metal-organic papers

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Decaaquadioxobis[μ3-N-(phosphonomethyl)-iminodiacetato]dimanganesedivanadium dihydrate

The crystal structure of the title compound, [$Mn_2V_2(C_5H_6NO_7P)_2O_2(H_2O)_{10}$]·$2H_2O$, contains a centrosymmetric dimeric [V_2O_2(pmida)$_2$]$^{4-}$ unit [where H$_4$pmida is N-(phosphonomethyl)iminodiacetic acid] connecting two neighbouring Mn^{2+} cations through the phosphonate groups. The crystal structure is characterized by the presence of 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-}.

Comment

Since the report by Hoskins & Robson (1990), research focused on the structural design and synthesis of novel coordination-based materials, in which the topology is extended from discrete complexes to one, two or three dimensions, has seen a great and exponential growth (for recent reviews see Cheetham et al., 2006; Kitagawa & Uemura, 2005). During the course of our ongoing research on novel multi-dimensional hybrid crystalline materials incorporating N-(phosphonomethyl)iminodiacetic acid (H$_4$pmida) residues (Mafra et al., 2006; Almeida Paz et al., 2004; Almeida Paz, Shi, Trindade et al., 2005; Almeida Paz, Shi, Mafra et al., 2005; Almeida Paz, Rocha, Klinowski et al., 2005; Shi et al., 2005; Shi, Almeida Paz, Trindade & Rocha, 2006; Shi, Almeida Paz, Girginova, Amaral et al., 2006; Shi, Almeida Paz, Girginova, Rocha et al., 2006), we have isolated the crystalline material [$Mn_2V_2O_2$(pmida)$_2$(H_2O)$_{10}$]·$2H_2O$ [where pmida^{4-} is ($C_5H_6NO_7P$)$^{4-}$], (I), whose crystal structure at the temperature of 180 (2) K we report here.

(I)
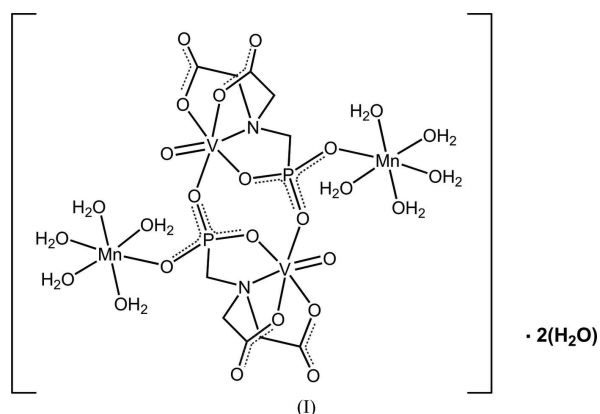
The title compound, (I), contains two crystallographically unique metal centres, Mn1 and V1, both exhibiting octahedral coordination geometries, {MnO_6} and {VO_5N} (Fig. 1; Table 1). Mn1 is coordinated by five water molecules plus one O atom

Figure 1
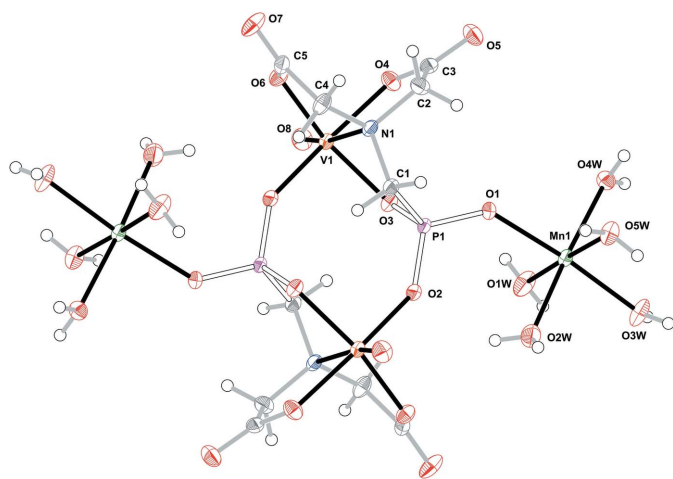The structure of the tetranuclear centrosymmetric [Mn$_2$V$_2$O$_2$(pmida)$_2$(H$_2$O)$_{10}$] complex, showing the labelling scheme for all non-H atoms belonging to the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres. The water molecule of crystallization, O6W, was omitted for clarity. Symmetry transformation used to generate non-labelled atoms: $2 - x$, $-y$, $-z$.

from the μ_3-bridging phosphonate group of pmida^{4-} (Fig. 1), with a coordination geometry resembling a quasi-regular octahedron [Mn—O bond lengths ranging from 2.092 (2) to 2.236 (2) Å; *cis* and *trans* O—Mn—O angles found in the 86.85 (10)–93.21 (11)° and 175.14 (10)–178.21 (9)° ranges, respectively; see Table 1]. The intermetallic Mn1···Mn1^i distance between *exo*-coordinated manganese(II) centres (and across the unit depicted in Fig. 1) is of 10.175 (3) Å, while the shortest Mn1···V1^i distance within the tetranuclear unit is 5.368 (1) Å [symmetry code: (i) $2 - x$, $-y$, $-z$].

The core of the neutral tetranuclear [Mn$_2$V$_2$O$_2$(pmida)$_2$-(H$_2$O)$_{10}$] molecule is composed of the anionic centrosym-

metric [V$_2$O$_2$(pmida)$_2$]$^{4-}$ dimeric unit, first described by Crans *et al.* (1998). The geometrical aspects of this unit, in particular the highly distorted octahedral coordination mode of V1 (Table 1) plus the coordination fashion of the pmida^{4-} ligand (which forms with V1 three five-membered chelate rings; see Fig. 1), are typical and in good agreement with those described in detail in our previous reports (Almeida Paz *et al.*, 2004; Almeida Paz, Shi, Trindade *et al.*, 2005; Almeida Paz, Shi, Mafra *et al.*, 2005; Almeida Paz, Rocha, Klinowski *et al.*, 2005; Shi *et al.*, 2005; Shi, Almeida Paz, Trindade & Rocha, 2006; Shi, Almeida Paz, Girginova, Amaral *et al.*, 2006; Shi, Almeida Paz, Girginova, Rocha *et al.*, 2006).

In the extended solid-state [Mn$_2$V$_2$O$_2$(pmida)$_2$(H$_2$O)$_{10}$] molecular units pack closely in a typical brick-wall-like fashion along the crystallographic [010] direction (Fig. 2a), mediated by an extensive network of strong and highly directional O—H···O hydrogen-bonding interactions, which also involve the water molecule of crystallization (Fig. 2 and Table 3).

Experimental

Synthesis was typically carried out in a PTFE-lined stainless steel reaction vessel (*ca* 40 ml), under autogeneous pressure and static conditions in a preheated oven at 393 K. The reaction took place over a period of 3 d, after which the vessel was removed from the oven and left to cool to ambient temperature before opening. The title compound proved to be air- and light-stable.

The title compound was synthesized from a mixture containing 0.40 g of VOSO$_4$·5H$_2$O, 0.61 g of MnC$_4$H$_6$O$_4$·4H$_2$O, and 0.40 g of
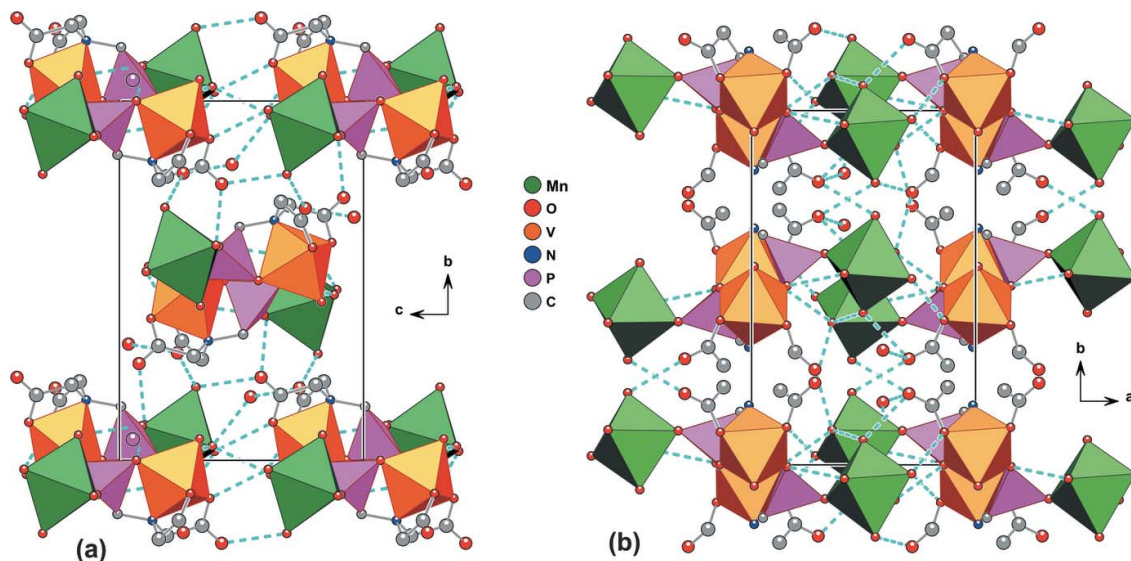

Figure 2
Perspective views of the crystal packing of the title compound, viewed along the (*a*) [100] and (*b*) [001] directions of the unit cell. Hydrogen bonds are represented as light-blue dashed lines. H atoms have been omitted for clarity. For details on the hydrogen-bonding geometry see Table 2.

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H$_4$pmida, and 0.24 g of TMD in *ca* 15 g of distilled water. The mixture was stirred thoroughly at ambient temperature for 30 minutes, yielding a suspension with a molar composition of 1.4:1.4:1.0:0.7:473, which was transferred to the reaction vessel. After reacting, a small quantity of green/blue single crystals of the title compound were isolated as a pure phase by vacuum filtering, washed with copious amounts of distilled water (*ca* 3 × 50 ml), and then air-dried at ambient temperature. The same material can also be isolated as large single crystals by slow evaporation (in the open air) of the autoclave mother liquor over a period of one month. It is of considerable interest to note that similar reactions where TMD was not included in the starting reactive mixture failed to lead to the isolation of the title material.

Crystal data

[Mn$_2$V$_2$(C$_5$H$_6$NO$_7$P)$_2$O$_2$-(H$_2$O)$_{10}$]·2H$_2$O
$M_r = 906.11$
Monoclinic, $P2_1/c$
$a = 10.096$ (2) Å
$b = 14.934$ (3) Å
$c = 10.848$ (2) Å
$\beta = 110.52$ (3)°

$V = 1531.8$ (6) Å^3
$Z = 2$
$D_x = 1.965$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.61$ mm^{-1}
$T = 180$ (2) K
Prism, brown
$0.15 \times 0.10 \times 0.09$ mm

Data collection

Nonius KappaCCD diffractometer
Thin–slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.794$, $T_{max} = 0.869$

17432 measured reflections
3502 independent reflections
2880 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.110$
$S = 1.05$
3502 reflections
233 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 3.2528P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.05$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.092 (2)	V1—O2^i	1.991 (2)
Mn1—O1W	2.164 (2)	V1—O3	1.988 (2)
Mn1—O2W	2.212 (2)	V1—O4	2.030 (2)
Mn1—O3W	2.152 (2)	V1—O6	2.028 (2)
Mn1—O4W	2.236 (2)	V1—O8	1.598 (2)
Mn1—O5W	2.187 (2)	V1—N1	2.370 (3)
O1—Mn1—O1W	88.63 (9)	O2^i—V1—O4	163.79 (9)
O1—Mn1—O2W	90.18 (9)	O2^i—V1—O6	86.89 (9)
O1—Mn1—O3W	175.14 (10)	O2^i—V1—N1	88.32 (9)
O1—Mn1—O4W	92.29 (8)	O3—V1—O2^i	90.96 (9)
O1—Mn1—O5W	93.12 (9)	O3—V1—O4	87.04 (9)
O1W—Mn1—O2W	93.21 (11)	O3—V1—O6	154.03 (9)
O1W—Mn1—O4W	89.40 (9)	O3—V1—N1	79.41 (9)
O1W—Mn1—O5W	178.21 (9)	O4—V1—N1	75.50 (9)
O2W—Mn1—O4W	176.45 (9)	O6—V1—O4	87.90 (9)
O3W—Mn1—O1W	87.68 (10)	O6—V1—N1	74.66 (9)
O3W—Mn1—O2W	86.85 (9)	O8—V1—O2^i	101.24 (11)
O3W—Mn1—O4W	90.85 (9)	O8—V1—O3	103.95 (11)
O3W—Mn1—O5W	90.58 (9)	O8—V1—O4	94.85 (11)
O5W—Mn1—O2W	87.12 (10)	O8—V1—O6	101.86 (11)
O5W—Mn1—O4W	90.21 (9)	O8—V1—N1	169.72 (10)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1C···O4W^{ii}	0.845 (10)	1.982 (12)	2.813 (3)	167 (4)
O1W—H1D···O5^{ii}	0.84 (3)	1.92 (3)	2.759 (3)	171 (3)
O2W—H2C···O2	0.83 (4)	2.15 (4)	2.847 (3)	142 (4)
O2W—H2D···O6W^{iii}	0.84 (4)	1.880 (17)	2.675 (6)	160 (4)
O3W—H3A···O4^{ii}	0.84 (3)	1.920 (16)	2.735 (3)	163 (4)
O3W—H3B···O6^{iv}	0.84 (3)	1.93 (3)	2.745 (3)	166 (4)
O4W—H4C···O7^v	0.844 (10)	1.856 (11)	2.698 (3)	175 (3)
O4W—H4D···O3^{ii}	0.85 (3)	1.94 (3)	2.778 (3)	173 (4)
O5W—H5A···O5^{vi}	0.84 (3)	1.996 (15)	2.803 (3)	161 (4)
O5W—H5B···O7^{iv}	0.841 (10)	1.989 (12)	2.823 (3)	171 (3)

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

H atoms bound to carbon were placed in idealized positions and allowed to ride on their parent atoms with U_{iso} fixed at 1.2 times U_{eq}(C) (C—H = 0.99 Å). H atoms associated with the five crystal-lographically unique coordinated water molecules were markedly visible in difference Fourier maps, and were included in subsequent least-squares refinement cycles with the O—H and H···H distances restrained to 0.84 (1) and 1.37 (1) Å, respectively, to ensure a chemically reasonable geometry of water molecules. These H atoms were also allowed to ride on their parent atoms with U_{iso} fixed at 1.5 times U_{eq}(O).

The crystallographically unique water molecule of crystallization was found to be severely affected by disorder, which prevented a sensible refinement using anisotropic displacement parameters. In fact, both the highest peak and deepest hole from the final difference Fourier synthesis were found close to this (0.01 and 0.64 Å, respectively). Therefore, the O atom from this molecule was refined assuming an isotropic displacement parameter. H atoms associated with this water molecule could not be located in difference Fourier maps, and attempts to place them in calculated positions did not lead to a reasonable model for the geometrical aspects of the resulting hydrogen-bonding interactions. Therefore, these H atoms were omitted from the present structural model but were included in the chemical formula of the compound.

Data collection: *COLLECT* (Nonius 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker 2001); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL*.

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supporting information

Decaaquadioxobis[μ_3-*N*-(phosphonomethyl)iminodiacetato]-dimanganesedivanadium dihydrate

Luís Cunha-Silva, Fa-Nian Shi, Jacek Klinowski, Tito Trindade, João Rocha and Filipe A. Almeida Paz

decaaquadioxobis[μ_3-*N*-(phosphonomethyl)iminodiacetato]dimanganesedivanadium dihydrate, [$Mn_2V_2(C_5H_6NO_7P)_2O_2(H_2O)_{10}$]·$2H_2O$

Crystal data

[$Mn_2V_2(C_5H_6NO_7P)_2O_2(H_2O)_{10}$]·$2H_2O$	$F(000) = 920$
$M_r = 906.11$	$D_x = 1.965$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 9712 reflections
$a = 10.096$ (2) Å	$\theta = 1.0$–27.5°
$b = 14.934$ (3) Å	$\mu = 1.61$ mm^{-1}
$c = 10.848$ (2) Å	$T = 180$ K
$\beta = 110.52$ (3)°	Prism, brown
$V = 1531.8$ (6) Å^3	$0.15 \times 0.10 \times 0.09$ mm
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	3502 independent reflections
Radiation source: fine-focus sealed tube	2880 reflections with $I > 2\sigma(I)$
Thin–slice ω and φ scans	$R_{int} = 0.059$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$
$T_{min} = 0.794$, $T_{max} = 0.869$	$h = -12 \rightarrow 13$
17432 measured reflections	$k = -19 \rightarrow 19$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.110$	$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 3.2528P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	
3502 reflections	$(\Delta/\sigma)_{max} = 0.001$
233 parameters	$\Delta\rho_{max} = 1.05$ e Å^{-3}
15 restraints	$\Delta\rho_{min} = -0.95$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.47798 (5)	0.06629 (3)	−0.23812 (4)	0.01467 (14)
O1W	0.5014 (3)	−0.07031 (16)	−0.1672 (2)	0.0285 (6)
H1C	0.531 (4)	−0.082 (3)	−0.0859 (12)	0.043*
H1D	0.438 (3)	−0.108 (2)	−0.205 (3)	0.043*
O2W	0.5853 (3)	0.0392 (2)	−0.3804 (2)	0.0316 (6)
H2C	0.657 (3)	0.009 (3)	−0.343 (4)	0.047*
H2D	0.599 (4)	0.074 (2)	−0.435 (4)	0.047*
O3W	0.2854 (2)	0.02509 (18)	−0.3901 (2)	0.0255 (5)
H3A	0.239 (3)	−0.017 (2)	−0.374 (4)	0.038*
H3B	0.235 (3)	0.052 (2)	−0.458 (3)	0.038*
O4W	0.3596 (2)	0.09866 (15)	−0.1040 (2)	0.0180 (5)
H4C	0.339 (3)	0.1530 (8)	−0.098 (4)	0.027*
H4D	0.291 (3)	0.0673 (17)	−0.101 (4)	0.027*
O5W	0.4474 (2)	0.20346 (16)	−0.3136 (2)	0.0222 (5)
H5A	0.525 (2)	0.227 (3)	−0.308 (3)	0.033*
H5B	0.391 (3)	0.209 (3)	−0.3914 (16)	0.033*
V1	1.00944 (5)	0.02657 (3)	0.24106 (5)	0.01255 (14)
N1	0.9881 (2)	0.16751 (18)	0.1354 (2)	0.0144 (5)
P1	0.82006 (8)	0.05841 (5)	−0.05527 (7)	0.01277 (18)
O1	0.6728 (2)	0.09610 (15)	−0.0929 (2)	0.0169 (4)
O2	0.8417 (2)	0.00520 (15)	−0.1674 (2)	0.0171 (5)
O3	0.8583 (2)	−0.00015 (14)	0.0697 (2)	0.0158 (4)
O4	0.8598 (2)	0.09240 (15)	0.2912 (2)	0.0190 (5)
O5	0.7024 (2)	0.20093 (16)	0.2621 (2)	0.0236 (5)
O6	1.1562 (2)	0.10601 (15)	0.3703 (2)	0.0173 (4)
O7	1.2826 (3)	0.23093 (16)	0.4190 (2)	0.0264 (5)
O8	1.0113 (2)	−0.05963 (15)	0.3290 (2)	0.0222 (5)
C1	0.9495 (3)	0.1494 (2)	−0.0073 (3)	0.0150 (6)
H1A	1.0349	0.1325	−0.0267	0.018*
H1B	0.9088	0.2040	−0.0582	0.018*
C2	0.8752 (3)	0.2192 (2)	0.1622 (3)	0.0184 (6)
H2A	0.8017	0.2360	0.0774	0.022*
H2B	0.9164	0.2752	0.2089	0.022*
C3	0.8069 (3)	0.1677 (2)	0.2439 (3)	0.0162 (6)
C4	1.1288 (3)	0.2098 (2)	0.1951 (3)	0.0187 (6)

H4A	1.1192	0.2757	0.1890	0.022*
H4B	1.1912	0.1910	0.1469	0.022*
C5	1.1943 (3)	0.1818 (2)	0.3395 (3)	0.0159 (6)
O6W	0.5865 (6)	0.1765 (4)	0.4618 (6)	0.1092 (17)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0117 (2)	0.0175 (3)	0.0126 (2)	−0.00012 (17)	0.00141 (18)	0.00099 (17)
O1W	0.0293 (14)	0.0205 (13)	0.0254 (13)	−0.0045 (10)	−0.0033 (11)	0.0034 (10)
O2W	0.0214 (12)	0.0543 (19)	0.0194 (13)	0.0064 (12)	0.0074 (10)	−0.0002 (11)
O3W	0.0173 (11)	0.0351 (15)	0.0179 (12)	−0.0091 (10)	−0.0015 (9)	0.0096 (10)
O4W	0.0173 (11)	0.0169 (11)	0.0210 (11)	−0.0006 (9)	0.0080 (9)	−0.0001 (9)
O5W	0.0189 (11)	0.0219 (12)	0.0221 (12)	−0.0027 (9)	0.0025 (10)	0.0047 (10)
V1	0.0118 (2)	0.0132 (3)	0.0118 (2)	−0.00010 (18)	0.00294 (19)	0.00108 (19)
N1	0.0120 (11)	0.0189 (13)	0.0108 (12)	−0.0015 (10)	0.0022 (10)	−0.0006 (10)
P1	0.0093 (3)	0.0163 (4)	0.0110 (4)	−0.0002 (3)	0.0015 (3)	−0.0009 (3)
O1	0.0106 (10)	0.0207 (12)	0.0172 (10)	0.0016 (8)	0.0022 (8)	−0.0026 (9)
O2	0.0109 (10)	0.0234 (12)	0.0154 (10)	−0.0003 (9)	0.0025 (8)	−0.0049 (9)
O3	0.0139 (10)	0.0179 (11)	0.0136 (10)	−0.0022 (8)	0.0021 (8)	−0.0001 (8)
O4	0.0199 (11)	0.0193 (12)	0.0221 (11)	0.0022 (9)	0.0125 (9)	0.0026 (9)
O5	0.0194 (11)	0.0220 (12)	0.0328 (13)	0.0016 (9)	0.0132 (10)	−0.0030 (10)
O6	0.0192 (11)	0.0168 (11)	0.0135 (10)	−0.0029 (9)	0.0026 (9)	0.0021 (8)
O7	0.0284 (13)	0.0232 (13)	0.0179 (11)	−0.0110 (10)	−0.0039 (10)	0.0012 (10)
O8	0.0244 (12)	0.0191 (12)	0.0237 (12)	0.0017 (9)	0.0091 (10)	0.0047 (9)
C1	0.0142 (13)	0.0177 (16)	0.0121 (14)	0.0006 (11)	0.0032 (11)	0.0003 (11)
C2	0.0220 (16)	0.0165 (16)	0.0181 (15)	0.0028 (12)	0.0088 (13)	0.0001 (12)
C3	0.0159 (14)	0.0154 (15)	0.0164 (15)	−0.0021 (12)	0.0043 (12)	−0.0047 (12)
C4	0.0160 (14)	0.0206 (16)	0.0160 (15)	−0.0064 (12)	0.0014 (12)	0.0034 (12)
C5	0.0121 (13)	0.0188 (16)	0.0153 (14)	0.0001 (11)	0.0029 (12)	0.0009 (12)

Geometric parameters (Å, º)

Mn1—O1	2.092 (2)	V1—N1	2.370 (3)
Mn1—O1W	2.164 (2)	N1—C4	1.480 (4)
Mn1—O2W	2.212 (2)	N1—C1	1.482 (4)
Mn1—O3W	2.152 (2)	N1—C2	1.488 (4)
Mn1—O4W	2.236 (2)	P1—O1	1.506 (2)
Mn1—O5W	2.187 (2)	P1—O2	1.531 (2)
O1W—H1C	0.845 (10)	P1—O3	1.544 (2)
O1W—H1D	0.84 (3)	P1—C1	1.830 (3)
O2W—H2C	0.83 (4)	O2—V1ⁱ	1.991 (2)
O2W—H2D	0.84 (4)	O4—C3	1.273 (4)
O3W—H3A	0.84 (3)	O5—C3	1.243 (4)
O3W—H3B	0.84 (3)	O6—C5	1.277 (4)
O4W—H4C	0.844 (10)	O7—C5	1.240 (4)
O4W—H4D	0.85 (3)	C1—H1A	0.9900
O5W—H5A	0.84 (3)	C1—H1B	0.9900

O5W—H5B	0.841 (10)	C2—C3	1.512 (4)
V1—O2ⁱ	1.991 (2)	C2—H2A	0.9900
V1—O3	1.988 (2)	C2—H2B	0.9900
V1—O4	2.030 (2)	C4—C5	1.529 (4)
V1—O6	2.028 (2)	C4—H4A	0.9900
V1—O8	1.598 (2)	C4—H4B	0.9900
O1—Mn1—O1W	88.63 (9)	O8—V1—O6	101.86 (11)
O1—Mn1—O2W	90.18 (9)	O8—V1—N1	169.72 (10)
O1—Mn1—O3W	175.14 (10)	C4—N1—C1	113.3 (2)
O1—Mn1—O4W	92.29 (8)	C4—N1—C2	112.1 (2)
O1—Mn1—O5W	93.12 (9)	C1—N1—C2	111.1 (2)
O1W—Mn1—O2W	93.21 (11)	C4—N1—V1	104.84 (18)
O1W—Mn1—O4W	89.40 (9)	C1—N1—V1	106.81 (18)
O1W—Mn1—O5W	178.21 (9)	C2—N1—V1	108.21 (17)
O2W—Mn1—O4W	176.45 (9)	O1—P1—O2	112.38 (12)
O3W—Mn1—O1W	87.68 (10)	O1—P1—O3	111.64 (12)
O3W—Mn1—O2W	86.85 (10)	O2—P1—O3	110.01 (12)
O3W—Mn1—O4W	90.85 (9)	O1—P1—C1	109.77 (14)
O3W—Mn1—O5W	90.58 (9)	O2—P1—C1	108.96 (13)
O5W—Mn1—O2W	87.12 (10)	O3—P1—C1	103.71 (13)
O5W—Mn1—O4W	90.21 (9)	P1—O1—Mn1	134.66 (13)
Mn1—O1W—H1C	121 (3)	P1—O2—V1ⁱ	141.30 (13)
Mn1—O1W—H1D	119 (3)	P1—O3—V1	125.51 (13)
H1C—O1W—H1D	108 (4)	C3—O4—V1	124.53 (19)
Mn1—O2W—H2C	109 (3)	C5—O6—V1	123.48 (19)
Mn1—O2W—H2D	128 (3)	N1—C1—P1	109.4 (2)
H2C—O2W—H2D	111 (4)	N1—C1—H1A	109.8
Mn1—O3W—H3A	118 (2)	P1—C1—H1A	109.8
Mn1—O3W—H3B	130 (2)	N1—C1—H1B	109.8
H3A—O3W—H3B	109.7 (17)	P1—C1—H1B	109.8
Mn1—O4W—H4C	117 (2)	H1A—C1—H1B	108.2
Mn1—O4W—H4D	123 (2)	N1—C2—C3	112.9 (3)
H4C—O4W—H4D	108.0 (16)	N1—C2—H2A	109.0
Mn1—O5W—H5A	112 (3)	C3—C2—H2A	109.0
Mn1—O5W—H5B	115 (3)	N1—C2—H2B	109.0
H5A—O5W—H5B	108.4 (16)	C3—C2—H2B	109.0
O2ⁱ—V1—O4	163.79 (9)	H2A—C2—H2B	107.8
O2ⁱ—V1—O6	86.89 (9)	O5—C3—O4	123.3 (3)
O2ⁱ—V1—N1	88.32 (9)	O5—C3—C2	118.5 (3)
O3—V1—O2ⁱ	90.96 (9)	O4—C3—C2	118.2 (3)
O3—V1—O4	87.04 (9)	N1—C4—C5	109.6 (2)
O3—V1—O6	154.03 (9)	N1—C4—H4A	109.7
O3—V1—N1	79.41 (9)	C5—C4—H4A	109.7
O4—V1—N1	75.50 (9)	N1—C4—H4B	109.7
O6—V1—O4	87.90 (9)	C5—C4—H4B	109.7
O6—V1—N1	74.66 (9)	H4A—C4—H4B	108.2
O8—V1—O2ⁱ	101.24 (11)	O7—C5—O6	123.4 (3)

O8—V1—O3	103.95 (11)	O7—C5—C4	119.9 (3)
O8—V1—O4	94.85 (11)	O6—C5—C4	116.6 (3)
O8—V1—N1—C4	97.0 (6)	N1—V1—O3—P1	14.95 (15)
O3—V1—N1—C4	−152.95 (19)	O8—V1—O4—C3	−176.3 (2)
O2ⁱ—V1—N1—C4	−61.66 (18)	O3—V1—O4—C3	−72.6 (2)
O6—V1—N1—C4	25.58 (18)	O2ⁱ—V1—O4—C3	10.7 (5)
O4—V1—N1—C4	117.39 (19)	O6—V1—O4—C3	81.9 (2)
O8—V1—N1—C1	−142.5 (6)	N1—V1—O4—C3	7.2 (2)
O3—V1—N1—C1	−32.42 (17)	O8—V1—O6—C5	176.7 (2)
O2ⁱ—V1—N1—C1	58.87 (18)	O3—V1—O6—C5	−9.9 (4)
O6—V1—N1—C1	146.11 (18)	O2ⁱ—V1—O6—C5	75.9 (2)
O4—V1—N1—C1	−122.08 (18)	O4—V1—O6—C5	−88.7 (2)
O8—V1—N1—C2	−22.8 (7)	N1—V1—O6—C5	−13.2 (2)
O3—V1—N1—C2	87.24 (19)	C4—N1—C1—P1	155.7 (2)
O2ⁱ—V1—N1—C2	178.53 (19)	C2—N1—C1—P1	−77.0 (3)
O6—V1—N1—C2	−94.24 (19)	V1—N1—C1—P1	40.8 (2)
O4—V1—N1—C2	−2.42 (18)	O1—P1—C1—N1	88.4 (2)
O2—P1—O1—Mn1	20.0 (2)	O2—P1—C1—N1	−148.10 (19)
O3—P1—O1—Mn1	−104.11 (19)	O3—P1—C1—N1	−31.0 (2)
C1—P1—O1—Mn1	141.47 (18)	C4—N1—C2—C3	−116.4 (3)
O1W—Mn1—O1—P1	55.1 (2)	C1—N1—C2—C3	115.7 (3)
O5W—Mn1—O1—P1	−125.19 (19)	V1—N1—C2—C3	−1.3 (3)
O2W—Mn1—O1—P1	−38.1 (2)	V1—O4—C3—O5	169.9 (2)
O4W—Mn1—O1—P1	144.48 (19)	V1—O4—C3—C2	−10.5 (4)
O1—P1—O2—V1ⁱ	149.0 (2)	N1—C2—C3—O5	−173.4 (3)
O3—P1—O2—V1ⁱ	−86.0 (2)	N1—C2—C3—O4	6.9 (4)
C1—P1—O2—V1ⁱ	27.1 (3)	C1—N1—C4—C5	−149.8 (3)
O1—P1—O3—V1	−115.47 (16)	C2—N1—C4—C5	83.5 (3)
O2—P1—O3—V1	119.05 (15)	V1—N1—C4—C5	−33.7 (3)
C1—P1—O3—V1	2.65 (18)	V1—O6—C5—O7	179.0 (2)
O8—V1—O3—P1	−175.00 (15)	V1—O6—C5—C4	−3.1 (4)
O2ⁱ—V1—O3—P1	−73.17 (16)	N1—C4—C5—O7	−154.2 (3)
O6—V1—O3—P1	11.7 (3)	N1—C4—C5—O6	27.8 (4)
O4—V1—O3—P1	90.74 (16)		

Symmetry code: (i) −*x*+2, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*W*—H1*C*⋯O4*W*ⁱ	0.85 (1)	1.98 (1)	2.813 (3)	167 (4)
O1*W*—H1*D*⋯O5ⁱⁱ	0.84 (3)	1.92 (3)	2.759 (3)	171 (3)
O2*W*—H2*C*⋯O2	0.83 (4)	2.15 (3)	2.847 (3)	142 (4)
O2*W*—H2*D*⋯O6*W*ⁱⁱⁱ	0.84 (4)	1.88 (2)	2.675 (6)	160 (4)
O3*W*—H3*A*⋯O4ⁱⁱ	0.84 (3)	1.92 (2)	2.735 (3)	163 (4)
O3*W*—H3*B*⋯O6ⁱᵛ	0.84 (3)	1.93 (3)	2.745 (3)	166 (4)
O4*W*—H4*C*⋯O7ᵛ	0.84 (1)	1.86 (1)	2.698 (3)	175 (3)

O4*W*—H4*D*···O3[ii]	0.85 (3)	1.94 (3)	2.778 (3)	173 (4)
O5*W*—H5*A*···O5[vi]	0.84 (3)	2.00 (2)	2.803 (3)	161 (4)
O5*W*—H5*B*···O7[iv]	0.84 (1)	1.99 (1)	2.823 (3)	171 (3)

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