

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

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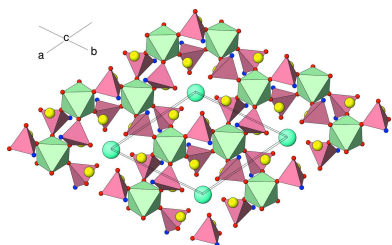
**Keywords:** crystal structure; zirconium; hafnium; arsenate; ionic conduction.**CCDC references:** 2179420; 2179419**Supporting information:** this article has supporting information at journals.iucr.org/e

The isostructural compounds caesium decasodium tetrazirconium nonaarsenate,  $\text{CsNa}_{10}\text{Zr}_4(\text{AsO}_4)_9$ , and caesium decasodium tetrahafnium nonaarsenate,  $\text{CsNa}_{10}\text{Hf}_4(\text{AsO}_4)_9$ , arose as unexpected single-crystal products from the reactions of  $\text{Na}_2\text{CO}_3$ ,  $\text{MO}_2$  ( $M = \text{Zr}, \text{Hf}$ ) and  $\text{As}_2\text{O}_5$  in a eutectic flux of  $\text{NaCl}$  and  $\text{CsCl}$ . They consist of  $\text{MO}_6$  octahedra and  $\text{AsO}_4$  tetrahedra sharing vertices to generate three-dimensional polyhedral networks encapsulating the caesium and sodium ions. The  $\text{MO}_6$  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  $\text{Cs}^+$  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  $\bar{3}$ ; M 3; As 1 and 2; O 1; Na 1, 2 and 3. The  $M = \text{Zr}$  crystal was refined as an obverse/reverse rhombohedral twin.

## 1. Chemical context

Potassium titanyl phosphate ( $\text{KTiOPO}_4$ ; 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  $\text{KTiOPO}_4$  structure type (space group  $Pna2_1$ ,  $a \simeq 12.8$ ,  $b \simeq 6.4$ ,  $c \simeq 10.6$  Å,  $Z = 8$ ,  $Z' = 2$ ) is remarkably accommodating with respect to partial or complete isovalent or aliovalent substitution at the potassium ( $\text{Na}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ti}^+$ ,  $\text{NH}_4^+$  . . .), titanium ( $\text{Zr}^{\text{IV}}$ ,  $\text{Hf}^{\text{IV}}$ ,  $\text{V}^{\text{IV}}$ ,  $\text{Sn}^{\text{IV}}$ ,  $\text{Sb}^{\text{V}}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  . . .), phosphorus ( $\text{As}^{\text{V}}$ ,  $\text{Si}^{\text{IV}}$ ,  $\text{Ge}^{\text{IV}}$ ) and even oxygen ( $\text{OH}^-$ ,  $\text{F}^-$ ) 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  $\text{NaZrOAsO}_4$  and  $\text{NaHfOAsO}_4$  by reacting  $\text{Na}_2\text{CO}_3$ ,  $\text{MO}_2$  ( $M = \text{Zr}, \text{Hf}$ ) and  $\text{As}_2\text{O}_5$  in a low-melting flux of  $\text{NaCl}$  and  $\text{CsCl}$ , the isostructural title compounds  $\text{CsNa}_{10}\text{Zr}_4(\text{AsO}_4)_9$  (I) and  $\text{CsNa}_{10}\text{Hf}_4(\text{AsO}_4)_9$  (II)



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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 12c), two arsenic atoms [As1 on a general position (36f) and As2 with site symmetry 2 (18e)] and six oxygen atoms, one of which is disordered over two adjacent sites (all lying on general positions, 36f), which leads to the unusual 4:9 stoichiometry for the  $Zr^{IV}$  and  $AsO_4^{3-}$  moieties with a net charge of  $-11$ . The structure of (I) is completed by a  $Cs^+$  ion (site symmetry  $\bar{3}$ , 6b) and four partly occupied sodium cations [one on a general position (36f), one with site symmetry 2 (18e) and two with site symmetry 3 (12c)]. 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  $3 \times O3$  and  $3 \times O5$ ) is 2.070 Å and the quadratic elongation and angular variance are 1.001 and  $4.43^\circ$ , respectively

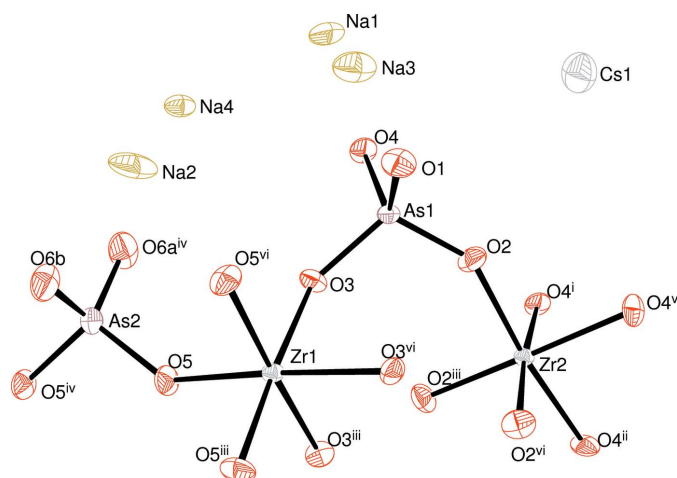


Figure 1

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)  $\frac{4}{3} - x, \frac{2}{3} - x + y, \frac{1}{6} - z$ ; (v)  $x - y, x, -z$ ; (vi)  $y - x, 1 - x, z$ .

(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  $9.86^\circ$ , respectively. The ‘extrapolated’ (Bresle & 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 =  $5.38^\circ$ ) and 2.065 Å for Hf2 (4.10, 1.004,  $13.20^\circ$ ). 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):  $r_6(Zr^{IV}) = 0.72$  (6 = six-coordinate) and  $r_6(Hf^{IV}) = 0.71$  Å and is presumed to arise from the lanthanide contraction effect.

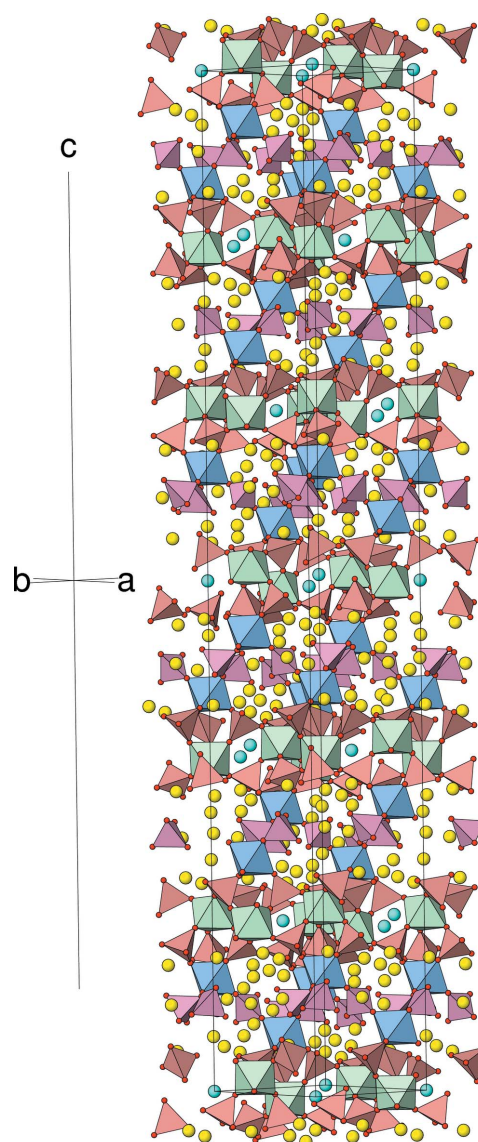
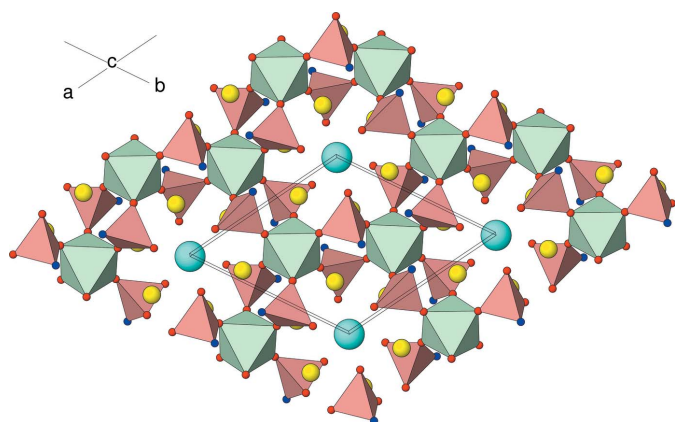


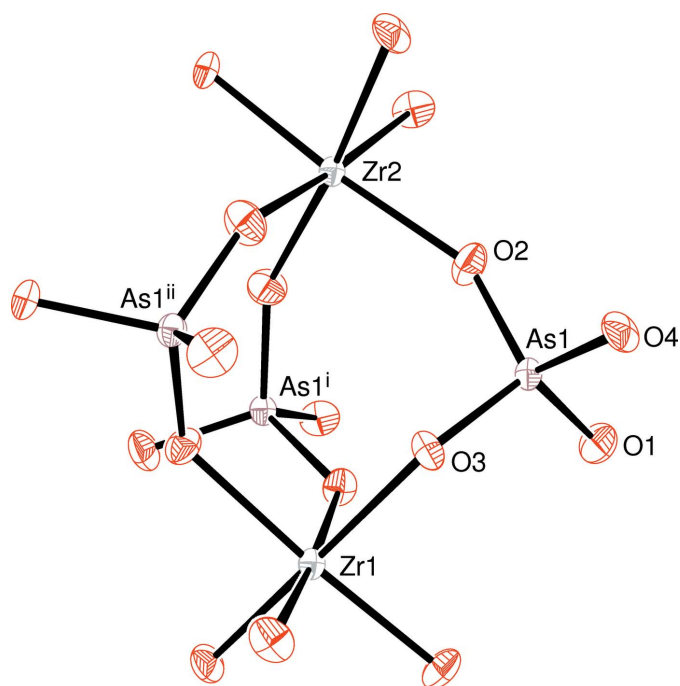
Figure 2

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.



**Figure 3**  
View down [001] of an 'A'-type layer in the structure of (I) in polyhedral representation. Atom and polyhedron colours as in Fig. 2 except O3 is blue.

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 × O5 and 2 × O6), with the latter O atom disordered over two adjacent sites in almost equal occupancies of 0.45 (3):0.55 (3) [O6A···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

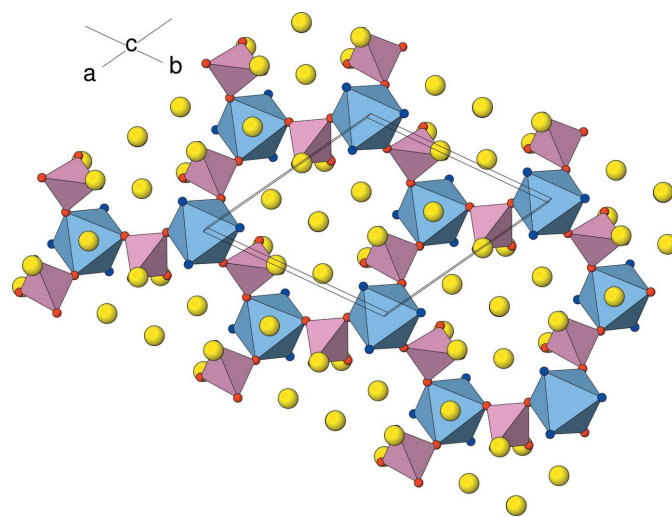


**Figure 4**  
Detail of the extended structure of (I) showing a  $Zr_2As_3O_{18}$  'lantern' motif of Zr1 and Zr2 octahedra linked by three As1 tetrahedra *via* atoms O2 and O3. In (I), this motif has crystallographically imposed threefold symmetry about a rotation axis passing through the zirconium atoms. Symmetry codes: (i)  $1 - y, 1 + x - y, z$ ; (ii)  $y - x, 1 - x, z$ .

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  $NaO_3$  geometries have been observed in dehydrated sodium aluminosilicate 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  $Zr_2O_6$  octahedron is connected by two  $As_1O_4$  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 *via* O3 leads to a distinctive 'lantern' motif (Fig. 4) in which three tetrahedra link two octahedra [ $Zr1 \cdots Zr2 = 4.886$  (2);  $Hf1 \cdots Hf2$  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  $M:X$  ratios compared to the 4:9 ratio for (I).



**Figure 5**  
View down [001] of a 'B'-type layer in the structure of (I) in polyhedral representation. Atom and polyhedron colours as in Fig. 2 except O3 is blue.

**Table 1**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	CsNa <sub>10</sub> Zr <sub>4</sub> (AsO <sub>4</sub> ) <sub>9</sub>	CsNa <sub>10</sub> Hf <sub>4</sub> (AsO <sub>4</sub> ) <sub>9</sub>
<i>M<sub>r</sub></i>	1977.97	2327.05
Crystal system, space group	Trigonal, <i>R</i> $\bar{3}c:H$	Trigonal, <i>R</i> $\bar{3}c:H$
Temperature (K)	293	120
<i>a</i> , <i>c</i> (Å)	9.2218 (5), 76.982 (5)	9.1795 (2), 76.527 (8)
<i>V</i> (Å <sup>3</sup> )	5669.6 (7)	5584.5 (6)
<i>Z</i>	6	6
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	10.07	20.25
Crystal size (mm)	0.10 × 0.10 × 0.10	0.08 × 0.08 × 0.08
Data collection		
Diffractometer	Bruker SMART CCD	Nonius KappaCCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 1999)	Multi-scan ( <i>SORTAV</i> ; Blessing, 1995)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.350, 0.495	0.40, 0.50
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	2288, 2288, 1694	11660, 1434, 1164
<i>R</i> <sub>int</sub>	–	0.070
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.756	0.650
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	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
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	1.85, -1.63	2.57, -2.00

Computer programs: *SMART* and *SAINT* (Bruker, 1999), *DENZO/SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS* and *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *ATOMS* (Dowty, 2005) and *publCIF* (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 Å<sup>3</sup> 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<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Chakir *et al.*, 2003) or KZr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Elbrahimi & Durand, 1990) as well as one KTP analogue, *viz.* RbZrOAsO<sub>4</sub> (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 Na<sub>2</sub>CO<sub>3</sub>, 0.581 g of ZrO<sub>2</sub> and 1.399 g of As<sub>2</sub>O<sub>5</sub> (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 (*T*<sub>melt</sub> ≈ 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<sup>-1</sup> 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 Na<sub>2</sub>CO<sub>3</sub>, 1.12 g HfO<sub>2</sub> and 1.57 g As<sub>2</sub>O<sub>5</sub> 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  $\sim 2 \text{ e } \text{Å}^{-3}$  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  $U_{\text{eq}}$  for Na4 is small, which might indicate partial occupancy of caesium on this site (*i.e.*, a formula of  $\text{Cs}_{1+x}\text{Na}_{10-x}\text{Hf}_4(\text{AsO}_4)_9$ , but attempts to model this were inconclusive.

### Acknowledgements

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## supporting information

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## Computing details

Data collection: *SMART* (Bruker, 1999) for (I); *DENZO/SCALEPACK* (Otwinowski & Minor, 1997) for (II). Cell refinement: *SAINTE* (Bruker, 1999) for (I); *DENZO/SCALEPACK* (Otwinowski & Minor, 1997) for (II). Data reduction: *SAINTE* (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 *pubCIF* (Westrip, 2010).

## Caesium decasodium tetrazirconium nonaarsenate (I)

## Crystal data

$\text{CsNa}_{10}\text{Zr}_4(\text{AsO}_4)_9$   
 $M_r = 1977.97$   
 Trigonal,  $R\bar{3}c:H$   
 $a = 9.2218$  (5) Å  
 $c = 76.982$  (5) Å  
 $V = 5669.6$  (7) Å<sup>3</sup>  
 $Z = 6$   
 $F(000) = 5460$

$D_x = 3.476$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 2999 reflections  
 $\theta = 2.6$ – $30.8^\circ$   
 $\mu = 10.07$  mm<sup>-1</sup>  
 $T = 293$  K  
 Prism, colourless  
 $0.10 \times 0.10 \times 0.10$  mm

## Data collection

Bruker SMART CCD  
 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 1999)  
 $T_{\min} = 0.350$ ,  $T_{\max} = 0.495$   
 2288 measured reflections

2288 independent reflections  
 1694 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 32.5^\circ$ ,  $\theta_{\min} = 2.6^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -13 \rightarrow 13$   
 $l = 0 \rightarrow 114$

## 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0452P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.85$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.63$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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)	0.3445 (5)	0.02328 (5)	0.0217 (8)	
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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cs1	0.0436 (4)	0.0436 (4)	0.0271 (4)	0.02182 (18)	0.000	0.000
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)	0.000	0.000
Na4	0.015 (3)	0.015 (3)	0.034 (5)	0.0074 (14)	0.000	0.000
Zr1	0.0109 (2)	0.0109 (2)	0.0153 (3)	0.00546 (10)	0.000	0.000
Zr2	0.0109 (2)	0.0109 (2)	0.0144 (3)	0.00543 (10)	0.000	0.000
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, °)

Cs1—O1 <sup>i</sup>	3.235 (4)	Na4—O6A <sup>vi</sup>	2.694 (17)
Cs1—O1 <sup>ii</sup>	3.235 (4)	Na4—O6A <sup>xii</sup>	2.694 (17)
Cs1—O1 <sup>iii</sup>	3.235 (4)	Zr1—O5	2.041 (3)
Cs1—O1	3.235 (4)	Zr1—O5 <sup>xiii</sup>	2.041 (3)
Cs1—O1 <sup>iv</sup>	3.235 (4)	Zr1—O5 <sup>ix</sup>	2.041 (3)
Cs1—O1 <sup>v</sup>	3.235 (4)	Zr1—O3 <sup>ix</sup>	2.099 (3)
Na1—O6B <sup>vi</sup>	2.193 (9)	Zr1—O3 <sup>xiii</sup>	2.099 (3)
Na1—O3 <sup>vii</sup>	2.394 (5)	Zr1—O3	2.099 (3)
Na1—O1 <sup>v</sup>	2.482 (5)	Zr2—O2 <sup>xiii</sup>	2.062 (4)
Na1—O6A <sup>vi</sup>	2.485 (16)	Zr2—O2 <sup>ix</sup>	2.062 (4)
Na1—O4	2.582 (5)	Zr2—O2	2.062 (4)
Na1—O1	2.632 (5)	Zr2—O4 <sup>xiv</sup>	2.081 (3)
Na2—O6A	2.185 (10)	Zr2—O4 <sup>iv</sup>	2.081 (3)
Na2—O6A <sup>vi</sup>	2.185 (10)	Zr2—O4 <sup>xv</sup>	2.081 (3)
Na2—O6B	2.361 (12)	As1—O1	1.647 (4)
Na2—O6B <sup>vi</sup>	2.361 (12)	As1—O2	1.673 (4)
Na2—O5 <sup>viii</sup>	2.495 (5)	As1—O4	1.691 (3)
Na2—O5 <sup>ix</sup>	2.495 (5)	As1—O3	1.694 (4)
Na3—O1 <sup>ii</sup>	2.463 (5)	As2—O6A	1.538 (10)
Na3—O1	2.463 (5)	As2—O6A <sup>xii</sup>	1.538 (10)
Na3—O1 <sup>v</sup>	2.463 (5)	As2—O5 <sup>xii</sup>	1.686 (4)
Na3—O6B <sup>viii</sup>	2.47 (2)	As2—O5	1.686 (4)
Na3—O6B <sup>x</sup>	2.47 (2)	As2—O6B	1.786 (13)
Na3—O6B <sup>vi</sup>	2.47 (2)	As2—O6B <sup>xii</sup>	1.786 (13)
Na4—O6A <sup>xi</sup>	2.694 (17)	O6A—O6B	0.909 (13)
O1 <sup>i</sup> —Cs1—O1 <sup>ii</sup>	180.0 (3)	O5 <sup>xiii</sup> —Zr1—O3 <sup>ix</sup>	87.67 (16)
O1 <sup>i</sup> —Cs1—O1 <sup>iii</sup>	62.30 (10)	O5 <sup>ix</sup> —Zr1—O3 <sup>ix</sup>	91.79 (15)
O1 <sup>ii</sup> —Cs1—O1 <sup>iii</sup>	117.70 (10)	O5—Zr1—O3 <sup>xiii</sup>	87.66 (16)
O1 <sup>i</sup> —Cs1—O1	117.70 (10)	O5 <sup>xiii</sup> —Zr1—O3 <sup>xiii</sup>	91.79 (15)
O1 <sup>ii</sup> —Cs1—O1	62.30 (10)	O5 <sup>ix</sup> —Zr1—O3 <sup>xiii</sup>	176.01 (15)
O1 <sup>iii</sup> —Cs1—O1	180.00 (9)	O3 <sup>ix</sup> —Zr1—O3 <sup>xiii</sup>	88.35 (14)
O1 <sup>i</sup> —Cs1—O1 <sup>iv</sup>	62.30 (10)	O5—Zr1—O3	91.79 (15)
O1 <sup>ii</sup> —Cs1—O1 <sup>iv</sup>	117.70 (10)	O5 <sup>xiii</sup> —Zr1—O3	176.01 (15)
O1 <sup>iii</sup> —Cs1—O1 <sup>iv</sup>	62.30 (10)	O5 <sup>ix</sup> —Zr1—O3	87.67 (16)
O1—Cs1—O1 <sup>iv</sup>	117.70 (10)	O3 <sup>ix</sup> —Zr1—O3	88.35 (14)
O1 <sup>i</sup> —Cs1—O1 <sup>v</sup>	117.70 (10)	O3 <sup>xiii</sup> —Zr1—O3	88.35 (14)
O1 <sup>ii</sup> —Cs1—O1 <sup>v</sup>	62.30 (10)	O2 <sup>xiii</sup> —Zr2—O2 <sup>ix</sup>	93.66 (15)
O1 <sup>iii</sup> —Cs1—O1 <sup>v</sup>	117.70 (10)	O2 <sup>xiii</sup> —Zr2—O2	93.66 (15)
O1—Cs1—O1 <sup>v</sup>	62.30 (10)	O2 <sup>ix</sup> —Zr2—O2	93.66 (15)
O1 <sup>iv</sup> —Cs1—O1 <sup>v</sup>	180.00 (16)	O2 <sup>xiii</sup> —Zr2—O4 <sup>xiv</sup>	92.00 (16)
O6B <sup>vi</sup> —Na1—O3 <sup>vii</sup>	104.6 (4)	O2 <sup>ix</sup> —Zr2—O4 <sup>xiv</sup>	88.01 (15)
O6B <sup>vi</sup> —Na1—O1 <sup>v</sup>	93.4 (5)	O2—Zr2—O4 <sup>xiv</sup>	173.98 (15)
O3 <sup>vii</sup> —Na1—O1 <sup>v</sup>	87.41 (15)	O2 <sup>xiii</sup> —Zr2—O4 <sup>iv</sup>	173.98 (15)
O6B <sup>vi</sup> —Na1—O6A <sup>vi</sup>	21.3 (3)	O2 <sup>ix</sup> —Zr2—O4 <sup>iv</sup>	92.00 (16)
O3 <sup>vii</sup> —Na1—O6A <sup>vi</sup>	90.3 (4)	O2—Zr2—O4 <sup>iv</sup>	88.01 (15)



O1 <sup>v</sup> —Na1—O6A <sup>vi</sup>	108.7 (4)	O4 <sup>xiv</sup> —Zr2—O4 <sup>iv</sup>	86.15 (14)
O6B <sup>vi</sup> —Na1—O4	118.5 (3)	O2 <sup>xiii</sup> —Zr2—O4 <sup>xv</sup>	88.01 (15)
O3 <sup>vii</sup> —Na1—O4	119.01 (18)	O2 <sup>ix</sup> —Zr2—O4 <sup>xv</sup>	173.98 (15)
O1 <sup>v</sup> —Na1—O4	127.39 (17)	O2—Zr2—O4 <sup>xv</sup>	92.01 (16)
O6A <sup>vi</sup> —Na1—O4	115.1 (3)	O4 <sup>xiv</sup> —Zr2—O4 <sup>xv</sup>	86.15 (14)
O6B <sup>vi</sup> —Na1—O1	85.3 (5)	O4 <sup>iv</sup> —Zr2—O4 <sup>xv</sup>	86.15 (14)
O3 <sup>vii</sup> —Na1—O1	165.74 (19)	O1—As1—O2	111.5 (2)
O1 <sup>v</sup> —Na1—O1	81.68 (19)	O1—As1—O4	108.17 (19)
O6A <sup>vi</sup> —Na1—O1	101.8 (5)	O2—As1—O4	109.94 (19)
O4—Na1—O1	62.47 (13)	O1—As1—O3	114.88 (19)
O6B <sup>vi</sup> —Na1—O4 <sup>vii</sup>	132.4 (6)	O2—As1—O3	108.98 (18)
O3 <sup>vii</sup> —Na1—O4 <sup>vii</sup>	58.02 (13)	O4—As1—O3	103.03 (18)
O1 <sup>v</sup> —Na1—O4 <sup>vii</sup>	125.80 (15)	O6A—As2—O6A <sup>xii</sup>	78.4 (18)
O6A <sup>vi</sup> —Na1—O4 <sup>vii</sup>	111.4 (6)	O6A—As2—O5 <sup>xii</sup>	112.1 (4)
O4—Na1—O4 <sup>vii</sup>	61.11 (16)	O6A <sup>xii</sup> —As2—O5 <sup>xii</sup>	125.4 (7)
O1—Na1—O4 <sup>vii</sup>	122.35 (15)	O6A—As2—O5	125.4 (7)
O6A—Na2—O6A <sup>vi</sup>	140.7 (13)	O6A <sup>xii</sup> —As2—O5	112.1 (4)
O6A—Na2—O6B	22.7 (4)	O5 <sup>xii</sup> —As2—O5	103.8 (3)
O6A <sup>vi</sup> —Na2—O6B	161.0 (11)	O6A—As2—O6B	30.6 (6)
O6A—Na2—O6B <sup>vi</sup>	161.0 (11)	O6A <sup>xii</sup> —As2—O6B	106.8 (15)
O6A <sup>vi</sup> —Na2—O6B <sup>vi</sup>	22.7 (4)	O5 <sup>xii</sup> —As2—O6B	103.3 (4)
O6B—Na2—O6B <sup>vi</sup>	176.2 (9)	O5—As2—O6B	103.1 (5)
O6A—Na2—O5 <sup>viii</sup>	118.7 (7)	O6A—As2—O6B <sup>xii</sup>	106.8 (15)
O6A <sup>vi</sup> —Na2—O5 <sup>viii</sup>	95.2 (5)	O6A <sup>xii</sup> —As2—O6B <sup>xii</sup>	30.6 (6)
O6B—Na2—O5 <sup>viii</sup>	96.8 (5)	O5 <sup>xii</sup> —As2—O6B <sup>xii</sup>	103.0 (5)
O6B <sup>vi</sup> —Na2—O5 <sup>viii</sup>	79.9 (4)	O5—As2—O6B <sup>xii</sup>	103.2 (4)
O6A—Na2—O5 <sup>ix</sup>	95.2 (5)	O6B—As2—O6B <sup>xii</sup>	136.7 (12)
O6A <sup>vi</sup> —Na2—O5 <sup>ix</sup>	118.7 (7)	As1—O1—Na3	157.7 (2)
O6B—Na2—O5 <sup>ix</sup>	79.9 (4)	As1—O1—Na1 <sup>ii</sup>	117.0 (2)
O6B <sup>vi</sup> —Na2—O5 <sup>ix</sup>	96.8 (5)	Na3—O1—Na1 <sup>ii</sup>	74.73 (13)
O5 <sup>viii</sup> —Na2—O5 <sup>ix</sup>	64.2 (2)	As1—O1—Na1	93.24 (18)
O6A—Na2—O6A <sup>vii</sup>	113.6 (6)	Na3—O1—Na1	72.10 (12)
O6A <sup>vi</sup> —Na2—O6A <sup>vii</sup>	40.3 (6)	Na1 <sup>ii</sup> —O1—Na1	146.6 (2)
O6B—Na2—O6A <sup>vii</sup>	124.1 (3)	As1—O1—Cs1	105.65 (17)
O6B <sup>vi</sup> —Na2—O6A <sup>vii</sup>	58.3 (4)	Na3—O1—Cs1	91.66 (16)
O5 <sup>viii</sup> —Na2—O6A <sup>vii</sup>	92.7 (2)	Na1 <sup>ii</sup> —O1—Cs1	93.89 (14)
O5 <sup>ix</sup> —Na2—O6A <sup>vii</sup>	149.8 (3)	Na1—O1—Cs1	91.09 (13)
O6A—Na2—O6A <sup>xii</sup>	40.3 (6)	As1—O2—Zr2	148.2 (2)
O6A <sup>vi</sup> —Na2—O6A <sup>xii</sup>	113.6 (6)	As1—O3—Zr1	130.8 (2)
O6B—Na2—O6A <sup>xii</sup>	58.3 (5)	As1—O3—Na1 <sup>xvi</sup>	108.79 (18)
O6B <sup>vi</sup> —Na2—O6A <sup>xii</sup>	124.1 (3)	Zr1—O3—Na1 <sup>xvi</sup>	120.42 (18)
O5 <sup>viii</sup> —Na2—O6A <sup>xii</sup>	149.8 (2)	As1—O4—Zr2 <sup>xv</sup>	148.4 (2)
O5 <sup>ix</sup> —Na2—O6A <sup>xii</sup>	92.7 (2)	As1—O4—Na1	93.97 (17)
O6A <sup>vii</sup> —Na2—O6A <sup>xii</sup>	114.9 (5)	Zr2 <sup>xv</sup> —O4—Na1	109.81 (17)
O1 <sup>ii</sup> —Na3—O1	85.6 (2)	As1—O4—Na1 <sup>xvi</sup>	87.30 (16)
O1 <sup>ii</sup> —Na3—O1 <sup>v</sup>	85.6 (2)	Zr2 <sup>xv</sup> —O4—Na1 <sup>xvi</sup>	96.88 (15)
O1—Na3—O1 <sup>v</sup>	85.6 (2)	Na1—O4—Na1 <sup>xvi</sup>	121.76 (18)
O1 <sup>ii</sup> —Na3—O6B <sup>viii</sup>	83.5 (2)	As2—O5—Zr1	138.4 (2)

O1—Na3—O6B <sup>viii</sup>	87.5 (2)	As2—O5—Na2 <sup>xiii</sup>	95.98 (16)
O1 <sup>v</sup> —Na3—O6B <sup>viii</sup>	167.5 (3)	Zr1—O5—Na2 <sup>xiii</sup>	124.11 (18)
O1 <sup>ii</sup> —Na3—O6B <sup>x</sup>	87.5 (2)	As2—O6A—Na2	118.8 (6)
O1—Na3—O6B <sup>x</sup>	167.5 (3)	As2—O6A—Na1 <sup>vi</sup>	116.7 (8)
O1 <sup>v</sup> —Na3—O6B <sup>x</sup>	83.5 (2)	Na2—O6A—Na1 <sup>vi</sup>	115.9 (6)
O6B <sup>viii</sup> —Na3—O6B <sup>x</sup>	102.1 (3)	As2—O6A—Na4 <sup>xi</sup>	147.0 (14)
O1 <sup>ii</sup> —Na3—O6B <sup>vi</sup>	167.5 (3)	Na2—O6A—Na4 <sup>xi</sup>	75.0 (4)
O1—Na3—O6B <sup>vi</sup>	83.5 (2)	Na1 <sup>vi</sup> —O6A—Na4 <sup>xi</sup>	75.8 (3)
O1 <sup>v</sup> —Na3—O6B <sup>vi</sup>	87.5 (2)	As2—O6A—Na2 <sup>xvi</sup>	83.8 (9)
O6B <sup>viii</sup> —Na3—O6B <sup>vi</sup>	102.1 (3)	Na2—O6A—Na2 <sup>xvi</sup>	106.0 (9)
O6B <sup>x</sup> —Na3—O6B <sup>vi</sup>	102.1 (3)	Na1 <sup>vi</sup> —O6A—Na2 <sup>xvi</sup>	109.3 (5)
O6A <sup>xi</sup> —Na4—O6A <sup>vi</sup>	108.1 (5)	Na4 <sup>xi</sup> —O6A—Na2 <sup>xvi</sup>	63.2 (5)
O6A <sup>xi</sup> —Na4—O6A <sup>xii</sup>	108.1 (5)	As2—O6B—Na1 <sup>vi</sup>	120.5 (5)
O6A <sup>vi</sup> —Na4—O6A <sup>xii</sup>	108.1 (5)	As2—O6B—Na2	101.0 (7)
O5—Zr1—O5 <sup>xiii</sup>	92.21 (16)	Na1 <sup>vi</sup> —O6B—Na2	120.8 (4)
O5—Zr1—O5 <sup>ix</sup>	92.21 (16)	As2—O6B—Na3 <sup>xvii</sup>	116.8 (7)
O5 <sup>xiii</sup> —Zr1—O5 <sup>ix</sup>	92.20 (16)	Na1 <sup>vi</sup> —O6B—Na3 <sup>xvii</sup>	79.9 (6)
O5—Zr1—O3 <sup>ix</sup>	176.01 (15)	Na2—O6B—Na3 <sup>xvii</sup>	118.3 (6)

Symmetry codes: (i)  $y, -x+y, -z$ ; (ii)  $-y, x-y, z$ ; (iii)  $-x, -y, -z$ ; (iv)  $x-y, x, -z$ ; (v)  $-x+y, -x, z$ ; (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)  $y+1/3, x-1/3, -z+1/6$ ; (xii)  $-x+4/3, -x+y+2/3, -z+1/6$ ; (xiii)  $-y+1, x-y+1, z$ ; (xiv)  $y, -x+y+1, -z$ ; (xv)  $-x+1, -y+1, -z$ ; (xvi)  $-x+y+1, -x+1, z$ ; (xvii)  $y+1/3, x+2/3, -z+1/6$ .

## Caesium decasodium tetrahafnium nonarsenate (II)

### Crystal data

CsNa<sub>10</sub>Hf<sub>4</sub>(AsO<sub>4</sub>)<sub>9</sub>

$M_r = 2327.05$

Trigonal,  $R\bar{3}c:H$

$a = 9.1795$  (2) Å

$c = 76.527$  (8) Å

$V = 5584.5$  (6) Å<sup>3</sup>

$Z = 6$

$F(000) = 6228$

$D_x = 4.152$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 22894 reflections

$\theta = 2.9$ – $27.5^\circ$

$\mu = 20.25$  mm<sup>-1</sup>

$T = 120$  K

Prism, colourless

$0.08 \times 0.08 \times 0.08$  mm

### Data collection

Nonius KappaCCD

diffractometer

$\omega$  scans

Absorption correction: multi-scan  
(SORTAV; Blessing, 1995)

$T_{\min} = 0.40$ ,  $T_{\max} = 0.50$

11660 measured reflections

1434 independent reflections

1164 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.070$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.2^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -99 \rightarrow 99$

### 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

Primary atom site location: structure-invariant  
direct methods

$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 136.7342P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 2.57$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -2.00$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cs1	0.000000	0.000000	0.000000	0.0162 (3)	
Na1	0.3354 (5)	0.0688 (5)	0.04043 (5)	0.0256 (11)	0.887 (7)
Na2	0.4061 (6)	0.333333	0.083333	0.0208 (15)*	0.846 (11)
Na3	0.000000	0.000000	0.05288 (11)	0.018 (2)	0.735 (16)
Na4	0.666667	0.333333	0.06123 (16)	0.002 (4)*	0.337 (14)
Hf1	0.333333	0.666667	0.05673 (2)	0.00710 (15)	
Hf2	0.333333	0.666667	-0.00682 (2)	0.00611 (15)	
As1	0.34520 (9)	0.39770 (9)	0.02639 (2)	0.00578 (18)	
As2	0.666667	0.73244 (13)	0.083333	0.0205 (3)	
O1	0.1730 (6)	0.2332 (6)	0.03369 (6)	0.0113 (11)	
O2	0.3086 (6)	0.4663 (6)	0.00745 (6)	0.0109 (11)	
O3	0.4389 (6)	0.5622 (6)	0.04043 (6)	0.0068 (10)	
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)	0.0942 (2)	0.008 (2)	0.35 (2)
O6B	0.5276 (16)	0.5861 (12)	0.09848 (14)	0.029 (4)	0.65 (2)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cs1	0.0181 (4)	0.0181 (4)	0.0125 (5)	0.0091 (2)	0.000	0.000
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)	0.000	0.000
Hf1	0.00580 (19)	0.00580 (19)	0.0097 (3)	0.00290 (9)	0.000	0.000
Hf2	0.00499 (19)	0.00499 (19)	0.0084 (3)	0.00250 (9)	0.000	0.000
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 ( $\text{\AA}$ ,  $^\circ$ )*

Cs1—O1	3.218 (5)	Na4—O6A <sup>vi</sup>	2.654 (18)
Cs1—O1 <sup>i</sup>	3.218 (5)	Na4—O6A <sup>xii</sup>	2.654 (18)

Cs1—O1 <sup>ii</sup>	3.218 (5)	Hf1—O5 <sup>xiii</sup>	2.039 (5)
Cs1—O1 <sup>iii</sup>	3.218 (5)	Hf1—O5 <sup>ix</sup>	2.039 (5)
Cs1—O1 <sup>iv</sup>	3.218 (5)	Hf1—O5	2.039 (5)
Cs1—O1 <sup>v</sup>	3.218 (5)	Hf1—O3 <sup>ix</sup>	2.084 (4)
Na1—O6B <sup>vi</sup>	2.212 (10)	Hf1—O3 <sup>xiii</sup>	2.084 (4)
Na1—O3 <sup>vii</sup>	2.377 (6)	Hf1—O3	2.084 (4)
Na1—O1 <sup>iii</sup>	2.443 (6)	Hf2—O2	2.051 (5)
Na1—O6A <sup>vi</sup>	2.467 (17)	Hf2—O2 <sup>ix</sup>	2.052 (5)
Na1—O4	2.524 (6)	Hf2—O2 <sup>xiii</sup>	2.052 (5)
Na1—O1	2.649 (6)	Hf2—O4 <sup>xiv</sup>	2.077 (5)
Na1—O4 <sup>vii</sup>	2.972 (6)	Hf2—O4 <sup>ii</sup>	2.077 (5)
Na2—O6A	2.170 (16)	Hf2—O4 <sup>xv</sup>	2.077 (5)
Na2—O6A <sup>vi</sup>	2.170 (16)	As1—O1	1.644 (5)
Na2—O6B	2.320 (10)	As1—O2	1.680 (5)
Na2—O6B <sup>vi</sup>	2.320 (10)	As1—O4	1.689 (5)
Na2—O5 <sup>viii</sup>	2.458 (7)	As1—O3	1.696 (4)
Na2—O5 <sup>ix</sup>	2.458 (7)	As2—O6A	1.552 (15)
Na3—O1 <sup>v</sup>	2.421 (7)	As2—O6A <sup>xi</sup>	1.552 (15)
Na3—O1 <sup>iii</sup>	2.421 (7)	As2—O5	1.684 (5)
Na3—O1	2.421 (7)	As2—O5 <sup>xi</sup>	1.684 (5)
Na3—O6B <sup>viii</sup>	2.534 (17)	As2—O6B	1.750 (11)
Na3—O6B <sup>x</sup>	2.534 (17)	As2—O6B <sup>xi</sup>	1.750 (11)
Na3—O6B <sup>vi</sup>	2.534 (17)	O6A—O6B	0.842 (15)
Na4—O6A <sup>xi</sup>	2.654 (18)		
O1—Cs1—O1 <sup>i</sup>	180.00 (19)	O5 <sup>ix</sup> —Hf1—O3	87.7 (2)
O1—Cs1—O1 <sup>ii</sup>	117.59 (14)	O5—Hf1—O3	92.3 (2)
O1 <sup>i</sup> —Cs1—O1 <sup>ii</sup>	62.41 (14)	O3 <sup>ix</sup> —Hf1—O3	87.88 (18)
O1—Cs1—O1 <sup>iii</sup>	62.41 (14)	O3 <sup>xiii</sup> —Hf1—O3	87.88 (18)
O1 <sup>i</sup> —Cs1—O1 <sup>iii</sup>	117.59 (14)	O2—Hf2—O2 <sup>ix</sup>	94.29 (18)
O1 <sup>ii</sup> —Cs1—O1 <sup>iii</sup>	180.00 (19)	O2—Hf2—O2 <sup>xiii</sup>	94.29 (18)
O1—Cs1—O1 <sup>iv</sup>	117.59 (14)	O2 <sup>ix</sup> —Hf2—O2 <sup>xiii</sup>	94.28 (18)
O1 <sup>i</sup> —Cs1—O1 <sup>iv</sup>	62.41 (14)	O2—Hf2—O4 <sup>xiv</sup>	92.38 (19)
O1 <sup>ii</sup> —Cs1—O1 <sup>iv</sup>	62.41 (14)	O2 <sup>ix</sup> —Hf2—O4 <sup>xiv</sup>	173.05 (19)
O1 <sup>iii</sup> —Cs1—O1 <sup>iv</sup>	117.59 (14)	O2 <sup>xiii</sup> —Hf2—O4 <sup>xiv</sup>	87.19 (19)
O1—Cs1—O1 <sup>v</sup>	62.41 (14)	O2—Hf2—O4 <sup>ii</sup>	87.18 (19)
O1 <sup>i</sup> —Cs1—O1 <sup>v</sup>	117.59 (14)	O2 <sup>ix</sup> —Hf2—O4 <sup>ii</sup>	92.38 (19)
O1 <sup>ii</sup> —Cs1—O1 <sup>v</sup>	117.59 (14)	O2 <sup>xiii</sup> —Hf2—O4 <sup>ii</sup>	173.05 (19)
O1 <sup>iii</sup> —Cs1—O1 <sup>v</sup>	62.41 (14)	O4 <sup>xiv</sup> —Hf2—O4 <sup>ii</sup>	85.96 (19)
O1 <sup>iv</sup> —Cs1—O1 <sup>v</sup>	180.0 (3)	O2—Hf2—O4 <sup>xv</sup>	173.04 (19)
O6B <sup>vi</sup> —Na1—O3 <sup>vii</sup>	103.8 (4)	O2 <sup>ix</sup> —Hf2—O4 <sup>xv</sup>	87.18 (19)
O6B <sup>vi</sup> —Na1—O1 <sup>iii</sup>	94.4 (4)	O2 <sup>xiii</sup> —Hf2—O4 <sup>xv</sup>	92.38 (19)
O3 <sup>vii</sup> —Na1—O1 <sup>iii</sup>	86.5 (2)	O4 <sup>xiv</sup> —Hf2—O4 <sup>xv</sup>	85.96 (19)
O6B <sup>vi</sup> —Na1—O6A <sup>vi</sup>	19.8 (4)	O4 <sup>ii</sup> —Hf2—O4 <sup>xv</sup>	85.96 (19)
O3 <sup>vii</sup> —Na1—O6A <sup>vi</sup>	90.7 (5)	O1—As1—O2	110.9 (3)
O1 <sup>iii</sup> —Na1—O6A <sup>vi</sup>	108.7 (5)	O1—As1—O4	108.0 (2)
O6B <sup>vi</sup> —Na1—O4	118.4 (3)	O2—As1—O4	110.3 (2)
O3 <sup>vii</sup> —Na1—O4	119.4 (2)	O1—As1—O3	115.4 (2)

O1 <sup>iii</sup> —Na1—O4	127.6 (2)	O2—As1—O3	108.7 (2)
O6A <sup>vi</sup> —Na1—O4	115.0 (4)	O4—As1—O3	103.3 (2)
O6B <sup>vi</sup> —Na1—O1	86.1 (4)	O6A—As2—O6A <sup>xi</sup>	78.0 (15)
O3 <sup>vii</sup> —Na1—O1	165.2 (2)	O6A—As2—O5	125.7 (7)
O1 <sup>iii</sup> —Na1—O1	81.7 (2)	O6A <sup>xi</sup> —As2—O5	112.6 (6)
O6A <sup>vi</sup> —Na1—O1	101.5 (5)	O6A—As2—O5 <sup>xi</sup>	112.6 (6)
O4—Na1—O1	62.78 (17)	O6A <sup>xi</sup> —As2—O5 <sup>xi</sup>	125.7 (7)
O6B <sup>vi</sup> —Na1—O4 <sup>vii</sup>	130.4 (5)	O5—As2—O5 <sup>xi</sup>	103.0 (3)
O3 <sup>vii</sup> —Na1—O4 <sup>vii</sup>	58.22 (16)	O6A—As2—O6B	28.8 (6)
O1 <sup>iii</sup> —Na1—O4 <sup>vii</sup>	126.1 (2)	O6A <sup>xi</sup> —As2—O6B	104.5 (12)
O6A <sup>vi</sup> —Na1—O4 <sup>vii</sup>	110.9 (5)	O5—As2—O6B	104.3 (5)
O4—Na1—O4 <sup>vii</sup>	61.4 (2)	O5 <sup>xi</sup> —As2—O6B	104.8 (4)
O1—Na1—O4 <sup>vii</sup>	123.09 (19)	O6A—As2—O6B <sup>xi</sup>	104.5 (12)
O6A—Na2—O6A <sup>vi</sup>	141.3 (12)	O6A <sup>xi</sup> —As2—O6B <sup>xi</sup>	28.8 (6)
O6A—Na2—O6B	21.3 (4)	O5—As2—O6B <sup>xi</sup>	104.8 (4)
O6A <sup>vi</sup> —Na2—O6B	160.8 (9)	O5 <sup>xi</sup> —As2—O6B <sup>xi</sup>	104.3 (5)
O6A—Na2—O6B <sup>vi</sup>	160.8 (9)	O6B—As2—O6B <sup>xi</sup>	132.5 (10)
O6A <sup>vi</sup> —Na2—O6B <sup>vi</sup>	21.3 (4)	As1—O1—Na3	157.3 (3)
O6B—Na2—O6B <sup>vi</sup>	177.8 (8)	As1—O1—Na1 <sup>v</sup>	118.2 (3)
O6A—Na2—O5 <sup>viii</sup>	118.4 (6)	Na3—O1—Na1 <sup>v</sup>	75.36 (17)
O6A <sup>vi</sup> —Na2—O5 <sup>viii</sup>	94.8 (5)	As1—O1—Na1	91.9 (2)
O6B—Na2—O5 <sup>viii</sup>	97.9 (4)	Na3—O1—Na1	71.66 (16)
O6B <sup>vi</sup> —Na2—O5 <sup>viii</sup>	80.2 (3)	Na1 <sup>v</sup> —O1—Na1	146.7 (3)
O6A—Na2—O5 <sup>ix</sup>	94.8 (5)	As1—O1—Cs1	105.5 (2)
O6A <sup>vi</sup> —Na2—O5 <sup>ix</sup>	118.4 (6)	Na3—O1—Cs1	90.6 (2)
O6B—Na2—O5 <sup>ix</sup>	80.2 (3)	Na1 <sup>v</sup> —O1—Cs1	94.33 (17)
O6B <sup>vi</sup> —Na2—O5 <sup>ix</sup>	97.9 (4)	Na1—O1—Cs1	90.47 (16)
O5 <sup>viii</sup> —Na2—O5 <sup>ix</sup>	64.8 (3)	As1—O2—Hf2	147.4 (3)
O1 <sup>v</sup> —Na3—O1 <sup>iii</sup>	87.0 (3)	As1—O3—Hf1	130.0 (3)
O1 <sup>v</sup> —Na3—O1	87.0 (3)	As1—O3—Na1 <sup>xvi</sup>	108.8 (2)
O1 <sup>iii</sup> —Na3—O1	87.0 (3)	Hf1—O3—Na1 <sup>xvi</sup>	121.1 (2)
O1 <sup>v</sup> —Na3—O6B <sup>viii</sup>	84.6 (2)	As1—O4—Hf2 <sup>xiv</sup>	146.9 (3)
O1 <sup>iii</sup> —Na3—O6B <sup>viii</sup>	170.0 (4)	As1—O4—Na1	95.3 (2)
O1—Na3—O6B <sup>viii</sup>	87.2 (2)	Hf2 <sup>xiv</sup> —O4—Na1	110.6 (2)
O1 <sup>v</sup> —Na3—O6B <sup>x</sup>	87.2 (2)	As1—O4—Na1 <sup>xvi</sup>	86.8 (2)
O1 <sup>iii</sup> —Na3—O6B <sup>x</sup>	84.5 (2)	Hf2 <sup>xiv</sup> —O4—Na1 <sup>xvi</sup>	95.70 (19)
O1—Na3—O6B <sup>x</sup>	170.0 (4)	Na1—O4—Na1 <sup>xvi</sup>	122.6 (2)
O6B <sup>viii</sup> —Na3—O6B <sup>x</sup>	100.3 (3)	As2—O5—Hf1	137.1 (3)
O1 <sup>v</sup> —Na3—O6B <sup>vi</sup>	170.0 (4)	As2—O5—Na2 <sup>xiii</sup>	96.1 (2)
O1 <sup>iii</sup> —Na3—O6B <sup>vi</sup>	87.2 (2)	Hf1—O5—Na2 <sup>xiii</sup>	125.3 (2)
O1—Na3—O6B <sup>vi</sup>	84.6 (2)	As2—O6A—Na2	119.0 (8)
O6B <sup>viii</sup> —Na3—O6B <sup>vi</sup>	100.3 (3)	As2—O6A—Na1 <sup>vi</sup>	116.5 (9)
O6B <sup>x</sup> —Na3—O6B <sup>vi</sup>	100.3 (3)	Na2—O6A—Na1 <sup>vi</sup>	116.2 (7)
O6A <sup>xi</sup> —Na4—O6A <sup>vi</sup>	110.0 (4)	As2—O6A—Na4 <sup>xii</sup>	146.0 (12)
O6A <sup>xi</sup> —Na4—O6A <sup>xii</sup>	110.0 (4)	Na2—O6A—Na4 <sup>xii</sup>	74.0 (5)
O6A <sup>vi</sup> —Na4—O6A <sup>xii</sup>	110.0 (4)	Na1 <sup>vi</sup> —O6A—Na4 <sup>xii</sup>	77.5 (5)
O5 <sup>xiii</sup> —Hf1—O5 <sup>ix</sup>	92.17 (19)	As2—O6A—Na2 <sup>xvi</sup>	83.9 (8)
O5 <sup>xiii</sup> —Hf1—O5	92.17 (19)	Na2—O6A—Na2 <sup>xvi</sup>	105.6 (8)



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>ix</sup>	87.7 (2)	Na4 <sup>xii</sup> —O6A—Na2 <sup>xvi</sup>	62.2 (5)
O5 <sup>ix</sup> —Hf1—O3 <sup>ix</sup>	92.3 (2)	As2—O6B—Na1 <sup>vi</sup>	120.8 (5)
O5—Hf1—O3 <sup>ix</sup>	175.57 (19)	As2—O6B—Na2	103.8 (6)
O5 <sup>xiii</sup> —Hf1—O3 <sup>xiii</sup>	92.3 (2)	Na1 <sup>vi</sup> —O6B—Na2	120.7 (4)
O5 <sup>ix</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>ix</sup> —Hf1—O3 <sup>xiii</sup>	87.89 (18)	Na2—O6B—Na3 <sup>xvii</sup>	117.8 (5)
O5 <sup>xiii</sup> —Hf1—O3	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)  $y, -x+y+1, -z$ ; (xvi)  $-x+y+1, -x+1, z$ ; (xvii)  $y+1/3, x+2/3, -z+1/6$ .