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# *In situ* decarbonylation of *N,N*-dimethylformamide to form dimethylammonium cations in the hybrid framework compound $\{[(\text{CH}_3)_2\text{NH}_2]_2[\text{Zn}\{\text{O}_3\text{PC}_6\text{H}_2(\text{OH})_2\text{PO}_3\}]\}_n$

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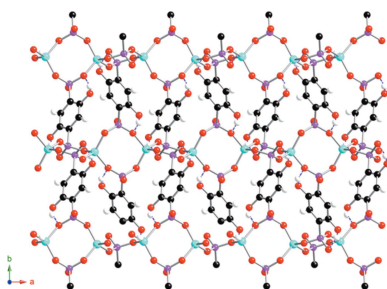
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The title phosphonate-based organic–inorganic hybrid framework, poly[bis(dimethylammonium)  $[(\mu_4\text{-}2,5\text{-dihydroxybenzene-}1,4\text{-diphosphonato})\text{zinc(II)}]]$ ,  $\{(\text{C}_2\text{H}_8\text{N})_2[\text{Zn}(\text{C}_6\text{H}_4\text{O}_8\text{P}_2)]\}_n$ , was formed unexpectedly when dimethylammonium cations were formed from the *in situ* decarbonylation of the *N,N*-dimethylformamide solvent. The framework is built up from  $\text{ZnO}_4$  tetrahedra and bridging diphosphonate tetra-anions to generate a three-dimensional network comprising [100] channels occupied by the  $(\text{CH}_3)_2\text{NH}_2^+$  cations. Within the channels, an array of  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds help to establish the structure. In addition, intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between the appended  $-\text{OH}$  groups of the phenyl ring and adjacent  $\text{PO}_3^{2-}$  groups are observed.

## 1. Chemical context

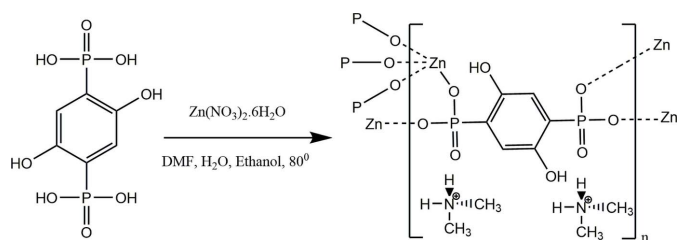
Studies on the structural chemistry of metal phosphonates developed as a result of the versatility of the phosphonate ligands (Zubieta *et al.*, 2011; Mao, 2007; Clearfield, 1996, 1998, 2002). A slight modification of the organic residues of the phosphonic acids ( $R\text{-PO}_3\text{H}_2$ , where  $R$  = organic residue) can lead to rich structural diversity. In general, phosphonates tend to assume various coordination modes as a result of the three coordinating oxygen atoms of the central phosphorus units. As a consequence, most metal phosphonates form a low-dimensional and dense layered structure (Deria *et al.*, 2015; Gagnon *et al.*, 2012). Nevertheless, a large number of isolated metal phosphonates have shown various potential applications in ion-exchange, ionic conductivity, gas storage, catalysis, and as small molecule sensors and magnetic interactions (Adelani & Albrecht-Schmitt, 2010; Ramaswamy *et al.*, 2015; Deria *et al.*, 2015; Kirumakki *et al.*, 2008; Brousseau *et al.*, 1997; Zheng *et al.*, 2011).

The majority of metal–organic frameworks (MOFs) are designed with carboxylate- and nitrogen-containing heterocyclic ligands, while phosphonate-based MOFs are less well studied. One possible explanation may have to do with the predisposition of phosphonates to precipitate rapidly into less ordered insoluble phases. However, carboxylate-based MOFs are less stable in air and water, and this poses a significant problem if they are to be used in industrial applications. Metal



carboxylate MOFs are subject to hydrolysis and are quite soluble in acidic solutions. On the contrary, phosphonates manifest stronger interactions with oxophilic metal ions than carboxylates and are not subject to hydrolysis (Deria *et al.*, 2015; Gagnon *et al.*, 2012).

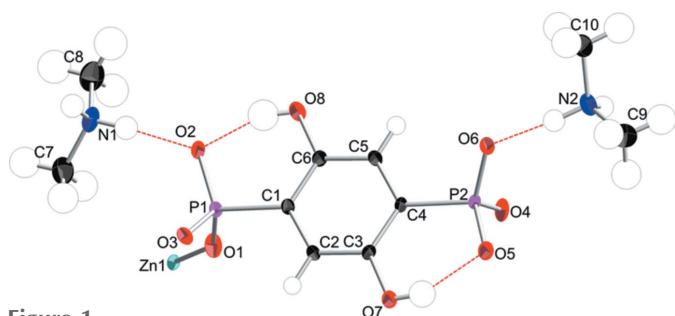
About a decade ago, a crystalline and porous zinc diphosphonate MOF,  $\{[\text{Zn}(\text{DHBP})](\text{DMF})_2\}$  (DMF = *N,N*-dimethylformamide) was reported (Liang & Shimizu, 2007). These researchers utilized a modified phosphonate ligand, 1,4-dihydroxy-2,5-benzenediphosphonate (DHBP), to cross-link one-dimensional  $\text{Zn}(\text{RPO}_3)$  columns into an ordered three-dimensional network. Herein, we report the synthesis and structure of the title inorganic–organic hybrid framework, (I), using 1,4-dihydroxy-2,5-benzenediphosphonate *via* the *in situ* formation of the guest cation.



## 2. Structural commentary

The structure of (I) crystallizes in the monoclinic space group  $P2_1/n$ . The asymmetric unit contains one  $\text{Zn}^{2+}$  cation, a  $\text{C}_6\text{H}_4\text{P}_2\text{O}_8^{4-}$  hydroxyphosphonate tetra-anion and two  $(\text{CH}_3)_2\text{NH}_2^+$  cations (Fig. 1). The extended structure is constructed from tetrahedral  $\text{ZnO}_4$  units with the O atoms arising from four rigid phenyl spacers into a three-dimensional framework (Fig. 2). Two of the oxygen atoms of each  $\text{PO}_3^{2-}$  moiety are involved in coordination to the  $\text{Zn}^{2+}$  ion and the others (O2 and O6) are not. The Zn–O bond distances range from 1.9055 (11) to 1.9671 (11) Å and the hydroxyphosphonate ligand is present in (I) with P–O bonds that range from 1.5129 (11) to 1.5337 (11) Å in length. The latter bond lengths are within the expected range for deprotonated P–O bonds (Liang & Shimizu, 2007).

The structure of (I) is similar to that of  $\{[\text{Zn}(\text{DHBP})](\text{DMF})_2\}$  (Liang & Shimizu, 2007; CCDC



**Figure 1**

The asymmetric unit of (I) in position  $1 - x, 1 - y, 1 - z$  showing 50% displacement ellipsoids.

**Table 1**

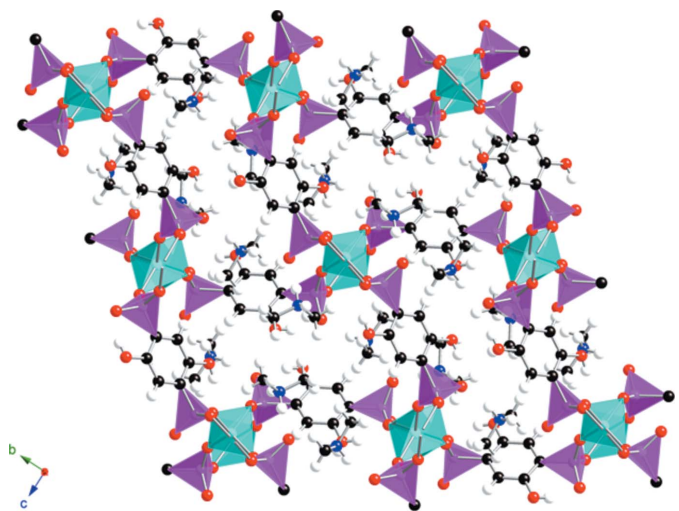
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7–H7A $\cdots$ O5	0.79 (2)	1.91 (2)	2.6510 (17)	156 (3)
O8–H8A $\cdots$ O2	0.87 (3)	1.73 (3)	2.5846 (18)	168 (3)
N1–H1A $\cdots$ O2	0.89 (2)	1.88 (2)	2.7168 (19)	155.2 (18)
N1–H1B $\cdots$ O6 <sup>i</sup>	0.89 (2)	2.02 (2)	2.8125 (19)	148.3 (18)
N2–H2B $\cdots$ O3 <sup>ii</sup>	0.83 (3)	2.07 (3)	2.8558 (19)	158 (2)
N2–H2C $\cdots$ O6	1.03 (2)	1.63 (2)	2.6518 (18)	173 (2)
C7–H7C $\cdots$ O4 <sup>iii</sup>	0.91 (2)	2.54 (2)	3.443 (3)	174 (2)
C9–H9B $\cdots$ O8 <sup>iv</sup>	1.03 (3)	2.57 (2)	3.445 (3)	142.6 (19)
C10–H10A $\cdots$ O8 <sup>iv</sup>	0.92 (3)	2.42 (3)	3.236 (3)	148 (3)

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

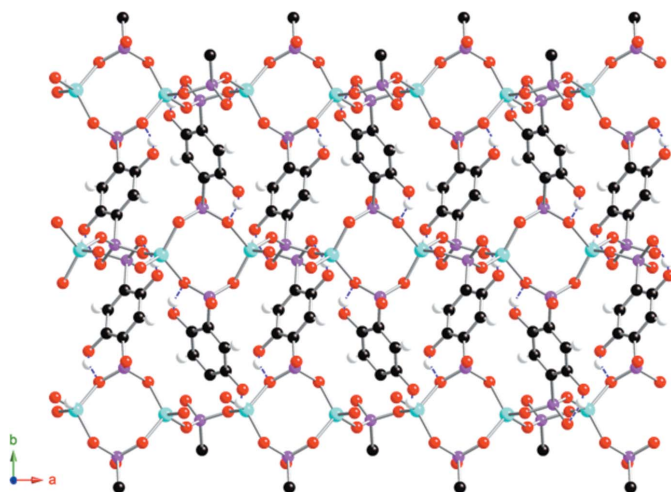
refcode JIVFUQ) in that the zinc–phosphonate framework comprises one-dimensional channels occupied by guest species, but with the significant difference that the guest species in JIVFUQ are neutral DMF molecules and the phosphonate groups are singly, rather than doubly deprotonated to form  $\text{C}_6\text{H}_6\text{P}_2\text{O}_8^{2-}$  dianions.

The channels reported here are smaller than those in JIVFUQ and measure approximately  $12.9 \times 7.1$  Å between phenyl groups and 9.9 Å between Zn centers. The  $(\text{CH}_3)_2\text{NH}_2^+$  cations in (I) have been formed by the *in situ* decarbonylation of the DMF solvent. It is known that *N,N*-dimethylformamide can undergo loss of CO to form dimethylamine in the presence of a metal catalyst or through slow decomposition at elevated temperature around 427 K (Hulushe *et al.*, 2016; Siddiqui *et al.*, 2012; Chen *et al.*, 2007; Karpova *et al.*, 2004). In the previous reports, the nitrate salts of  $\text{Mg}^{2+}/\text{Pb}^{2+}/\text{Ho}^{3+}$  and chloride salts of  $\text{Nd}^{3+}/\text{Zr}^{4+}$  were suggested to act as a metal catalyst in the decarbonylation of the DMF solvent.



**Figure 2**

View down [100] of the three-dimensional framework structure of (I) with the  $\text{ZnO}_4$  and  $\text{PO}_3\text{C}$  moieties shown as polyhedra. Color key:  $\text{ZnO}_4$  groups = cyan,  $\text{PO}_3\text{C}$  groups = magenta, oxygen = red, carbon = black, hydrogen = white. The  $(\text{CH}_3)_2\text{NH}_2^+$  cations are omitted for clarity.



**Figure 3**  
Ball-and-stick representation of the structure of (I) viewed along the [001] axis. The hydrogen bonds involving the –OH groups are drawn as blue dashed lines. Color key as in Fig. 2.

### 3. Supramolecular features

The C6–O8H and C3–O7H groups appended on the phenyl ring of the ligand form intramolecular O–H···O hydrogen bonds with the adjacent  $RPO_3^{2-}$  moieties (Figs. 1 and 3). Within the channels, the  $(CH_3)_2NH_2^+$  cations are linked by N–H···O hydrogen bonds to the  $RPO_3^{2-}$  groups of the framework (Table 1). Some short C–H···O contacts (Table 1) may help to consolidate the structure.

### 4. Synthesis and crystallization

The title compound was synthesized by placing  $Zn(NO_3)_2 \cdot 6H_2O$  (29.7 mg, 0.1 mmol) and 2,5-dihydroxy-1,4-benzenediphosphonic acid (27.0 mg, 0.1 mmol) into a 125 ml PTFE-lined Parr reaction vessel along with DMF/ $H_2O$ /ethanol (2.0/0.5/0.5 ml, respectively). The vessel was heated in a programmable furnace at 353 K for 3 d, and then the autoclave was cooled to 296 K at an average rate of  $274 \text{ K h}^{-1}$ . The mother liquor was decanted from the products and then placed in a petri dish. The solid products were washed with distilled water, dispersed with ethanol and allowed to dry in air. Colorless tablets of the title compound were isolated and studied for single-crystal X-ray diffraction.

### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

### Acknowledgements

We thank St. Mary's University, the School of Science, Engineering and Technology, and the Department of Chemistry and Biochemistry for supporting undergraduate research. Single-crystal X-ray analyses were conducted at the Materials

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$(C_2H_8N)_2[Zn(C_6H_4O_8P_2)]$
$M_r$	423.59
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	220
$a, b, c$ (Å)	8.8455 (5), 16.4492 (9), 11.2721 (6)
$\beta$ (°)	97.338 (1)
$V$ (Å <sup>3</sup> )	1626.67 (15)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.75
Crystal size (mm)	0.09 × 0.03 × 0.03
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}$ , $T_{\max}$	0.706, 0.746
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	19692, 4040, 3582
$R_{\text{int}}$	0.027
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.681
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.022, 0.060, 1.05
No. of reflections	4040
No. of parameters	288
No. of restraints	1
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.42, –0.31

Computer programs: APEX3 and SAINT (Bruker, 2015), SHELXT2014/2 (Sheldrick, 2015a), SHELXL2016/6 (Sheldrick, 2015b), XP in SHELXTL (Sheldrick, 2008a) and CIFTAB (Sheldrick, 2008b).

Characterization Facility of the Center of Sustainable Energy at the University of Notre Dame.

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## supporting information

*Acta Cryst.* (2019). E75, 1540-1543 [https://doi.org/10.1107/S2056989019012969]

## *In situ* decarbonylation of *N,N*-dimethylformamide to form dimethylammonium cations in the hybrid framework compound



**Josemaria S. Soriano, Bryan E. Galeas, Paul Garrett, Ryan A. Flores, Juan L. Pinedo, Tsuyoshi A. Kohlgruber, Daniel Felton and Pius O. Adelani**

### Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT2014/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008a); software used to prepare material for publication: *CIFTAB* (Sheldrick, 2008b).

Poly[bis(dimethylammonium) [ $\mu_4$ -2,5-dihydroxybenzene-1,4-diphosphonato]zinc(II)]

### Crystal data

(C<sub>2</sub>H<sub>8</sub>N)<sub>2</sub>[Zn(C<sub>6</sub>H<sub>4</sub>O<sub>8</sub>P<sub>2</sub>)

*M<sub>r</sub>* = 423.59

Monoclinic, *P2<sub>1</sub>/n*

*a* = 8.8455 (5) Å

*b* = 16.4492 (9) Å

*c* = 11.2721 (6) Å

$\beta$  = 97.338 (1)°

*V* = 1626.67 (15) Å<sup>3</sup>

*Z* = 4

*F*(000) = 872

*D<sub>x</sub>* = 1.730 Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 8723 reflections

$\theta$  = 2.2–28.8°

$\mu$  = 1.75 mm<sup>-1</sup>

*T* = 220 K

Block, colorless

0.09 × 0.03 × 0.03 mm

### Data collection

Bruker APEXII  
diffractometer

Radiation source: Incoatec micro-focus

Detector resolution: 8.33 pixels mm<sup>-1</sup>

combination of  $\omega$  and  $\varphi$ -scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

*T<sub>min</sub>* = 0.706, *T<sub>max</sub>* = 0.746

19692 measured reflections

4040 independent reflections

3582 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.027

$\theta_{\text{max}}$  = 29.0°,  $\theta_{\text{min}}$  = 2.2°

*h* = -11 → 11

*k* = -22 → 21

*l* = -14 → 14

### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.022

*wR*(*F*<sup>2</sup>) = 0.060

*S* = 1.05

4040 reflections

288 parameters

1 restraint

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 0.4955P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

### 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.73693 (2)	0.50748 (2)	-0.00920 (2)	0.01208 (6)
P1	0.53496 (4)	0.52463 (2)	0.21300 (3)	0.01348 (9)
P2	0.52017 (4)	0.86078 (2)	0.50529 (3)	0.01240 (8)
O1	0.61568 (13)	0.54669 (7)	0.10670 (10)	0.0251 (3)
O2	0.61879 (14)	0.46378 (7)	0.29864 (11)	0.0241 (3)
O3	0.37005 (12)	0.49818 (6)	0.17307 (10)	0.0173 (2)
O4	0.66080 (13)	0.90494 (6)	0.47282 (10)	0.0217 (2)
O5	0.37382 (13)	0.90513 (7)	0.45507 (10)	0.0220 (2)
O6	0.53036 (13)	0.84096 (7)	0.63713 (9)	0.0216 (2)
O7	0.31114 (15)	0.80860 (7)	0.26689 (12)	0.0287 (3)
O8	0.71416 (17)	0.57148 (8)	0.45775 (13)	0.0382 (4)
C1	0.52417 (16)	0.61778 (9)	0.29782 (13)	0.0137 (3)
C2	0.42525 (17)	0.67996 (9)	0.25376 (13)	0.0161 (3)
C3	0.41615 (17)	0.75253 (9)	0.31601 (13)	0.0155 (3)
C4	0.51147 (16)	0.76540 (8)	0.42426 (13)	0.0128 (3)
C5	0.60872 (17)	0.70290 (9)	0.46917 (14)	0.0176 (3)
C6	0.61546 (17)	0.62969 (9)	0.40804 (14)	0.0186 (3)
C7	0.5494 (3)	0.29794 (13)	0.13241 (19)	0.0387 (5)
N1	0.57872 (18)	0.30131 (9)	0.26452 (15)	0.0277 (3)
C8	0.7362 (3)	0.27776 (15)	0.3120 (2)	0.0443 (5)
C9	0.5188 (3)	1.01513 (14)	0.8070 (2)	0.0356 (4)
N2	0.63088 (18)	0.94927 (9)	0.80290 (13)	0.0246 (3)
C10	0.6615 (3)	0.90359 (13)	0.91563 (18)	0.0371 (5)
H1A	0.568 (2)	0.3527 (14)	0.287 (2)	0.038 (6)*
H1B	0.515 (2)	0.2695 (14)	0.2980 (19)	0.037 (6)*
H2A	0.360 (2)	0.6731 (12)	0.1787 (17)	0.026 (5)*
H2B	0.709 (3)	0.9705 (14)	0.783 (2)	0.041 (6)*
H2C	0.588 (3)	0.9111 (15)	0.735 (2)	0.054 (7)*
H5A	0.676 (2)	0.7101 (11)	0.5433 (17)	0.024 (5)*
H7A	0.306 (3)	0.8427 (16)	0.316 (2)	0.050 (7)*
H7B	0.450 (3)	0.3113 (17)	0.109 (2)	0.071 (9)*
H7C	0.620 (2)	0.3284 (16)	0.101 (2)	0.055 (7)*
H7D	0.566 (3)	0.2430 (15)	0.109 (2)	0.044 (6)*
H8A	0.691 (3)	0.5308 (18)	0.410 (3)	0.064 (8)*
H8B	0.806 (3)	0.3177 (15)	0.281 (2)	0.052 (7)*
H8C	0.750 (3)	0.2805 (15)	0.402 (2)	0.053 (7)*

H8D	0.748 (3)	0.2232 (16)	0.278 (2)	0.056 (7)*
H9A	0.501 (2)	1.0337 (13)	0.729 (2)	0.036 (6)*
H9B	0.569 (3)	1.0562 (16)	0.869 (2)	0.054 (7)*
H9C	0.431 (3)	0.9924 (13)	0.828 (2)	0.042 (7)*
H10A	0.719 (4)	0.936 (2)	0.970 (3)	0.088 (11)*
H10B	0.564 (4)	0.8940 (17)	0.947 (3)	0.077 (9)*
H10C	0.716 (3)	0.8557 (17)	0.902 (2)	0.062 (8)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.01243 (9)	0.01005 (9)	0.01414 (9)	-0.00104 (6)	0.00319 (6)	-0.00073 (6)
P1	0.01327 (18)	0.01165 (17)	0.01539 (18)	0.00072 (13)	0.00134 (14)	-0.00453 (14)
P2	0.01391 (18)	0.00907 (17)	0.01421 (18)	0.00096 (13)	0.00174 (14)	-0.00254 (13)
O1	0.0271 (6)	0.0243 (6)	0.0268 (6)	-0.0033 (5)	0.0146 (5)	-0.0084 (5)
O2	0.0287 (6)	0.0141 (5)	0.0268 (6)	0.0053 (5)	-0.0070 (5)	-0.0053 (5)
O3	0.0153 (5)	0.0196 (5)	0.0167 (5)	-0.0027 (4)	0.0006 (4)	-0.0046 (4)
O4	0.0219 (6)	0.0142 (5)	0.0302 (6)	-0.0051 (4)	0.0085 (5)	-0.0057 (4)
O5	0.0210 (6)	0.0185 (5)	0.0253 (6)	0.0094 (4)	-0.0018 (5)	-0.0068 (5)
O6	0.0331 (6)	0.0162 (5)	0.0152 (5)	-0.0024 (5)	0.0023 (5)	-0.0024 (4)
O7	0.0350 (7)	0.0169 (6)	0.0293 (7)	0.0113 (5)	-0.0149 (5)	-0.0073 (5)
O8	0.0463 (8)	0.0237 (7)	0.0367 (8)	0.0212 (6)	-0.0249 (6)	-0.0140 (6)
C1	0.0132 (7)	0.0125 (7)	0.0156 (7)	0.0004 (5)	0.0019 (5)	-0.0032 (5)
C2	0.0177 (7)	0.0144 (7)	0.0152 (7)	-0.0005 (6)	-0.0020 (6)	-0.0025 (6)
C3	0.0158 (7)	0.0123 (6)	0.0176 (7)	0.0023 (5)	-0.0005 (6)	0.0002 (5)
C4	0.0142 (7)	0.0105 (6)	0.0141 (7)	-0.0008 (5)	0.0029 (5)	-0.0016 (5)
C5	0.0184 (7)	0.0160 (7)	0.0168 (7)	0.0018 (6)	-0.0032 (6)	-0.0032 (6)
C6	0.0192 (7)	0.0147 (7)	0.0207 (8)	0.0062 (6)	-0.0028 (6)	-0.0032 (6)
C7	0.0482 (13)	0.0331 (11)	0.0375 (11)	-0.0098 (10)	0.0162 (10)	-0.0045 (9)
N1	0.0312 (8)	0.0175 (7)	0.0373 (9)	-0.0035 (6)	0.0154 (7)	-0.0030 (6)
C8	0.0363 (11)	0.0374 (12)	0.0601 (16)	0.0052 (9)	0.0091 (11)	-0.0063 (11)
C9	0.0353 (11)	0.0405 (11)	0.0326 (11)	0.0034 (9)	0.0096 (9)	0.0022 (9)
N2	0.0254 (8)	0.0297 (8)	0.0202 (7)	-0.0096 (6)	0.0087 (6)	-0.0050 (6)
C10	0.0577 (14)	0.0300 (10)	0.0236 (9)	0.0000 (10)	0.0052 (9)	-0.0045 (8)

*Geometric parameters (Å, °)*

Zn1—O1	1.9055 (11)	C5—C6	1.392 (2)
Zn1—O3 <sup>i</sup>	1.9671 (11)	C5—H5A	0.971 (19)
Zn1—O4 <sup>ii</sup>	1.9330 (11)	C7—N1	1.480 (3)
Zn1—O5 <sup>iii</sup>	1.9543 (10)	C7—H7B	0.92 (2)
P1—O1	1.5151 (12)	C7—H7C	0.91 (2)
P1—O2	1.5169 (12)	C7—H7D	0.96 (2)
P1—O3	1.5337 (11)	N1—C8	1.479 (3)
P1—C1	1.8150 (14)	N1—H1A	0.89 (2)
P2—O6	1.5129 (11)	N1—H1B	0.89 (2)
P2—O4	1.5249 (11)	C8—H8B	1.00 (3)
P2—O5	1.5301 (11)	C8—H8C	1.01 (3)

P2—C4	1.8121 (14)	C8—H8D	0.98 (3)
O7—C3	1.3743 (18)	C9—N2	1.473 (3)
O7—H7A	0.79 (3)	C9—H9A	0.92 (2)
O8—C6	1.3668 (19)	C9—H9B	1.03 (3)
O8—H8A	0.86 (3)	C9—H9C	0.92 (3)
C1—C2	1.395 (2)	N2—C10	1.471 (2)
C1—C6	1.406 (2)	N2—H2B	0.83 (2)
C2—C3	1.392 (2)	N2—H2C	1.02 (3)
C2—H2A	0.968 (19)	C10—H10A	0.92 (4)
C3—C4	1.408 (2)	C10—H10B	0.98 (3)
C4—C5	1.394 (2)	C10—H10C	0.95 (3)
O1—Zn1—O4 <sup>ii</sup>	116.04 (5)	O8—C6—C5	117.94 (14)
O1—Zn1—O5 <sup>iii</sup>	108.06 (5)	O8—C6—C1	121.95 (13)
O4 <sup>ii</sup> —Zn1—O5 <sup>iii</sup>	113.58 (5)	C5—C6—C1	120.11 (13)
O1—Zn1—O3 <sup>i</sup>	114.48 (5)	N1—C7—H7B	108.8 (17)
O4 <sup>ii</sup> —Zn1—O3 <sup>i</sup>	108.30 (5)	N1—C7—H7C	109.5 (15)
O5 <sup>iii</sup> —Zn1—O3 <sup>i</sup>	94.45 (4)	H7B—C7—H7C	116 (2)
O1—P1—O2	114.83 (7)	N1—C7—H7D	107.5 (14)
O1—P1—O3	111.25 (7)	H7B—C7—H7D	109 (2)
O2—P1—O3	111.65 (7)	H7C—C7—H7D	106 (2)
O1—P1—C1	106.03 (7)	C8—N1—C7	112.97 (17)
O2—P1—C1	106.03 (7)	C8—N1—H1A	106.0 (14)
O3—P1—C1	106.38 (6)	C7—N1—H1A	107.9 (14)
O6—P2—O4	112.98 (7)	C8—N1—H1B	108.3 (14)
O6—P2—O5	114.05 (7)	C7—N1—H1B	111.4 (14)
O4—P2—O5	111.20 (7)	H1A—N1—H1B	110 (2)
O6—P2—C4	107.57 (6)	N1—C8—H8B	107.3 (14)
O4—P2—C4	105.95 (6)	N1—C8—H8C	110.0 (14)
O5—P2—C4	104.29 (6)	H8B—C8—H8C	109 (2)
P1—O1—Zn1	145.53 (8)	N1—C8—H8D	104.0 (15)
P1—O3—Zn1 <sup>i</sup>	127.91 (7)	H8B—C8—H8D	111 (2)
P2—O4—Zn1 <sup>iv</sup>	137.62 (7)	H8C—C8—H8D	115 (2)
P2—O5—Zn1 <sup>v</sup>	142.34 (7)	N2—C9—H9A	104.4 (14)
C3—O7—H7A	107.0 (18)	N2—C9—H9B	105.8 (14)
C6—O8—H8A	101.6 (19)	H9A—C9—H9B	116 (2)
C2—C1—C6	118.38 (13)	N2—C9—H9C	107.6 (14)
C2—C1—P1	120.27 (11)	H9A—C9—H9C	109 (2)
C6—C1—P1	121.34 (11)	H9B—C9—H9C	113 (2)
C3—C2—C1	121.54 (14)	C10—N2—C9	113.51 (16)
C3—C2—H2A	118.3 (11)	C10—N2—H2B	112.3 (17)
C1—C2—H2A	120.1 (11)	C9—N2—H2B	106.7 (16)
O7—C3—C2	116.88 (13)	C10—N2—H2C	110.0 (14)
O7—C3—C4	123.19 (13)	C9—N2—H2C	106.8 (14)
C2—C3—C4	119.93 (13)	H2B—N2—H2C	107 (2)
C5—C4—C3	118.52 (13)	N2—C10—H10A	108 (2)
C5—C4—P2	118.11 (11)	N2—C10—H10B	108.4 (17)
C3—C4—P2	123.32 (11)	H10A—C10—H10B	107 (2)



C6—C5—C4	121.45 (14)	N2—C10—H10C	109.3 (16)
C6—C5—H5A	118.1 (11)	H10A—C10—H10C	110 (3)
C4—C5—H5A	120.4 (11)	H10B—C10—H10C	114 (2)
O2—P1—O1—Zn1	37.88 (16)	C1—C2—C3—O7	-177.72 (14)
O3—P1—O1—Zn1	-90.15 (14)	C1—C2—C3—C4	2.0 (2)
C1—P1—O1—Zn1	154.59 (13)	O7—C3—C4—C5	176.85 (14)
O1—P1—O3—Zn1 <sup>i</sup>	-0.87 (10)	C2—C3—C4—C5	-2.8 (2)
O2—P1—O3—Zn1 <sup>i</sup>	-130.59 (8)	O7—C3—C4—P2	-5.8 (2)
C1—P1—O3—Zn1 <sup>i</sup>	114.17 (8)	C2—C3—C4—P2	174.51 (11)
O6—P2—O4—Zn1 <sup>iv</sup>	-63.56 (12)	O6—P2—C4—C5	-43.03 (13)
O5—P2—O4—Zn1 <sup>iv</sup>	66.18 (12)	O4—P2—C4—C5	78.06 (13)
C4—P2—O4—Zn1 <sup>iv</sup>	178.91 (10)	O5—P2—C4—C5	-164.49 (12)
O6—P2—O5—Zn1 <sup>v</sup>	43.33 (14)	O6—P2—C4—C3	139.65 (13)
O4—P2—O5—Zn1 <sup>v</sup>	-85.85 (13)	O4—P2—C4—C3	-99.26 (13)
C4—P2—O5—Zn1 <sup>v</sup>	160.39 (11)	O5—P2—C4—C3	18.19 (14)
O1—P1—C1—C2	71.83 (13)	C3—C4—C5—C6	1.5 (2)
O2—P1—C1—C2	-165.68 (12)	P2—C4—C5—C6	-175.95 (12)
O3—P1—C1—C2	-46.70 (14)	C4—C5—C6—O8	179.76 (15)
O1—P1—C1—C6	-107.45 (13)	C4—C5—C6—C1	0.7 (2)
O2—P1—C1—C6	15.04 (15)	C2—C1—C6—O8	179.40 (15)
O3—P1—C1—C6	134.02 (13)	P1—C1—C6—O8	-1.3 (2)
C6—C1—C2—C3	0.2 (2)	C2—C1—C6—C5	-1.6 (2)
P1—C1—C2—C3	-179.06 (12)	P1—C1—C6—C5	177.73 (12)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H7A $\cdots$ O5	0.79 (2)	1.91 (2)	2.6510 (17)	156 (3)
O8—H8A $\cdots$ O2	0.87 (3)	1.73 (3)	2.5846 (18)	168 (3)
N1—H1A $\cdots$ O2	0.89 (2)	1.88 (2)	2.7168 (19)	155.2 (18)
N1—H1B $\cdots$ O6 <sup>vi</sup>	0.89 (2)	2.02 (2)	2.8125 (19)	148.3 (18)
N2—H2B $\cdots$ O3 <sup>vii</sup>	0.83 (3)	2.07 (3)	2.8558 (19)	158 (2)
N2—H2C $\cdots$ O6	1.03 (2)	1.63 (2)	2.6518 (18)	173 (2)
C7—H7C $\cdots$ O4 <sup>ii</sup>	0.91 (2)	2.54 (2)	3.443 (3)	174 (2)
C9—H9B $\cdots$ O8 <sup>viii</sup>	1.03 (3)	2.57 (2)	3.445 (3)	142.6 (19)
C10—H10A $\cdots$ O8 <sup>viii</sup>	0.92 (3)	2.42 (3)	3.236 (3)	148 (3)

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