A new form of NaMnAsO$_4$

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A new form of NaMnAsO$_4$, sodium manganese(II) orthoarsenate, has been obtained under hydrothermal conditions, and is referred to as the β-polymorph. In contrast to the previously reported orthorhombic α-polymorph that crystallizes in the olivine-type of structure and has one manganese(II) cation in a distorted octahedral coordination, the current β-polymorph contains two manganese(II) cations in [5]-coordination, intermediate between a square-pyramid and a trigonal bipyramid. In the crystal structure of β-NaMnAsO$_4$, four [MnO$_5$] polyhedra are linked through vertex- and edge-sharing into finite {Mn$_4$O$_{16}$} units strung into rows parallel to [100]. These units are linked through two distinct orthoarsenate groups into a framework structure with channels propagating parallel to the manganese oxide rows. Both unique sodium cations are situated inside the channels and exhibit coordination numbers of six and seven. β-NaMnAsO$_4$ is isotypic with one form of NaCoPO$_4$ and with NaCuAsO$_4$.

1. Chemical context

Magnussonite is a rare manganese(II) arsenite mineral and has been described with an ideal formula of Mn$^{II}_{10}$As$^{III}_6$O$_{18}$(OH,Cl)$_2$ (Moore & Araki, 1979). In a recent project on hydrothermal crystal growth of phases in the system Mn^{II}/As^{III}/O (Priestner *et al.*, 2018a) and a precise structure refinement of magnussonite, it could be shown that the obtained synthetic material has a composition of Mn$^{II}_3$As$^{III}_2$O$_6$·1/3H$_2$O whereas naturally occurring material (type locality Långban, Sweden) is better described as Mn$^{II}_3$As$^{III}_2$O$_6$(Cu^{II}(OH,Cl)$_2$)$_x$ (Priestner *et al.*, 2018b). Building on that knowledge, a subsequent project was started to incorporate divalent transition-metal cations under hydrothermal conditions into synthetic magnussonite for obtaining similar compositions to those in the natural material. In one of the batches, containing manganese(II) acetate, sodium hydroxide, nickel chloride and arsenic(III) oxide as the arsenic source, we observed a partial oxidation of arsenic to yield monoclinic NaMnAsO$_4$ as a by-product with arsenic in an oxidation state of +V. NaMnAsO$_4$ was reported previously, as obtained from a high-temperature synthesis in a molten salt medium (Ulutagay-Kartin *et al.*, 2002). This form crystallizes in the orthorhombic system with space-group type *Pnma* and adopts an olivine-type of structure.

In the following, we refer to the previously reported orthorhombic polymorph (Ulutagay-Kartin *et al.*, 2002) as the α-form, and the new monoclinic polymorph as the β-form of NaMnAsO$_4$.

research communications
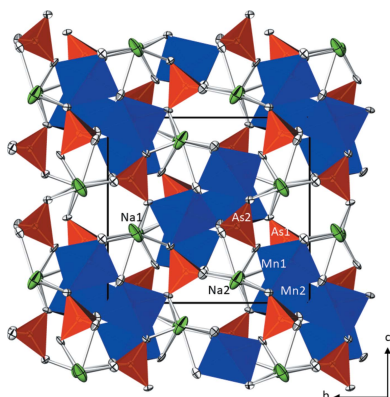
Table 1
Selected bond lengths (Å).

Na1—O6^i	2.368 (3)	Mn1—O7	2.162 (3)
Na1—O1^{ii}	2.407 (3)	Mn1—O3	2.205 (3)
Na1—O2^{iii}	2.411 (3)	Mn2—O2^v	2.095 (3)
Na1—O5^{ii}	2.496 (3)	Mn2—O4^{vii}	2.124 (3)
Na1—O3^i	2.526 (4)	Mn2—O1	2.139 (3)
Na1—O7^{iv}	2.547 (3)	Mn2—O8^v	2.150 (3)
Na2—O3	2.376 (3)	Mn2—O4^v	2.155 (3)
Na2—O2^v	2.409 (4)	As1—O2	1.683 (3)
Na2—O7^i	2.539 (3)	As1—O5^{vii}	1.689 (3)
Na2—O5	2.540 (3)	As1—O1	1.694 (3)
Na2—O1	2.580 (4)	As1—O7	1.703 (3)
Na2—O6	2.712 (4)	As2—O6	1.647 (3)
Na2—O8	2.829 (4)	As2—O3^{viii}	1.676 (3)
Mn1—O6	2.061 (3)	As2—O4^{ix}	1.684 (3)
Mn1—O5^{vi}	2.144 (3)	As2—O8	1.696 (3)
Mn1—O8^{vi}	2.144 (3)		

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

2. Structural commentary

β-NaMnAsO₄ crystallizes isotypically with one of the three modifications of the phosphate NaCoPO₄ (Feng *et al.*, 1997) and with the copper analogue NaCuAsO₄ (Ulutagay-Kartin *et al.*, 2003). The asymmetric unit of β-NaMnAsO₄ comprises of two formula units, and the principal building units are two manganese(II) cations in [5]-coordination, two orthoarsenate anions AsO₄$^{3-}$, and two sodium cations in a six- and sevenfold coordination by oxygen (Fig. 1).
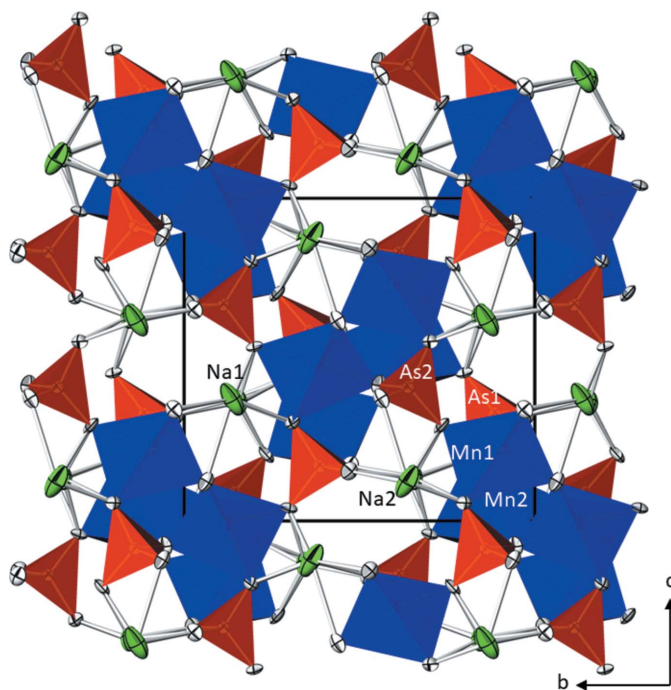
Figure 1
The crystal structure of β-NaMnAsO₄ in a projection along [$\bar{1}$00]. [MnO₅] polyhedra are shown in blue, [AsO₄] tetrahedra in red, Na^I cations in green and O atoms in shaded grey. Displacement ellipsoids are drawn at the 90% probability level.

The τ_5 descriptor (Addison *et al.*, 1984) was calculated as 0.59 for the polyhedron around Mn1 and 0.54 for that around Mn2, meaning that the shapes of the polyhedra are intermediate between a square pyramid ($\tau_5 = 0$) and a trigonal bipyramid ($\tau_5 = 1$). The Mn—O bond lengths range from 2.061 (3)–2.205 (3) Å whereby those involving Mn1 scatter in a greater range than those involving Mn2 (Table 1). Two [Mn2O₅] polyhedra are fused into a centrosymmetric dimer by sharing an edge. To each side of the dimer two [Mn1O₅] polyhedra are attached by sharing a common vertex, thus establishing a finite {Mn₄O₁₆} unit. In the crystal structure of the α-polymorph (Ulutagay-Kartin *et al.*, 2002), the unique Mn^{II} site has a distorted octahedral environment with bond lengths ranging from 2.121 (2)–2.339 (2) Å. Here the [MnO₆] units are connected through sharing four of their vertices into perovskite-type sheets. The isolated {Mn₄O₁₆} units in the β-polymorph are strung into rows parallel to [100] and are connected into a three-dimensional framework structure by AsO₄$^{3-}$ tetrahedra sharing common vertices. The As—O bond lengths (Table 1) are characteristic for isolated orthoarsenate groups, and their mean values of 1.692 Å (As1) and 1.676 Å (As2) conform with literature data (1.687 Å; Gagné & Hawthorne, 2018). This framework delimits channels parallel to [100] in which the two sodium cations are situated. They are surrounded by six (Na1) and seven (Na2) oxygen atoms, each displaying a distorted coordination polyhedron. Relevant Na—O distances are collated in Table 1. The results of bond-valence-sum calculations (Brown, 2002; Brese & O'Keeffe, 1991) are consistent with the expected oxidation states of +I for Na, +II for Mn, +V for As, and −II for O (values in valence units): Na1 = 1.03, Na2 = 0.95, Mn1 = 1.94, Mn2 = 1.98, As1 = 4.90, As2 = 5.12, O atoms = 1.83–2.16.

The previously reported α-form of NaMnAsO₄ has a calculated X-ray density $D_x = 4.03$ g cm^{-3} and thus is denser than the current β-form (3.95 g cm^{-3}). Based on the rule of thumb that the denser polymorph is (in the majority of cases) the stable form, these values point to α-NaMnAsO₄ as the thermodynamically stable polymorph. This assumption is supported by the preparation conditions of the different polymorphs. The α-polymorph was obtained under high-temperature conditions (Ulutagay-Kartin *et al.*, 2002) whereas the β-polymorph crystallized under much milder temperature conditions. As a result of the scarcity of β-NaMnAsO₄ material, a detailed investigation of the thermal behaviour was not conducted. However, a possible $\beta \rightarrow \alpha$ phase transition would be of the reconstructive type because the building units in the two structures exhibit a completely different arrangement.

For a quantitative structural comparison of β-NaMnAsO₄ with the isotypic sodium copper(II) arsenate analogue, NaCuAsO₄ (Ulutagay-Kartin *et al.*, 2003), the program *compstru* (de la Flor *et al.*, 2016) available at the Bilbao Crystallographic Server (Aroyo *et al.*, 2006) was used. The comparison revealed a degree of lattice distortion of 0.0170, the maximum distance between the atomic positions of paired atoms of 0.1834 Å for pair Na1, the arithmetic mean of all distances of 0.1150 Å, and the measure of similarity of 0.050. All these values show a high similarity between the two crystal

Table 2
Experimental details.

Crystal data	
Chemical formula	$NaMnAsO_4$
M_r	216.85
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	6.0917 (6), 11.4072 (10), 10.5008 (9)
β (°)	91.517 (3)
V (Å^3)	729.44 (11)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	12.60
Crystal size (mm)	$0.12 \times 0.02 \times 0.01$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.476, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10811, 2336, 1682
R_{int}	0.075
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.726
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.059, 1.00
No. of reflections	2336
No. of parameters	128
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, −0.94

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXL2017* (Sheldrick, 2015), *ATOMS* (Dowty, 2006) and *publCIF* (Westrip, 2010).

structures. This is supported by the similar τ_5 values of 0.57 and 0.47 for the two copper(II) cations in $NaCuAsO_4$.

3. Synthesis and crystallization

A stoichiometric mixture of $Mn(CH_3COO)_2 \cdot 4H_2O$, NaOH, As_2O_3 and $NiCl_2$ in the ratio 1:6:1:1/6 was loaded in a Teflon container that was filled with 3 ml of water to two-thirds of its volume. Then the container was sealed with a Teflon lid and placed in a steel autoclave that was heated at 483 K for five days. After cooling to room temperature, the solid material was filtered off, washed with mother liquor, water and ethanol and air-dried. The main phase identified by single crystal and powder X-ray diffraction was synthetic magnussonite, $Mn_3As_2O_6 \cdot 1/3H_2O$ (Priestner *et al.*, 2018b). Synthetic sarkinite, a basic manganese(II) arsenate(V) with formula $Mn_2AsO_4(OH)$ (Stock *et al.*, 2002), and the title compound were also present as minor by-products, with β-$NaMnAsO_4$ typically appearing in the form of needles.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Coordinates of isotypic $NaCuAsO_4$ (Ulutagay-Kartin *et al.*, 2003) were standardized using the program *STRUCTURE-TIDY* (Gelato & Parthé, 1987) and then used as starting parameters for refinement. Free refinement of the site occupation factors for the two Mn sites resulted in a value of 1.000 (3) in each case, thus revealing no incorporation of Ni at these sites.

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A new form of NaMnAsO₄

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Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: coordinates taken from isotypic compound; program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Sodium manganese(II) orthoarsenate

Crystal data

NaMnAsO₄	$F(000) = 808$
$M_r = 216.85$	$D_x = 3.949$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.0917$ (6) Å	Cell parameters from 1472 reflections
$b = 11.4072$ (10) Å	$\theta = 2.6$–29.1°
$c = 10.5008$ (9) Å	$\mu = 12.60$ mm^{-1}
$\beta = 91.517$ (3)°	$T = 296$ K
$V = 729.44$ (11) Å³	Needle, colourless
$Z = 8$	$0.12 \times 0.02 \times 0.01$ mm

Data collection

Bruker APEXII CCD diffractometer	2336 independent reflections
ω– and φ–scans	1682 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)	$R_{int} = 0.075$
	$\theta_{max} = 31.1°$, $\theta_{min} = 3.4°$
$T_{min} = 0.476$, $T_{max} = 0.746$	$h = -8 \rightarrow 8$
10811 measured reflections	$k = -16 \rightarrow 16$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0138P)^2]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.059$	$\Delta\rho_{max} = 0.93$ e Å^{-3}
$S = 1.00$	$\Delta\rho_{min} = -0.94$ e Å^{-3}
2336 reflections	Extinction correction: SHELXL2017
128 parameters	(Sheldrick, 2015),
0 restraints	Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]$^{-1/4}$
	Extinction coefficient: 0.00083 (19)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
As1	0.12080 (7)	0.11305 (3)	0.33114 (4)	0.00717 (10)
As2	0.62792 (7)	0.35882 (3)	0.41290 (4)	0.00749 (10)
Mn1	0.61290 (11)	0.09632 (5)	0.23084 (6)	0.00943 (14)
Mn2	0.14942 (11)	0.12113 (5)	0.00555 (6)	0.00920 (14)
Na1	0.1190 (3)	0.84466 (15)	0.36519 (18)	0.0193 (4)
Na2	0.3740 (3)	0.36374 (17)	0.1217 (2)	0.0294 (5)
O1	0.1342 (5)	0.1909 (2)	0.1942 (3)	0.0135 (7)
O2	0.1143 (5)	0.2010 (2)	0.4596 (3)	0.0117 (6)
O3	0.5901 (5)	0.2026 (3)	0.0556 (3)	0.0148 (7)
O4	0.1471 (5)	0.5556 (2)	0.5782 (3)	0.0111 (6)
O5	0.1034 (5)	0.5259 (2)	0.1712 (3)	0.0123 (6)
O6	0.6572 (5)	0.2657 (2)	0.2946 (3)	0.0145 (7)
O7	0.3513 (5)	0.0291 (2)	0.3453 (3)	0.0117 (6)
O8	0.3980 (5)	0.4378 (2)	0.3788 (3)	0.0117 (6)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0078 (2)	0.0068 (2)	0.0069 (2)	−0.00017 (16)	−0.00021 (16)	−0.00042 (16)
As2	0.0079 (2)	0.0072 (2)	0.0073 (2)	−0.00031 (16)	−0.00027 (16)	0.00011 (16)
Mn1	0.0117 (3)	0.0073 (3)	0.0093 (3)	−0.0010 (2)	−0.0009 (2)	−0.0003 (2)
Mn2	0.0104 (3)	0.0079 (3)	0.0094 (3)	0.0007 (2)	0.0008 (2)	0.0000 (2)
Na1	0.0179 (10)	0.0133 (9)	0.0271 (11)	0.0000 (8)	0.0083 (8)	−0.0007 (8)
Na2	0.0195 (10)	0.0250 (11)	0.0432 (13)	0.0032 (8)	−0.0086 (9)	−0.0179 (9)
O1	0.0214 (17)	0.0099 (14)	0.0094 (17)	0.0012 (13)	0.0032 (13)	0.0014 (11)
O2	0.0176 (17)	0.0121 (14)	0.0055 (15)	0.0001 (13)	0.0038 (12)	−0.0022 (11)
O3	0.0245 (18)	0.0115 (15)	0.0082 (16)	0.0030 (13)	0.0001 (13)	0.0001 (12)
O4	0.0068 (15)	0.0102 (14)	0.0161 (17)	−0.0040 (12)	−0.0019 (12)	−0.0019 (12)
O5	0.0088 (16)	0.0123 (15)	0.0157 (17)	0.0025 (12)	−0.0002 (12)	−0.0013 (12)
O6	0.0217 (18)	0.0104 (15)	0.0115 (17)	−0.0022 (12)	0.0028 (13)	−0.0064 (12)
O7	0.0083 (15)	0.0127 (15)	0.0141 (16)	0.0028 (12)	0.0005 (12)	0.0015 (12)
O8	0.0075 (15)	0.0114 (15)	0.0161 (17)	0.0024 (12)	0.0005 (12)	0.0039 (12)

Geometric parameters (Å, º)

Na1—O6[i]	2.368 (3)	Mn1—O7	2.162 (3)
Na1—O1[ii]	2.407 (3)	Mn1—O3	2.205 (3)
Na1—O2[iii]	2.411 (3)	Mn2—O2[v]	2.095 (3)
Na1—O5[ii]	2.496 (3)	Mn2—O4[vii]	2.124 (3)

Na1—O3[i]	2.526 (4)	Mn2—O1	2.139 (3)
Na1—O7[iv]	2.547 (3)	Mn2—O8[v]	2.150 (3)
Na2—O3	2.376 (3)	Mn2—O4[v]	2.155 (3)
Na2—O2[v]	2.409 (4)	As1—O2	1.683 (3)
Na2—O7[i]	2.539 (3)	As1—O5[vii]	1.689 (3)
Na2—O5	2.540 (3)	As1—O1	1.694 (3)
Na2—O1	2.580 (4)	As1—O7	1.703 (3)
Na2—O6	2.712 (4)	As2—O6	1.647 (3)
Na2—O8	2.829 (4)	As2—O3[viii]	1.676 (3)
Mn1—O6	2.061 (3)	As2—O4[ix]	1.684 (3)
Mn1—O5[vi]	2.144 (3)	As2—O8	1.696 (3)
Mn1—O8[vi]	2.144 (3)		
O2—As1—O5[vii]	109.07 (14)	O3—Na2—O6	61.90 (10)
O2—As1—O1	111.74 (14)	O2[v]—Na2—O6	137.80 (12)
O5[vii]—As1—O1	110.68 (15)	O7[i]—Na2—O6	79.02 (11)
O2—As1—O7	107.60 (15)	O5—Na2—O6	124.60 (12)
O5[vii]—As1—O7	109.56 (14)	O1—Na2—O6	80.96 (11)
O1—As1—O7	108.11 (14)	O3—Na2—O8	119.67 (12)
O6—As2—O3[viii]	115.17 (14)	O2[v]—Na2—O8	141.48 (13)
O6—As2—O4[ix]	108.13 (15)	O7[i]—Na2—O8	68.33 (10)
O3[viii]—As2—O4[ix]	108.90 (15)	O5—Na2—O8	66.72 (10)
O6—As2—O8	106.78 (15)	O1—Na2—O8	87.83 (11)
O3[viii]—As2—O8	106.17 (15)	O6—Na2—O8	57.89 (9)
O4[ix]—As2—O8	111.73 (14)	As1—O1—Mn2	126.51 (15)
O6—Mn1—O5[vi]	95.67 (12)	As1—O1—Na1[vii]	123.87 (15)
O6—Mn1—O8[vi]	165.34 (12)	Mn2—O1—Na1[vii]	94.27 (12)
O5[vi]—Mn1—O8[vi]	87.40 (11)	As1—O1—Na2	133.73 (16)
O6—Mn1—O7	104.14 (12)	Mn2—O1—Na2	88.43 (11)
O5[vi]—Mn1—O7	101.37 (11)	Na1[vii]—O1—Na2	74.38 (10)
O8[vi]—Mn1—O7	89.23 (11)	As1—O2—Mn2[viii]	139.26 (16)
O6—Mn1—O3	76.13 (11)	As1—O2—Na2[viii]	110.78 (15)
O5[vi]—Mn1—O3	129.69 (11)	Mn2[viii]—O2—Na2[viii]	94.20 (12)
O8[vi]—Mn1—O3	90.86 (11)	As1—O2—Na1[iii]	120.64 (15)
O7—Mn1—O3	128.90 (12)	Mn2[viii]—O2—Na1[iii]	95.30 (11)
O2[v]—Mn2—O4[vii]	99.50 (12)	Na2[viii]—O2—Na1[iii]	77.51 (11)
O2[v]—Mn2—O1	81.14 (11)	As2[v]—O3—Mn1	120.63 (15)
O4[vii]—Mn2—O1	117.21 (12)	As2[v]—O3—Na2	132.47 (17)
O2[v]—Mn2—O8[v]	103.27 (11)	Mn1—O3—Na2	101.81 (12)
O4[vii]—Mn2—O8[v]	103.81 (11)	As2[v]—O3—Na1[vi]	116.79 (15)
O1—Mn2—O8[v]	137.57 (12)	Mn1—O3—Na1[vi]	92.86 (12)
O2[v]—Mn2—O4[v]	170.23 (11)	Na2—O3—Na1[vi]	78.27 (11)
O4[vii]—Mn2—O4[v]	78.69 (12)	As2[ix]—O4—Mn2[ii]	120.06 (15)
O1—Mn2—O4[v]	91.11 (11)	As2[ix]—O4—Mn2[viii]	123.30 (15)
O8[v]—Mn2—O4[v]	86.45 (11)	Mn2[ii]—O4—Mn2[viii]	101.31 (12)
O6[i]—Na1—O1[ii]	85.20 (12)	As1[ii]—O5—Mn1[i]	115.32 (14)
O6[i]—Na1—O2[iii]	145.14 (12)	As1[ii]—O5—Na1[vii]	92.86 (13)
O1[ii]—Na1—O2[iii]	69.73 (11)	Mn1[i]—O5—Na1[vii]	144.25 (14)

O6^i—Na1—O5^{ii}	121.79 (12)	As1^{ii}—O5—Na2	162.63 (17)
O1^{ii}—Na1—O5^{ii}	102.84 (12)	Mn1^i—O5—Na2	81.48 (10)
O2^{iii}—Na1—O5^{ii}	88.13 (11)	Na1^{vii}—O5—Na2	73.62 (10)
O6^i—Na1—O3^i	64.99 (11)	As2—O6—Mn1	146.46 (18)
O1^{ii}—Na1—O3^i	93.26 (11)	As2—O6—Na1^{vi}	111.42 (15)
O2^{iii}—Na1—O3^i	91.88 (11)	Mn1—O6—Na1^{vi}	101.49 (12)
O5^{ii}—Na1—O3^i	162.80 (13)	As2—O6—Na2	99.17 (13)
O6^i—Na1—O7^{iv}	85.65 (11)	Mn1—O6—Na2	95.37 (12)
O1^{ii}—Na1—O7^{iv}	159.09 (13)	Na1^{vi}—O6—Na2	74.75 (11)
O2^{iii}—Na1—O7^{iv}	125.53 (12)	As1—O7—Mn1	111.73 (14)
O5^{ii}—Na1—O7^{iv}	66.66 (10)	As1—O7—Na2^{vi}	165.60 (16)
O3^i—Na1—O7^{iv}	99.82 (11)	Mn1—O7—Na2^{vi}	81.17 (10)
O3—Na2—O2^v	85.11 (12)	As1—O7—Na1^x	90.74 (12)
O3—Na2—O7^i	104.26 (12)	Mn1—O7—Na1^x	139.29 (14)
O2^v—Na2—O7^i	137.92 (14)	Na2^{vi}—O7—Na1^x	74.98 (10)
O3—Na2—O5	172.25 (14)	As2—O8—Mn1^i	125.11 (15)
O2^v—Na2—O5	87.16 (12)	As2—O8—Mn2^{viii}	107.14 (14)
O7^i—Na2—O5	81.95 (11)	Mn1^i—O8—Mn2^{viii}	125.73 (13)
O3—Na2—O1	79.48 (11)	As2—O8—Na2	93.68 (12)
O2^v—Na2—O1	66.91 (11)	Mn1^i—O8—Na2	74.88 (10)
O7^i—Na2—O1	154.63 (13)	Mn2^{viii}—O8—Na2	118.54 (13)
O5—Na2—O1	96.92 (11)		

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