

Aquabis[1-hydroxy-2-(imidazol-3-ium-1-yl)-1,1'-ethylenediphosphonato- κ^2 O,O']-zinc(II) dihydrate

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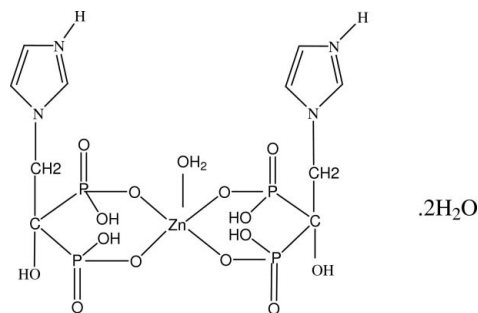
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.032; wR factor = 0.096; data-to-parameter ratio = 13.2.

In the title complex, $[\text{Zn}(\text{C}_5\text{H}_9\text{NO}_7\text{P}_2)_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$, the zinc atom is coordinated by two zoledronate anions [zoledronate = (2-(1-imidazole)-1-hydroxy-1,1'-ethylenediphosphonate)] and one water molecule. The coordination number is 5. There is one half-molecule in the asymmetric unit, the zinc atom being located on a twofold rotation axis passing through the metal centre and the coordinating water O atom. The anion exists as a zwitterion with an overall charge of -1 ; the protonated nitrogen in the ring has a positive charge and the two phosphonates groups each have a single negative charge. Intermolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds link the molecules. An $\text{N}-\text{H} \cdots \text{O}$ interaction is also present.

Related literature

For general background to bisphosphonates, see: Fleisch *et al.* (1968); Green *et al.* (1994); Fleisch (2000); Ross *et al.* (2004); Smith (2005); Ralston *et al.* (1989); Reid *et al.* (2005); Rauch & Glorieux (2005); Chesnut *et al.* (2004). For structures of transition metal (Ni, Co and Cu) complexes with the zoledronate anion, see: Cao *et al.* (2007, 2008). For metal complexes of other bisphosphonates (Etidronate and Pamidronate), see: Fernández *et al.* (2002); Li *et al.* (2008); Chen *et al.* (2008); Uchtman (1972). For a hexacoordinated zinc(II)-zoledronate complex, see: Freire & Vega (2009).



Experimental

Crystal data

$[\text{Zn}(\text{C}_5\text{H}_9\text{N}_2\text{O}_7\text{P}_2)_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

$M_r = 661.58$

Monoclinic, $C2/c$

$a = 12.089$ (2) Å

$b = 9.858$ (2) Å

$c = 18.831$ (4) Å

$\beta = 95.09$ (3)°

$V = 2235.3$ (8) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 1.48$ mm⁻¹

$T = 293$ K

$0.20 \times 0.18 \times 0.09$ mm

Data collection

Rigaku AFC6 diffractometer

Absorption correction: ψ scan

(North *et al.*, 1968)

$T_{\min} = 0.75$, $T_{\max} = 0.87$

2847 measured reflections

2208 independent reflections

1528 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

3 standard reflections

every 150 reflections

intensity decay: <3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.096$

$S = 1.00$

2208 reflections

167 parameters

H-atom parameters constrained

$\Delta\rho_{\max} = 0.35$ e Å⁻³

$\Delta\rho_{\min} = -0.87$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--------------------------|-------------|---------------------------|-------------|
| Zn1—O1W | 1.999 (4) | Zn1—O21 | 2.041 (2) |
| Zn1—O11 | 2.006 (2) | | |
| O1W—Zn1—O11 | 112.97 (8) | O1W—Zn1—O21 | 88.48 (7) |
| O11—Zn1—O11 ⁱ | 134.06 (15) | O11—Zn1—O21 | 92.16 (9) |
| O11—Zn1—O21 ⁱ | 89.03 (9) | O21 ⁱ —Zn1—O21 | 176.96 (14) |

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| O12—H12 ⁱⁱ ···O2W | 0.82 | 1.75 | 2.566 (3) | 171 |
| O22—H22 ⁱⁱⁱ ···O13 ⁱⁱⁱ | 0.82 | 1.84 | 2.645 (3) | 167 |
| O2W—H2WA···O21 ⁱⁱⁱ | 0.82 | 2.38 | 2.990 (3) | 132 |
| O2W—H2WB···O13 ^{iv} | 0.82 | 1.94 | 2.758 (4) | 173 |
| N2—H2 ^v ···O12 ^v | 0.86 | 2.11 | 2.917 (4) | 157 |
| O1W—H1W···O23 ⁱⁱ | 0.82 | 1.81 | 2.632 (3) | 177 |
| O1—H1···O23 ⁱⁱ | 0.82 | 1.80 | 2.581 (3) | 160 |

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

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Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

We acknowledge PICT 25409, the Spanish Research Council (CSIC) for providing us with a free-of-charge licence to use the CSD system (Allen, 2002) and Professor Judith Howard for the donation of a Rigaku AFC6S four-circle diffractometer. EF is a member of the research staff of Conicet. The authors are grateful to Laboratorios Gador for providing the zoledronic acid.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2166).

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supplementary materials

Acta Cryst. (2009). E65, m1430-m1431 [doi:10.1107/S160053680904286X]

Aquabis[1-hydroxy-2-(imidazol-3-ium-1-yl)-1,1'-ethylidenediphosphonato- κ^2O,O']zinc(II) dihydrate

E. Freire and D. R. Vega

Comment

The following work is part of a project directed to the preparation and characterization of coordination complexes obtained by the interaction among metals and organic molecules of relevant pharmacological interest like bisphosphonates. An informative introduction on bisphosphonates has been made in the previous paper (Freire & Vega, 2009). Although few metal derivatives of Zoledronic acid have been reported in CSD (Allen, 2002), an isostructural compound of copper has been synthesized (Cao *et al.*, 2008).

So, we present herein the crystal structure of a Zinc-Zoledronate complex: monozinc dizoledronate trihydrate, (I), Zn.(H₂O).2(P₂O₇N₂C₅H₉).2H₂O. In (I), as in the similar hexacoordinated compound (Freire & Vega, 2009), the zoledronate anion exists as a zwitterion with an overall charge of -1; the protonated nitrogen in the ring has a positive charge and the two phosphonates groups each have a single negative charge.

The coordination number of Zn is 5 (Fig. 1) and the resulting coordination polyhedron is a trigonal bipyramid defined by O21, O21A, O11, O11A and O1W. Atoms O11A and O21A are generated by the symmetry operation (1 - x, y, 3/2 - z). The equatorial plane is defined by O11, O11A and O1W, the apexes are defined by O21 and O21A. The apical Zn—O distance is 2.041 (2) Å while in the equatorial plane the mean value for the Zn—O distance is 2.004 (4) Å. The coordination angles in the equatorial plane are a little turned aside from the expected 120° theoretically due to the "bite" of the ligand: O11—Zn—O11A 134.08 (15)°, O11—Zn—O1W and O11A—Zn—O1W are 112.96 (8)°. The angle between the line defined by O21 and O21A with the normal to the equatorial plane (O11, O11A, O1W and Zn1) is 2.3°.

Considering the bisphosphonates groups, there are two distinct types of P—O bonds, as shown by the mean value in the following bond distances and angles: P—OH 1.576 (8), P - O 1.505 (5) Å, O—P—OH 109.4° (11), O—P—O 116.4° (14). The staggered conformation of PO₃ groups in compound (II) is more prominent than in the hexacoordinated complex (Freire & Vega, 2009), the non bonded torsion angle O12—P1...P2 O22 is -16.1°. In (I), the imidazol ring is planar, maximum deviation from the *L. S.* mean plane is 0.0026 Å for C3, and it is not coplanar with C2, between the plane of the ring and the bond N1—C2 is 3.4° and C2 is 0.0837 Å far from the ring. The torsion angle C1—C2—N1—C3 is of -78.62° and it is possible to describe it like - Syn-Clinal (-*sc*).

Five hydrogen bonds, involving, H22, H1W, H1, H2WA and H2WB, provide intermolecular cohesion, defining a two-dimensional arrangement, while the three-dimensional net completes with two more hydrogen bonds, involving H2 from the aromatic ring and H12 from the bisphosphonate group (Fig. 2 and Table 2).

Experimental

Zoledronic Acid was obtained from Gador S. A. laboratory. Compound (II) was obtained by direct mix of a water solution of Zoledronic Acid and a water solution of ZnCl₂. Colorless prismatic crystals were grown after a few days.

Refinement

The H atoms attached to O were found in a difference Fourier map, further idealized (O—H: 0.82 Å - 0.90 Å) and finally allowed to ride. Those attached to C and N were placed at calculated positions (C—H: 0.93 Å; C—H₂: 0.97 Å; N—H₂: 0.90 Å) and allowed to ride. Displacement factors were taken as $U(\text{H})_{\text{isot}} = x \cdot U(\text{host})$, x : 1.2 (C—H); 1.5 (C—H₂, N—H₂, O—H).

Figures

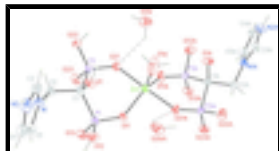


Fig. 1. : Molecular view of (I), showing the labeling scheme used. Hydrogen bonding is shown in dashed lines.

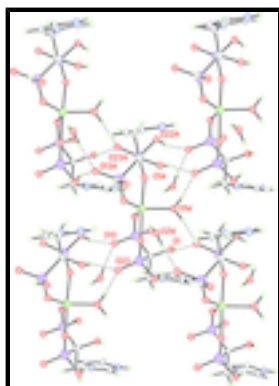


Fig. 2. : Full packing diagram of (I).

Aquabis[1-hydroxy-2-(imidazol-3-ium-1-yl)-1,1'-ethylidenediphosphonato- $\kappa^2\text{O},\text{O}'$]zinc(II) dihydrate

Crystal data

$[\text{Zn}(\text{C}_5\text{H}_9\text{N}_2\text{O}_7\text{P}_2)_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

$M_r = 661.58$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 12.089$ (2) Å

$b = 9.858$ (2) Å

$c = 18.831$ (4) Å

$\beta = 95.09$ (3)°

$V = 2235.3$ (8) Å³

$Z = 4$

$F_{000} = 1352$

$D_x = 1.966$ Mg m⁻³

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

Cell parameters from 42 reflections

$\theta = 8\text{--}25^\circ$

$\mu = 1.48$ mm⁻¹

$T = 293$ K

Prism, colorless

$0.20 \times 0.18 \times 0.09$ mm

Data collection

Rigaku AFC6 diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$R_{\text{int}} = 0.054$

$\theta_{\text{max}} = 26.0^\circ$

$\theta_{\text{min}} = 2.2^\circ$

$T = 293$ K $h = -1 \rightarrow 14$
 $\omega/2\theta$ scans $k = -1 \rightarrow 12$
Absorption correction: ψ scan $l = -23 \rightarrow 23$
(North *et al.*, 1968)
 $T_{\min} = 0.75$, $T_{\max} = 0.87$ 3 standard reflections
2847 measured reflections every 150 reflections
2208 independent reflections intensity decay: <3%
1528 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.032$ H-atom parameters constrained
 $wR(F^2) = 0.096$ $w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 1.3378P]$
 $S = 1.00$ where $P = (F_o^2 + 2F_c^2)/3$
2208 reflections $(\Delta/\sigma)_{\max} = 0.001$
167 parameters $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods $\Delta\rho_{\min} = -0.87 \text{ e } \text{\AA}^{-3}$
Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| Zn1 | 0.5000 | 0.50532 (5) | 0.7500 | 0.02015 (15) |
| P1 | 0.64482 (6) | 0.41327 (8) | 0.61862 (4) | 0.01916 (19) |
| P2 | 0.76934 (6) | 0.48891 (8) | 0.75923 (4) | 0.01749 (19) |
| O1 | 0.71512 (19) | 0.6590 (2) | 0.64590 (11) | 0.0237 (5) |
| H1 | 0.7154 | 0.7093 | 0.6806 | 0.043 (12)* |
| O11 | 0.54208 (18) | 0.4259 (3) | 0.65807 (12) | 0.0299 (5) |
| O12 | 0.6205 (2) | 0.4826 (2) | 0.54319 (13) | 0.0288 (5) |
| H12 | 0.6271 | 0.4369 | 0.5075 | 0.050 (14)* |
| O13 | 0.68721 (19) | 0.2707 (2) | 0.61059 (12) | 0.0277 (5) |
| O21 | 0.66152 (17) | 0.5108 (2) | 0.79201 (11) | 0.0253 (5) |

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| | | | | |
|------|--------------|------------|--------------|-------------|
| O22 | 0.85809 (18) | 0.5945 (2) | 0.79009 (12) | 0.0269 (5) |
| H22 | 0.8339 | 0.6491 | 0.8177 | 0.051 (14)* |
| O23 | 0.81904 (19) | 0.3498 (2) | 0.76479 (12) | 0.0280 (5) |
| O1W | 0.5000 | 0.7080 (4) | 0.7500 | 0.0727 (17) |
| H1W | 0.5565 | 0.7530 | 0.7470 | 0.109* |
| O2W | 0.6191 (2) | 0.3463 (3) | 0.42704 (13) | 0.0394 (6) |
| H2WA | 0.5899 | 0.3910 | 0.3937 | 0.059* |
| H2WB | 0.6790 | 0.3124 | 0.4196 | 0.059* |
| N1 | 0.8788 (2) | 0.5706 (3) | 0.56618 (13) | 0.0218 (5) |
| N2 | 0.8895 (2) | 0.7275 (3) | 0.48801 (15) | 0.0328 (7) |
| H2 | 0.8972 | 0.8060 | 0.4691 | 0.039* |
| C1 | 0.7536 (2) | 0.5248 (3) | 0.66243 (16) | 0.0183 (6) |
| C2 | 0.8707 (2) | 0.5064 (3) | 0.63530 (16) | 0.0216 (6) |
| H2A | 0.9262 | 0.5453 | 0.6698 | 0.026* |
| H2B | 0.8865 | 0.4103 | 0.6315 | 0.026* |
| C3 | 0.8930 (3) | 0.7035 (3) | 0.55705 (18) | 0.0278 (7) |
| H3 | 0.9034 | 0.7680 | 0.5931 | 0.033* |
| C4 | 0.8718 (3) | 0.6092 (4) | 0.45095 (19) | 0.0351 (8) |
| H4 | 0.8657 | 0.5991 | 0.4017 | 0.042* |
| C5 | 0.8649 (3) | 0.5096 (4) | 0.49990 (17) | 0.0282 (7) |
| H5 | 0.8530 | 0.4178 | 0.4907 | 0.034* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Zn1 | 0.0189 (2) | 0.0212 (3) | 0.0206 (3) | 0.000 | 0.00281 (18) | 0.000 |
| P1 | 0.0201 (4) | 0.0188 (4) | 0.0187 (4) | -0.0007 (3) | 0.0023 (3) | -0.0026 (3) |
| P2 | 0.0181 (4) | 0.0171 (4) | 0.0172 (4) | 0.0010 (3) | 0.0010 (3) | 0.0012 (3) |
| O1 | 0.0348 (12) | 0.0148 (10) | 0.0211 (11) | 0.0063 (9) | -0.0003 (9) | 0.0005 (9) |
| O11 | 0.0207 (11) | 0.0397 (14) | 0.0304 (13) | -0.0072 (10) | 0.0080 (9) | -0.0142 (11) |
| O12 | 0.0363 (13) | 0.0275 (12) | 0.0217 (11) | 0.0036 (10) | -0.0033 (10) | -0.0023 (10) |
| O13 | 0.0378 (13) | 0.0175 (11) | 0.0282 (11) | 0.0015 (10) | 0.0044 (10) | -0.0035 (10) |
| O21 | 0.0190 (10) | 0.0362 (13) | 0.0208 (11) | 0.0021 (9) | 0.0029 (8) | -0.0011 (10) |
| O22 | 0.0231 (11) | 0.0291 (13) | 0.0284 (12) | -0.0052 (9) | 0.0019 (9) | -0.0081 (11) |
| O23 | 0.0360 (13) | 0.0193 (11) | 0.0296 (12) | 0.0064 (9) | 0.0072 (10) | 0.0062 (9) |
| O1W | 0.025 (2) | 0.0195 (19) | 0.177 (6) | 0.000 | 0.027 (3) | 0.000 |
| O2W | 0.0535 (17) | 0.0414 (15) | 0.0233 (12) | 0.0094 (13) | 0.0041 (11) | -0.0019 (11) |
| N1 | 0.0212 (12) | 0.0244 (13) | 0.0203 (13) | -0.0008 (10) | 0.0051 (10) | -0.0006 (12) |
| N2 | 0.0363 (16) | 0.0302 (15) | 0.0324 (15) | -0.0009 (12) | 0.0062 (13) | 0.0132 (14) |
| C1 | 0.0207 (14) | 0.0144 (13) | 0.0197 (14) | 0.0035 (11) | 0.0020 (11) | 0.0013 (11) |
| C2 | 0.0193 (14) | 0.0239 (16) | 0.0217 (15) | -0.0002 (12) | 0.0025 (12) | 0.0034 (13) |
| C3 | 0.0288 (17) | 0.0252 (16) | 0.0304 (18) | -0.0040 (13) | 0.0073 (13) | 0.0004 (14) |
| C4 | 0.0333 (19) | 0.049 (2) | 0.0230 (17) | 0.0047 (16) | 0.0012 (14) | 0.0041 (17) |
| C5 | 0.0291 (17) | 0.0322 (18) | 0.0237 (16) | -0.0001 (14) | 0.0044 (13) | -0.0070 (15) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|---------|-----------|----------|--------|
| Zn1—O1W | 1.999 (4) | O1W—H1W | 0.8200 |
| Zn1—O11 | 2.006 (2) | O2W—H2WA | 0.8200 |

| | | | |
|--|-------------|---------------|-------------|
| Zn1—O11 ⁱ | 2.006 (2) | O2W—H2WB | 0.8200 |
| Zn1—O21 ⁱ | 2.041 (2) | N1—C3 | 1.335 (4) |
| Zn1—O21 | 2.041 (2) | N1—C5 | 1.382 (4) |
| P1—O13 | 1.508 (2) | N1—C2 | 1.458 (4) |
| P1—O11 | 1.508 (2) | N2—C3 | 1.318 (4) |
| P1—O12 | 1.580 (2) | N2—C4 | 1.366 (5) |
| P1—C1 | 1.851 (3) | N2—H2 | 0.8600 |
| P2—O23 | 1.497 (2) | C1—C2 | 1.558 (4) |
| P2—O21 | 1.506 (2) | C2—H2A | 0.9700 |
| P2—O22 | 1.569 (2) | C2—H2B | 0.9700 |
| P2—C1 | 1.850 (3) | C3—H3 | 0.9300 |
| O1—C1 | 1.427 (3) | C4—C5 | 1.355 (5) |
| O1—H1 | 0.8200 | C4—H4 | 0.9300 |
| O12—H12 | 0.8200 | C5—H5 | 0.9300 |
| O22—H22 | 0.8200 | | |
| O1W—Zn1—O11 | 112.97 (8) | H2WA—O2W—H2WB | 114.6 |
| O1W—Zn1—O11 ⁱ | 112.97 (7) | C3—N1—C5 | 108.5 (3) |
| O11—Zn1—O11 ⁱ | 134.06 (15) | C3—N1—C2 | 124.1 (3) |
| O1W—Zn1—O21 ⁱ | 88.48 (7) | C5—N1—C2 | 127.2 (3) |
| O11—Zn1—O21 ⁱ | 89.03 (9) | C3—N2—C4 | 109.9 (3) |
| O11 ⁱ —Zn1—O21 ⁱ | 92.16 (9) | C3—N2—H2 | 125.0 |
| O1W—Zn1—O21 | 88.48 (7) | C4—N2—H2 | 125.0 |
| O11—Zn1—O21 | 92.16 (9) | O1—C1—C2 | 108.9 (2) |
| O11 ⁱ —Zn1—O21 | 89.03 (9) | O1—C1—P2 | 113.3 (2) |
| O21 ⁱ —Zn1—O21 | 176.96 (14) | C2—C1—P2 | 106.45 (19) |
| O13—P1—O11 | 115.37 (14) | O1—C1—P1 | 104.41 (18) |
| O13—P1—O12 | 110.54 (13) | C2—C1—P1 | 114.5 (2) |
| O11—P1—O12 | 108.12 (14) | P2—C1—P1 | 109.42 (15) |
| O13—P1—C1 | 111.36 (13) | N1—C2—C1 | 112.1 (2) |
| O11—P1—C1 | 108.35 (13) | N1—C2—H2A | 109.2 |
| O12—P1—C1 | 102.23 (13) | C1—C2—H2A | 109.2 |
| O23—P2—O21 | 117.33 (14) | N1—C2—H2B | 109.2 |
| O23—P2—O22 | 108.95 (14) | C1—C2—H2B | 109.2 |
| O21—P2—O22 | 109.95 (13) | H2A—C2—H2B | 107.9 |
| O23—P2—C1 | 104.47 (13) | N2—C3—N1 | 108.1 (3) |
| O21—P2—C1 | 111.03 (13) | N2—C3—H3 | 126.0 |
| O22—P2—C1 | 104.20 (13) | N1—C3—H3 | 126.0 |
| C1—O1—H1 | 114.1 | C5—C4—N2 | 106.7 (3) |
| P1—O11—Zn1 | 137.76 (14) | C5—C4—H4 | 126.6 |
| P1—O12—H12 | 118.4 | N2—C4—H4 | 126.6 |
| P2—O21—Zn1 | 132.07 (13) | C4—C5—N1 | 106.8 (3) |
| P2—O22—H22 | 113.5 | C4—C5—H5 | 126.6 |
| Zn1—O1W—H1W | 122.7 | N1—C5—H5 | 126.6 |
| O13—P1—O11—Zn1 | 114.0 (2) | O13—P1—C1—O1 | 162.06 (18) |
| O12—P1—O11—Zn1 | -121.6 (2) | O11—P1—C1—O1 | -70.0 (2) |
| C1—P1—O11—Zn1 | -11.6 (3) | O12—P1—C1—O1 | 44.0 (2) |
| O1W—Zn1—O11—P1 | 70.5 (2) | O13—P1—C1—C2 | 43.0 (2) |

supplementary materials

| | | | |
|------------------------------|--------------|--------------|-------------|
| O11 ⁱ —Zn1—O11—P1 | -109.5 (2) | O11—P1—C1—C2 | 170.9 (2) |
| O21 ⁱ —Zn1—O11—P1 | 158.5 (2) | O12—P1—C1—C2 | -75.0 (2) |
| O21—Zn1—O11—P1 | -18.7 (2) | O13—P1—C1—P2 | -76.38 (17) |
| O23—P2—O21—Zn1 | -95.2 (2) | O11—P1—C1—P2 | 51.53 (18) |
| O22—P2—O21—Zn1 | 139.62 (18) | O12—P1—C1—P2 | 165.57 (14) |
| C1—P2—O21—Zn1 | 24.8 (2) | C3—N1—C2—C1 | 78.5 (4) |
| O1W—Zn1—O21—P2 | -102.54 (19) | C5—N1—C2—C1 | -96.1 (3) |
| O11—Zn1—O21—P2 | 10.4 (2) | O1—C1—C2—N1 | -39.8 (3) |
| O11 ⁱ —Zn1—O21—P2 | 144.5 (2) | P2—C1—C2—N1 | -162.3 (2) |
| O23—P2—C1—O1 | -175.2 (2) | P1—C1—C2—N1 | 76.6 (3) |
| O21—P2—C1—O1 | 57.4 (2) | C4—N2—C3—N1 | 0.6 (4) |
| O22—P2—C1—O1 | -60.9 (2) | C5—N1—C3—N2 | -0.6 (4) |
| O23—P2—C1—C2 | -55.5 (2) | C2—N1—C3—N2 | -176.1 (3) |
| O21—P2—C1—C2 | 177.09 (19) | C3—N2—C4—C5 | -0.3 (4) |
| O22—P2—C1—C2 | 58.8 (2) | N2—C4—C5—N1 | 0.0 (4) |
| O23—P2—C1—P1 | 68.72 (17) | C3—N1—C5—C4 | 0.4 (4) |
| O21—P2—C1—P1 | -58.67 (18) | C2—N1—C5—C4 | 175.7 (3) |
| O22—P2—C1—P1 | -176.99 (13) | | |

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

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

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O12—H12 \cdots O2W | 0.82 | 1.75 | 2.566 (3) | 171 |
| O22—H22 \cdots O13 ⁱⁱ | 0.82 | 1.84 | 2.645 (3) | 167 |
| O2W—H2WA \cdots O21 ⁱⁱⁱ | 0.82 | 2.38 | 2.990 (3) | 132 |
| O2W—H2WB \cdots O13 ^{iv} | 0.82 | 1.94 | 2.758 (4) | 173 |
| N2—H2 \cdots O12 ^v | 0.86 | 2.11 | 2.917 (4) | 157 |
| O1W—H1W \cdots O23 ⁱⁱ | 0.82 | 1.81 | 2.632 (3) | 177 |
| O1—H1 \cdots O23 ⁱⁱ | 0.82 | 1.80 | 2.581 (3) | 160 |

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

Fig. 1

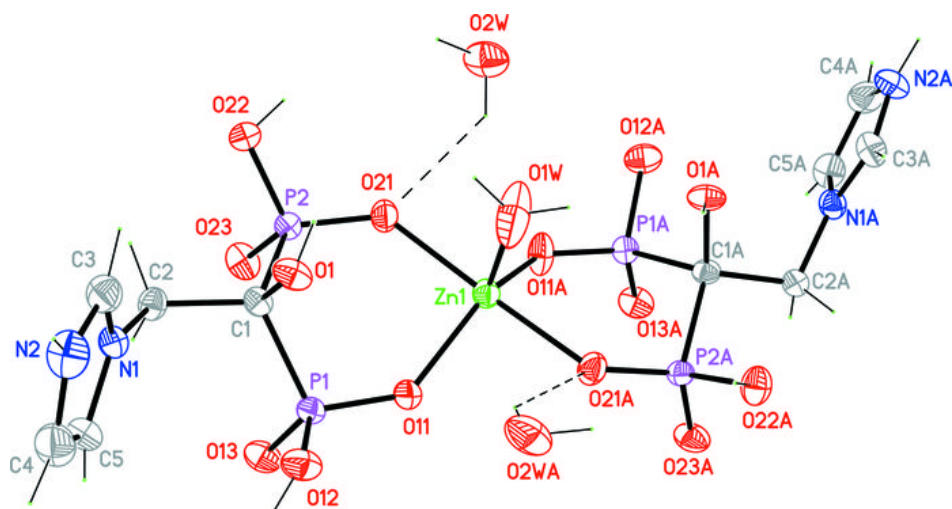


Fig. 2

