Flux syntheses and single-crystal structures of CsNa$_{10}M_4$(AsO$_4$)$_9$ ($M = Zr, Hf$)

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The isostructural compounds caesium decasodium tetrazirconium nonaarsenate, CsNa$_{10}$Zr$_4$(AsO$_4$)$_9$, and caesium decasodium tetrahafnium nonaarsenate, CsNa$_{10}$Hf$_4$(AsO$_4$)$_9$, arose as unexpected single-crystal products from the reactions of Na$_2$CO$_3$, MO$_2$ ($M = Zr$, Hf) and As$_2$O$_5$ in a eutectic flux of NaCl and CsCl. They consist of MO$_6$ octahedra and AsO$_4$ tetrahedra sharing vertices to generate three-dimensional polyhedral networks encapsulating the caesium and sodium ions. The MO$_6$ groups share all their vertices with adjacent As atoms but the As atoms have one or two ‘terminal’ O atoms not bonded to Zr or Hf. The Cs$^+$ ion adopts a squashed octahedral geometry and the coordination polyhedra of the partially occupied sodium ions are variously trigonal bipyramidal, tetrahedral, square pyramidal and trigonal pyramidal. Site symmetries: Cs 3; M 3; As 1 and 2; O 1; Na 1, 2 and 3. The $M = Zr$ crystal was refined as an obverse/reverse rhombohedral twin.

1. Chemical context
Potassium titanyl phosphate (KTiOPO$_4$; KTP) has long been recognized as an important non-linear optical (NLO) material (Zumsteg et al., 1976) due to its unique combination of desirable physical properties including ‘a large hyperpolarizability, excellent temperature window, wide wavelength for phase matching and outstanding crystal stability’ (Stucky et al., 1989). Work continues to improve the performance of KTP waveguides in optoelectronics (Kores et al., 2021) and it is finding new uses as a frequency doubler (to 532 nm green light) for 1064 nm Nd–YAG laser radiation in many areas of medicine (Shim & Kim, 2021; McGarey et al., 2021). So far as crystal chemistry is concerned, the KTiOPO$_4$ structure type (space group $P$na$2_1$, $a \approx 12.8$, $b \approx 6.4$, $c \approx 10.6$ Å, $Z = 8$, $Z' = 2$) is remarkably accommodating with respect to partial or complete isoivalent or aleovalent substitution at the potassium (Na$^+$, Rb$^+$, Cs$^+$, Ti$^{4+}$, NH$_4^+$ ...), titanium (Zr$^{4+}$, Hf$^{4+}$, V$^{4+}$, Sn$^{4+}$, Sb$^{3+}$, Ga$^{3+}$, Fe$^{3+}$, Al$^{3+}$, Cr$^{3+}$ ...), phosphorus (As$^V$, Si$^{4+}$, Ge$^{4+}$) and even oxygen (OH$^-$, F$^-$) sites and comprehensive reviews on its substitution chemistry have appeared (Sorokina & Voronkova, 2007).

In an attempt to grow single crystals of the possible new KTP analogues NaZrOAsO$_4$ and NaHfOAsO$_4$ by reacting Na$_2$CO$_3$, MO$_2$ ($M = Zr$, Hf) and As$_2$O$_5$ in a low-melting flux of NaCl and CsCl, the isostructural title compounds CsNa$_{10}$Zr$_4$(AsO$_4$)$_9$ (I) and CsNa$_{10}$Hf$_4$(AsO$_4$)$_9$ (II)
were the unexpected result and their crystal structures are now described.

2. Structural commentary

Compounds (I) and (II) are isostructural and crystallize in the rhombohedral space group $R\bar{3}c$ (No. 167) with an unusually long $c$ unit-cell parameter of nearly 77 Å. This is of course partly a consequence of our choosing the hexagonal ($R$-centred) setting of the unit cell [the equivalent primitive rhombohedral lattice for (I) has $a = b = c \simeq 26.21$ Å and $\alpha = \beta = \gamma \simeq 20.3^\circ$] but even so, it is notable that the $l$ index runs well into three figures for (I) in the $R$-centred setting. This description will focus on the structure of (I) and note significant differences for (II) where applicable.

The asymmetric unit of (I), expanded to show the full coordination polyhedra of the zirconium and arsenic atoms, is shown in Fig. 1. It consists of two zirconium atoms (both with site symmetry 3 on Wyckoff site 12$c$), two arsenic atoms [As1 on a general position (36$f$) and As2 with site symmetry 2 (18$e$)] and six oxygen atoms, one of which is disordered over two adjacent sites (all lying on general positions, 36$f$), which leads to the unusual 4:9 stoichiometry for the ZrIV and AsO$_4^{3-}$ moieties with a net charge of $-11$. The structure of (I) is completed by a Cs$^+$ ion (site symmetry 3, 6$b$) and four partly occupied sodium cations [one on a general position (36$f$), one with site symmetry 2 (18$e$) and two with site symmetry 3 (12$c$)]. To maintain charge balance, the four sodium ions must have a total occupancy of 10 based on $Z = 6$ (full occupancy of the four sites would give 13 sodium ions per caesium ion).

Both zirconium atoms adopt almost regular ZrO$_6$ octahedral geometries (Müller-Buschbaum, 2010) when crystal symmetry is taken into account: the mean Zr1–O separation (to O3$^i$ and O5$^i$) is 2.070 Å and the quadratic elongation and angular variance are 1.001 and 4.43$^2$, respectively (Robinson et al., 1971). Equivalent data for Zr2 (bonded to to $3 \times$ O2 and $3 \times$ O4) are 2.072 Å, 1.003 and 9.86$^2$, respectively. The ‘extrapolated’ (Brese & O’Keeffe, 1991) bond-valence sums (BVS) in valence units are 4.10 and 4.07 for Zr1 and Zr2, respectively, in acceptable agreement with the expected value of 4.00. The mean Hf–O distances in (II) are 2.062 Å for Hf1 (BVS = 4.13, quadratic elongation = 1.002, angular variance = 5.38$^2$) and 2.065 Å for Hf2 (4.10, 1.004, 13.20$^2$). It may be seen that the Hf–O bonds are slightly shorter than the Zr–O bonds, which is in accordance with ionic radii data (Shannon, 1976): $r_6$(ZrIV) = 0.72 Å (six-coordinate) and $r_6$(HfIV) = 0.71 Å and is presumed to arise from the lanthanide contraction effect.

Figure 1

The asymmetric unit of (I) expanded to include the full Zr and As coordination polyhedra showing 50% displacement ellipsoids. Only one disorder component about As2 is shown. Symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $y$, $1 - x - y$, $-z$; (iii) $1 - y$, $1 + x - y$, $z$; (iv) $\frac{1}{2} - x$, $\frac{1}{2} - x + y$, $\frac{1}{2} - z$; (v) $x - y$, $x$, $-z$; (vi) $y - x$, $1 - x$, $z$.

Figure 2

The unit-cell of (I) in polyhedral representation viewed approximately down [110]. A single O atom at the average location of O6a and O6b in the asymmetric unit has been used to construct the As2 tetrahedron. Colour code: Zr1O$_6$ octahedra blue, Zr2O$_6$ octahedra green, As1O$_4$ tetrahedra peach, As2O$_4$ tetrahedra rose, Cs sky blue, Na yellow, O (polyhedral corners) red.
The As1 atom in (I) is surrounded by four oxygen atoms (O1–O4) in the geometry of a slightly distorted tetrahedron [mean As—O = 1.677 Å, spread of O—As—O angles = 103.0 (2)–114.9 (2)] \( \tau_4 \) (Yang et al., 2007) = 0.95]. Atom As2 is also tetrahedral (to \( 2_{\text{C}2} \) O5 and \( 2_{\text{C}2} \) O6), with the latter O atom disordered over two adjacent sites in almost equal occupancies of 0.45 (3):0.55 (3) \([\text{O6A}]:0.45(3)=[\text{O6B}]=0.909(13)\) Å.

Of the six oxygen atoms in the structure of (I), four of them (O2–O5) bridge zirconium and arsenic atoms with a mean Zr—O—As bond angle of 141.5° (equivalent mean Hf—O—As bond angle in (II) = 140.4°) and two (O1 and O6) are ‘terminal’ and only bonded to arsenic: all of the O atoms also form one or more bonds to nearby caesium and/or sodium ions.

The caesium ion in (I) adopts a grossly squashed octahedral coordination to six O1 atoms with Cs1—O1 = 3.235 (4) Å: the cis O—Cs—O bond angles are compressed to 62.30 (10) or expanded to 117.70 (10): the Cs1 BVS of 0.61 compared to an expected value of 1.00 suggests significant underbonding. The interpretation of the sodium-ion coordination polyhedra are complicated by the positional disorder of atom O6 but can be described as distorted trigonal bipyramidal (Na1), very distorted tetrahedral (Na2), square-based pyramidal (Na3) and squashed trigonal pyramidal (Na4). It is notable that Na4 is only three coordinate but similar NaO4 geometries have been observed in dehydrated sodium aluminoisilicate zeolites (Adams et al., 1982).

The extended structure of (I) (Fig. 2) can be conceptually broken down into two different types of layers lying parallel to (001). The first layer (type ‘A’) occurs at \( z \approx 0, 1/6, 1/3, 1/2, 2/3 \) and \( 5/6 \) with adjacent A-layers laterally displaced by \( 1/3 \) in \( x \) and \( 2/3 \) in \( y \) and consists of the Zr2 and As1 centred polyhedra as well as the caesium ions. Fig. 3 shows that each Zr2O6 octahedron is connected by two As1O4 tetrahedra (via O2 and O4) to result in a ‘honeycomb’ array of polyhedral 12-rings (six octahedra and 12 tetrahedra) encapsulating the Cs+ ions. Atom O3 of the arsenate group provides the link to the type ‘B’ layers on either side of the A layer. This inter-octahedral connectivity \( \text{via} \) O3 leads to a distinctive ‘lantern’ motif (Fig. 4) in which three tetrahedra link two octahedra [Zr1—O2 = 4.886 (2); Hf1—O2 in (II) = 4.863 (2) Å]: similar ‘lanterns’ are a feature of the polyhedral connectivity in the scandium tungstate \([M_2(XO_4)_3]\) (Abrahams & Bernstein, 1966), Nasicon \([AM_2(XO_4)_3]\) (Anantharamulu et al., 2011) and langbeinite \([A_2M_2(XO_4)_3]\) (Norberg, 2002) structure types but they differ from (I) because all the vertices of the constituent tetrahedra in these structures link to adjacent octahedra, hence their 2:3 \( M:X \) ratio compared to the 4:9 ratio for (I).
Table 1
Experimental details.

|                          | (I)                                      | (II)                                      |
|--------------------------|------------------------------------------|------------------------------------------|
| Crystal data             | CsNa₁₀Zr₄(AsO₄)₉                         | CsNa₁₀Hf₄(AsO₄)₉                         |
| Chemical formula         | M₆                                      | M₆                                      |
| Crystal system, space    | Trigonal, R₅c-H                         | Trigonal, R₅c-H                         |
| group                    |                                          |                                          |
| Temperature (K)          | 293                                      | 120                                      |
| a, c (Å)                 | 9.2218 (5), 76.982 (5)                   | 9.1795 (2), 76.527 (8)                   |
| V (Å³)                   | 5669.6 (7)                               | 5584.5 (6)                               |
| Z                        | 6                                        | 6                                        |
| Radiation type           | Mo Ka                                    | Mo Ka                                    |
| µ (mm⁻¹)                 | 10.0                                    | 20.25                                    |
| Crystal size (mm)        | 0.10 × 0.10 × 0.10                       | 0.08 × 0.08 × 0.08                       |
| Data collection          | Bruker SMART CCD                        | Nonius KappaCCD                          |
| Diffractometer           |                                          |                                          |
| Absorption correction    | Multi-scan (SADABs; Bruker, 1999)        | Multi-scan (SORTAV; Blessing, 1995)      |
| Tmin–Tmax                | 0.350, 0.495                             | 0.40, 0.50                               |
| No. of measured, independent and observed | 2288, 2288, 1694 | 11660, 1434, 1164 |
| Dmax                     | –                                        | 0.070                                    |
| (sin θ/λ)max (Å⁻¹)       | 0.756                                    | 0.650                                    |
| Refinement               |                                          |                                          |
| R(F² > 2σ(F²))           | 0.040, 0.093, 1.00                       | 0.032, 0.078, 1.06                       |
| No. of reflections       | 2288                                    | 1434                                    |
| No. of parameters        | 112                                      | 107                                      |
| No. of restraints        | 1                                        | 7                                        |
| Δρmax, Δρmin (e Å⁻³)     | 1.85, −1.63                             | 2.57, −2.00                             |

Computer programs: SMART and SAINT (Bruker, 1999), DENZOSCALEPACK (Ortwinski & Minor, 1997), SHELXS and SHELXS97 (Sheldrick, 2008), SHELXL2018/3 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012), ATOMS (Dowty, 2005) and pubCIF (Westrip, 2010).

The B layers in (I) (Fig. 5) lie at z ≃ 1/12, 1/4, 5/12, 7/12, 3/4 and 11/12 and are associated with the Zr1 and As2 species. These also feature polyhedral 12-rings (six octahedra and six tetrahedra) but only one As2 tetrahedron (with two terminal As2—O6 bonds) links adjacent Zr1 octahedra via atom O5. There are numerous sodium sites associated with the B layers. The disorder of the sodium ions in the vicinities of the B layers and possible small [110] channels (see Fig. 2) suggests the possibility of ionic conductivity (Norberg, 2002). An analysis of the structure with PLATON (Spek, 2020) with the sodium ions removed indicated that there was 119.4 Å³ of free space per unit cell (~2.1%).

3. Database survey
A survey of the Inorganic Crystal Structure Database (ICSD) (Belsky et al., 2002) revealed 11 matches for crystal structures containing Zr + As + O, the majority of these being Nasicon (Anantharamulu et al., 2011) derivatives such as NaZr(AsO₄)₃ (Chakir et al., 2003) or KZr(AsO₄)₃ (Elbrachimi & Durand, 1990) as well as one KTP analogue, viz. RbZrOAsO₅ (Simpson & Harrison, 2004). There were no hits for the combination of Hf + As + O.

4. Synthesis and crystallization
Compound (I) was prepared by mixing 1.00 g of Na₂CO₃, 0.581 g of ZrO₂ and 1.399 g of As₂O₅ (Na:Zr:As molar ratio ≃ 4:1:3) in an agate mortar; 1.00 g of this mixture was added to 3.0 g of a eutectic-melt mixture (Tₘelt ≃ 500°C) of NaCl/CsCl (~0.35:0.65 mol) and placed in a flat-bottom alumina crucible. The crucible was rapidly heated to 500°C in a muffle furnace and then ramped at 12°C min⁻¹ to 700°C and cooled at the same rate to 400°C and then removed from the furnace and left to cool. The gummy white product was washed with copious amounts of hot water followed by acetone to result in a mass of tiny colourless rods of (I). Compound (II) was made in the same way starting from a pre-mixture of 1.00 g Na₂CO₃, 1.12 g HfO₂ and 1.57 g As₂O₅ and tiny colourless rods of (II) were the result.

Caution! Arsenic compounds are highly toxic and carcinogenic. Take all appropriate safety precautions, especially with respect to dust contamination.

5. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 1. The crystal chosen for data collection for (I) was found to be twinned over its rhombohedral obverse and reverse settings (Herbst-Irmer & Sheldrick, 2002) in a 0.797 (3):0.203 (3) ratio, which was processed as a SHELXL HKLF 5 refinement. To ensure charge balance, the occupancies of the four partially occupied sodium sites must sum to 10.0 Na per caesium ion and this was achieved by using a SUMP card (linear free variable restraint) in SHELXL, as unrestrained refinements tended to drift to a collective occupancy of above 10 (full occupancy of the four sodium sites would give 13 Na to 1 Cs). This needed cautious...
damped refinement cycles to begin with, but as the refinement converged, the damping could be removed to give refined fractional site occupancies of Na1 = 0.852 (5), Na2 = 0.860 (9), Na3 = 0.731 (12) and Na4 = 0.423 (11) for (I) and Na1 = 0.887 (7), Na2 = 0.846 (11), Na3 = 0.735 (16) and Na4 = 0.337 (14) for (II). The final difference map for (II) features electron density peaks of \( \pm 2 \text{ e}\, \text{Å}^{-3} \) near some of the sodium ions, perhaps suggesting that they are localizing over split multiple sites at low temperatures, but efforts to model this did not lead to satisfactory refinements. The value of \( U_{eq} \) for Na4 is small, which might indicate partial occupancy of caesium on this site (i.e., a formula of Cs\(_{1+x}\)Na\(_{10-x}\)Hf\(_4\)(AsO\(_4\))\(_9\), but attempts to model this were inconclusive.

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Flux syntheses and single-crystal structures of CsNa\textsubscript{10}M\textsubscript{4}(AsO\textsubscript{4})\textsubscript{9} (M = Zr, Hf)

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Computing details
Data collection: SMART (Bruker, 1999) for (I); DENZO/SCALEPACK (Otwinowski & Minor, 1997) for (II). Cell refinement: SAINT (Bruker, 1999) for (I); DENZO/SCALEPACK (Otwinowski & Minor, 1997) for (II). Data reduction: SAINT (Bruker, 1999) for (I); DENZO/SCALEPACK (Otwinowski & Minor, 1997) for (II). Program(s) used to solve structure: SHELXS (Sheldrick, 2008) for (I); SHELXS97 (Sheldrick, 2008) for (II). For both structures, program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and ATOMS (Dowty, 2005); software used to prepare material for publication: SHELXL2018/3 (Sheldrick, 2015) and publCIF (Westrip, 2010).

Caesium decasodium tetrazirconium nonaarsenate (I)

Crystal data
Cs\textsubscript{Na}\textsubscript{10}Zr\textsubscript{4}(AsO\textsubscript{4})\textsubscript{9}
Mr = 1977.97
Trigonal, R\textsubscript{3c}:H
a = 9.2218 (5) Å
b = 76.982 (5) Å
V = 5669.6 (7) Å\textsuperscript{3}
Z = 6
F(000) = 5460

$D_\text{c}$ = 3.476 Mg m\textsuperscript{-3}
Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2999 reflections
$\theta$ = 2.6–30.8°
$\mu$ = 10.07 mm\textsuperscript{-1}
$T$ = 293 K
Prism, colourless
0.10 × 0.10 × 0.10 mm

Data collection
Bruker SMART CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan
(SADABS; Bruker, 1999)
$T_{\text{min}} = 0.350, T_{\text{max}} = 0.495$
2288 measured reflections
2288 independent reflections
1694 reflections with $I > 2\sigma(I)$
$\theta_{\text{max}} = 32.5^\circ, \theta_{\text{min}} = 2.6^\circ$
$h = -12\rightarrow 12$
$k = -13\rightarrow 13$
$l = 0\rightarrow 114$

Refinement
Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]= 0.040$
$wR(F^2) = 0.093$
$S = 1.00$
2288 reflections
112 parameters
1 restraint

Primary atom site location: structure-invariant direct methods
$w = 1/\sigma^2(F^2) + (0.0452P)^2$
where $P = (F^2 + 2F'^2)/3$
$(\Delta\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 1.85 \text{ e Å}^{-3}$
$\Delta\rho_{\text{min}} = -1.63 \text{ e Å}^{-3}$
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. Refined as a 2-component obverse/reverse twin.

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

|    | x      | y      | z      | U(eq)  | Occ. (<1) |
|----|--------|--------|--------|--------|-----------|
| Cs1| 0.000000 | 0.000000 | 0.000000 | 0.0381 (2) |
| Na1| 0.3350 (5) | 0.0681 (4) | 0.04049 (4) | 0.0410 (9) | 0.852 (5) |
| Na2| 0.4054 (5) | 0.333333 | 0.083333 | 0.0411 (13) | 0.860 (9) |
| Na3| 0.000000 | 0.000000 | 0.05355 (8) | 0.0321 (17) | 0.731 (12) |
| Na4| 0.666667 | 0.333333 | 0.06014 (12) | 0.021 (2) | 0.423 (11) |
| Zr1| 0.333333 | 0.666667 | 0.05681 (2) | 0.01237 (15) |
| Zr2| 0.333333 | 0.666667 | −0.00666 (2) | 0.01204 (15) |
| As1| 0.34556 (6) | 0.39774 (6) | 0.02640 (2) | 0.01350 (11) |
| As2| 0.666667 | 0.73010 (9) | 0.083333 | 0.0309 (2) |
| O1 | 0.1757 (5) | 0.2319 (4) | 0.03370 (5) | 0.0251 (8) |
| O2 | 0.3084 (5) | 0.4671 (5) | 0.00779 (5) | 0.0251 (8) |
| O3 | 0.4373 (5) | 0.5591 (4) | 0.04062 (5) | 0.0192 (7) |
| O4 | 0.4946 (5) | 0.73010 (9) | 0.083333 | 0.01350 (11) |
| O5 | 0.5457 (5) | 0.7825 (5) | 0.07152 (5) | 0.0234 (8) |
| O6A| 0.603 (2) | 0.5691 (13) | 0.09411 (18) | 0.036 (5) | 0.45 (3) |
| O6B| 0.5238 (19) | 0.5873 (11) | 0.09900 (16) | 0.034 (4) | 0.55 (3) |

Atomic displacement parameters (Å²)

|    | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|----|-----|-----|-----|-----|-----|-----|
| Cs1| 0.0436 (4) | 0.0436 (4) | 0.0271 (4) | 0.02182 (18) | 0.0000 | 0.0000 |
| Na1| 0.072 (2) | 0.0286 (15) | 0.0375 (16) | 0.0369 (17) | −0.0102 (17) | −0.0033 (13) |
| Na2| 0.0307 (18) | 0.0138 (18) | 0.073 (3) | 0.0069 (9) | −0.0044 (10) | −0.009 (2) |
| Na3| 0.0216 (19) | 0.0216 (19) | 0.053 (4) | 0.0108 (9) | 0.0000 | 0.0000 |
| Na4| 0.015 (3) | 0.015 (3) | 0.034 (5) | 0.0074 (14) | 0.0000 | 0.0000 |
| Zr1| 0.0109 (2) | 0.0109 (2) | 0.0153 (3) | 0.00546 (10) | 0.0000 | 0.0000 |
| Zr2| 0.0109 (2) | 0.0109 (2) | 0.0144 (3) | 0.00543 (10) | 0.0000 | 0.0000 |
| As1| 0.0135 (2) | 0.0114 (2) | 0.0162 (2) | 0.00670 (18) | 0.00020 (18) | 0.00004 (18) |
| As2| 0.0460 (5) | 0.0276 (3) | 0.0254 (4) | 0.0230 (3) | −0.0191 (4) | −0.0095 (2) |
| O1 | 0.0227 (19) | 0.0166 (17) | 0.029 (2) | 0.0041 (15) | 0.0059 (16) | 0.0051 (16) |
| O2 | 0.029 (2) | 0.0199 (18) | 0.0268 (19) | 0.0131 (17) | −0.0026 (17) | 0.0055 (16) |
| O3 | 0.0199 (17) | 0.0165 (16) | 0.0220 (17) | 0.0097 (14) | 0.0002 (15) | −0.0050 (15) |
| O4 | 0.0246 (19) | 0.0293 (19) | 0.0227 (18) | 0.0219 (17) | 0.0003 (15) | −0.0034 (17) |
| O5 | 0.0178 (17) | 0.028 (2) | 0.0252 (18) | 0.0123 (16) | −0.0095 (15) | −0.0076 (17) |
| O6A| 0.034 (8) | 0.024 (5) | 0.034 (6) | 0.001 (4) | −0.010 (6) | 0.003 (4) |
| O6B| 0.032 (7) | 0.021 (4) | 0.032 (5) | 0.000 (4) | −0.014 (5) | 0.004 (4) |
### Geometric parameters (Å, °)

| Bond          | Distance (Å) | Angle (°)       | Bond          | Distance (Å) | Angle (°)       |
|---------------|--------------|----------------|---------------|--------------|----------------|
| Cs1—O1i       | 3.235 (4)    | Na4—O6Aiv      | 2.694 (17)    |
| Cs1—O1ii      | 3.235 (4)    | Na4—O6Axii     | 2.694 (17)    |
| Cs1—O1iii     | 3.235 (4)    | Zr1—O5         | 2.041 (3)     |
| Cs1—O1iv      | 3.235 (4)    | Zr1—O5ix       | 2.041 (3)     |
| Na1—O6Bvii    | 2.193 (9)    | Zr1—O3xii      | 2.099 (3)     |
| Na1—O3xvii    | 2.394 (5)    | Zr1—O3         | 2.099 (3)     |
| Na1—O1v       | 2.482 (5)    | Zr2—O2xii      | 2.062 (4)     |
| Na1—O6Aiv     | 2.485 (16)   | Zr2—O2x        | 2.062 (4)     |
| Na1—O4        | 2.582 (5)    | Zr2—O2         | 2.062 (4)     |
| Na1—O1        | 2.632 (5)    | Zr2—O4xiv      | 2.081 (3)     |
| Na2—O6A       | 2.185 (10)   | Zr2—O4xvi      | 2.081 (3)     |
| Na2—O6Aiv     | 2.185 (10)   | Zr2—O4vi       | 2.081 (3)     |
| Na2—O6B       | 2.361 (12)   | As1—O1         | 1.647 (4)     |
| Na2—O6Bvii    | 2.361 (12)   | As1—O2         | 1.673 (4)     |
| Na2—O5xviii   | 2.495 (5)    | As1—O4         | 1.691 (3)     |
| Na2—O5xv      | 2.495 (5)    | As1—O3         | 1.694 (4)     |
| Na3—O1vi      | 2.463 (5)    | As2—O6A        | 1.538 (10)    |
| Na3—O1        | 2.463 (5)    | As2—O6Aii      | 1.538 (10)    |
| Na3—O1v       | 2.463 (5)    | As2—O5xii      | 1.686 (4)     |
| Na3—O6Bvii    | 2.47 (2)     | As2—O5         | 1.686 (4)     |
| Na3—O6Bvi     | 2.47 (2)     | As2—O6B        | 1.786 (13)    |
| Na3—O6Bv      | 2.47 (2)     | As2—O6Bvii     | 1.786 (13)    |
| Na4—O6Aiv     | 2.694 (17)   | O6A—O6B        | 0.909 (13)    |

| Bond          | Angle (°)       | Bond          | Angle (°)       |
|---------------|----------------|---------------|----------------|
| O1iv—Cs1—O1ii| 180.0 (3)      | O5xiii—Zr1—O3x| 87.67 (16)     |
| O1iv—Cs1—O1iii| 62.30 (10)    | O5xix—Zr1—O3x| 91.79 (15)     |
| O1iv—Cs1—O1iv| 117.70 (10)   | O5—Zr1—O3xii | 87.66 (16)     |
| O1iv—Cs1—O1v | 117.70 (10)   | O5—Zr1—O3xiii| 87.66 (16)     |
| O1v—Cs1—O1v  | 62.30 (10)    | O5—Zr1—O3xiii| 176.01 (15)    |
| O1v—Cs1—O1vi | 180.00 (9)    | O3x—Zr1—O3xiii| 88.35 (14)    |
| O1v—Cs1—O1v  | 62.30 (10)    | O5—Zr1—O3    | 91.79 (15)     |
| O1iv—Cs1—O1v | 117.70 (10)   | O5xiii—Zr1—O3| 176.01 (15)    |
| O1v—Cs1—O1v  | 62.30 (10)    | O5—Zr1—O3    | 87.67 (16)     |
| O1iv—Cs1—O1v | 117.70 (10)   | O3x—Zr1—O3   | 88.35 (14)     |
| O1v—Cs1—O1v  | 117.70 (10)   | O3x—Zr1—O3   | 88.35 (14)     |
| O1v—Cs1—O1v  | 62.30 (10)    | O2xii—Zr2—O2x| 93.66 (15)     |
| O1iv—Cs1—O1v | 117.70 (10)   | O2xii—Zr2—O2  | 93.66 (15)     |
| O1v—Cs1—O1v  | 62.30 (10)    | O2xii—Zr2—O2  | 93.66 (15)     |
| O1iv—Cs1—O1v | 180.00 (16)   | O2xii—Zr2—O4xv| 92.00 (16)    |
| O6Bvi—Na1—O3xii| 104.6 (4)    | O2x—Zr2—O4xv | 88.01 (15)     |
| O6Bvi—Na1—O1v| 93.4 (5)      | O2—Zr2—O4xv  | 173.98 (15)    |
| O3x—Na1—O1v  | 87.41 (15)    | O2—Zr2—O4xv  | 173.98 (15)    |
| O6Bvi—Na1—O6Avi| 21.3 (3)     | O2x—Zr2—O4xv | 92.00 (16)     |
| O3x—Na1—O6A vi| 90.3 (4)      | O2—Zr2—O4xv  | 88.01 (15)     |
O1v—Na1—O6Avi 108.7 (4) O4xiv—Zr2—O4xv 86.15 (14)
O6Bvi—Na1—O4 118.5 (3) O2viii—Zr2—O4vi 88.01 (15)
O3viii—Na1—O1 119.01 (18) O2v—Zr2—O4vvi 173.98 (15)
O1v—Na1—O4 127.39 (17) O4xiv—Zr2—O4vvi 92.01 (16)
O6Avi—Na1—O4 115.1 (3) O4v—Zr2—O4vvi 86.15 (14)
O3viii—Na1—O1 85.3 (5) O4v—Zr2—O4vvi 86.15 (14)
O1v—Na1—O1 165.74 (19) O1v—As1—O2 111.5 (2)
O6Avi—Na1—O1 81.68 (19) O1v—As1—O4 108.17 (19)
O4—Na1—O1 101.8 (5) O2—As1—O4 109.94 (19)
O6Bvi—Na1—O4viii 62.47 (13) O1v—As1—O3 114.88 (19)
O3viii—Na1—O4viii 132.4 (6) O2—As1—O3 108.98 (18)
O1v—Na1—O4viii 58.02 (13) O4—As1—O3 103.03 (18)
O6Avi—Na1—O4viii 125.80 (15) O6A—As2—O6Avi 78.4 (18)
O6Avi—Na1—O4viii 111.4 (6) O6A—As2—O5xviii 112.1 (4)
O4—Na1—O4viii 61.11 (16) O6Avi—As2—O5xviii 125.4 (7)
O1—Na1—O4viii 122.35 (15) O6A—As2—O5xviii 125.4 (7)
O6A—Na2—O6Avi 140.7 (13) O6Avi—As2—O5xviii 112.1 (4)
O6A—Na2—O6B 22.7 (4) O5xviii—As2—O5xviii 103.8 (3)
O6Avi—Na2—O6Bv 161.0 (11) O6A—As2—O6B 30.6 (6)
O6Avi—Na2—O6Bvi 161.0 (11) O6Avi—As2—O6Bvi 106.8 (15)
O6B—Na2—O6Bvi 22.7 (4) O5xviii—As2—O6Bvi 103.3 (4)
O6B—Na2—O6Bvi 176.2 (9) O5—As2—O6Bvi 103.1 (5)
O6Avi—Na2—O6Bvi 118.7 (7) O6A—As2—O6Bvi 106.8 (15)
O6B—Na2—O5xviii 95.2 (5) O6Avi—As2—O6Bv 30.6 (6)
O6Bv—Na2—O5xviii 96.8 (5) O5xviii—As2—O6Bv 103.0 (5)
O6Avi—Na2—O5xviii 79.9 (4) O5—As2—O6Bv 103.2 (4)
O6Avi—Na2—O5xviii 95.2 (5) O6B—As2—O6Bv 136.7 (12)
O6Avi—Na2—O5xviii 118.7 (7) As1—O1—Na3 157.7 (2)
O6B—Na2—O5xviii 79.9 (4) As1—O1—Na1ii 117.0 (2)
O6Bv—Na2—O5xvi 96.8 (5) Na3—O1—Na1ii 74.3 (13)
O5xviii—Na2—O5xvi 64.2 (2) As1—O1—Na1 93.24 (18)
O6Avi—Na2—O5xvi 113.6 (6) Na3—O1—Na1 72.10 (12)
O6Avi—Na2—O5xvi 40.3 (6) Na1ii—O1—Na1 146.6 (2)
O6B—Na2—O5xvi 124.1 (3) As1—O1—Cs1 105.65 (17)
O6Bv—Na2—O5xvi 58.3 (4) Na3—O1—Cs1 91.66 (16)
O5xviii—Na2—O5xvi 92.7 (2) Na1ii—O1—Cs1 93.89 (14)
O5xv—Na2—O6Avii 149.8 (3) Na1—O1—Cs1 91.09 (13)
O6Avi—Na2—O6Avii 40.3 (6) As1—O2—Zr2 148.2 (2)
O6Avi—Na2—O6Avii 113.6 (6) As1—O3—Zr1 130.8 (2)
O6B—Na2—O6Avii 58.3 (5) As1—O3—Na1xvi 108.79 (18)
O6Bv—Na2—O6Avii 124.1 (3) Zr1—O3—Na1xvi 120.42 (18)
O5xv—Na2—O6Avii 149.8 (2) As1—O4—Zr2vii 148.4 (2)
O5v—Na2—O6Avii 92.7 (2) As1—O4—Na1 93.97 (17)
O6Avi—Na2—O6Avii 214.9 (5) Zr2vii—O4—Na1 109.81 (17)
O1v—Na3—O1 85.6 (2) As1—O4—Na1xvi 87.30 (16)
O1v—Na3—O1v 85.6 (2) Zr2vii—O4—Na1xvi 96.88 (15)
O1v—Na3—O1v 85.6 (2) Na1—O4—Na1xvi 121.76 (18)
O1v—Na3—O6Bviii 83.5 (2) As2—O5—Zr1 138.4 (2)
### Crystal data

\[ \text{CsNa}_{10}\text{Hf}_4(\text{AsO}_4)_9 \]

\[ M_r = 2327.05 \]

Trigonal, \( R\overline{3}c \): \( H \)

\[ a = 9.1795 (2) \text{ Å} \]

\[ c = 76.527 (8) \text{ Å} \]

\[ V = 5584.5 (6) \text{ Å}^3 \]

\[ Z = 6 \]

\[ F(000) = 6228 \]

### Data collection

Nonius KappaCCD diffractometer

\( \omega \) scans

Absorption correction: multi-scan

(SORTAV; Blessing, 1995)

\[ T_{\text{min}} = 0.40, T_{\text{max}} = 0.50 \]

11640 measured reflections

1164 independent reflections

\[ \bar{R} = 0.070 \]

Primary atom site location: structure-invariant direct methods

\[ \Delta \rho \text{max} = 2.57 \text{ e Å}^{-3} \]

\[ \Delta \rho \text{min} = -2.00 \text{ e Å}^{-3} \]

### Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R[F^2 > 2\sigma(F^2)] = 0.032 \]

\[ wR(F^2) = 0.078 \]

\[ S = 1.06 \]

1434 reflections

107 parameters

7 restraints

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**O1—Na3—O6B^{iii} 87.5 (2)**  \[ \text{As2—O5—Na2}^{xiii} 95.98 (16) \]

**O1^{v}—Na3—O6B^{xiii} 167.5 (3)**  \[ \text{Zr1—O5—Na2}^{xiii} 124.11 (18) \]

**O1^{vi}—Na3—O6B^{x} 87.5 (2)**  \[ \text{As2—O6A—Na2} 118.8 (6) \]

**O1^{vii}—Na3—O6B^{x} 167.5 (3)**  \[ \text{Na2—O6A—Na1}^{vi} 116.7 (8) \]

**O1^{viii}—Na3—O6B^{vi} 87.5 (2)**  \[ \text{As2—O6A—Na4}^{xi} 147.0 (14) \]

**O1^{ix}—Na3—O6B^{vi} 83.5 (2)**  \[ \text{Na2—O6A—Na4}^{xi} 75.0 (4) \]

**O1^{x}—Na3—O6B^{vi} 87.5 (2)**  \[ \text{Na1}^{vi}—O6A—Na4^{xi} 75.8 (3) \]

**O1^{xi}—Na3—O6B^{vi} 83.5 (2)**  \[ \text{Na1}^{vi}—O6A—Na2^{xvi} 83.8 (9) \]

**O1^{xii}—Na3—O6B^{vi} 102.1 (3)**  \[ \text{Na2—O6A—Na2}^{xvi} 106.0 (9) \]

**O1^{xiii}—Na3—O6B^{vi} 102.1 (3)**  \[ \text{Na1}^{vi}—O6A—Na2^{xvi} 109.3 (5) \]

**O1^{xiv}—Na3—O6B^{vi} 108.1 (5)**  \[ \text{Na4}^{vi}—O6A—Na2^{xvi} 63.2 (5) \]

**O1^{xv}—Na3—O6B^{vi} 108.1 (5)**  \[ \text{As2—O6B—Na1}^{vi} 120.5 (5) \]

**O1^{xvi}—Na3—O6B^{vi} 108.1 (5)**  \[ \text{As2—O6B—Na3}^{xvii} 116.8 (7) \]

**O1^{xvii}—Na3—O6B^{vi} 108.1 (5)**  \[ \text{Na2—O6B—Na3}^{xvii} 79.9 (6) \]

**O1^{xviii}—Na3—O6B^{vi} 108.1 (5)**  \[ \text{Na2—O6B—Na3}^{xvii} 118.3 (6) \]

**O1^{xix}—Na3—O6B^{vi} 108.1 (5)**  \[ \text{Na2—O6B—Na3}^{xvii} 118.3 (6) \]

**O1^{xx}—Na3—O6B^{vi} 108.1 (5)**  \[ \text{Na2—O6B—Na3}^{xvii} 118.3 (6) \]

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**Caesium decasodium tetrahafnium nonaarsenate (II)**

\[ D_r = 4.152 \text{ Mg m}^{-3} \]

\[ \text{Mo Kα radiation, } \lambda = 0.71073 \text{ Å} \]

Cell parameters from 22894 reflections

\[ \theta = 2.9–27.5^\circ \]

\[ \mu = 20.25 \text{ mm}^{-1} \]

\[ T = 120 \text{ K} \]

Prism, colourless

0.08 × 0.08 × 0.08 mm

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Supporting information
**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 (Å²)

|          | x        | y        | z        | U₁₁       | U₂₂       | U₃₃       | U₁₂       | U₁₃       | U₂₃       | Occ. (<1) |
|----------|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Cs1      | 0.000000 | 0.000000 | 0.000000 | 0.0162    |           |           |           |           |           | 0.887 (7) |
| Na1      | 0.3354 (5)| 0.0688 (5)| 0.04043 (5)| 0.0256 (11)| 0.0208 (15)*| 0.846 (11)| 0.018 (2) | 0.735 (16) |           |
| Na2      | 0.4061 (6)| 0.333333 | 0.083333 | 0.018 (2) | 0.0113 (11)|           |           |           |           | 0.337 (14)|
| Na3      | 0.000000 | 0.000000 | 0.05288 (11)| 0.00710 (15)| 0.0068 (15)| 0.00578 (18)| 0.0205 (3)|           |           |
| Na4      | 0.666667 | 0.333333 | 0.06123 (16)| 0.002 (4)*| 0.870 (16)|           |           |           |           | 0.35 (2) |
| Hf1      | 0.333333 | 0.666667 | 0.05673 (2) | 0.00710 (15) | 0.00611 (15) |           |           |           |           | 0.65 (2) |
| Hf2      | 0.333333 | 0.666667 | −0.00682 (2) | 0.00611 (15) |           |           |           |           |           |           |
| As1      | 0.34520 (9) | 0.39770 (9)| 0.02639 (2) | 0.00578 (18)| 0.0205 (3) |           |           |           |           |           |
| As2      | 0.666667 | 0.73244 (13)| 0.083333 | 0.02170 (18)| 0.0205 (3) |           |           |           |           |           |
| O1       | 0.1730 (6)| 0.2332 (6)| 0.03369 (6) | 0.0113 (11)| 0.00745 (6) | 0.0068 (10)| 0.0109 (11)| 0.00578 (18)| 0.0205 (3)|           |
| O2       | 0.3086 (6)| 0.4663 (6)| 0.00745 (6) | 0.0113 (11)| 0.00745 (6) | 0.0068 (10)| 0.0109 (11)|           |           |           |
| O3       | 0.4389 (6)| 0.5622 (6)| 0.04043 (6) | 0.0068 (10)|           |           |           |           |           | 0.0127 (11)|
| O4       | 0.4922 (6)| 0.3405 (6)| 0.02356 (6) | 0.0097 (11)|           |           |           |           |           |           |
| O5       | 0.5461 (6)| 0.7864 (6)| 0.07152 (6) | 0.0127 (11)|           |           |           |           |           |           |
| O6A      | 0.602 (2) | 0.569 (2) | 0.09842 (2) | 0.008 (2) | 0.00578 (18)| 0.0205 (3) |           |           |           | 0.35 (2) |
| O6B      | 0.5276 (16)| 0.5861 (12)| 0.09848 (14)| 0.029 (4) | 0.00578 (18)| 0.0205 (3) |           |           |           | 0.65 (2) |

**Atomic displacement parameters (Å²)**

|          | U₁₁       | U₂₂       | U₃₃       | U₁₂       | U₁₃       | U₂₃       |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Cs1      | 0.0181 (4)| 0.0181 (4)| 0.0125 (5)| 0.0091 (2)| 0.0000     | 0.0000     |
| Na1      | 0.049 (3) | 0.014 (2) | 0.023 (2) | 0.023 (2) | −0.0094 (18)| −0.0012 (16)|
| Na3      | 0.002 (3) | 0.002 (3) | 0.049 (5) | 0.0012 (13)| 0.0000     | 0.0000     |
| Hf1      | 0.00580 (19)| 0.00580 (19)| 0.0097 (3)| 0.00290 (9)| 0.0000     | 0.0000     |
| Hf2      | 0.00499 (19)| 0.00499 (19)| 0.0084 (3)| 0.00250 (9)| 0.0000     | 0.0000     |
| As1      | 0.0056 (4)| 0.0037 (4)| 0.0086 (3)| 0.0027 (3)| 0.0002 (3) | 0.0002 (3) |
| As2      | 0.0312 (7)| 0.0178 (4)| 0.0170 (6)| 0.0156 (4)| −0.0165 (5)| −0.0083 (3)|
| O1       | 0.007 (3) | 0.007 (3) | 0.015 (3) | 0.000 (2) | 0.001 (2) | 0.001 (2) |
| O2       | 0.015 (3) | 0.009 (3) | 0.011 (2) | 0.007 (2) | −0.003 (2) | 0.000 (2) |
| O3       | 0.005 (2) | 0.005 (2) | 0.011 (2) | 0.003 (2) | −0.0006 (19)| −0.0054 (19)|
| O4       | 0.010 (3) | 0.013 (3) | 0.010 (2) | 0.010 (2) | 0.002 (2) | 0.000 (2) |
| O5       | 0.007 (3) | 0.017 (3) | 0.012 (2) | 0.004 (2) | −0.006 (2) | −0.006 (2) |
| O6A      | 0.008 (2) | 0.008 (2) | 0.008 (2) | 0.0042 (11)| 0.00000 (10)| 0.00000 (10)|
| O6B      | 0.030 (7) | 0.021 (5) | 0.022 (5) | 0.003 (5) | −0.014 (5) | 0.002 (4) |

**Geometric parameters (Å, °)**

|          | Cs1—O1 | Na4—O6A | Na4—O6A |
|----------|--------|---------|---------|
| Cs1—O1  | 3.218 (5)| 2.654 (18)| 2.654 (18)|
Cs1—O1ii 3.218 (5) Hf1—O5iii 2.039 (5)
Cs1—O1iii 3.218 (5) Hf1—O5iv 2.039 (5)
Cs1—O1iv 3.218 (5) Hf1—O3viii 2.084 (4)
Cs1—O1v 3.218 (5) Hf1—O3ix 2.084 (4)
Na1—O6Bvi 2.212 (10) Hf1—O3xi 2.084 (4)
Na1—O3viii 2.377 (6) Hf1—O3xii 2.084 (4)
Na1—O3ix 2.443 (6) Hf2—O2 2.051 (5)
Na1—O6Avi 2.467 (17) Hf2—O2xii 2.052 (5)
Na1—O6 iv 2.524 (6) Hf2—O2xiii 2.052 (5)
Na1—O1 2.649 (6) Hf2—O4xiv 2.077 (5)
Na1—O4vii 2.972 (6) Hf2—O4 2.077 (5)
Na2—O6Avi 2.170 (16) Hf2—O4xiv 2.077 (5)
Na2—O6A 2.170 (16) O6Avi—O6A 0.842 (15)
Na2—O6B 2.320 (10) O6Avi—O6A 0.842 (15)
Na2—O6Bvi 2.320 (10) O6Avi—O6A 0.842 (15)
Na3—O5viii 2.458 (7) O6Avi—O6A 0.842 (15)
Na3—O5ix 2.458 (7) O6Avi—O6A 0.842 (15)
Na3—O5x 2.458 (7) O6Avi—O6A 0.842 (15)
Na3—O5vi 2.458 (7) O6Avi—O6A 0.842 (15)
Na3—O5vii 2.458 (7) O6Avi—O6A 0.842 (15)
Na4—O6Avi 2.654 (18)

O1—Cs1—O1i 180.00 (19) O5ix—Hf1—O3 87.7 (2)
O1—Cs1—O1ii 117.59 (14) O5—Hf1—O3 92.3 (2)
O1—Cs1—O1iii 62.41 (14) O3ix—Hf1—O3 87.88 (18)
O1—Cs1—O1iv 62.41 (14) O3xiii—Hf1—O3 87.88 (18)
O1—Cs1—O1v 117.59 (14) O2—Hf2—O2xii 94.29 (18)
O1—Cs1—O1vi 117.59 (14) O2—Hf2—O2xiii 94.29 (18)
O1—Cs1—O1vii 62.41 (14) O2—Hf2—O4xii 92.38 (19)
O1—Cs1—O1viii 62.41 (14) O2—Hf2—O4xiv 173.05 (19)
O1—Cs1—O1ix 117.59 (14) O2—Hf2—O4xiv 173.05 (19)
O1—Cs1—O1x 117.59 (14) O2—Hf2—O4xiv 173.05 (19)
O1—Cs1—O1xi 117.59 (14) O2—Hf2—O4xiv 173.05 (19)
O1—Cs1—O1xii 117.59 (14) O2—Hf2—O4xiv 173.05 (19)
O1—Cs1—O1xiii 62.41 (14) O2—Hf2—O4xiv 173.05 (19)
O1—Cs1—O1xiv 180.0 (3) O2—Hf2—O4xiv 173.05 (19)
O6B—Na1—O3viii 103.3 (4) O2—Hf2—O4xiv 173.05 (19)
O6B—Na1—O3ix 94.4 (4) O2—Hf2—O4xiv 173.05 (19)
O3—Na1—O1i 86.5 (2) O4xv—Hf2—O4xiv 85.96 (19)
O6B—Na1—O6Avi 19.8 (4) O4xv—Hf2—O4xiv 85.96 (19)
O3—Na1—O6A 90.7 (5) O1—As1—O2 110.9 (3)
O1—Na1—O6Avi 108.7 (5) O1—As1—O4 108.0 (2)
O6B—Na1—O4 118.4 (3) O2—As1—O4 110.3 (3)
O3—Na1—O4 119.4 (2) O1—As1—O3 115.4 (2)
| Bond 1 | Bond 2 | Bond 3 | Angle (°) |
|-------|-------|-------|-----------|
| O1iii—Na1—O4 | 127.6 (2) | O2—As1—O3 | 108.7 (2) |
| O6Avi—Na1—O4 | 115.0 (4) | O4—As1—O3 | 103.3 (2) |
| O6Bvi—Na1—O4i | 86.1 (4) | O6A—As2—O6Ai | 78.0 (15) |
| O3viii—Na1—O1 | 165.2 (2) | O6A—As2—O5 | 125.7 (7) |
| O1v—Na1—O1 | 81.7 (2) | O6Aviii—As2—O5i | 112.6 (6) |
| O6Avi—Na1—O1 | 101.5 (5) | O6Aviii—As2—O5ii | 112.6 (6) |
| O4—Na1—O1 | 62.78 (17) | O6Aviii—As2—O5iii | 125.7 (7) |
| O6Bvi—Na1—O4ii | 130.4 (5) | O5—As2—O5ii | 103.0 (3) |
| O3viii—Na1—O4iii | 58.22 (16) | O6Av—As2—O6B | 28.8 (6) |
| O1v—Na1—O4iv | 126.1 (2) | O6Av—As2—O6B | 104.5 (12) |
| O6Avi—Na1—O4iv | 110.9 (5) | O5—As2—O6B | 104.3 (5) |
| O4—Na1—O4v | 61.4 (2) | O5v—As2—O6B | 104.8 (4) |
| O1—Na1—O4vii | 123.09 (19) | O6A—As2—O6Bvii | 104.5 (12) |
| O6A—Na2—O6Avi | 141.3 (12) | O6A—As2—O6Bvii | 28.8 (6) |
| O6A—Na2—O6B | 21.3 (4) | O5—As2—O6Bvii | 104.8 (4) |
| O6Av—Na2—O6B | 160.8 (9) | O5v—As2—O6Bvii | 104.3 (5) |
| O6Av—Na2—O6Bii | 160.8 (9) | O6B—As2—O6Bvi | 132.5 (10) |
| O6B—Na2—O6Bvi | 21.3 (4) | As1—O1—Na3 | 157.3 (3) |
| O6B—Na2—O6Bvii | 177.8 (8) | As1—O1—Na1v | 118.2 (3) |
| O6Av—Na2—O5viii | 118.4 (6) | Na3—O1—Na1v | 75.36 (17) |
| O6Av—Na2—O5viii | 94.8 (5) | As1—O1—Na1 | 91.9 (2) |
| O6B—Na2—O5viii | 97.9 (4) | Na3—O1—Na1 | 71.66 (16) |
| O6Av—Na2—O5viii | 80.2 (3) | Na1′—O1—Na1 | 146.7 (3) |
| O6A—Na2—O5v | 94.8 (5) | Na1′—O1—Cs1 | 105.5 (2) |
| O6Av—Na2—O5v | 118.4 (6) | Na3—O1—Cs1 | 90.6 (2) |
| O6B—Na2—O5v | 80.2 (3) | Na1′—O1—Cs1 | 94.33 (17) |
| O6Bv—Na2—O5v | 97.9 (4) | Na1—O1—Cs1 | 90.47 (16) |
| O5viii—Na2—O5v | 64.8 (3) | As1—O2—Hf2 | 147.4 (3) |
| O1v—Na3—O1viii | 87.0 (3) | As1—O3—Hf1 | 130.0 (3) |
| O1v—Na3—O1viii | 87.0 (3) | As1—O3—Na1vi | 108.8 (2) |
| O1v—Na3—O1viii | 87.0 (3) | Hf1—O3—Na1vi | 121.1 (2) |
| O1v—Na3—O6Bviii | 84.6 (2) | As1—O4—Hf2iv | 146.9 (3) |
| O1v—Na3—O6Bviii | 170.0 (4) | As1—O4—Na1 | 95.3 (2) |
| O1—Na3—O6Biii | 87.2 (2) | Hf2iv—O4—Na1 | 110.6 (2) |
| O1v—Na3—O6B | 87.2 (2) | As1—O4—Na1vi | 86.8 (2) |
| O1v—Na3—O6B | 84.5 (2) | Hf2iv—O4—Na1vi | 95.70 (19) |
| O1—Na3—O6Bvii | 170.0 (4) | Na1—O4—Na1vi | 122.6 (2) |
| O6Bviii—Na3—O6Bvii | 100.3 (3) | As2—O5—Hf1 | 137.1 (3) |
| O1v—Na3—O6Bviii | 170.0 (4) | As2—O5—Na2viii | 96.1 (2) |
| O1v—Na3—O6Bviii | 87.2 (2) | Hf1—O5—Na2viii | 125.3 (2) |
| O1v—Na3—O6Bviii | 84.6 (2) | As2—O6A—Na2 | 119.0 (8) |
| O6Bviii—Na3—O6Bvii | 100.3 (3) | As2—O6A—Na1v | 116.5 (9) |
| O6Bviii—Na3—O6Bvii | 100.3 (3) | Na2—O6A—Na1v | 116.2 (7) |
| O6Av—Na4—O6Avi | 110.0 (4) | As2—O6A—Na4vii | 146.0 (12) |
| O6Av—Na4—O6Avi | 110.0 (4) | Na2—O6A—Na4vii | 74.0 (5) |
| O6Av—Na4—O6Avi | 110.0 (4) | Na1vi—O6A—Na4vii | 77.5 (5) |
| O5viii—Hf1—O5v | 92.17 (19) | As2—O6A—Na2vii | 83.9 (8) |
| O5viii—Hf1—O5v | 92.17 (19) | Na2—O6A—Na2vii | 105.6 (8) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| O5<sup>ix</sup>—Hf1—O5 | 92.17 (19)   | Na1<sup>vi</sup>—O6A—Na2<sup>xvi</sup> | 109.2 (6)    |
| O5<sup>xiii</sup>—Hf1—O3<sup>x</sup> | 87.7 (2)     | Na4<sup>xii</sup>—O6A—Na2<sup>xvi</sup> | 62.2 (5)     |
| O5<sup>xiii</sup>—Hf1—O3<sup>x</sup> | 92.3 (2)     | As2—O6B—Na1<sup>vi</sup> | 120.8 (5)    |
| O5—Hf1—O3<sup>xiii</sup> | 175.57 (19)  | As2—O6B—Na2 | 103.8 (6)    |
| O5<sup>xii</sup>—Hf1—O3<sup>xiii</sup> | 92.3 (2)     | Na1<sup>vi</sup>—O6B—Na2 | 120.7 (4)    |
| O5<sup>xii</sup>—Hf1—O3<sup>xiii</sup> | 175.56 (19)  | As2—O6B—Na3<sup>xvii</sup> | 115.6 (6)    |
| O5—Hf1—O3<sup>xiii</sup> | 87.7 (2)     | Na1<sup>vi</sup>—O6B—Na3<sup>xvii</sup> | 77.3 (5)     |
| O3<sup>xiii</sup>—Hf1—O3<sup>xiii</sup> | 87.89 (18)   | Na2—O6B—Na3<sup>xvii</sup> | 117.8 (5)    |
| O5<sup>xiii</sup>—Hf1—O3<sup>xiii</sup> | 175.56 (19)  |                     |              |

Symmetry codes: (i) −x, −y, −z; (ii) x+y, x, −z; (iii) −x+y, −x, z; (iv) y, −x+y, −z; (v) −y, x−y, z; (vi) x−y+1/3, −y+2/3, −z+1/6; (vii) −y+1, x−y, z; (viii) y−2/3, x−1/3, −z+1/6; (ix) −x+y, −x+1, z; (x) −x+1/3, −x+y−1/3, −z+1/6; (xi) −x+4/3, −x+y+2/3, −z+1/6; (xii) y+1/3, x−1/3, −z+1/6; (xiii) −y+1, x−y+1, z; (xiv) −x+1, −y+1, −z; (xv) −x+y+1, −z; (xvi) −x+y+1, −x+1, z; (xvii) y+1/3, x+2/3, −z+1/6;