.5
C4—C5—H5	120.1	H12A—C12—H12B	109.5
N1—C5—H5	120.1	C8—C12—H12C	109.5
C2—C6—H6A	109.5	H12A—C12—H12C	109.5
C2—C6—H6B	109.5	H12B—C12—H12C	109.5
H6A—C6—H6B	109.5	C7—N3—C11	124.4 (5)
C2—C6—H6C	109.5	C7—N3—H3A	117.8
H6A—C6—H6C	109.5	C11—N3—H3A	117.8
H6B—C6—H6C	109.5	C7—N4—H4A	120.0
C1—N1—C5	123.3 (5)	C7—N4—H4B	120.0
C1—N1—H1	118.3	H4A—N4—H4B	120.0
C5—N1—H1	118.3	Cl2—Zn1—Cl3	113.75 (5)
C1—N2—H2A	120.0	Cl2—Zn1—Cl1	109.26 (5)
C1—N2—H2B	120.0	Cl3—Zn1—Cl1	110.27 (5)
H2A—N2—H2B	120.0	Cl2—Zn1—Cl4	109.40 (5)
N4—C7—N3	119.5 (5)	Cl3—Zn1—Cl4	104.48 (5)
N4—C7—C8	122.7 (5)	Cl1—Zn1—Cl4	109.55 (5)
N3—C7—C8	117.8 (5)	H1O—O1—H2O	105.6
C9—C8—C7	118.3 (5)		
N2—C1—C2—C3	-171.5 (7)	N4—C7—C8—C9	-179.1 (5)

N1—C1—C2—C3	9.1 (12)	N3—C7—C8—C9	0.6 (8)
N2—C1—C2—C6	-0.9 (13)	N4—C7—C8—C12	1.9 (8)
N1—C1—C2—C6	179.8 (7)	N3—C7—C8—C12	-178.5 (5)
C1—C2—C3—C4	-10.1 (12)	C7—C8—C9—C10	-1.3 (7)
C6—C2—C3—C4	179.9 (7)	C12—C8—C9—C10	177.7 (5)
C2—C3—C4—C5	1.5 (11)	C8—C9—C10—C11	2.2 (8)
C3—C4—C5—N1	8.0 (13)	C9—C10—C11—N3	-2.5 (8)
N2—C1—N1—C5	-179.6 (8)	N4—C7—N3—C11	178.7 (5)
C2—C1—N1—C5	-0.2 (12)	C8—C7—N3—C11	-1.0 (8)
C4—C5—N1—C1	-8.8 (14)	C10—C11—N3—C7	2.0 (9)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...C14	0.88	2.35	3.134 (5)	148
N2—H2 <i>A</i> ...C11	0.88	2.54	3.375 (4)	158
N2—H2 <i>B</i> ...O1	0.88	2.03	2.838 (5)	152
N3—H3 <i>A</i> ...C14	0.88	2.66	3.306 (4)	132
N4—H4 <i>A</i> ...C13	0.88	2.40	3.268 (4)	170
N4—H4 <i>B</i> ...C12 <sup>i</sup>	0.88	2.51	3.333 (5)	155
O1—H1 <i>O</i> ...C13 <sup>ii</sup>	0.88	2.95	3.669 (4)	141
O1—H1 <i>O</i> ...C14 <sup>ii</sup>	0.88	2.98	3.675 (4)	138
O1—H2 <i>O</i> ...C11 <sup>iii</sup>	0.88	2.45	3.302 (4)	162
C10—H10...C13 <sup>iv</sup>	0.95	2.92	3.696 (5)	140

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