CRYSTALLOGRAPHIC COMMUNICATIONS

Received 14 April 2017
Accepted 16 April 2017

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; zinc phosphite; unsymmetrical dimethyl hydrazine; open framework.

CCDC reference: 1544227

Supporting information: this article has supporting information at journals.iucr.org/e


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# The crystal structure of $\left(\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}\right)_{2}\left[\mathrm{Zn}_{3}\left(\mathrm{HPO}_{3}\right)_{4}\right]$, a three-dimensional zincophosphite framework containing 16-membered rings templated by the unsymmetrical dimethyl hydrazinium cation 

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The solution-mediated synthesis and crystal structure of 1,1-dimethylhydrazinium tetraphoshonoatotrizincate, $\left(\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}\right)_{2}\left[\mathrm{Zn}_{3}\left(\mathrm{HPO}_{3}\right)_{4}\right]$, are described. The anionic $\left[\mathrm{Zn}_{3}\left(\mathrm{HPO}_{3}\right)_{4}\right]^{2-}$ framework is built up from alternating $\mathrm{ZnO}_{4}$ tetrahedra and $\mathrm{HPO}_{3}$ pseudo-pyramids to generate a three-dimensional 4,3-net encapsulating the $\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}{ }^{+}$cations. The organic cations, which are protonated at their central N atoms, occupy pores delineated by large 16membered polyhedral rings and interact with the framework by way of $\mathrm{N}-$ $\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds and possible $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ interactions. One of the zinc ions lies on a crystallographic twofold rotation axis and all the other atoms lie on general positions. The crystal studied was found to be rotationally twinned about the [001] axis in reciprocal space in a 0.585 (5):0.415 (5) ratio.

## 1. Chemical context

Organically templated zinc phosphites are now a well-established family of open frameworks (e.g.: Phillips et al., 2002; Luo et al., 2010; Wang et al., 2011; Dong et al., 2015; Huang et al., 2017). As part of our occasional studies in this area (Harrison \& McNamee, 2010), we now describe the synthesis and structure of the title compound, (I), which represents the first example of a protonated unsymmetrical dimethyl hydrazine $\left(\mathrm{C}_{2} \mathrm{H}_{8} \mathrm{~N}_{2}\right.$ or UDMH is the neutral molecule and $\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}{ }^{+}$ is the cation) acting as a templating agent for an inorganic open framework. So far as we are aware, the only crystal structures containing $\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}{ }^{+}$that have been reported previously are molecular salts with different simple counterions (Katinaite \& Harrison, 2016, and references therein).


## 2. Structural commentary

The asymmetric unit of (I) comprises two zinc cations ( Zn 1 with site symmetry 2 and Zn 2 on a general position), two $\mathrm{HPO}_{3}{ }^{2-}$ hydrogen phosphite groups and one $\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}{ }^{+}$cation


Figure 1
The asymmetric unit of (I) expanded to show the zinc coordination polyhedra ( $50 \%$ displacement ellipsoids). For symmetry codes, see Table 1.
(Fig. 1). Both zinc ions adopt their usual tetrahedral coordination geometries (Table 1) to four nearby O atoms with mean $\mathrm{Zn}-\mathrm{O}$ separations of 1.942 and $1.945 \AA$ for Zn 1 and Zn 2 , respectively. The range of $\mathrm{O}-\mathrm{Zn}-\mathrm{O}$ bond angles for Zn 1 of 100.0 (2)-121.0 (2) ${ }^{\circ}$ indicates considerable distortion from the ideal tetrahedral value of $109.5^{\circ}$; the spread of values for Zn 2 of $99.8(2)-115.1(2)^{\circ}$ is somewhat smaller. Bond-valence-sum values (in valence units; Brown \& Altermatt, 1985) for Zn 1 and Zn 2 of 2.11 and 2.09 , respectively, are in adequate agreement with the expected values of 2.00 .

Both phosphorus atoms in (I) display their expected $\mathrm{HPO}_{3}$ pseudo-tetrahedral geometries with mean $\mathrm{P}-\mathrm{O}$ distances ( $1.517 \AA$ for P 1 and $1.516 \AA$ for P 2 ) and $\mathrm{O}-\mathrm{P}-\mathrm{O}$ angles ( $112.7^{\circ}$ for P1 and $112.6^{\circ}$ for P2) that are consistent with previous results (Dong et al., 2015). P1 deviates from its pyramid of attached O atoms by 0.418 (4) and the equivalent deviation for P 2 is 0.420 (3) $\AA$.

The structure of (I) is completed by the charge-balancing $\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}{ }^{+}$cation, which is protonated at the central (methylated) N 2 atom, as is most commonly seen for this species


Figure 2
Fragment of (I) showing a 16-ring channel occupied side-by-side by two $\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}{ }^{+}$template cations.

Table 1
Selected geometric parameters $\left(\AA,{ }^{\circ}\right)$.

| $\mathrm{Zn} 1-\mathrm{O} 4$ | $1.938(5)$ | $\mathrm{P} 1-\mathrm{O} 2$ | $1.504(5)$ |
| :--- | :---: | :--- | :--- |
| $\mathrm{Zn} 1-\mathrm{O} 4^{\mathrm{i}}$ | $1.938(5)$ | $\mathrm{P} 1-\mathrm{O} 1$ | $1.515(6)$ |
| $\mathrm{Zn} 2-\mathrm{O} 5^{\text {ii }}$ | $1.936(6)$ | $\mathrm{P} 1-\mathrm{O} 3$ | $1.533(5)$ |
| $\mathrm{Zn} 2-\mathrm{O} 2^{\text {iii }}$ | $1.943(5)$ | $\mathrm{P} 2-\mathrm{O} 5$ | $1.500(6)$ |
| $\mathrm{Zn} 2-6^{\text {iv }}$ | $1.946(5)$ | $\mathrm{P} 2-\mathrm{O} 6$ | $1.520(5)$ |
| $\mathrm{Zn} 2-\mathrm{O} 1$ | $1.954(6)$ | $\mathrm{P} 2-\mathrm{O} 4$ | $1.529(5)$ |
|  |  |  |  |
| $\mathrm{P} 1-\mathrm{O} 1-\mathrm{Zn} 2$ | $128.0(3)$ | $\mathrm{P} 2-\mathrm{O} 4-\mathrm{Zn} 1$ | $123.6(3)$ |
| $\mathrm{P} 1-\mathrm{O} 2-\mathrm{Zn} 2^{\text {iii }}$ | $140.3(3)$ | $\mathrm{P} 2-\mathrm{O} 5-\mathrm{Zn} 2^{\mathrm{v}}$ | $138.4(4)$ |
| $\mathrm{P} 1-\mathrm{O} 3-\mathrm{Zn} 1$ | $137.2(3)$ | $\mathrm{P} 2-\mathrm{O} 6-\mathrm{Zn} 2^{\text {vi }}$ | $120.8(3)$ |

Symmetry codes: (i) $-x, y,-z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2},-z+\frac{1}{2}$; (iii) $-x+\frac{1}{2},-y+\frac{1}{2},-z+1$; (iv) $x+\frac{1}{2},-y+\frac{1}{2}, z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, y-\frac{1}{2},-z+\frac{1}{2}$; (vi) $x-\frac{1}{2},-y+\frac{1}{2}, z-\frac{1}{2}$.
(Katinaite \& Harrison, 2016). The $\mathrm{C}-\mathrm{N}$ and $\mathrm{N}-\mathrm{N}$ bond lengths are indistinguishable and N 2 deviates from the plane of N1, C1 and C2 by 0.434 (8) $\AA$.

In the extended framework structure of (I), the zinc- and phosphorus-centred building units strictly alternate: every O atom forms a $\mathrm{Zn}-\mathrm{O}-\mathrm{P}$ bridge (mean angle $=131.4^{\circ}$ ), thus there are no 'dangling' $\mathrm{Zn}-\mathrm{OH}_{2}, \mathrm{P}=\mathrm{O}$ or $\mathrm{P}-\mathrm{OH}$ bonds as found in some zincophosphite frameworks (Shi et al., 2004; Liu et al., 2008), which is fully consistent with the $3: 4 \mathrm{Zn}: P$ stoichiometry of the anionic $\left[\mathrm{Zn}_{3}\left(\mathrm{HPO}_{3}\right)_{4}\right]^{2-}$ component of the structure (Harrison \& McNamee, 2010). In addition, there are no $\mathrm{Zn}-\mathrm{N}$ bonds (direct metal-to-template links) in (I); compare Kirkpatrick \& Harrison (2004), Lin et al. (2004) and Harrison (2006).

The polyhedral connectivity in (I) can be broken down as follows: the $\mathrm{Zn} 2, \mathrm{P} 1$ and P2 polyhedra form four-ring (i.e.: a loop of two Zn atoms and two P atoms) chains, with the zinc


Figure 3
The unit-cell packing in (I) viewed approximately along [110] with the framework represented topologically (i.e. as $\mathrm{Zn}-\mathrm{P}$ links).

Table 2
Hydrogen-bond geometry $\left(\AA^{\circ},{ }^{\circ}\right)$.

| $D-\mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :---: | :---: | :---: | :---: | :---: |
| N1-H1N...O1 | 0.91 | 2.34 | 3.130 (9) | 146 |
| $\mathrm{N} 1-\mathrm{H} 2 \mathrm{~N} \cdots \mathrm{O}^{\text {vii }}$ | 0.91 | 2.35 | 3.133 (9) | 144 |
| $\mathrm{N} 2-\mathrm{H} 3 \mathrm{~N} \cdots \mathrm{O} 3$ | 1.00 | 1.79 | 2.762 (8) | 163 |
| $\mathrm{C} 1-\mathrm{H} 1 A \cdots \mathrm{O} 1^{\text {v }}$ | 0.98 | 2.50 | 3.474 (11) | 173 |
| $\mathrm{C} 1-\mathrm{H} 1 C \cdots \mathrm{O} 5^{\text {viii }}$ | 0.98 | 2.50 | 3.295 (11) | 138 |
| $\mathrm{C} 2-\mathrm{H} 2 \mathrm{C} \cdots \mathrm{O} 2^{\text {ix }}$ | 0.98 | 2.43 | 3.355 (9) | 157 |

Symmetry codes: (v) $-x+\frac{1}{2}, y-\frac{1}{2},-z+\frac{1}{2}$; (vii) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (viii) $-x,-y,-z$; (ix) $x,-y+1, z-\frac{1}{2}$.
atoms as the linking nodes, which propagate alternately in the [ 110 ] and [110] directions with respect to the $c$-axis direction. Atom Zn 1 serves to link these criss-cross chains into a threedimensional open framework. If the template is omitted, a PLATON (Spek, 2009) analysis indicates that $878 \AA^{3}$ ( $43.3 \%$ ) of the unit cell is 'empty space' and the 'framework density' (FD) (number of Zn and P atoms per $1000 \AA^{3}$; Brunner \& Meier, 1989) of (I) is 13.8. This low FD is comparable to that of the unusual open-framework MAPSO-46, which contains Mg , $\mathrm{Al}, \mathrm{P}$ and Si as its tetrahedral framework atoms (Bennett \& Marcus, 1988). When the template is included in the calculation, PLATON indicates no free space, suggesting that the template is a 'snug fit' within the inorganic framework of (I).

In the extended structure, large 16-ring pores (Figs. 2 and 3) are apparent in the framework, which alternately propagate in [110] and [110] with respect to the $c$-axis direction. Measured atom-to-atom, the 16 -ring has a dimension of $\sim 5.7 \times 14.6 \AA$. Pairs of template cations lie roughly in the plane of the 16 rings and interact with framework oxygen atoms by way of $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds (Table 2). It is notable that the $\mathrm{H} \cdots \mathrm{O}$ separation for the charge-assisted $\mathrm{N}^{2}-\mathrm{H} 3 N \cdots \mathrm{O} 3$ bond is much shorter than the $\mathrm{H} \cdots \mathrm{O}$ separations for the terminal $\mathrm{N} 1 \mathrm{H}_{2}$ grouping. Within the asymmetric unit, an $R_{2}^{2}(7)$ loop is apparent (Fig. 1). Possible weak $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ interactions (Table 2) consolidate the structure.

## 3. Database survey

A survey of of the Cambridge Structural Database (Groom et al., 2016: updated to April 2017) for organically templated zinc phosphite frameworks (those containing a $\mathrm{Zn}-\mathrm{O}-\mathrm{P}-\mathrm{H}$ fragment) revealed 172 matches.

## 4. Synthesis and crystallization

Caution! UDMH is toxic, potentially carcinogenic and may form explosive mixtures with oxidizing agents: all appropriate safety precautions should be taken when handling it. Zinc oxide $(1.63 \mathrm{~g})$, phosphorus acid $(1.64 \mathrm{~g})$ and 20 ml of a 1.0 M aqueous UDMH solution were mixed in a 1:1:1 molar ratio in a sealed PTFE bottle and heated to 353 K for 24 h and then cooled to room temperature over a few hours. Product recovery by vacuum filtration yielded some colourless blocks of (I) accompanied by an unidentified white powder.

Table 3
Experimental details.
Crystal data
Chemical formula
$M_{\mathrm{r}}$
Crystal system, space group
Temperature (K)
$a, b, c(\AA)$
$\beta\left({ }^{\circ}\right)$
$V\left(\AA^{3}\right)$
Z
Radiation type
$\mu\left(\mathrm{mm}^{-1}\right)$
Crystal size (mm)
Data collection
Diffractometer
Absorption correction
$T_{\text {min }}, T_{\text {max }}$
No. of measured, independent and observed $[I>2 \sigma(I)]$ reflections $(\sin \theta / \lambda)_{\max }\left(\AA^{-1}\right)$

Refinement
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right], w R\left(F^{2}\right), S \quad 0.068,0.239,1.22$
No. of reflections
No. of parameters
H -atom treatment
$\Delta \rho_{\text {max }}, \Delta \rho_{\text {min }}\left(\mathrm{e} \AA^{-3}\right)$

2273

```
\(\left(\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}\right)_{2}\left[\mathrm{Zn}_{3}\left(\mathrm{HPO}_{3}\right)_{4}\right]\)
638.24
Monoclinic, \(C 2 / c\)
100
15.1154 (5), 8.7269 (3), 16.1675 (6)
108.156 (1)
2026.48 (12)
4
Mo \(K \alpha\)
3.90
\(0.19 \times 0.11 \times 0.05\)
```

Rigaku Mercury CCD
Multi-scan (SADABS; Sheldrick,
2004)
0.527, 1.000
2273, 2273, 2169
0.650
2273
127
H -atom parameters constrained
1.51, -1.24

Computer programs: CrysAlis PRO (Rigaku, 2015), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012), ATOMS (Shape Software, 2005) and publCIF (Westrip, 2010).

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3 . The N -bound H atoms were located in difference maps, relocated to idealized locations ( $\mathrm{N}-\mathrm{H}=0.91-1.00 \AA$ ) and refined as riding atoms. The other hydrogen atoms were placed geometrically ( $\mathrm{P}-\mathrm{H}=1.32, \mathrm{C}-$ $\mathrm{H}=0.98 \AA$ ) and refined as riding atoms. The constraint $U_{\text {iso }}(\mathrm{H})=1.2 U_{\text {eq }}$ (carrier) or $1.5 U_{\text {eq }}$ (methyl carrier) was applied in all cases. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The crystal chosen for data collection was found to be rotationally twinned about the [001] axis in reciprocal space in a 0.585 (5):0.415 (5) ratio.

## Acknowledgements

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

## References

Bennett, J. M. \& Marcus, B. K. (1988). Stud. Surf. Sci. Catal. 37, 269279.

Brunner, G. O. \& Meier, W. M. (1989). Nature (London), 337, 146147.

Brown, I. D. \& Altermatt, D. (1985). Acta Cryst. B41, 244-247.
Dong, Z.-J., Yan, Y., Zhang, W.-Q., Wang, Y. \& Li, J.-Y. (2015). Chem. Res. Chin. Univ. 31, 498-502.
Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849-854.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. \& Ward, S. C. (2016). Acta Cryst. B72, 171-179.
Harrison, W. T. A. (2006). Acta Cryst. C62, m156-m158.
Harrison, W. T. A. \& McNamee, P. M. (2010). J. Chem. Res. (S), 34, 641-642.
Huang, H.-L., Lin, H.-Y., Chen, P.-S., Lee, J.-J., Kung, H.-C. \& Wang, S.-L. (2017). Dalton Trans. 46, 364-368.

Katinaitė, J. \& Harrison, W. T. A. (2016). Acta Cryst. E72, 12061210.

Kirkpatrick, A. \& Harrison, W. T. A. (2004). Solid State Sci. 6, 593598.

Lin, Z.-E., Zhang, J., Zheng, S.-T. \& Yang, G.-Y. (2004). Microporous Mesoporous Mater. 68, 65-70.
Liu, L., Zhang, L., Wang, X., Li, G., Liu, Y. \& Pang, W. (2008). Dalton Trans. pp. 2009-2014.
Luo, X.-C., Gong, M.-C., Chen, Y.-Q. \& Lin, Z.-E. (2010). Microporous Mesoporous Mater. 131, 418-422.

Phillips, M. L. F., Nenoff, T. M., Thompson, C. T. \& Harrison, W. T. A. (2002). J. Solid State Chem. 167, 337-343.

Rigaku (2015). CrysAlis PRO. Rigaku Corporation, Tokyo, Japan.
Shape Software (2005). ATOMS. Shape Software Inc., Kingsport, Tennessee, USA.
Sheldrick, G. M. (2004). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8.
Spek, A. L. (2009). Acta Cryst. D65, 148-155.
Shi, S., Qian, W., Li, G., Wang, L., Yuan, H., Xu, J., Zhu, G., Song, T. \& Qiu, S. (2004). J. Solid State Chem. 177, 3038-3044.
Wang, S.-D., Luo, D.-B., Luo, X.-C., Chen, Y.-Q. \& Lin, Z.-E. (2011). Solid State Sci. 13, 904-907.
Westrip, S. P. (2010). J. Appl. Cryst. 43, 920-925.

## supporting information

Acta Cryst. (2017). E73, 759-762 [https://doi.org/10.1107/S2056989017005758]

## The crystal structure of $\left(\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}\right)_{2}\left[\mathrm{Zn}_{3}\left(\mathrm{HPO}_{3}\right)_{4}\right]$, a three-dimensional zincophosphite framework containing 16-membered rings templated by the unsymmetrical dimethyl hydrazinium cation

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## Computing details

Data collection: CrysAlis PRO (Rigaku, 2015); cell refinement: CrysAlis PRO (Rigaku, 2015); data reduction: CrysAlis PRO (Rigaku, 2015); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and ATOMS (Shape Software, 2005); software used to prepare material for publication: publCIF (Westrip, 2010).

## 1,1-Dimethylhydrazinium tetraphoshonoatotrizincate(II)

## Crystal data

$\left(\mathrm{C}_{2} \mathrm{H}_{9} \mathrm{~N}_{2}\right)_{2}\left[\mathrm{Zn}_{3}\left(\mathrm{HPO}_{3}\right)_{4}\right]$
$M_{r}=638.24$
Monoclinic, $C 2 / c$
$a=15.1154(5) \AA$
$b=8.7269$ (3) $\AA$
$c=16.1675$ (6) $\AA$
$\beta=108.156(1)^{\circ}$
$V=2026.48(12) \AA^{3}$
$Z=4$

## Data collection

Rigaku Mercury CCD
diffractometer
$\omega$ scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 2004)
$T_{\min }=0.527, T_{\max }=1.000$
2273 measured reflections

## Refinement

Refinement on $F^{2}$
Least-squares matrix: full
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.068$
$w R\left(F^{2}\right)=0.239$
$S=1.22$
2273 reflections
127 parameters
0 restraints

$$
\begin{aligned}
& F(000)=1280 \\
& D_{\mathrm{x}}=2.092 \mathrm{Mg} \mathrm{~m}^{-3} \\
& \text { Mo } K \alpha \text { radiation, } \lambda=0.71073 \AA \\
& \text { Cell parameters from } 6272 \text { reflections } \\
& \theta=2.6-27.6^{\circ} \\
& \mu=3.90 \mathrm{~mm}^{-1} \\
& T=100 \mathrm{~K} \\
& \text { Block, colourless } \\
& 0.19 \times 0.11 \times 0.05 \mathrm{~mm}
\end{aligned}
$$

2273 independent reflections
2169 reflections with $I>2 \sigma(I)$
$\theta_{\text {max }}=27.5^{\circ}, \theta_{\text {min }}=2.7^{\circ}$
$h=-19 \rightarrow 18$
$k=-11 \rightarrow 11$
$l=-11 \rightarrow 20$

$$
\begin{aligned}
& \text { Primary atom site location: structure-invariant } \\
& \quad \text { direct methods } \\
& \text { Hydrogen site location: mixed } \\
& \text { H-atom parameters constrained } \\
& w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}^{2}\right)+(0.1587 P)^{2}+13.6003 P\right] \\
& \text { where } P=\left(F_{\mathrm{o}}^{2}+2 F_{\mathrm{c}}^{2}\right) / 3 \\
& (\Delta / \sigma)_{\max }<0.001 \\
& \Delta \rho_{\max }=1.51 \mathrm{e} \AA^{-3} \\
& \Delta \rho_{\min }=-1.24 \mathrm{e} \AA^{-3}
\end{aligned}
$$

Extinction correction: SHELXL2014
(Sheldrick, 2015),
$\mathrm{Fc}^{*}=\mathrm{kFc}\left[1+0.001 \mathrm{xFc}^{2} \lambda^{3} / \sin (2 \theta)\right]^{-1 / 4}$
Extinction coefficient: 0.011 (2)

## Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refined as a 2-component twin with components rotated about (001) in reciprocal space

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

|  | $x$ | $y$ | $z$ | $U_{\text {iso }}^{*} / U_{\mathrm{eq}}$ |
| :--- | :--- | :--- | :--- | :--- |
| Zn1 | 0.0000 | $0.16565(13)$ | 0.2500 | $0.0076(4)$ |
| Zn2 | $0.36570(6)$ | $0.37073(9)$ | $0.48484(5)$ | $0.0096(4)$ |
| P1 | $0.15444(13)$ | $0.3885(2)$ | $0.37817(11)$ | $0.0091(5)$ |
| H1 | 0.1147 | 0.5248 | 0.3662 | $0.011^{*}$ |
| P2 | $-0.01597(13)$ | $-0.0917(2)$ | $0.11747(11)$ | $0.0088^{(5)}$ |
| H2 | -0.0253 | -0.1970 | 0.1728 | $0.011^{*}$ |
| O1 | $0.2557(4)$ | $0.4152(7)$ | $0.3858(3)$ | $0.0193(12)$ |
| O2 | $0.1393(5)$ | $0.3246(6)$ | $0.4592(3)$ | $0.0180(12)$ |
| O3 | $0.1081(4)$ | $0.2975(7)$ | $0.2948(3)$ | $0.0160(11)$ |
| O4 | $0.0428(4)$ | $0.0362(6)$ | $0.1728(3)$ | $0.0146(11)$ |
| O5 | $0.0321(4)$ | $-0.1690(6)$ | $0.0604(4)$ | $0.0169(12)$ |
| O6 | $-0.1139(4)$ | $-0.0379(6)$ | $0.0684(3)$ | $0.0124(10)$ |
| C1 | $0.1591(7)$ | $0.2877(11)$ | $0.0880(5)$ | $0.028(2)$ |
| H1A | 0.1821 | 0.1825 | 0.1002 | $0.043^{*}$ |
| H1B | 0.1847 | 0.3339 | 0.0452 | $0.043^{*}$ |
| H1C | 0.0909 | 0.2867 | 0.0649 | $0.043^{*}$ |
| C2 | $0.1529(8)$ | $0.5365(10)$ | $0.1562(6)$ | $0.029(2)$ |
| H2A | 0.1818 | 0.5963 | 0.2091 | $0.043^{*}$ |
| H2B | 0.0852 | 0.5358 | 0.1439 | $0.043^{*}$ |
| H2C | 0.1683 | 0.5827 | 0.1072 | $0.043^{*}$ |
| N1 | $0.2898(6)$ | $0.3663(9)$ | $0.2063(5)$ | $0.0249(17)$ |
| H1N | 0.3067 | 0.3880 | 0.2642 | $0.030^{*}$ |
| H2N | 0.3170 | 0.4346 | 0.1793 | $0.030^{*}$ |
| N2 | $0.1884(5)$ | $0.3781(7)$ | $0.1691(4)$ | $0.0132(13)$ |
| H3N | 0.1608 | 0.3280 | 0.2110 | $0.016^{*}$ |
|  |  |  |  |  |

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

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Zn1 | $0.0064(7)$ | $0.0080(6)$ | $0.0076(6)$ | 0.000 | $0.0008(4)$ | 0.000 |
| Zn2 | $0.0093(6)$ | $0.0109(5)$ | $0.0078(5)$ | $-0.0032(3)$ | $0.0015(4)$ | $0.0003(3)$ |
| P1 | $0.0106(10)$ | $0.0085(8)$ | $0.0076(8)$ | $-0.0011(6)$ | $0.0021(7)$ | $0.0010(6)$ |
| P2 | $0.0085(9)$ | $0.0093(8)$ | $0.0077(8)$ | $0.0008(6)$ | $0.0014(7)$ | $0.0001(6)$ |
| O1 | $0.020(3)$ | $0.024(3)$ | $0.012(2)$ | $-0.006(2)$ | $0.001(2)$ | $0.002(2)$ |


| O2 | $0.033(3)$ | $0.009(2)$ | $0.013(2)$ | $-0.002(2)$ | $0.009(2)$ | $0.0000(18)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| O3 | $0.013(3)$ | $0.023(3)$ | $0.012(2)$ | $-0.010(2)$ | $0.004(2)$ | $-0.006(2)$ |
| O4 | $0.015(3)$ | $0.014(2)$ | $0.014(2)$ | $0.000(2)$ | $0.002(2)$ | $-0.006(2)$ |
| O5 | $0.025(3)$ | $0.012(2)$ | $0.016(2)$ | $0.005(2)$ | $0.009(2)$ | $-0.0021(19)$ |
| O6 | $0.008(3)$ | $0.016(2)$ | $0.013(2)$ | $0.000(2)$ | $0.0020(19)$ | $0.004(2)$ |
| C1 | $0.039(5)$ | $0.024(4)$ | $0.015(3)$ | $-0.003(4)$ | $-0.002(4)$ | $-0.008(3)$ |
| C2 | $0.048(6)$ | $0.020(4)$ | $0.024(4)$ | $0.005(4)$ | $0.020(4)$ | $0.006(3)$ |
| N1 | $0.019(4)$ | $0.034(4)$ | $0.020(3)$ | $-0.004(3)$ | $0.004(3)$ | $0.002(3)$ |
| N2 | $0.017(4)$ | $0.013(3)$ | $0.011(3)$ | $-0.004(2)$ | $0.008(3)$ | $-0.001(2)$ |

Geometric parameters ( $\mathrm{A},{ }^{\circ}$ )

| $\mathrm{Zn} 1-\mathrm{O} 4$ | 1.938 (5) | $\mathrm{O} 2-\mathrm{Zn} 2^{\text {iii }}$ | 1.943 (5) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Zn} 1-\mathrm{O} 4^{\text {i }}$ | 1.938 (5) | $\mathrm{O} 5-\mathrm{Zn} 2^{\text {v }}$ | 1.936 (6) |
| $\mathrm{Zn} 1-\mathrm{O}^{\text {i }}$ | 1.945 (5) | O6-Zn2 ${ }^{\text {vi }}$ | 1.946 (5) |
| $\mathrm{Zn} 1-\mathrm{O} 3$ | 1.945 (5) | C1-N2 | 1.475 (9) |
| $\mathrm{Zn} 2-\mathrm{O} 5^{\text {ii }}$ | 1.936 (6) | C1-H1A | 0.9800 |
| $\mathrm{Zn} 2-\mathrm{O} 2{ }^{\text {iii }}$ | 1.943 (5) | C1-H1B | 0.9800 |
| $\mathrm{Zn} 2-\mathrm{O}^{\text {iv }}$ | 1.946 (5) | $\mathrm{C} 1-\mathrm{H} 1 \mathrm{C}$ | 0.9800 |
| Zn2-O1 | 1.954 (6) | C2-N2 | 1.474 (10) |
| P1-O2 | 1.504 (5) | $\mathrm{C} 2-\mathrm{H} 2 \mathrm{~A}$ | 0.9800 |
| P1-O1 | 1.515 (6) | $\mathrm{C} 2-\mathrm{H} 2 \mathrm{~B}$ | 0.9800 |
| P1-O3 | 1.533 (5) | $\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | 0.9800 |
| P1-H1 | 1.3200 | N1-N2 | 1.465 (10) |
| P2-O5 | 1.500 (6) | N1-H1N | 0.9100 |
| P2-O6 | 1.520 (5) | N1—H2N | 0.9100 |
| P2-O4 | 1.529 (5) | N2-H3N | 1.0000 |
| P2-H2 | 1.3200 |  |  |
| $\mathrm{O} 4-\mathrm{Znl}-\mathrm{O} 4{ }^{\text {i }}$ | 108.7 (3) | $\mathrm{P} 1-\mathrm{O} 3-\mathrm{Zn} 1$ | 137.2 (3) |
| $\mathrm{O} 4-\mathrm{Znl}-\mathrm{O}^{\text {i }}$ | 121.0 (2) | $\mathrm{P} 2-\mathrm{O} 4-\mathrm{Zn} 1$ | 123.6 (3) |
| $\mathrm{O} 4{ }^{\mathrm{i}}-\mathrm{Zn} 1-\mathrm{O}^{\text {i }}$ | 100.0 (2) | $\mathrm{P} 2-\mathrm{O} 5-\mathrm{Zn} 2^{\text {v }}$ | 138.4 (4) |
| $\mathrm{O} 4-\mathrm{Zn} 1-\mathrm{O} 3$ | 100.0 (2) | $\mathrm{P} 2-\mathrm{O} 6-\mathrm{Zn} 2^{\text {vi }}$ | 120.8 (3) |
| $\mathrm{O} 4 \mathrm{i}-\mathrm{Zn} 1-\mathrm{O} 3$ | 121.0 (2) | $\mathrm{N} 2-\mathrm{C} 1-\mathrm{H} 1 \mathrm{~A}$ | 109.5 |
| O3i-Zn1-O3 | 107.4 (4) | N2-C1-H1B | 109.5 |
| $\mathrm{O} 5 \mathrm{ii}-\mathrm{Zn} 2-\mathrm{O} 2^{\text {iii }}$ | 99.8 (2) | $\mathrm{H} 1 \mathrm{~A}-\mathrm{C} 1-\mathrm{H} 1 \mathrm{~B}$ | 109.5 |
| $\mathrm{O} 5{ }^{\text {iii }} \mathrm{Zn} 2-\mathrm{O}^{\text {iv }}$ | 115.1 (2) | N2-C1-H1C | 109.5 |
| $\mathrm{O} 2{ }^{\text {iii] }} \mathrm{Z} \mathrm{Zn} 2-\mathrm{O}^{\text {iv }}$ | 110.8 (2) | $\mathrm{H} 1 \mathrm{~A}-\mathrm{C} 1-\mathrm{H} 1 \mathrm{C}$ | 109.5 |
| $\mathrm{O} 5^{\mathrm{ii}}-\mathrm{Zn} 2-\mathrm{O} 1$ | 107.5 (3) | $\mathrm{H} 1 \mathrm{~B}-\mathrm{C} 1-\mathrm{H} 1 \mathrm{C}$ | 109.5 |
| $\mathrm{O} 2{ }^{\text {iii- }} \mathrm{Zn} 2-\mathrm{O} 1$ | 114.1 (3) | $\mathrm{N} 2-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~A}$ | 109.5 |
| $\mathrm{O6}^{\text {iv }}-\mathrm{Zn} 2-\mathrm{O} 1$ | 109.3 (2) | N2-C2-H2B | 109.5 |
| $\mathrm{O} 2-\mathrm{P} 1-\mathrm{O} 1$ | 114.2 (3) | $\mathrm{H} 2 \mathrm{~A}-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~B}$ | 109.5 |
| $\mathrm{O} 2-\mathrm{P} 1-\mathrm{O} 3$ | 115.0 (3) | $\mathrm{N} 2-\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | 109.5 |
| $\mathrm{O} 1-\mathrm{P} 1-\mathrm{O} 3$ | 108.9 (3) | $\mathrm{H} 2 \mathrm{~A}-\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | 109.5 |
| $\mathrm{O} 2-\mathrm{P} 1-\mathrm{H} 1$ | 106.0 | $\mathrm{H} 2 \mathrm{~B}-\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | 109.5 |
| $\mathrm{O} 1-\mathrm{P} 1-\mathrm{H} 1$ | 106.0 | $\mathrm{N} 2-\mathrm{N} 1-\mathrm{H} 1 \mathrm{~N}$ | 109.3 |
| O3-P1-H1 | 106.0 | $\mathrm{N} 2-\mathrm{N} 1-\mathrm{H} 2 \mathrm{~N}$ | 109.2 |
| O5-P2-O6 | 113.4 (3) | $\mathrm{H} 1 \mathrm{~N}-\mathrm{N} 1-\mathrm{H} 2 \mathrm{~N}$ | 109.5 |


| O5-P2-O4 | 112.6 (3) | N1-N2-C2 | 114.3 (7) |
| :---: | :---: | :---: | :---: |
| O6-P2-O4 | 111.9 (3) | $\mathrm{N} 1-\mathrm{N} 2-\mathrm{C} 1$ | 108.3 (6) |
| O5-P2-H2 | 106.1 | C2-N2-C1 | 112.4 (7) |
| O6-P2-H2 | 106.1 | N1-N2-H3N | 107.2 |
| $\mathrm{O} 4-\mathrm{P} 2-\mathrm{H} 2$ | 106.1 | C2-N2-H3N | 107.2 |
| $\mathrm{P} 1-\mathrm{O} 1-\mathrm{Zn} 2$ | 128.0 (3) | $\mathrm{C} 1-\mathrm{N} 2-\mathrm{H} 3 \mathrm{~N}$ | 107.2 |
| $\mathrm{P} 1-\mathrm{O} 2-\mathrm{Zn} 2{ }^{\text {iii }}$ | 140.3 (3) |  |  |
| $\mathrm{O} 2-\mathrm{P} 1-\mathrm{O} 1-\mathrm{Zn} 2$ | 2.2 (6) | $\mathrm{O} 5-\mathrm{P} 2-\mathrm{O} 4-\mathrm{Zn} 1$ | 177.2 (3) |
| $\mathrm{O} 3-\mathrm{P} 1-\mathrm{O} 1-\mathrm{Zn} 2$ | -127.8 (4) | O6-P2-O4-Zn1 | 48.1 (4) |
| $\mathrm{O} 1-\mathrm{P} 1-\mathrm{O} 2-\mathrm{Zn} 2{ }^{\text {iii }}$ | -86.8 (7) | O6-P2-O5-Zn2 ${ }^{\text {v }}$ | 110.4 (6) |
| $\mathrm{O} 3-\mathrm{P} 1-\mathrm{O} 2-\mathrm{Zn} 2{ }^{\text {iii }}$ | 40.2 (8) | O4-P2-O5-Zn2 ${ }^{\text {v }}$ | -18.0 (7) |
| $\mathrm{O} 2-\mathrm{P} 1-\mathrm{O} 3-\mathrm{Zn} 1$ | 28.0 (7) | O5-P2-O6-Zn2 ${ }^{\text {vi }}$ | -68.4 (4) |
| $\mathrm{O} 1-\mathrm{P} 1-\mathrm{O} 3-\mathrm{Zn} 1$ | 157.6 (5) | O4-P2-O6-Zn2 ${ }^{\text {vi }}$ | 60.3 (4) |

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

Hydrogen-bond geometry ( $A,{ }^{\circ}$ )

| $D — \mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{~N} 1 — \mathrm{H} 1 N \cdots \mathrm{O} 1$ | 0.91 | 2.34 | $3.130(9)$ | 146 |
| $\mathrm{~N} 1 — \mathrm{H} 2 N \cdots \mathrm{O} 6^{\text {vii }}$ | 0.91 | 2.35 | $3.133(9)$ | 144 |
| $\mathrm{~N} 2 — \mathrm{H} 3 N \cdots \mathrm{O} 3$ | 1.00 | 1.79 | $2.762(8)$ | 163 |
| $\mathrm{C} 1 — \mathrm{H} 1 A \cdots \mathrm{O}^{\text {v }}$ | 0.98 | 2.50 | $3.474(11)$ | 173 |
| $\mathrm{C} 1 — \mathrm{H} 1 C \cdots \mathrm{O} 5^{\text {viii }}$ | 0.98 | 2.50 | $3.295(11)$ | 138 |
| $\mathrm{C} 2 — \mathrm{H} 2 C \cdots \mathrm{O} 2^{\text {ix }}$ | 0.98 | 2.43 | $3.355(9)$ | 157 |

Symmetry codes: (v) $-x+1 / 2, y-1 / 2,-z+1 / 2$; (vii) $x+1 / 2, y+1 / 2, z$; (viii) $-x,-y,-z$; (ix) $x,-y+1, z-1 / 2$.

