

Tetraquatetramanganese(II) catena-[germanodihydroxidodi(hydrogen-phosphate)diphosphate]

Xin Zhang, Lei Wen, Hong-Ming Chen, Jin-Xiao Mi and Ya-Xi Huang*

Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, Fujian Province, People's Republic of China

Correspondence e-mail: yaxihuang@xmu.edu.cn

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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{Mn}-\text{O}) = 0.003$ Å; R factor = 0.042; wR factor = 0.064; data-to-parameter ratio = 14.0.

The title compound, $\text{Mn}_4(\text{H}_2\text{O})_4[\text{Ge}(\text{OH})_2(\text{HPO}_4)_2(\text{PO}_4)_2]$, was synthesized by the solvothermal method. Its crystal structure is isotypic with the iron and cobalt analogues [Huang *et al.* (2012). *Inorg. Chem.* **51**, 3316–3323]. In the crystal structure, the framework is built from undulating manganese phosphate sheets parallel to (010) interconnected by GeO_6 octahedra (at the inversion center), resulting in a three-dimensional network with eight-membered ring channels into which all the protons point. The undulating manganese phosphate sheet consists of zigzag manganese octahedral chains along $[10\bar{1}]$, built from $\text{MnO}_4(\text{OH})(\text{OH}_2)$ octahedra and $\text{MnO}_5(\text{OH}_2)$ octahedra by sharing their *trans* or skew edges, which are interconnected by $\text{PO}_3(\text{OH})$ and PO_4 tetrahedra *via* corner-sharing. The crystal structure features extensive $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions.

Related literature

For background to germanophosphates, see: Brock *et al.* (1998); Corma (1997); Li *et al.* (2000); Liu, Yang, Wang *et al.* (2008); Liu, Yang, Zhang *et al.* (2008); Zhao *et al.* (2009); Zubietta (1994). For isotypic structures of the Fe^{II} and Co^{II} analogues, see: Huang *et al.* (2012).

Experimental

Crystal data

$\text{Mn}_4(\text{H}_2\text{O})_4[\text{Ge}(\text{OH})_2(\text{HPO}_4)_2(\text{PO}_4)_2]$	$\beta = 98.506$ (4)°
$M_r = 780.33$	$V = 815.84$ (6) Å ³
Monoclinic, $P2_1/n$	$Z = 2$
$a = 6.5336$ (3) Å	Mo $K\alpha$ radiation
$b = 16.3869$ (7) Å	$\mu = 5.35$ mm ⁻¹
$c = 7.7048$ (3) Å	$T = 173$ K
	$0.10 \times 0.08 \times 0.05$ mm

Data collection

Oxford Diffraction CCD area-detector diffractometer	5173 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2005)	2215 independent reflections
$T_{\text{min}} = 0.604$, $T_{\text{max}} = 0.765$	1808 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.064$	$\Delta\rho_{\text{max}} = 0.67$ e Å ⁻³
$S = 1.11$	$\Delta\rho_{\text{min}} = -0.71$ e Å ⁻³
2215 reflections	
158 parameters	
5 restraints	

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O9}^{\text{i}}$	0.82 (1)	2.49 (5)	3.039 (5)	126 (5)
$\text{O1}-\text{H1}\cdots\text{O7}^{\text{i}}$	0.82 (1)	2.60 (5)	3.166 (4)	127 (5)
$\text{O1}-\text{H2}\cdots\text{O8}^{\text{ii}}$	0.82 (1)	2.33 (3)	3.101 (4)	157 (6)
$\text{O1}-\text{H2}\cdots\text{O11}^{\text{iii}}$	0.82 (1)	2.39 (5)	2.878 (4)	119 (5)
$\text{O2}-\text{H3}\cdots\text{O9}^{\text{iv}}$	0.82 (1)	2.01 (3)	2.733 (4)	147 (5)
$\text{O2}-\text{H4}\cdots\text{O1}^{\text{iii}}$	0.82 (1)	2.03 (3)	2.765 (5)	149 (6)
$\text{O2}-\text{H3}\cdots\text{O10}^{\text{v}}$	0.82 (1)	2.63 (5)	3.161 (4)	123 (5)
$\text{O8}-\text{H5}\cdots\text{O10}^{\text{vi}}$	0.83	2.11	2.692 (4)	126 (1)
$\text{O9}-\text{H6}\cdots\text{O5}^{\text{vii}}$	0.82 (1)	1.80 (2)	2.584 (4)	160 (6)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005) and *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2199).

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supplementary materials

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Tetraaquatetramanganese(II) *catena*-[germanodihydroxidodi(hydrogenphosphate)diphosphate]

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Comment

Open-framework compounds attract much attention due to their rich structural chemistry and potential catalytic, electrical, optical, and magnetic properties (Brock *et al.*, 1998; Corma, 1997; Zubieta, 1994). Germanophosphates, as one kind of open-framework compounds, have not been fully explored, and only a few compounds had been synthesized up to date (Li *et al.*, 2000; Liu, Yang, Wang *et al.*, 2008; Liu, Yang, Zhang *et al.*, 2008; Zhao *et al.*, 2009). During our systematical investigation on the transition metal germanophosphate system, we obtain the first manganese compound, $\text{Mn}^{\text{II}}_4(\text{H}_2\text{O})_4[\text{Ge}(\text{OH})_2(\text{HPO}_4)_2(\text{PO}_4)_2]$, which is isostructural with its Fe and Co-analogues (Huang *et al.*, 2012) published recently.

The asymmetric unit of the title compound consists of two distinct Mn atoms, one Ge atom, and two crystallographically independent P atoms (Figure 1). Mn1 is surrounded by four O atoms, an OH-group, and a H_2O molecule forming a distorted octahedron $\text{Mn1O}_4(\text{OH})(\text{OH}_2)$ with bond distances of 2.159–2.207 Å. Mn2 adopts a nearly regular octahedral coordination to five O atoms and a water molecule with bond distances ranging from 2.176 to 2.224 Å. Ge atom coordinates to four O-atoms in the equatorial plane with shorter bond lengths of 1.846–1.871 Å and two hydroxyl groups in trans-position with longer distance of 1.913 Å. Both P atoms are in tetrahedral coordination with bond lengths of 1.526–1.573 Å. All the bond lengths and angles of the title compound are similar to those of the known germanophosphates (Huang *et al.*, 2012; Liu, Yang, Wang *et al.*, 2008; Liu, Yang, Zhang *et al.*, 2008; Zhao *et al.*, 2009). The $\text{Mn2O}_5(\text{OH}_2)$ octahedra share their trans-edges with two adjacent $\text{Mn1O}_4(\text{OH})(\text{OH}_2)$ octahedra, in turn, Mn1-octahedra share skew-edges to two neighboring Mn2-octahedra, resulting in a zigzag chain running along [10-1] (Figure 2a). These manganese octahedral chains are further linked by the $\text{P1O}_3(\text{OH})$ and P2O_4 tetrahedra through corner sharing to form undulating sheets (Figure 2b). These sheets are further interconnected by $\text{GeO}_4(\text{OH})_2$ octahedra, sitting at the inverse center, along [010] via common O-corners (Figure 2c) to form a neutral 3-D network with 8-membered ring channels parallel to [100] where all the protons protrude to (Figure 2d). Compared with the two isotopic Fe- and Co-compounds, the Mn–O distances are longer than those of Co- and Fe-compound which is consistent to the longer ionic radius of Mn than those of Fe and Co analogues.

Experimental

The crystals of the title compound were solvothermally synthesized by a mixture of GeO_2 (0.073 g), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.171 g), H_3PO_4 (85 wt%, 1 mL), H_2O (2 mL), triethylamine (1 mL), and 1,2-propanediol (2 mL). The mixture was transferred into a Teflon-lined stainless steel autoclave (internal volume of 15 mL) and heated at 423 K for 7 days under static conditions. After the autoclaves cooling to room temperature, the products were filtered off and washed by distilled water for several times and dried in air. Finally light-pink block-shaped crystals were obtained. It is needed to note that the products often contain a minor impurity of GeO_2 . Many efforts have been made to get pure phase.

However, even the pure phase was obtained but the yield is so low that not enough for further characterization. Thus only single crystal X-ray diffraction of the title compound was carried out.

Refinement

Originally, all hydrogen positions were located from the difference Fourier map and refined by applying the constraint of displacement parameters as 0.05 \AA^3 and a bond distance of $d(\text{O-H}) = 0.82 (1) \text{ \AA}$. After the refinement, O8-H5 turned out to have no acceptor atom. Therefore, the H5 position was calculated geometrically and fixed without applying further refinement.

Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2005); data reduction: *CrysAlis CCD* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005) and *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 1999).

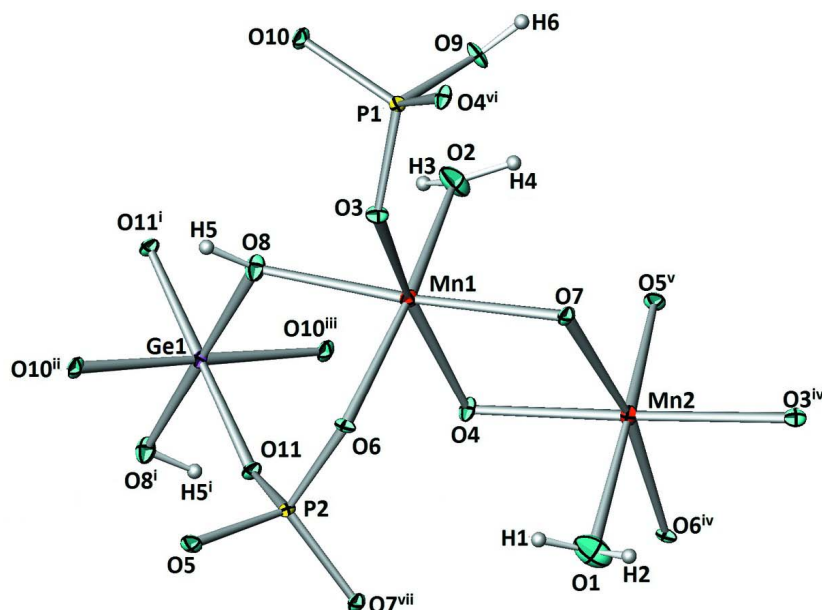
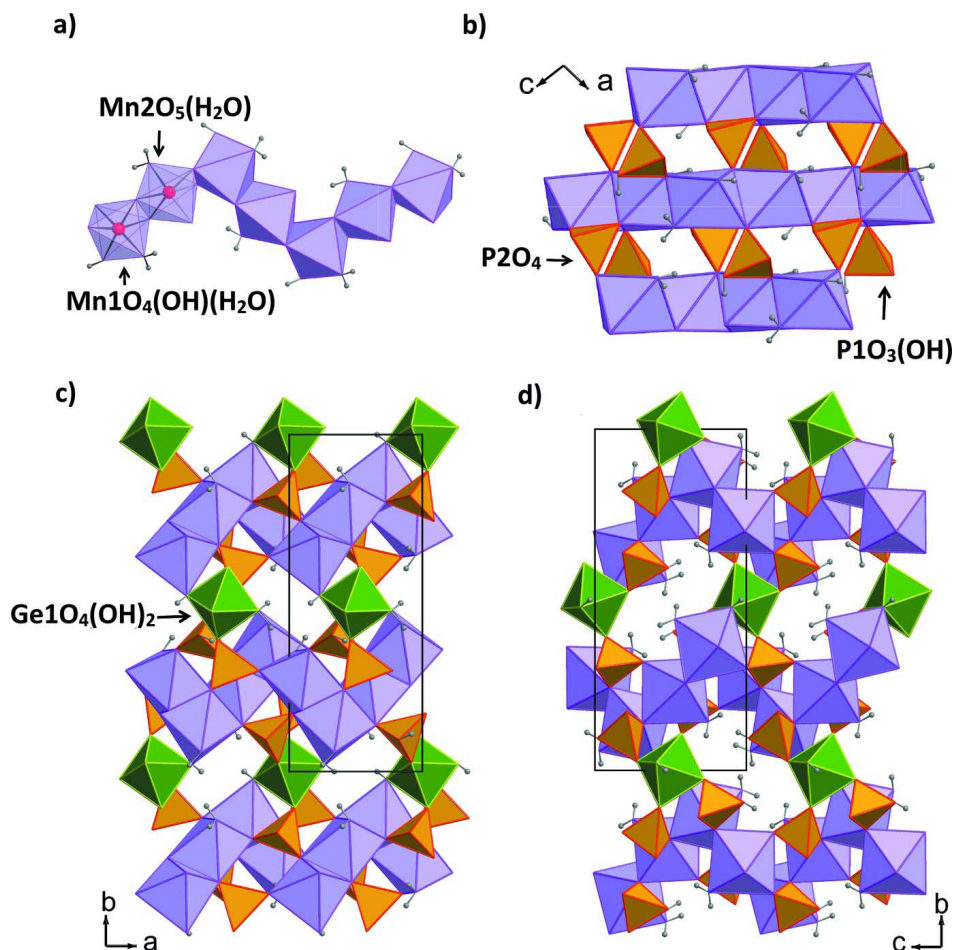


Figure 1

Asymmetric unit of the title compound, showing the coordination environments of Ge, Mn and P atoms. Thermal ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x-1, y, z$; (iv) $x-1/2, -y+1/2, z+1/2$; (v) $x, y, z+1$; (vi) $x+1, y, z$; (vii) $x-1/2, -y+1/2, z-1/2$.


Figure 2

Polyhedral presentation of the title compound, a) manganese octahedra share their trans or skew edges to form zigzag chains parallel to $[10\bar{1}]$, b) these manganese octahedral chains are linked by phosphate tetrahedra via common O-corners to form undulating manganese phosphate sheets parallel to (010) , c) the undulating sheets are further connected by $\text{GeO}_4(\text{OH})_2$ octahedra along $[010]$, resulting in a three-dimensional network structure, d) the network structure comprises 8-membered ring channels running along $[100]$ direction where all the protons protrude to. MnO_6 octahedra: purple, GeO_6 octahedra: green, PO_4 tetrahedra: orange, H atoms: light grey spheres.

Tetraquatetramanganese(II) catena-[germanodihydroxidodi(hydrogenphosphate)diphosphate]
Crystal data

 $M_r = 780.33$

 Monoclinic, $P2_1/n$

 Hall symbol: $-P 2_1/n$
 $a = 6.5336 (3) \text{ \AA}$
 $b = 16.3869 (7) \text{ \AA}$
 $c = 7.7048 (3) \text{ \AA}$
 $\beta = 98.506 (4)^\circ$
 $V = 815.84 (6) \text{ \AA}^3$
 $Z = 2$
 $F(000) = 760$
 $D_x = 3.176 \text{ Mg m}^{-3}$

 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 $\theta = 3.0\text{--}32.5^\circ$
 $\mu = 5.35 \text{ mm}^{-1}$
 $T = 173 \text{ K}$

Block-shaped, light pink

 $0.10 \times 0.08 \times 0.05 \text{ mm}$

Data collection

Oxford Diffraction CCD area-detector diffractometer	5173 measured reflections
Radiation source: fine-focus sealed tube	2215 independent reflections
Graphite monochromator	1808 reflections with $I > 2\sigma(I)$
326 images, $\Delta\omega=1^\circ$, Exp time: 40 s. scans	$R_{\text{int}} = 0.049$
Absorption correction: multi-scan (<i>CrysAlis CCD</i> ; Oxford Diffraction, 2005)	$\theta_{\text{max}} = 30.7^\circ$, $\theta_{\text{min}} = 3.0^\circ$
$T_{\text{min}} = 0.604$, $T_{\text{max}} = 0.765$	$h = -8 \rightarrow 8$
	$k = -23 \rightarrow 21$
	$l = -10 \rightarrow 5$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.007P)^2]$
$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2215 reflections	$\Delta\rho_{\text{max}} = 0.67 \text{ e } \text{\AA}^{-3}$
158 parameters	$\Delta\rho_{\text{min}} = -0.71 \text{ e } \text{\AA}^{-3}$
5 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0025 (3)
Secondary atom site location: difference Fourier map	

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. 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 $F^2 > 2\sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ge1	0.0000	0.0000	0.5000	0.00570 (15)
Mn1	0.33624 (9)	0.13618 (4)	0.73967 (8)	0.00616 (15)
Mn2	0.10405 (9)	0.27193 (4)	0.97488 (8)	0.00687 (15)
P1	0.85555 (15)	0.10913 (6)	0.78765 (14)	0.0048 (2)
P2	0.06543 (15)	0.18774 (6)	0.37557 (14)	0.0048 (2)
O1	0.0486 (5)	0.3570 (2)	0.7515 (5)	0.0212 (8)
O2	0.3396 (5)	0.05675 (19)	0.9714 (4)	0.0169 (7)
O3	0.6508 (4)	0.13783 (16)	0.6846 (4)	0.0068 (6)
O4	0.0282 (4)	0.17242 (16)	0.7897 (4)	0.0075 (6)
O5	0.0928 (4)	0.18148 (16)	0.1813 (4)	0.0071 (6)
O6	0.2743 (4)	0.20020 (16)	0.4915 (4)	0.0063 (6)
O7	0.4116 (4)	0.24382 (15)	0.9032 (4)	0.0071 (6)
O8	0.2712 (4)	0.02156 (17)	0.5966 (4)	0.0099 (6)
O9	0.8236 (4)	0.09402 (17)	0.9835 (4)	0.0094 (6)
O10	0.9176 (4)	0.02614 (16)	0.7215 (4)	0.0078 (6)

O11	−0.0403 (4)	0.10841 (16)	0.4270 (4)	0.0074 (6)
H1	0.101 (8)	0.336 (3)	0.672 (5)	0.050*
H2	0.117 (8)	0.399 (2)	0.768 (8)	0.050*
H3	0.252 (6)	0.020 (2)	0.959 (8)	0.050*
H4	0.364 (9)	0.076 (3)	1.070 (3)	0.050*
H5	0.296	0.014	0.495	0.050*
H6	0.917 (6)	0.111 (3)	1.056 (6)	0.050*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ge1	0.0067 (3)	0.0038 (3)	0.0065 (3)	−0.0004 (2)	0.0006 (2)	−0.0006 (2)
Mn1	0.0059 (3)	0.0056 (3)	0.0069 (3)	0.0000 (2)	0.0010 (2)	−0.0001 (2)
Mn2	0.0075 (3)	0.0062 (3)	0.0069 (3)	−0.0002 (2)	0.0011 (2)	−0.0009 (3)
P1	0.0050 (5)	0.0048 (5)	0.0048 (5)	−0.0003 (4)	0.0008 (4)	0.0003 (4)
P2	0.0048 (5)	0.0038 (5)	0.0056 (5)	0.0009 (4)	0.0006 (4)	0.0006 (4)
O1	0.0201 (19)	0.024 (2)	0.0185 (19)	−0.0062 (15)	−0.0014 (15)	0.0063 (16)
O2	0.0222 (18)	0.0140 (18)	0.0122 (17)	−0.0081 (13)	−0.0054 (15)	0.0033 (14)
O3	0.0040 (13)	0.0076 (15)	0.0088 (15)	−0.0006 (11)	0.0005 (12)	0.0015 (12)
O4	0.0070 (14)	0.0081 (15)	0.0083 (15)	−0.0002 (11)	0.0043 (12)	−0.0025 (11)
O5	0.0092 (14)	0.0059 (15)	0.0061 (15)	−0.0004 (11)	0.0003 (12)	0.0024 (11)
O6	0.0042 (13)	0.0082 (15)	0.0061 (15)	0.0010 (11)	−0.0010 (11)	0.0011 (11)
O7	0.0080 (14)	0.0040 (14)	0.0090 (15)	0.0000 (11)	0.0000 (12)	−0.0013 (12)
O8	0.0097 (14)	0.0117 (16)	0.0087 (15)	−0.0027 (11)	0.0023 (12)	−0.0027 (12)
O9	0.0110 (15)	0.0136 (16)	0.0031 (15)	−0.0034 (12)	−0.0009 (12)	0.0003 (12)
O10	0.0119 (14)	0.0037 (14)	0.0078 (15)	0.0001 (11)	0.0018 (12)	−0.0005 (11)
O11	0.0089 (14)	0.0038 (14)	0.0092 (15)	0.0008 (11)	0.0000 (12)	0.0004 (12)

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

Ge1—O8 ⁱ	1.851 (3)	Mn2—O7	2.210 (3)
Ge1—O8	1.851 (3)	Mn2—O6 ^{iv}	2.225 (3)
Ge1—O11 ⁱ	1.870 (3)	P1—O3	1.525 (3)
Ge1—O11	1.870 (3)	P1—O10	1.528 (3)
Ge1—O10 ⁱⁱ	1.913 (3)	P1—O4 ^{vi}	1.531 (3)
Ge1—O10 ⁱⁱⁱ	1.913 (3)	P1—O9	1.573 (3)
Ge1—H5	1.9535	P2—O6	1.530 (3)
Mn1—O3	2.159 (3)	P2—O5	1.537 (3)
Mn1—O6	2.166 (3)	P2—O7 ^{vii}	1.542 (3)
Mn1—O7	2.181 (3)	P2—O11	1.551 (3)
Mn1—O4	2.186 (3)	O1—H1	0.817 (10)
Mn1—O8	2.188 (3)	O1—H2	0.818 (10)
Mn1—O2	2.207 (3)	O2—H3	0.822 (10)
Mn2—O4	2.175 (3)	O2—H4	0.815 (10)
Mn2—O3 ^{iv}	2.178 (3)	O8—H5	0.83
Mn2—O5 ^v	2.183 (3)	O9—H6	0.816 (10)
Mn2—O1	2.203 (4)		
O8 ⁱ —Ge1—O8	180.00 (7)	O5 ^v —Mn2—O7	99.81 (10)
O8 ⁱ —Ge1—O11 ⁱ	91.35 (12)	O1—Mn2—O7	89.26 (12)

O8—Ge1—O11 ⁱ	88.65 (12)	O4—Mn2—O6 ^{iv}	93.62 (10)
O8 ⁱ —Ge1—O11	88.65 (12)	O3 ^{iv} —Mn2—O6 ^{iv}	81.31 (10)
O8—Ge1—O11	91.35 (12)	O5 ^v —Mn2—O6 ^{iv}	87.72 (10)
O11 ⁱ —Ge1—O11	180.0	O1—Mn2—O6 ^{iv}	82.32 (12)
O8 ⁱ —Ge1—O10 ⁱⁱ	91.28 (12)	O7—Mn2—O6 ^{iv}	168.93 (11)
O8—Ge1—O10 ⁱⁱ	88.72 (12)	O3—P1—O10	110.87 (15)
O11 ⁱ —Ge1—O10 ⁱⁱ	89.43 (12)	O3—P1—O4 ^{vi}	112.63 (16)
O11—Ge1—O10 ⁱⁱ	90.57 (12)	O10—P1—O4 ^{vi}	112.02 (16)
O8 ⁱ —Ge1—O10 ⁱⁱⁱ	88.72 (12)	O3—P1—O9	108.50 (16)
O8—Ge1—O10 ⁱⁱⁱ	91.28 (12)	O10—P1—O9	105.01 (16)
O11 ⁱ —Ge1—O10 ⁱⁱⁱ	90.57 (12)	O4 ^{vi} —P1—O9	107.40 (16)
O11—Ge1—O10 ⁱⁱⁱ	89.43 (12)	O6—P2—O5	110.80 (16)
O10 ⁱⁱ —Ge1—O10 ⁱⁱⁱ	180.0	O6—P2—O7 ^{vii}	111.45 (15)
O3—Mn1—O6	83.08 (10)	O5—P2—O7 ^{vii}	110.81 (16)
O3—Mn1—O7	87.89 (10)	O6—P2—O11	110.82 (15)
O6—Mn1—O7	96.60 (10)	O5—P2—O11	108.25 (16)
O3—Mn1—O4	163.50 (10)	O7 ^{vii} —P2—O11	104.49 (16)
O6—Mn1—O4	88.13 (10)	H1—O1—H2	101 (6)
O7—Mn1—O4	79.25 (10)	H3—O2—H4	115 (6)
O3—Mn1—O8	91.79 (10)	P1—O3—Mn1	132.90 (17)
O6—Mn1—O8	88.50 (10)	P1—O3—Mn2 ^{viii}	127.70 (16)
O7—Mn1—O8	174.81 (11)	Mn1—O3—Mn2 ^{viii}	96.96 (10)
O4—Mn1—O8	101.94 (10)	P1 ⁱⁱ —O4—Mn2	127.63 (17)
O3—Mn1—O2	105.70 (12)	P1 ⁱⁱ —O4—Mn1	120.69 (15)
O6—Mn1—O2	167.96 (11)	Mn2—O4—Mn1	101.13 (10)
O7—Mn1—O2	92.02 (11)	P2—O5—Mn2 ^{ix}	133.27 (16)
O4—Mn1—O2	85.22 (12)	P2—O6—Mn1	119.00 (15)
O8—Mn1—O2	83.08 (11)	P2—O6—Mn2 ^{viii}	141.41 (17)
O4—Mn2—O3 ^{iv}	171.44 (11)	Mn1—O6—Mn2 ^{viii}	95.39 (10)
O4—Mn2—O5 ^v	86.56 (10)	P2 ^x —O7—Mn1	127.21 (17)
O3 ^{iv} —Mn2—O5 ^v	86.36 (10)	P2 ^x —O7—Mn2	121.22 (15)
O4—Mn2—O1	88.11 (12)	Mn1—O7—Mn2	100.20 (10)
O3 ^{iv} —Mn2—O1	97.96 (12)	Ge1—O8—Mn1	118.00 (13)
O5 ^v —Mn2—O1	168.39 (12)	P1—O10—Ge1 ^{vi}	128.35 (17)
O4—Mn2—O7	78.87 (10)	P2—O11—Ge1	145.55 (17)
O3 ^{iv} —Mn2—O7	107.09 (10)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O9 ^{vii}	0.82 (1)	2.49 (5)	3.039 (5)	126 (5)
O1—H1 \cdots O7 ^{vii}	0.82 (1)	2.60 (5)	3.166 (4)	127 (5)
O1—H2 \cdots O8 ^{xi}	0.82 (1)	2.33 (3)	3.101 (4)	157 (6)
O1—H2 \cdots O11 ^x	0.82 (1)	2.39 (5)	2.878 (4)	119 (5)
O2—H3 \cdots O9 ^{xii}	0.82 (1)	2.01 (3)	2.733 (4)	147 (5)
O2—H4 \cdots O1 ^x	0.82 (1)	2.03 (3)	2.765 (5)	149 (6)
O2—H3 \cdots O10 ⁱⁱ	0.82 (1)	2.63 (5)	3.161 (4)	123 (5)

O8—H5···O10 ⁱⁱⁱ	0.83	2.11	2.692 (4)	126 (1)
O9—H6···O5 ^{xiii}	0.82 (1)	1.80 (2)	2.584 (4)	160 (6)

Symmetry codes: (ii) $x-1, y, z$; (iii) $-x+1, -y, -z+1$; (vii) $x-1/2, -y+1/2, z-1/2$; (x) $x+1/2, -y+1/2, z+1/2$; (xi) $-x+1/2, y+1/2, -z+3/2$; (xii) $-x+1, -y, -z+2$; (xiii) $x+1, y, z+1$.