Decaaquadioxidobis[μ₃-N-(phosphonatomethyl)iminodiacetato]dizinc(II)divanadium(IV) dihydrate

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The title compound, $[Zn_2V_2(C_5H_6NO_7P)_2O_2(H_2O)_{10}]\cdot 2H_2O$, contains a $[V_2O_2(pmida)_2]^{4-}$ dimeric anionic unit [where H_4pmida is N-(phosphonomethyl)iminodiacetic acid] lying on a centre of symmetry which is *exo*-coordinated *via* the two deprotonated phosphonate groups to two Zn^{2+} cations, with the coordination environment of Zn completed by five water molecules. The crystal packing is mediated by an extensive network of strong and highly directional O—H···O hydrogen bonds involving the water molecules (coordinated and uncoordinated) and the functional groups of pmida^{4-}, leading to a three-dimensional supramolecular network.

Related literature

For related literature, see: Cunha-Silva, Mafra *et al.* (2007); Cunha-Silva, Shi *et al.* (2007); Shi *et al.* (2007); Mafra *et al.* (2006); Shi, Paz, Girginova, Amaral *et al.* (2006); Shi, Paz, Girginova, Rocha *et al.* (2006); Shi, Almeida Paz, Trindade & Rocha (2006); Paz, Rocha, Klinowski *et al.* (2005); Almeida Paz, Shi, Mafra *et al.* (2005); Almeida Paz, Shi, Trindade *et al.* (2005); Shi *et al.* (2005); Paz *et al.* (2004).
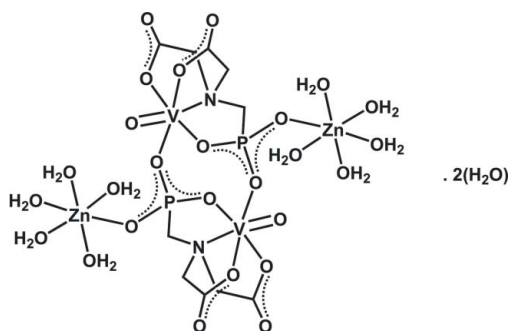
Experimental

Crystal data

$[Zn_2V_2(C_5H_6NO_7P)_2O_2(H_2O)_{10}]\cdot 2H_2O$	$\beta = 111.147$ (2)°
$M_r = 926.97$	$V = 1505.48$ (12) Å³
Monoclinic, $P2_1/c$	$Z = 2$
$a = 10.0161$ (5) Å	Mo $K\alpha$ radiation
$b = 14.8811$ (7) Å	$\mu = 2.40$ mm^{-1}
$c = 10.8298$ (5) Å	$T = 293$ (2) K
	$0.22 \times 0.14 \times 0.10$ mm

Data collection

Bruker Kappa APEXII diffractometer	95509 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)	4040 independent reflections
$T_{min} = 0.621$, $T_{max} = 0.796$	3765 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.077$	
$S = 1.04$	$\Delta\rho_{max} = 1.06$ e Å^{-3}
4040 reflections	$\Delta\rho_{min} = -0.87$ e Å^{-3}
238 parameters	
15 restraints	

Table 1
Selected bond lengths (Å).

Zn1—O7	2.0133 (14)	V1—O8	1.6086 (16)
Zn1—O3W	2.0609 (16)	V1—O6^i	1.9890 (14)
Zn1—O1W	2.0860 (17)	V1—O5	1.9932 (14)
Zn1—O4W	2.0974 (16)	V1—O2	2.0312 (15)
Zn1—O5W	2.1440 (18)	V1—O4	2.0321 (14)
Zn1—O2W	2.1660 (15)	V1—N1	2.3590 (16)

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O1^{ii}	0.90 (2)	1.88 (2)	2.770 (2)	169 (3)
O1W—H2W···O2W^{ii}	0.90 (2)	1.95 (2)	2.828 (2)	164 (3)
O2W—H3W···O3^{iii}	0.88 (2)	1.85 (2)	2.725 (2)	172 (3)
O2W—H4W···O5^{ii}	0.87 (2)	1.93 (2)	2.795 (2)	173 (3)
O3W—H6W···O2^{ii}	0.88 (2)	1.87 (2)	2.733 (2)	171 (3)
O3W—H5W···O4^{iv}	0.89 (2)	1.86 (2)	2.726 (2)	164 (4)
O4W—H7W···O3^{iv}	0.86 (2)	1.98 (2)	2.837 (2)	174 (3)
O4W—H8W···O1^v	0.88 (2)	1.94 (2)	2.799 (2)	167 (3)
O5W—H9W···O6	0.90 (2)	1.98 (3)	2.805 (2)	150 (4)
O5W—H10W···O6W	0.86 (2)	1.84 (3)	2.656 (6)	159 (4)

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL*.

metal-organic compounds

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supplementary materials

Decaaquadioxidobis[μ_3-*N*-(phosphonatomethyl)iminodiacetato]dizinc(II)divanadium(IV)   dihydrate

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Comment

Research on highly crystalline organic–inorganic hybrids, in particular those belonging to the family of coordination polymers, has received a considerable attention over the last two decades. Such occurs as a direct consequence of the fascinating structural architectures achieved by assembling organic ligands and metal centres which, in many cases, can be allied with interesting potential applications (*e.g.* gas storage, separation, catalysis, guest exchange, magnetic or optical sensors). Following our ongoing research toward the hydrothermal synthesis and structural characterization of this type of materials, we recently focused our attention on the use of multifunctional ligands such as *N*-(phosphonomethyl)iminodiacetic acid (H$_4$pmida) (Cunha-Silva, Shi *et al.*, 2007; Mafra *et al.*, 2006; Shi, Paz, Girginova, Amaral *et al.*, 2006; Shi, Paz, Girginova, Rocha *et al.*, 2006; Shi, Almeida Paz, Trindade & Rocha, 2006; Paz, Rocha, Klinowski *et al.*, 2005; Almeida Paz, Shi, Mafra *et al.*, 2005; Almeida Paz, Shi, Trindade *et al.*, 2005; Shi *et al.*, 2005; Paz *et al.*, 2004), 1-hydroxyethylidene-1,1-diphosphonic acid (H$_5$hedp) (Shi *et al.*, 2007), and nitrilotris(methylenephosphonic acid) (H$_6$nmp) (Cunha-Silva, Mafra *et al.*, 2007), we report here the structural details of the title compound, [Zn$_2$V$_2$O$_2$(pmida)$_2$(H$_2$O)$_{10}$].2H$_2$O (I) [where pmida^{4-} stands for C$_5$H$_6$NO$_7$P^{4-}].

The structure of (I) contains two crystallographically unique metal centres, Zn1 and V1, both exhibiting octahedral coordination geometries, {ZnO$_6$} and {VO$_5$N} (see table of selected geometric parameters and Fig. 1). Zn1 is coordinated by five O atoms of five crystalographically independent water molecules and one O atom from the μ_3-bridging phosphonate group of pmida^{4-} (Fig. 1), with the overall coordination geometry resembling a slightly distorted octahedron [Zn—O bond lengths found in the 2.0133 (14)–2.1660 (15) Å range; *cis* and *trans* O—Zn—O octahedral angles ranging from 87.09 (8) to 91.64 (6)° and from 177.27 (7) to 178.11 (7)°, respectively; see table of selected geometric parameters].

The two symmetry-related Zn^{2+} cations of the neutral tetranuclear [Zn$_2$V$_2$O$_2$(pmida)$_2$(H$_2$O)$_{10}$] molecule depicted in Fig. 1 are connected through the phosphonate groups belonging to the central centrosymmetric dimeric anionic [V$_2$O$_2$(pmida)$_2$]$^{4-}$ unit, with intermetallic Zn1···Zn1^i, Zn1···V1 and V1···V1^i distances of 10.0170 (5), 3.2447 (5) and 3.8773 (5) Å, respectively [symmetry code: (i) *2 - x, 1 - y, 1 - z*]. It is of considerable importance to emphasize that the geometrical aspects of this dimeric anionic unit are typical and in good agreement with those described in detail in our previous publications (Shi *et al.*, 2007; Shi, Paz, Girginova, Amaral *et al.*, 2006; Shi, Paz, Girginova, Rocha *et al.*, 2006; Shi, Almeida Paz, Trindade & Rocha, 2006; Paz, Rocha, Klinowski *et al.*, 2005; Almeida Paz, Shi, Mafra *et al.*, 2005; Almeida Paz, Shi, Trindade *et al.*, 2005; Shi *et al.*, 2005; Paz *et al.*, 2004). V1 is connected to one oxo group and to two pmida^{4-} ligands, with the geometry of the first coordination sphere resembling a highly distorted octahedron, which is composed by one short V—O bond [1.6088 (16) Å], four intermediate V—O bonds [1.9890 (12)–2.0321 (14) Å] and a long V—N bond [2.3590 (16) Å]; the *cis* and *trans* internal octahedral angles range from 86.67 (6) to 103.84 (8)°, and from 154.45 (6) to 169.79 (8)°,

supplementary materials

respectively. Noteworthy is the structural evidence of the notable *trans* effect of the oxo group over the long V—N distance (see Table of selected geometric parameters).

Individual $[Zn_2V_2O_2(pmida)_2(H_2O)_{10}]$ molecular units close pack with the water molecules of crystallization in a typical brick-wall-like fashion in the *bc* plane of the unit cell (Fig. 2), mediated by an extensive network of strong and highly directional O—H$\cdots$O hydrogen bonding interactions (see Table summarizing the geometrical aspects of the hydrogen bonds).

Experimental

Starting materials were purchased from commercial sources and were used as received without further purification: *N*-(phosphonomethyl)iminodiacetic acid hydrate (H$_4$pmida, $C_5H_{10}NO_7P$, 97%, Fluka), potassium metavanadate (KVO$_3$, 98%, Aldrich), zinc oxide (ZnO, 98%, Panreac), imidazole ($C_3H_4N_2$, 99.0%, Panreac) and adipic acid (HOOC(CH$_2$)$_4$COOH, 99%, Aldrich).

A mixture containing 0.26 g of KVO$_3$, 0.15 g of ZnO, 0.42 g of H$_4$pmida, 0.13 g of imidazole and 0.27 g of adipic acid in *ca* 9 g of distilled water, was stirred thoroughly at ambient temperature for 30 minutes, yielding a suspension with a molar composition of *ca* 1:1:1:1:1:270, respectively, which was transferred to a PTFE-lined stainless steel reaction vessel (total volume *ca* 40 ml). The reaction vessel was placed inside a preheated oven at 473 K for one day, after which the temperature was decreased to 373 K allowing the reaction to proceed for another four days. After reacting, under autogeneous pressure and static conditions, the vessel was removed from the oven and left to cool to ambient temperature before opening. Small amounts of green and/or blue mixed powders of unknown phases were readily separated from the mother liquor by vacuum filtering. Large single crystals of the title compound were isolated by slow evaporation (in open air) of the mother liquor over the period of one week. It is of considerable importance to emphasize that similar reactions where imidazole and adipic acid were not included in the starting reactive mixture failed in the isolation of the title material.

Refinement

H atoms bound to carbon were placed at idealized positions and allowed to ride on their parent atoms with U_{iso} fixed at $1.2 \times U_{eq}(C)$. H atoms associated with the five coordinated water molecules were markedly visible in difference Fourier maps and were included in the structural model for subsequent least-squares refinement cycles with the O—H and H$\cdots$H distances restrained to 0.90 (3) and 1.47 (3) Å, respectively, in order to ensure a chemically reasonable geometry for these chemical moieties. These H atoms were allowed to ride on their parent atoms with U_{iso} fixed at $1.5 \times U_{eq}(O)$.

The crystallographically unique O6W water molecule of crystallization was directly located from difference Fourier maps and refined assuming a full site occupancy and a thermal anisotropic displacement behaviour. The H atoms associated with this chemical moiety could not be unequivocally located from difference Fourier maps. Additionally, attempts to place the two H atoms in calculated positions did not produce a chemically reasonable structural model, in particular concerning the geometry of the resulting hydrogen bonding interactions. Therefore, these H atoms were omitted from the final structural model but were included in the empirical chemical formula.
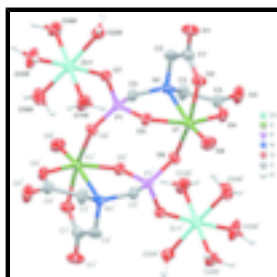
Figures

Fig. 1. Schematic representation of the tetranuclear centrosymmetric $[Zn_2V_2O_2(pmida)_2(H_2O)_{10}]$ molecular unit, showing the labelling scheme for all non-H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as small spheres with arbitrary radii. The water molecule of crystallization O6W was omitted for clarity. Symmetry transformation used to generate equivalent atoms (in grey): *2 - x, 1 - y, 1 - z*.
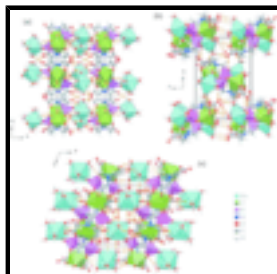
Fig. 2. Crystal packing of the title compound viewed in perspective along the (**a**) [001], (**b**) [100] and (**c**) [010] directions of the unit cell. Hydrogen bonds are represented as orange dashed lines.

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Crystal data

$[Zn_2V_2(C_5H_6NO_7P)_2O_2(H_2O)_{10}]·2H_2O$	$F_{000} = 940$
$M_r = 926.97$	$D_x = 2.045$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 9009 reflections
$a = 10.0161$ (5) Å	$\theta = 2.6–37.6°$
$b = 14.8811$ (7) Å	$\mu = 2.40$ mm^{-1}
$c = 10.8298$ (5) Å	$T = 293$ (2) K
$\beta = 111.147$ (2)°	Prism, blue
$V = 1505.48$ (12) Å^3	$0.22 \times 0.14 \times 0.10$ mm
$Z = 2$	

Data collection

Bruker X8 APEXII Kappa CCD diffractometer	4040 independent reflections
Radiation source: fine-focus sealed tube	3765 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.028$
$T = 293(2)$ K	$\theta_{max} = 29.1°$
Thin–slice ω and φ scans	$\theta_{min} = 3.6°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)	$h = -13 \rightarrow 13$
$T_{min} = 0.621$, $T_{max} = 0.796$	$k = -20 \rightarrow 20$
95509 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.077$	$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 2.056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.002$
4040 reflections	$\Delta\rho_{max} = 1.06$ e Å^{-3}
238 parameters	$\Delta\rho_{min} = -0.87$ e Å^{-3}
15 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. See dedicated section in the main paper

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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Zn1	0.47946 (2)	0.566124 (16)	0.26276 (2)	0.02202 (7)
V1	1.01192 (3)	0.52639 (2)	0.74230 (3)	0.01679 (8)
P1	0.81721 (5)	0.55866 (3)	0.44467 (5)	0.01775 (10)
N1	0.98913 (17)	0.66771 (11)	0.63798 (15)	0.0188 (3)
O5	0.85567 (14)	0.49988 (10)	0.57024 (13)	0.0223 (3)
O7	0.66854 (14)	0.59666 (10)	0.40459 (14)	0.0242 (3)
O4	1.16206 (16)	0.60558 (10)	0.87361 (13)	0.0252 (3)
C5	0.9481 (2)	0.65025 (13)	0.49415 (17)	0.0199 (3)
H5A	1.0323	0.6340	0.4747	0.024*
H5B	0.9072	0.7041	0.4446	0.024*
O6	0.83989 (15)	0.50552 (10)	0.33263 (14)	0.0249 (3)
O2	0.86146 (16)	0.59104 (10)	0.79428 (16)	0.0275 (3)
C4	1.1990 (2)	0.68247 (13)	0.84317 (19)	0.0229 (4)
C1	0.8075 (2)	0.66657 (14)	0.7474 (2)	0.0239 (4)
O8	1.0159 (2)	0.43890 (11)	0.83081 (18)	0.0348 (4)

C3	1.1313 (2)	0.71027 (15)	0.69835 (19)	0.0263 (4)
H3A	1.1213	0.7751	0.6922	0.032*
H3B	1.1924	0.6920	0.6509	0.032*
C2	0.8762 (2)	0.71885 (14)	0.6657 (2)	0.0266 (4)
H2A	0.8027	0.7359	0.5824	0.032*
H2B	0.9176	0.7736	0.7125	0.032*
O3	1.28796 (19)	0.73187 (12)	0.92367 (16)	0.0371 (4)
O1	0.70218 (18)	0.69941 (11)	0.76509 (19)	0.0360 (4)
O1W	0.5041 (2)	0.43314 (11)	0.32805 (19)	0.0392 (4)
H1W	0.440 (3)	0.390 (2)	0.288 (3)	0.059*
H2W	0.528 (4)	0.419 (2)	0.414 (2)	0.059*
O2W	0.36824 (16)	0.59655 (11)	0.39610 (15)	0.0266 (3)
H3W	0.348 (3)	0.6535 (14)	0.402 (3)	0.040*
H4W	0.298 (3)	0.5638 (17)	0.401 (3)	0.040*
O3W	0.28954 (18)	0.52927 (14)	0.11685 (17)	0.0409 (4)
H5W	0.238 (4)	0.560 (2)	0.045 (3)	0.061*
H6W	0.234 (4)	0.491 (2)	0.136 (3)	0.061*
O4W	0.45023 (17)	0.69926 (11)	0.19464 (16)	0.0304 (3)
H7W	0.397 (3)	0.706 (2)	0.113 (2)	0.046*
H8W	0.531 (3)	0.727 (2)	0.205 (3)	0.046*
O5W	0.58091 (19)	0.53840 (17)	0.12317 (18)	0.0446 (5)
H9W	0.666 (3)	0.513 (2)	0.170 (3)	0.067*
H10W	0.598 (4)	0.574 (2)	0.068 (3)	0.067*
O6W	0.5884 (6)	0.6734 (4)	−0.0345 (5)	0.1474 (18)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01727 (12)	0.02490 (13)	0.01985 (12)	−0.00060 (8)	0.00183 (8)	0.00210 (8)
V1	0.01574 (14)	0.01789 (15)	0.01586 (14)	0.00001 (10)	0.00464 (11)	0.00076 (10)
P1	0.01270 (19)	0.0220 (2)	0.0165 (2)	−0.00024 (16)	0.00279 (16)	−0.00184 (16)
N1	0.0182 (7)	0.0201 (7)	0.0165 (7)	−0.0029 (6)	0.0045 (5)	−0.0002 (5)
O5	0.0185 (6)	0.0238 (6)	0.0206 (6)	−0.0037 (5)	0.0023 (5)	0.0009 (5)
O7	0.0142 (6)	0.0304 (7)	0.0239 (6)	0.0025 (5)	0.0018 (5)	−0.0048 (6)
O4	0.0279 (7)	0.0252 (7)	0.0171 (6)	−0.0049 (6)	0.0017 (5)	0.0016 (5)
C5	0.0195 (8)	0.0232 (8)	0.0152 (7)	−0.0024 (7)	0.0041 (6)	0.0014 (6)
O6	0.0177 (6)	0.0331 (7)	0.0233 (6)	−0.0002 (5)	0.0067 (5)	−0.0079 (6)
O2	0.0287 (7)	0.0247 (7)	0.0357 (8)	0.0029 (6)	0.0196 (6)	0.0039 (6)
C4	0.0210 (8)	0.0251 (9)	0.0190 (8)	−0.0035 (7)	0.0026 (7)	0.0003 (7)
C1	0.0227 (9)	0.0225 (9)	0.0270 (9)	−0.0022 (7)	0.0094 (7)	−0.0053 (7)
O8	0.0410 (9)	0.0272 (8)	0.0383 (9)	0.0017 (7)	0.0169 (7)	0.0086 (7)
C3	0.0248 (9)	0.0288 (10)	0.0202 (8)	−0.0110 (8)	0.0021 (7)	0.0036 (7)
C2	0.0337 (10)	0.0189 (8)	0.0299 (10)	0.0036 (8)	0.0148 (8)	0.0009 (7)
O3	0.0405 (9)	0.0334 (8)	0.0242 (7)	−0.0151 (7)	−0.0043 (7)	0.0007 (6)
O1	0.0305 (8)	0.0297 (8)	0.0538 (10)	0.0047 (6)	0.0226 (8)	−0.0033 (7)
O1W	0.0428 (10)	0.0270 (8)	0.0340 (9)	−0.0057 (7)	−0.0029 (7)	0.0044 (7)
O2W	0.0235 (7)	0.0261 (7)	0.0316 (7)	−0.0003 (6)	0.0117 (6)	0.0027 (6)
O3W	0.0269 (8)	0.0578 (12)	0.0266 (8)	−0.0179 (8)	−0.0040 (6)	0.0167 (8)

O4W	0.0274 (7)	0.0287 (8)	0.0303 (8)	−0.0041 (6)	0.0046 (6)	0.0066 (6)
O5W	0.0281 (8)	0.0761 (14)	0.0268 (8)	0.0078 (9)	0.0064 (7)	−0.0058 (9)
O6W	0.163 (4)	0.159 (5)	0.143 (4)	−0.009 (4)	0.083 (4)	0.009 (3)

Geometric parameters (Å, °)

Zn1—O7	2.0133 (14)	C5—H5B	0.9700
Zn1—O3W	2.0609 (16)	O6—V1^i	1.9890 (14)
Zn1—O1W	2.0860 (17)	O2—C1	1.271 (3)
Zn1—O4W	2.0974 (16)	C4—O3	1.238 (2)
Zn1—O5W	2.1440 (18)	C4—C3	1.524 (3)
Zn1—O2W	2.1660 (15)	C1—O1	1.239 (3)
V1—O8	1.6086 (16)	C1—C2	1.517 (3)
V1—O6^i	1.9890 (14)	C3—H3A	0.9700
V1—O5	1.9932 (14)	C3—H3B	0.9700
V1—O2	2.0312 (15)	C2—H2A	0.9700
V1—O4	2.0321 (14)	C2—H2B	0.9700
V1—N1	2.3590 (16)	O1W—H1W	0.90 (2)
P1—O7	1.5030 (14)	O1W—H2W	0.90 (2)
P1—O6	1.5324 (15)	O2W—H3W	0.88 (2)
P1—O5	1.5443 (14)	O2W—H4W	0.87 (2)
P1—C5	1.8323 (19)	O3W—H5W	0.89 (2)
N1—C3	1.478 (2)	O3W—H6W	0.88 (2)
N1—C2	1.481 (3)	O4W—H7W	0.86 (2)
N1—C5	1.484 (2)	O4W—H8W	0.88 (2)
O4—C4	1.282 (2)	O5W—H9W	0.90 (2)
C5—H5A	0.9700	O5W—H10W	0.86 (2)
O7—Zn1—O3W	177.43 (8)	P1—O7—Zn1	134.17 (9)
O7—Zn1—O1W	89.53 (7)	C4—O4—V1	123.17 (12)
O3W—Zn1—O1W	88.34 (7)	N1—C5—P1	109.58 (12)
O7—Zn1—O4W	91.64 (6)	N1—C5—H5A	109.8
O3W—Zn1—O4W	90.49 (7)	P1—C5—H5A	109.8
O1W—Zn1—O4W	178.81 (7)	N1—C5—H5B	109.8
O7—Zn1—O5W	91.53 (6)	P1—C5—H5B	109.8
O3W—Zn1—O5W	87.09 (8)	H5A—C5—H5B	108.2
O1W—Zn1—O5W	91.61 (9)	P1—O6—V1^i	142.36 (9)
O4W—Zn1—O5W	88.58 (8)	C1—O2—V1	123.99 (13)
O7—Zn1—O2W	90.73 (6)	O3—C4—O4	123.37 (18)
O3W—Zn1—O2W	90.71 (7)	O3—C4—C3	120.23 (18)
O1W—Zn1—O2W	89.93 (7)	O4—C4—C3	116.37 (16)
O4W—Zn1—O2W	89.83 (6)	O1—C1—O2	123.4 (2)
O5W—Zn1—O2W	177.27 (7)	O1—C1—C2	118.61 (19)
O8—V1—O6^i	100.84 (8)	O2—C1—C2	118.02 (17)
O8—V1—O5	103.84 (8)	N1—C3—C4	109.82 (15)
O6^i—V1—O5	91.21 (6)	N1—C3—H3A	109.7
O8—V1—O2	94.57 (8)	C4—C3—H3A	109.7
O6^i—V1—O2	164.50 (7)	N1—C3—H3B	109.7
O5—V1—O2	86.67 (6)	C4—C3—H3B	109.7

O8—V1—O4	101.49 (8)	H3A—C3—H3B	108.2
O6i—V1—O4	87.20 (6)	N1—C2—C1	113.27 (16)
O5—V1—O4	154.45 (6)	N1—C2—H2A	108.9
O2—V1—O4	88.12 (6)	C1—C2—H2A	108.9
O8—V1—N1	169.79 (8)	N1—C2—H2B	108.9
O6i—V1—N1	88.57 (6)	C1—C2—H2B	108.9
O5—V1—N1	79.69 (6)	H2A—C2—H2B	107.7
O2—V1—N1	75.95 (6)	Zn1—O1W—H1W	122 (2)
O4—V1—N1	74.78 (6)	Zn1—O1W—H2W	121 (2)
O7—P1—O6	112.33 (8)	H1W—O1W—H2W	103 (3)
O7—P1—O5	111.96 (8)	Zn1—O2W—H3W	115.9 (19)
O6—P1—O5	110.11 (9)	Zn1—O2W—H4W	123 (2)
O7—P1—C5	109.55 (9)	H3W—O2W—H4W	109 (2)
O6—P1—C5	108.69 (8)	Zn1—O3W—H5W	128 (2)
O5—P1—C5	103.82 (8)	Zn1—O3W—H6W	119 (2)
C3—N1—C2	111.98 (16)	H5W—O3W—H6W	109 (3)
C3—N1—C5	113.40 (15)	Zn1—O4W—H7W	115 (2)
C2—N1—C5	111.14 (15)	Zn1—O4W—H8W	113 (2)
C3—N1—V1	105.00 (11)	H7W—O4W—H8W	106 (3)
C2—N1—V1	108.06 (11)	Zn1—O5W—H9W	106 (2)
C5—N1—V1	106.80 (11)	Zn1—O5W—H10W	130 (3)
P1—O5—V1	124.99 (8)	H9W—O5W—H10W	105 (3)
O8—V1—N1—C3	95.2 (5)	O5—V1—O4—C4	−10.3 (3)
O6i—V1—N1—C3	−62.07 (12)	O2—V1—O4—C4	−88.53 (16)
O5—V1—N1—C3	−153.56 (13)	N1—V1—O4—C4	−12.59 (15)
O2—V1—N1—C3	117.32 (13)	C3—N1—C5—P1	155.80 (14)
O4—V1—N1—C3	25.42 (12)	C2—N1—C5—P1	−77.01 (17)
O8—V1—N1—C2	−24.5 (5)	V1—N1—C5—P1	40.64 (13)
O6i—V1—N1—C2	178.27 (13)	O7—P1—C5—N1	89.70 (14)
O5—V1—N1—C2	86.78 (13)	O6—P1—C5—N1	−147.23 (12)
O2—V1—N1—C2	−2.35 (12)	O5—P1—C5—N1	−30.04 (15)
O4—V1—N1—C2	−94.24 (13)	O7—P1—O6—V1i	147.90 (15)
O8—V1—N1—C5	−144.1 (4)	O5—P1—O6—V1i	−86.60 (17)
O6i—V1—N1—C5	58.62 (11)	C5—P1—O6—V1i	26.51 (19)
O5—V1—N1—C5	−32.88 (11)	O8—V1—O2—C1	−176.55 (17)
O2—V1—N1—C5	−122.00 (12)	O6i—V1—O2—C1	9.6 (4)
O4—V1—N1—C5	146.11 (12)	O5—V1—O2—C1	−72.91 (17)
O7—P1—O5—V1	−116.85 (10)	O4—V1—O2—C1	82.07 (17)
O6—P1—O5—V1	117.44 (10)	N1—V1—O2—C1	7.29 (16)
C5—P1—O5—V1	1.24 (12)	V1—O4—C4—O3	178.20 (17)
O8—V1—O5—P1	−173.68 (11)	V1—O4—C4—C3	−4.0 (3)
O6i—V1—O5—P1	−72.20 (11)	V1—O2—C1—O1	169.44 (16)
O2—V1—O5—P1	92.43 (11)	V1—O2—C1—C2	−10.6 (3)
O4—V1—O5—P1	13.8 (2)	C2—N1—C3—C4	83.0 (2)
N1—V1—O5—P1	16.12 (10)	C5—N1—C3—C4	−150.29 (17)
O6—P1—O7—Zn1	21.40 (16)	V1—N1—C3—C4	−34.07 (19)
O5—P1—O7—Zn1	−103.09 (13)	O3—C4—C3—N1	−153.7 (2)

C5—P1—O7—Zn1	142.29 (12)	O4—C4—C3—N1	28.5 (3)
O1W—Zn1—O7—P1	52.88 (14)	C3—N1—C2—C1	−116.61 (19)
O4W—Zn1—O7—P1	−127.34 (14)	C5—N1—C2—C1	115.43 (18)
O5W—Zn1—O7—P1	−38.72 (15)	V1—N1—C2—C1	−1.4 (2)
O2W—Zn1—O7—P1	142.81 (13)	O1—C1—C2—N1	−172.84 (19)
O8—V1—O4—C4	177.18 (16)	O2—C1—C2—N1	7.2 (3)
O6^i—V1—O4—C4	76.69 (16)		

Symmetry codes: (i) −x+2, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1W—H1W⋯O1^{ii}	0.90 (2)	1.88 (2)	2.770 (2)	169 (3)
O1W—H2W⋯O2W^{ii}	0.90 (2)	1.95 (2)	2.828 (2)	164 (3)
O2W—H3W⋯O3^{iii}	0.88 (2)	1.85 (2)	2.725 (2)	172 (3)
O2W—H4W⋯O5^{ii}	0.87 (2)	1.93 (2)	2.795 (2)	173 (3)
O3W—H6W⋯O2^{ii}	0.88 (2)	1.87 (2)	2.733 (2)	171 (3)
O3W—H5W⋯O4^{iv}	0.89 (2)	1.86 (2)	2.726 (2)	164 (4)
O4W—H7W⋯O3^{iv}	0.86 (2)	1.98 (2)	2.837 (2)	174 (3)
O4W—H8W⋯O1^{v}	0.88 (2)	1.94 (2)	2.799 (2)	167 (3)
O5W—H9W⋯O6	0.90 (2)	1.98 (3)	2.805 (2)	150 (4)
O5W—H10W⋯O6W	0.86 (2)	1.84 (3)	2.656 (6)	159 (4)

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

Fig. 1

Fig. 2