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Synthesis and crystal structure of $Na_4Ni_7(AsO_4)_6$

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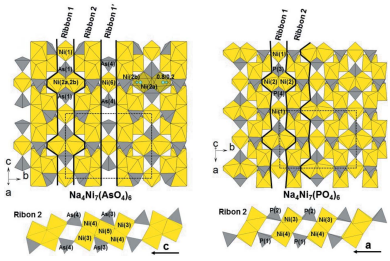
The title compound, tetrasodium heptanickel hexaarsenate, was obtained by ceramic synthesis and crystallizes in the monoclinic space group *C*2/*m*. The asymmetric unit contains seven Ni atoms of which two have site symmetry 2/*m* and three site symmetry 2, four As atoms of which two have site symmetry *m* and two site symmetry 2, three Na atoms of which two have site symmetry 2, and fifteen O atoms of which four have site symmetry *m*. The structure of $Na_4Ni_7(AsO_4)_6$ is made of layers of Ni octahedra and As tetrahedra assembled in sheets parallel to the *bc* plane. These layers are interconnected by corner-sharing between NiO_6 octahedra and AsO_4 tetrahedra. This linkage creates tunnels running along the *c* axis in which the Na atoms are located. This arrangement is similar to the one observed in $Na_4Ni_7(PO_4)_6$, but the layers of the two compounds are slightly different because of the disorder of one of the Ni sites in the structure of the title compound.

1. Chemical context

Although the structures of transition metal phosphates have been widely investigated during the last decades, very little work has been done on comparable arsenates due to the toxicity of arsenic. The latter phases can exhibit, however, peculiar properties. $BaCo_2(AsO_4)_2$ is a good example of a quasi-2D system with a magnetically frustrated honeycomb lattice (Regnault *et al.*, 1977). $BaCoAs_2O_7$ appears as the first example of a magnetization step promoted by a structural modulation (David *et al.*, 2013*a*). $LiCoAsO_4$ shows reversible electrochemical activity at high potential (Satya Kishore & Varadaraju, 2006). Moreover, a recent study reveals the interest of arsenate groups in playing the role of efficient disconnecting units in the magnetic compound $BaCo_2(As_3O_6)_2{\cdot}H_2O$, being the first pure inorganic compound with slow spin dynamics (David *et al.*, 2013*b*). From the crystal chemistry point of view, substitution of phosphate by arsenate gives the possibility of stabilizing new phases. For example, $NaNiPO_4$ crystallizes with the maricite structure (Senthilkumar *et al.*, 2014), whereas $NaNiAsO_4$ has a honeycomb layer structure (Range & Meister, 1984). In this study, we describe the structure of $Na_4Ni_7(AsO_4)_6$ and compare it with its phosphate analogue.



2. Structural commentary

The structure of the title compound $Na_4Ni_7(AsO_4)_6$ is quite similar to the one of the phosphate homologue $Na_4Ni_7(PO_4)_6$. Both are made of interconnected $Ni_7(XO_4)_6$ layers with tunnels in between where the Na atoms are located, as shown in Fig. 1*a*. The arrangement of NiO_6 and XO_4 in the layer is, however, slightly different, as evidenced in Fig. 2. As described

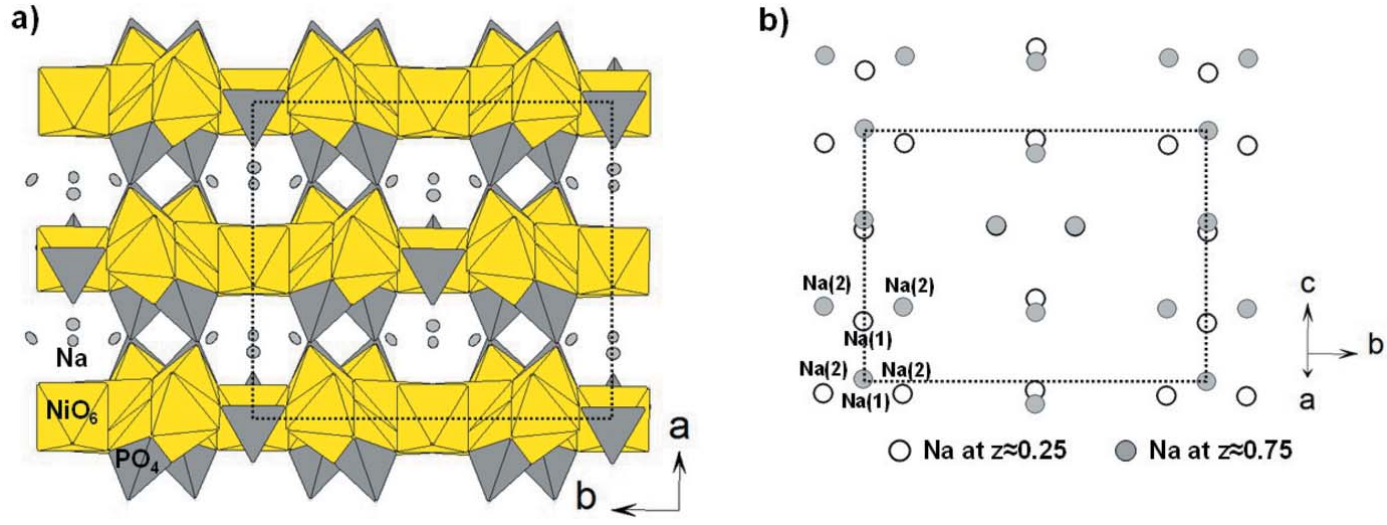


Figure 1
Description of the crystal structure of $Na_4Ni_7(AsO_4)_6$ with (*a*) a view of the stacking and (*b*) a view of the Na layers. The dotted lines show the cell edges. Displacement ellipsoids are drawn at the 50% probability level.

by Moring & Kostiner (1986), $Na_4Ni_7(PO_4)_6$ layers are made of parallel ribbons (called ribbon 1) containing Ni1, Ni2, P3 and P4 polyhedra. These ribbons 1 are interconnected by another kind of ribbon (called ribbon 2) made of dimers consisting of edge-sharing NiO_6 octahedra (Ni3 and Ni4). The latter are linked to PO_4 tetrahedra (P1 and P2) by edge- and corner-sharing. The difference between the two compounds is associated with the possibility of the Ni2 atom in

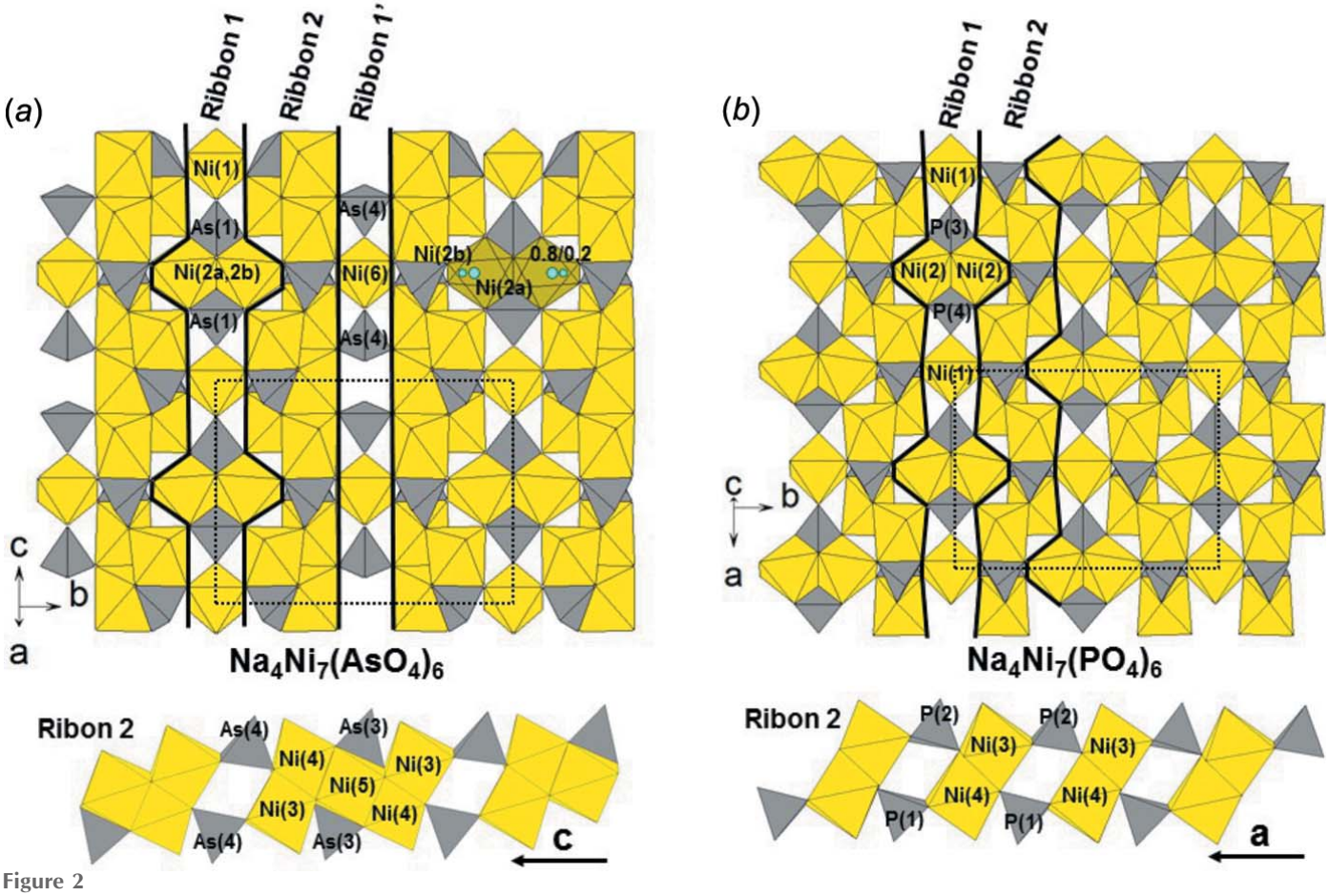


Figure 2
Description of the layers (top) and the ribbon 2 (bottom) of (*a*) $Na_4Ni_7(AsO_4)_6$ and (*b*) $Na_4Ni_7(PO_4)_6$. The dotted lines show the cell edges.

Table 1
Experimental details.

Crystal data	
Chemical formula	$Na_4Ni_7(AsO_4)_6$
M_r	1336.3
Crystal system, space group	Monoclinic, *C*2/*m*
Temperature (K)	293
a, *b*, *c* (Å)	14.5383 (11), 14.5047 (11), 10.6120 (8)
β (°)	118.299 (2)
V (Å^3)	1970.3 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	16.76
Crystal size (mm)	0.07 × 0.06 × 0.04
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.640, 0.747
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	48075, 3773, 2901
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.772
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.052, 2.73
No. of reflections	3773
No. of parameters	146
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.34, −2.22

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014, *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

$Na_4Ni_7(PO_4)_6$ occupying two octahedral sites. The first site, belonging to ribbon 1, is equivalent to the Ni2*a* site in $Na_4Ni_7(AsO_4)_6$. The other, equivalent to the Ni2*b* and Ni5 sites in $Na_4Ni_7(AsO_4)_6$, belongs to ribbon 2, forming pentamers of edge-sharing NiO_6 octahedra. The layers of the title compound $Na_4Ni_7(AsO_4)_6$ can thus be described with three kinds of ribbons, as shown in Fig. 2. The linkage between the layers is done by corner-sharing between NiO_6 and AsO_4 units of two consecutive ribbons 2 along the stacking axis (Fig. 1*a*). This linkage is identical to the one of the phosphorus homologue. However, since in $Na_4Ni_7(AsO_4)_6$ layers are made of three different kinds of ribbons, two adjacent layers are shifted to align ribbon 1 with ribbon 1′. That is why in $Na_4Ni_7(AsO_4)_6$ the stacking axis is roughly doubled compared to $Na_4Ni_7(PO_4)_6$ [c = 6.398 (2) Å *versus* a = 14.5383 (11) Å in the title structure]. It implies two different kinds of Na layers, as shown in Fig. 1*b*.

3. Synthesis and crystallization

Sodium carbonate (>99.5%), arsenic oxide (99%) and nickel sulfate hexahydrate (>99.9%) were purchased from Sigma–Aldrich. They were used as received without further purification. Reagents were ground together in stoichiometric ratio in an agate mortar. The obtained mixture was pelletized, placed in an alumina boat and annealed at 573 K for 1h. The obtained mixture was reground, pelletized and heated at 1073 K (5 K min^{-1}) for 48 h, after which the alumina boat was removed from the furnace and cooled to room temperature. The brown crystals of the title compound were isolated by hand.

4. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 1. The (001) reflection, affected by the beamstop, has been removed from the refinement. Another reflection ($\bar{2}$01), flagged as potentially affected by the beamstop, was in fact not and was kept in the refinement. After positioning and refining all the atom positions except Ni2*b*, the difference Fourier map revealed residual density (≃8 e Å^{-3}) near Ni2*a* (at ≃0.6 Å). It was refined introducing a second position Ni2*b* with complementary occupation. The occupancy ratio was refined to 0.80 (4):0.20 (4) for the Ni2*a*/Ni2*b* site, constraining the sum to be equal to 1.

Acknowledgements

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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: SUPERFLIP (Palatinus & Chapuis, 2007); program(s) used to refine structure: JANA2006 (Petříček *et al.*, 2014; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Tetrasodium heptanickel hexaarsenate

Crystal data

$Na_4Ni_7(AsO_4)_6$
M_r = 1336.3
Monoclinic, *C*2/*m*
Hall symbol: -C 2y
a = 14.5383 (11) Å
b = 14.5047 (11) Å
c = 10.6120 (8) Å
β = 118.299 (2)°
V = 1970.3 (3) Å^3
Z = 4
F(000) = 2520
D_x = 4.505 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 38754 reflections
θ = 2.1–33.3°
μ = 16.76 mm^{-1}
T = 293 K
Irregular, brown
0.07 × 0.06 × 0.04 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: X-ray tube
phi scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)
T_{min} = 0.640, T_{max} = 0.747
48075 measured reflections
3773 independent reflections
2901 reflections with $I > 3\sigma(I)$
R_{int} = 0.036
θ_{max} = 33.3°, θ_{min} = 2.1°
h = −21→20
k = −22→21
l = −16→16

Refinement

Refinement on *F*
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.052
S = 2.73
3773 reflections
146 parameters
0 restraints
0 constraints
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(F) + 0.0001F^2)$
$(\Delta/\sigma)_{max}$ = 0.015
$\Delta\rho_{max}$ = 3.34 e Å^{-3}
$\Delta\rho_{min}$ = −2.22 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.5	0	0	0.0068 (4)	
Ni2a	0.5	0.1306 (6)	0.5	0.0078 (8)	0.80 (4)
Ni2b	0.5	0.166 (5)	0.5	0.027 (7)	0.20 (4)
Ni3	0.91312 (4)	0.18257 (3)	0.23065 (6)	0.00542 (19)	
Ni4	0.59336 (4)	0.18693 (3)	0.26615 (6)	0.00530 (19)	
Ni5	0.5	0.32688 (6)	0	0.0112 (3)	
Ni6	0	0	0.5	0.0061 (4)	
As1	0.85957 (3)	0.18473 (3)	0.45674 (4)	0.00503 (16)	
As2	0.65106 (3)	0.18354 (3)	0.05278 (4)	0.00470 (15)	
As3	0.47038 (5)	0	0.28662 (6)	0.0062 (2)	
As4	0.45990 (5)	0.5	−0.20991 (6)	0.0056 (2)	
Na1	0.2934 (2)	0.5	−0.0189 (3)	0.0304 (13)	
Na2	0.25173 (16)	0.11586 (14)	0.3367 (2)	0.0305 (9)	
Na3	0.7399 (2)	0	0.3103 (4)	0.0435 (15)	
O1	0.6079 (2)	0.09855 (19)	0.1237 (3)	0.0067 (5)*	
O2	0.8783 (2)	0.2776 (2)	0.3717 (3)	0.0125 (6)*	
O3	0.4137 (3)	0	0.1101 (4)	0.0104 (8)*	
O4	0.4391 (2)	0.21767 (19)	0.1132 (3)	0.0090 (6)*	
O5	0.7665 (2)	0.1552 (2)	0.0682 (3)	0.0097 (6)*	
O6	0.5380 (2)	0.4081 (2)	−0.1240 (3)	0.0096 (6)*	
O8	0.3535 (3)	0.5	−0.1899 (5)	0.0140 (9)*	
O9	0.3901 (4)	0	0.3581 (5)	0.0232 (11)*	
O10	0.9333 (2)	0.20454 (19)	0.6329 (3)	0.0089 (6)*	
O11	0.5468 (2)	0.0939 (2)	0.3604 (3)	0.0115 (6)*	
O12	0.7395 (2)	0.1588 (2)	0.4274 (3)	0.0096 (6)*	
O13	0.6448 (2)	0.27433 (19)	0.1522 (3)	0.0092 (6)*	
O14	0.4220 (3)	0.5	−0.3841 (4)	0.0108 (9)*	
O15	0.8965 (2)	0.10027 (18)	0.3788 (3)	0.0062 (5)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0070 (5)	0.0067 (5)	0.0068 (5)	0	0.0032 (4)	0
Ni2a	0.0102 (7)	0.006 (2)	0.0096 (7)	0	0.0068 (5)	0
Ni2b	0.021 (3)	0.04 (2)	0.019 (3)	0	0.010 (2)	0
Ni3	0.0047 (2)	0.0062 (3)	0.0048 (3)	−0.00029 (18)	0.0018 (2)	0.00088 (18)
Ni4	0.0050 (2)	0.0057 (3)	0.0048 (3)	0.00053 (18)	0.0020 (2)	−0.00048 (18)
Ni5	0.0097 (4)	0.0149 (4)	0.0084 (4)	0	0.0039 (3)	0
Ni6	0.0070 (5)	0.0048 (5)	0.0066 (5)	0	0.0033 (4)	0
As1	0.0049 (2)	0.0058 (2)	0.0047 (2)	0.00044 (14)	0.00248 (16)	0.00007 (14)
As2	0.00360 (19)	0.0057 (2)	0.0046 (2)	0.00079 (14)	0.00184 (16)	0.00099 (14)
As3	0.0082 (3)	0.0051 (3)	0.0054 (3)	0	0.0032 (2)	0
As4	0.0061 (3)	0.0044 (3)	0.0058 (3)	0	0.0024 (2)	0
Na1	0.0270 (17)	0.0353 (17)	0.0297 (17)	0	0.0141 (14)	0
Na2	0.0251 (11)	0.0240 (11)	0.0399 (14)	−0.0090 (9)	0.0134 (10)	−0.0080 (10)

Na3	0.0236 (17)	0.0179 (15)	0.061 (2)	0	−0.0026 (16)	0

Geometric parameters (Å, º)

Ni1—O1	2.068 (2)	Ni6—O15^{iv}	2.049 (2)
Ni1—O1^{i}	2.068 (2)	Ni6—O15^{xiii}	2.049 (2)
Ni1—O1^{ii}	2.068 (2)	Ni6—O15^{xiv}	2.049 (2)
Ni1—O1^{iii}	2.068 (2)	As1—Na2^{vii}	3.249 (2)
Ni1—O3	2.081 (6)	As1—Na3	3.1713 (16)
Ni1—O3^{i}	2.081 (6)	As1—O2	1.714 (3)
Ni2a—Ni2b	0.51 (7)	As1—O10	1.681 (3)
Ni2a—Na2	3.185 (2)	As1—O12	1.664 (3)
Ni2a—Na2^{iv}	3.185 (2)	As1—O15	1.702 (3)
Ni2a—O11	1.974 (4)	As2—O1	1.711 (3)
Ni2a—O11^{iv}	1.974 (4)	As2—O4^{i}	1.696 (3)
Ni2b—Na2	3.260 (17)	As2—O5	1.659 (3)
Ni2b—Na2^{iv}	3.260 (17)	As2—O13	1.716 (3)
Ni2b—O2^{v}	1.83 (3)	As3—O3	1.650 (4)
Ni2b—O2^{vi}	1.83 (3)	As3—O9	1.667 (7)
Ni3—O4^{vii}	2.058 (3)	As3—O11	1.697 (3)
Ni3—O5	2.047 (3)	As3—O11^{iii}	1.697 (3)
Ni3—O6^{viii}	2.069 (3)	As4—Na1^{i}	3.240 (3)
Ni3—O10^{ix}	2.029 (3)	As4—Na2^{xv}	3.190 (2)
Ni3—O15	2.077 (3)	As4—Na2^{xvi}	3.190 (2)
Ni4—O1	2.068 (3)	As4—O6	1.707 (3)
Ni4—O4	2.101 (3)	As4—O6^{xvii}	1.707 (3)
Ni4—O10^{v}	2.042 (3)	As4—O8	1.658 (6)
Ni4—O11	1.980 (4)	As4—O14	1.660 (5)
Ni4—O12	2.041 (3)	Na1—Na2^{xv}	3.540 (4)
Ni5—O6	2.029 (3)	Na1—Na2^{xvi}	3.540 (4)
Ni5—O6^{i}	2.029 (3)	Na1—Na3^{xviii}	3.923 (6)
Ni5—O13	2.097 (3)	Na1—O8	2.358 (7)
Ni5—O13^{i}	2.097 (3)	Na2—Na2^{iii}	3.361 (3)
Ni6—O14^{x}	2.030 (6)	Na2—O2^{vi}	2.294 (4)
Ni6—O14^{xi}	2.030 (6)	Na2—O8^{xi}	2.309 (3)
Ni6—O15^{xii}	2.049 (2)	Na2—O13^{vi}	2.429 (3)
O1—Ni1—O1^{i}	92.53 (10)	Na1^{i}—As4—Na2^{xvi}	145.04 (5)
O1—Ni1—O1^{ii}	180.0 (5)	Na1^{i}—As4—O6	51.71 (9)
O1—Ni1—O1^{iii}	87.47 (10)	Na1^{i}—As4—O6^{xvii}	51.71 (9)
O1—Ni1—O3	96.97 (12)	Na1^{i}—As4—O8	132.24 (16)
O1—Ni1—O3^{i}	83.03 (12)	Na1^{i}—As4—O14	119.95 (18)
O1^{i}—Ni1—O1^{ii}	87.47 (10)	Na2^{xv}—As4—Na2^{xvi}	63.58 (5)
O1^{i}—Ni1—O1^{iii}	180.0 (5)	Na2^{xv}—As4—O6	154.25 (13)
O1^{i}—Ni1—O3	83.03 (12)	Na2^{xv}—As4—O6^{xvii}	94.48 (10)
O1^{i}—Ni1—O3^{i}	96.97 (12)	Na2^{xv}—As4—O8	44.13 (10)
O1^{ii}—Ni1—O1^{iii}	92.53 (10)	Na2^{xv}—As4—O14	77.65 (15)
O1^{ii}—Ni1—O3	83.03 (12)	Na2^{xvi}—As4—O6	94.48 (10)

O1^{ii}—Ni1—O3^{i}	96.97 (12)	Na2^{xvi}—As4—O6^{xvii}	154.25 (13)
O1^{iii}—Ni1—O3	96.97 (12)	Na2^{xvi}—As4—O8	44.13 (10)
O1^{iii}—Ni1—O3^{i}	83.03 (12)	Na2^{xvi}—As4—O14	77.65 (15)
O3—Ni1—O3^{i}	180.0 (5)	O6—As4—O6^{xvii}	102.64 (12)
Ni2b—Ni2a—Na2	93.85 (16)	O6—As4—O8	110.86 (15)
Ni2b—Ni2a—Na2^{iv}	93.85 (16)	O6—As4—O14	112.34 (14)
Ni2b—Ni2a—O11	105.6 (3)	O6^{xvii}—As4—O8	110.86 (15)
Ni2b—Ni2a—O11^{iv}	105.6 (3)	O6^{xvii}—As4—O14	112.34 (14)
Na2—Ni2a—Na2^{iv}	172.3 (3)	O8—As4—O14	107.8 (2)
Na2—Ni2a—O11	106.17 (12)	As4^{i}—Na1—Na2^{xv}	110.70 (11)
Na2—Ni2a—O11^{iv}	71.66 (9)	As4^{i}—Na1—Na2^{xvi}	110.70 (11)
Na2^{iv}—Ni2a—O11	71.66 (9)	As4^{i}—Na1—Na3^{xviii}	87.08 (8)
Na2^{iv}—Ni2a—O11^{iv}	106.17 (12)	As4^{i}—Na1—O8	83.94 (14)
O11—Ni2a—O11^{iv}	148.7 (5)	Na2^{xv}—Na1—Na2^{xvi}	56.69 (7)
Ni2a—Ni2b—Na2	77.1 (13)	Na2^{xv}—Na1—Na3^{xviii}	145.38 (8)
Ni2a—Ni2b—Na2^{iv}	77.1 (13)	Na2^{xv}—Na1—O8	40.16 (9)
Ni2a—Ni2b—O2^{v}	116 (2)	Na2^{xvi}—Na1—Na3^{xviii}	145.38 (8)
Ni2a—Ni2b—O2^{vi}	116 (2)	Na2^{xvi}—Na1—O8	40.16 (9)
Na2—Ni2b—Na2^{iv}	154 (3)	Na3^{xviii}—Na1—O8	171.02 (14)
Na2—Ni2b—O2^{v}	158 (2)	Ni2a—Na2—Ni2b	9.1 (13)
Na2—Ni2b—O2^{vi}	43.1 (7)	Ni2a—Na2—As1^{vi}	61.00 (16)
Na2^{iv}—Ni2b—O2^{v}	43.1 (7)	Ni2a—Na2—As4^{xi}	151.93 (17)
Na2^{iv}—Ni2b—O2^{vi}	158 (2)	Ni2a—Na2—Na1^{xi}	101.59 (12)
O2^{v}—Ni2b—O2^{vi}	127 (4)	Ni2a—Na2—Na2^{iii}	93.85 (17)
O4^{vii}—Ni3—O5	92.46 (12)	Ni2a—Na2—O2^{vi}	41.55 (17)
O4^{vii}—Ni3—O6^{viii}	84.64 (13)	Ni2a—Na2—O8^{xi}	129.3 (2)
O4^{vii}—Ni3—O10^{ix}	82.32 (12)	Ni2a—Na2—O13^{vi}	121.44 (17)
O4^{vii}—Ni3—O15	169.39 (11)	Ni2b—Na2—As1^{vi}	52.1 (12)
O5—Ni3—O6^{viii}	84.66 (12)	Ni2b—Na2—As4^{xi}	160.9 (13)
O5—Ni3—O10^{ix}	170.33 (16)	Ni2b—Na2—Na1^{xi}	105.7 (6)
O5—Ni3—O15	94.46 (12)	Ni2b—Na2—Na2^{iii}	102.9 (13)
O6^{viii}—Ni3—O10^{ix}	86.74 (12)	Ni2b—Na2—O2^{vi}	33.1 (12)
O6^{viii}—Ni3—O15	103.99 (12)	Ni2b—Na2—O8^{xi}	137.2 (11)
O10^{ix}—Ni3—O15	91.91 (12)	Ni2b—Na2—O13^{vi}	114.0 (11)
O1—Ni4—O4	90.49 (11)	As1^{vi}—Na2—As4^{xi}	145.50 (8)
O1—Ni4—O10^{v}	166.43 (12)	As1^{vi}—Na2—Na1^{xi}	129.31 (10)
O1—Ni4—O11	97.17 (13)	As1^{vi}—Na2—Na2^{iii}	152.92 (7)
O1—Ni4—O12	93.57 (12)	As1^{vi}—Na2—O2^{vi}	30.22 (10)
O4—Ni4—O10^{v}	80.96 (11)	As1^{vi}—Na2—O8^{xi}	162.71 (11)
O4—Ni4—O11	92.27 (12)	As1^{vi}—Na2—O13^{vi}	74.79 (8)
O4—Ni4—O12	175.26 (15)	As4^{xi}—Na2—Na1^{xi}	69.02 (7)
O10^{v}—Ni4—O11	93.70 (14)	As4^{xi}—Na2—Na2^{iii}	58.21 (5)
O10^{v}—Ni4—O12	95.48 (12)	As4^{xi}—Na2—O2^{vi}	164.23 (11)
O11—Ni4—O12	84.81 (12)	As4^{xi}—Na2—O8^{xi}	30.00 (15)
O6—Ni5—O6^{i}	108.95 (13)	As4^{xi}—Na2—O13^{vi}	83.39 (9)
O6—Ni5—O13	103.20 (12)	Na1^{xi}—Na2—Na2^{iii}	61.65 (6)
O6—Ni5—O13^{i}	101.19 (12)	Na1^{xi}—Na2—O2^{vi}	104.27 (14)
O6^{i}—Ni5—O13	101.19 (12)	Na1^{xi}—Na2—O8^{xi}	41.18 (16)

O6^{i}—Ni5—O13^{i}	103.20 (12)	Na1^{xi}—Na2—O13^{vi}	77.57 (10)
O13—Ni5—O13^{i}	137.37 (11)	Na2^{iii}—Na2—O2^{vi}	132.33 (13)
O14^{x}—Ni6—O14^{xi}	180.0 (5)	Na2^{iii}—Na2—O8^{xi}	43.30 (8)
O14^{x}—Ni6—O15^{xii}	85.74 (12)	Na2^{iii}—Na2—O13^{vi}	130.98 (10)
O14^{x}—Ni6—O15^{iv}	94.26 (12)	O2^{vi}—Na2—O8^{xi}	145.4 (2)
O14^{x}—Ni6—O15^{xiii}	94.26 (12)	O2^{vi}—Na2—O13^{vi}	81.18 (12)
O14^{x}—Ni6—O15^{xiv}	85.74 (12)	O8^{xi}—Na2—O13^{vi}	88.13 (11)
O14^{xi}—Ni6—O15^{xii}	94.26 (12)	As1—Na3—As1^{iii}	115.32 (9)
O14^{xi}—Ni6—O15^{iv}	85.74 (12)	As1—Na3—Na1^{xix}	98.15 (10)
O14^{xi}—Ni6—O15^{xiii}	85.74 (12)	As1^{iii}—Na3—Na1^{xix}	98.15 (10)
O14^{xi}—Ni6—O15^{xiv}	94.26 (12)	Ni1—O1—Ni4	125.67 (17)
O15^{xii}—Ni6—O15^{iv}	89.57 (10)	Ni1—O1—As2	123.00 (15)
O15^{xii}—Ni6—O15^{xiii}	180.0 (5)	Ni4—O1—As2	93.49 (12)
O15^{xii}—Ni6—O15^{xiv}	90.43 (10)	Ni2b^{v}—O2—As1	107.3 (16)
O15^{iv}—Ni6—O15^{xiii}	90.43 (10)	Ni2b^{v}—O2—Na2^{vii}	103.8 (19)
O15^{iv}—Ni6—O15^{xiv}	180.0 (5)	As1—O2—Na2^{vii}	107.4 (2)
O15^{xiii}—Ni6—O15^{xiv}	89.57 (10)	Ni1—O3—As3	121.8 (2)
Na2^{vii}—As1—Na3	120.62 (5)	Ni3^{vi}—O4—Ni4	96.68 (11)
Na2^{vii}—As1—O2	42.36 (13)	Ni3^{vi}—O4—As2^{i}	124.13 (16)
Na2^{vii}—As1—O10	102.64 (10)	Ni4—O4—As2^{i}	139.19 (19)
Na2^{vii}—As1—O12	81.93 (11)	Ni3—O5—As2	129.51 (19)
Na2^{vii}—As1—O15	130.93 (11)	Ni3^{viii}—O6—Ni5	104.78 (13)
Na3—As1—O2	126.42 (12)	Ni3^{viii}—O6—As4	121.23 (17)
Na3—As1—O10	127.00 (12)	Ni5—O6—As4	118.91 (19)
Na3—As1—O12	55.54 (13)	As4—O8—Na1	143.8 (2)
Na3—As1—O15	51.68 (13)	As4—O8—Na2^{xv}	105.9 (2)
O2—As1—O10	105.90 (14)	As4—O8—Na2^{xvi}	105.9 (2)
O2—As1—O12	119.59 (14)	Na1—O8—Na2^{xv}	98.65 (19)
O2—As1—O15	98.30 (17)	Na1—O8—Na2^{xvi}	98.65 (19)
O10—As1—O12	107.84 (17)	Na2^{xv}—O8—Na2^{xvi}	93.40 (14)
O10—As1—O15	118.79 (13)	Ni3^{ix}—O10—Ni4^{v}	99.49 (11)
O12—As1—O15	106.93 (14)	Ni3^{ix}—O10—As1	132.3 (2)
O1—As2—O4^{i}	113.78 (13)	Ni4^{v}—O10—As1	122.37 (14)
O1—As2—O5	110.07 (15)	Ni2a—O11—Ni4	121.2 (3)
O1—As2—O13	98.34 (16)	Ni2a—O11—As3	100.3 (3)
O4^{i}—As2—O5	114.98 (17)	Ni4—O11—As3	128.29 (18)
O4^{i}—As2—O13	100.05 (14)	Ni4—O12—As1	134.0 (2)
O5—As2—O13	118.36 (14)	Ni5—O13—As2	97.57 (12)
O3—As3—O9	115.8 (2)	Ni5—O13—Na2^{vii}	114.05 (13)
O3—As3—O11	112.91 (14)	As2—O13—Na2^{vii}	142.98 (18)
O3—As3—O11^{iii}	112.91 (14)	Ni6^{xx}—O14—As4	133.6 (2)
O9—As3—O11	103.68 (16)	Ni3—O15—Ni6^{xxi}	124.68 (17)
O9—As3—O11^{iii}	103.68 (16)	Ni3—O15—As1	97.52 (13)
O11—As3—O11^{iii}	106.83 (13)	Ni6^{xxi}—O15—As1	120.85 (15)
Na1^{i}—As4—Na2^{xv}	145.04 (5)		

Symmetry codes: (i) −*x*+1, *y*, −*z*; (ii) −*x*+1, −*y*, −*z*; (iii) *x*, −*y*, *z*; (iv) −*x*+1, *y*, −*z*+1; (v) −*x*+3/2, −*y*+1/2, −*z*+1; (vi) *x*−1/2, −*y*+1/2, *z*; (vii) *x*+1/2, −*y*+1/2, *z*; (viii) −*x*+3/2, −*y*+1/2, −*z*; (ix) −*x*+2, *y*, −*z*+1; (x) *x*−1/2, *y*−1/2, *z*+1; (xi) −*x*+1/2, *y*−1/2, −*z*; (xii) *x*−1, *y*, *z*; (xiii) −*x*+1, −*y*, −*z*+1; (xiv) *x*−1, −*y*, *z*; (xv) −*x*+1/2, *y*+1/2, −*z*; (xvi) −*x*+1/2, −*y*+1/2, −*z*; (xvii) *x*, −*y*+1, *z*; (xviii) *x*−1/2, *y*+1/2, *z*; (xix) *x*+1/2, *y*−1/2, *z*; (xx) *x*+1/2, *y*+1/2, *z*−1; (xxi) *x*+1, *y*, *z*.