

## A novel zirconium polyoxometalate compound: $(\text{NH}_4)_9[\text{Zr}_2(\mu\text{-OH})\text{-(H}_2\text{O)}_2(\text{AsOH})_2(\text{AsW}_7\text{O}_{28})\text{-(AsW}_{10}\text{O}_{36})]\cdot 26\text{H}_2\text{O}$

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The crystal structure of the title compound, nonaammonium (arsenic decatungstido)(arsenic heptatungstido)diaqua- $\mu$ -hydroxo-(hydroxyarsenido)dizirconium hexacosahydrate, which was obtained from the reaction of  $[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]^{27-}$  with  $\text{Zr}^{\text{IV}}$ , has been determined. The anionic complex consists of two hydroxyl-bridged seven-coordinate capped trigonal-prismatic zirconium ions, which are bonded to an  $[\text{AsW}_{10}\text{O}_{36}]^{9-}$  anion and to an  $[\text{AsW}_7\text{O}_{28}]^{11-}$  anion that has two  $\{\text{AsOH}\}^{2+}$  capping units. The asymmetric unit contains half of the complex, with one crystallographically independent Zr atom. Crystallographic  $m$  symmetry imposed by the monoclinic  $C2/m$  space group gives rise to the asymmetric unit comprising half of the complex with one crystallographically independent Zr atom.

### Comment

Polyoxometalates have been extensively studied because of their useful properties in fields as diverse as catalysis and medicine (Pope, 1983; Baker & Glick, 1998). Recently, there has been much interest in the use of polyoxometalates as potential sequestration/separation agents in nuclear waste remediation, with most attention focused on coordination to the  $f$ -elements (Williams *et al.*, 2000; Kamoshida *et al.*, 1998; Bion *et al.*, 1999; Gaunt *et al.*, 2002). Relatively little attention has been given to aspects of this chemistry with zirconium, which is another important element in some nuclear waste processes (Doucet *et al.*, 2002). In addition,  $\text{Zr}^{\text{IV}}$  can be used as a non-radioactive analogue for actinide ions, including  $\text{Pu}^{\text{IV}}$ . During our studies to increase the understanding of the interaction of  $\text{Zr}^{\text{IV}}$  with heteropolyanions, we obtained the title compound, (I).

The crystal structure of (I) has one symmetrically unique Zr atom, with the whole complex anion grown from the asymmetric unit by the operation  $(x, -y, z)$  (Figs. 1 and 2). The

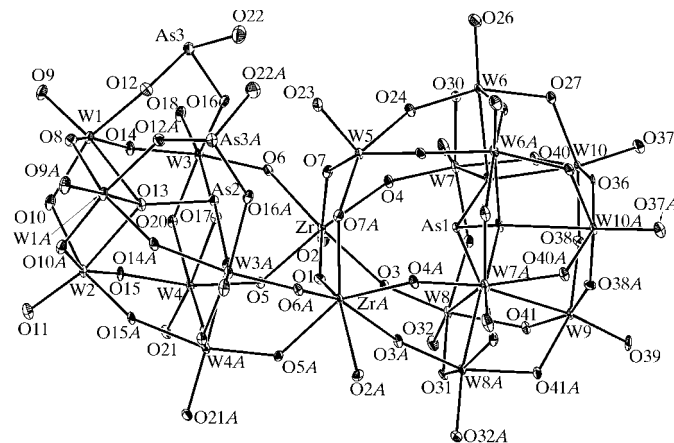


Figure 1

A view of the anion of (I). Displacement ellipsoids are shown at the 50% probability level. Atoms As1, As2, O1, O8, O11, O13, O19, O23, O25, O29, O31, O36, O39, W2, W5 and W9 lie on the mirror plane. Atoms marked with the suffix A are at the symmetry position  $(x, -y, z)$ .

reacting  $[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]^{27-}$  anion, itself composed of four linked  $[\text{AsW}_9\text{O}_{33}]^{9-}$  anions, has fragmented and the two units that coordinate to the  $\text{Zr}^{4+}$  ions are formally  $[\text{AsW}_{10}\text{O}_{36}]^{9-}$  and  $[\text{AsW}_7\text{O}_{28}]^{11-}$ . The  $\text{Zr}^{4+}$  ion is seven-coordinate, with an arrangement of O-donor ligands that conforms to capped trigonal-prismatic geometry. Five O atoms from the polyoxometalate fragments are bonded to Zr, with distances ranging from 2.093 (7) Å for  $\text{Zr}-\text{O}7$  to 2.136 (6) Å for  $\text{Zr}1-\text{O}4$  (Table 1). The Zr atoms are linked by a bridging hydroxyl group, with a  $\text{Zr}-\text{O}1$  distance of 2.151 (2) Å. The coordination sphere of Zr is completed by an O atom from a water molecule in the capping position of the trigonal prism, with a  $\text{Zr}-\text{O}2$  distance of 2.326 (6) Å. A bond-valence sum (BVS; Brown & Altermatt, 1985) of 1.095 was calculated for atom O1, which bridges the two Zr atoms, indicating an attached H atom, and thus O1 was assigned as an  $\text{OH}^-$  group. By comparison, a BVS of 0.341 was calculated for water atom O2. Upon coordination of Zr, the remaining unsaturated O atoms of the  $[\text{AsW}_7\text{O}_{28}]^{11-}$  anion are bonded to capping  $\{\text{AsOH}\}^{2+}$  groups. The assignment of the H atom was made based on the similarity of the As—O terminal bond length [ $\text{As}3-\text{O}22 = 1.769$  (8) Å] to the  $\text{As}3-\text{O}12$  bond [1.771 (7) Å], in which O12 is a  $\mu_2$ -O atom, and on the similarity in bond length to those in a previously reported polyoxometalate compound containing assigned  $\{\text{AsOH}\}^{2+}$  groups (Müller *et al.*, 1996). The

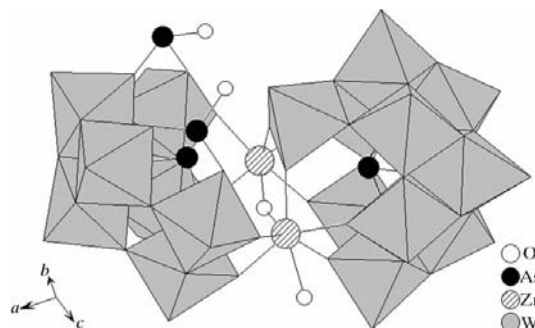


Figure 2

A polyhedral representation of the anion of (I).

[AsW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup> unit has the unusual structural feature, for a heteropolytungstate, of a five-coordinated W5 atom with distorted square-pyramidal geometry. This coordination probably arises because the lone pair of electrons on the As<sup>III</sup> atom occupy the space where an O atom would need to be in order for atom W5 to achieve an octahedral geometry.

## Experimental

Na<sub>27</sub>[NaAs<sub>4</sub>W<sub>40</sub>O<sub>140</sub>]·60H<sub>2</sub>O (2.00 g, 0.17 mmol; Klemperer, 1990) and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (0.224 g, 0.68 mmol) were successively suspended in H<sub>2</sub>O (100 ml). ZrCl<sub>4</sub> (0.158 g, 0.68 mmol) was added to the suspension, which was then heated at reflux for 1 h to yield a colourless solution. NH<sub>4</sub>Cl (11 g, 20.56 mmol) was dissolved in the hot solution, which was allowed to cool to room temperature and was then filtered under gravity and stored at 276 K. After three months, a few colourless prismatic crystals (<0.1 g) of (I) had grown from the solution. FT-IR (ATR): 945 (W=O), 878 (W-O-W), 1618 (H-O-H), 1417 cm<sup>-1</sup> (N-H).

### Crystal data

(NH <sub>4</sub> ) <sub>9</sub> [Zr <sub>2</sub> (OH)(H <sub>2</sub> O) <sub>2</sub> - (AsOH) <sub>2</sub> (AsW <sub>7</sub> O <sub>28</sub> )- (AsW <sub>10</sub> O <sub>36</sub> )]·26H <sub>2</sub> O	$Z = 4$
$M_r = 5349.42$	$D_x = 3.859 \text{ Mg m}^{-3}$
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 32.200 (4) \text{ \AA}$	Cell parameters from 5091 reflections
$b = 15.993 (2) \text{ \AA}$	$\theta = 2.4\text{--}28.3^\circ$
$c = 18.415 (2) \text{ \AA}$	$\mu = 23.05 \text{ mm}^{-1}$
$\beta = 105.228 (2)^\circ$	$T = 100 (0) \text{ K}$
$V = 9150 (2) \text{ \AA}^3$	Prism, colourless
	$0.31 \times 0.08 \times 0.03 \text{ mm}$

### Data collection

Bruker SMART Platform CCD diffractometer	10 914 independent reflections
$\omega$ scans	8830 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$R_{\text{int}} = 0.047$
$T_{\text{min}} = 0.126$ , $T_{\text{max}} = 0.501$	$\theta_{\text{max}} = 28.3^\circ$
39 187 measured reflections	$h = -42 \rightarrow 41$
	$k = -20 \rightarrow 20$
	$l = -24 \rightarrow 24$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 201.8467P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.03$	$\Delta\rho_{\text{max}} = 3.36 \text{ e \AA}^{-3}$
10 914 reflections	$\Delta\rho_{\text{min}} = -1.95 \text{ e \AA}^{-3}$
525 parameters	
H-atom parameters not refined	

All the Zr, W, As and O atoms of the anionic complex were refined with anisotropic displacement parameters. All solvent water O atoms and ammonium N atoms were refined isotropically. Data did not allow direct discrimination between O and N atoms, so in the later stages of refinement, the water O atoms with the highest displacement parameters were assigned as N atoms to account for the NH<sub>4</sub><sup>+</sup> cations, which balance the charge. The positions of the H atoms were

**Table 1**

Selected interatomic distances (Å).

As3—O12	1.772 (7)	Zr—O7	2.093 (7)
As3—O16	1.787 (6)	W1—O12	1.946 (7)
As3—O22	1.770 (8)	W3—O6	1.823 (6)
Zr—O1	2.150 (2)	W3—O16	1.952 (7)
Zr—O2	2.327 (6)	W4—O5	1.816 (6)
Zr—O3	2.130 (6)	W5—O7	1.807 (6)
Zr—O4	2.136 (6)	W7—O4	1.811 (6)
Zr—O5	2.107 (6)	W8—O3	1.801 (6)
Zr—O6	2.123 (6)		

not determined. The locations of the highest peak and deepest hole in the final residual electron-density map were 0.79 and 0.62 Å, respectively, from W1.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSHELL* in *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *XP* in *SHELXTL*, and *DIAMOND* (Crystal Impact, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1008). Services for accessing these data are described at the back of the journal.

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