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Alkali scandium arsenates. II. The framework structures of α- and β-$CsSc(HAsO_4)_2$

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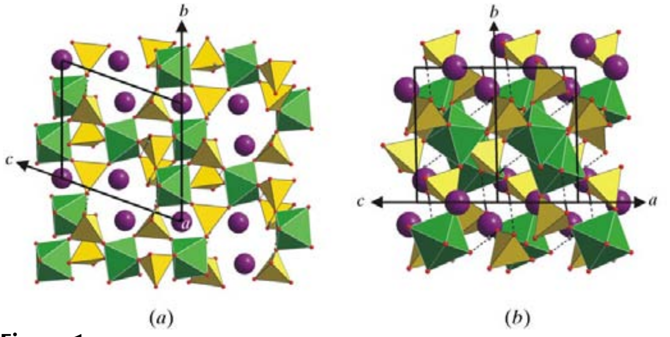
The crystal structures of hydrothermally synthesized α-, (I), and β-caesium scandium bis[hydrogen arsenate(V)], (II), both $CsSc(HAsO_4)_2$, have been determined from single-crystal X-ray diffraction data collected at room temperature. The dimorphs are both characterized by a three-dimensional negatively charged framework of corner-sharing alternating ScO_6 octahedra and $HAsO_4$ tetrahedra. The charge-balancing Cs^+ cations are located in a system of three intersecting tunnels in (I) and in tunnels parallel to the *a* axis in (II). Strong to weak hydrogen bonds reinforce both frameworks. The average Sc—O bond lengths are 2.098 and 2.094 Å, respectively. Compound (I) is triclinic and isotypic with $(NH_4)Fe^{III}(HPO_4)_2$, α-$A^IV^{III}(HPO_4)_2$ (*A* is NH_4 or Rb) and α-$(NH_4)(Al_{0.64}Ga_{0.36})(HPO_4)_2$. Compound (II) is monoclinic and isotypic with $(H_3O)Fe^{III}(HPO_4)_2$, β-$A^IV^{III}(HPO_4)_2$ (*A* is NH_4 or Rb), $CsIn(HPO_4)_2$ and $RbSc(HPO_4)_2$. Both (I) and (II) represent the first arsenate examples of their structure types. The Cs and Sc atoms in (I) lie on inversion centres. In (II), all atoms are in general positions. A brief overview is presented of the six structure types shown by $A^IM^{III}(HXO_4)_2$ compounds (*X* is P or As).

Comment

We have recently started to investigate the crystallography and topology of metal scandium arsenates, in order to study the crystal–chemical behaviour of Sc^{III} cations in oxy salts, and to compare it with that of trivalent cations with similar ionic radii (*e.g.* V^{III}, Fe^{III}, Cr^{III} and Ga^{III}). In the first part of our series on alkali scandium arsenates (Schwendtner & Kolitsch, 2004), we have reported the acid arsenate $KSc(HAsO_4)_2$, representing a new microporous structure type, designated MCV-3, and the diarsenate $RbScAs_2O_7$, which represents the first diarsenate known to crystallize with a $KAlP_2O_7$-type structure (Ng & Calvo, 1973). This second part of our series describes triclinic α-$CsSc(HAsO_4)_2$, (I), and monoclinic β-$CsSc(HAsO_4)_2$, (II). Furthermore, a brief overview is presented of the six structure types presently known for the compounds $A^IM^{III}(HXO_4)_2$ (A^I is a monovalent cation, M^{III} is a trivalent cation, and *X* is P or As).

The crystal structure of (I) contains two Cs, two Sc, three As, twelve O and three H atoms in the asymmetric unit, and has space-group symmetry $P\bar{1}$. The structure can be described as a complex three-dimensional negatively charged $[Sc(HAsO_4)_2]^-$ framework, built of ScO_6 octahedra sharing corners with $HAsO_4$ tetrahedra (Figs. 1 and 2). The polyhedral connectivity results in a complex system of intersecting tunnels extending parallel to all three principal axes (Fig. 1, only the largest tunnel is shown). These tunnels host the Cs^+ cations, which balance the negative charge of the framework. Each of the two ScO_6 octahedra shares all its vertices with adjacent $HAsO_4$ tetrahedra. Each of the three $HAsO_4$ tetrahedra shares three (unprotonated) vertices with adjacent ScO_6 octahedra.

The average Sc—O bond lengths are 2.104 (Sc1) and 2.092 Å (Sc2). The average As—O bond lengths in the three protonated arsenate groups (1.680 Å for As1, 1.687 Å for As2 and 1.682 Å for As3) show good agreement with the mean



(*a*) (*b*)

Figure 1
A view of the framework structure of (I) along (*a*) [100] and (*b*) [101]. Protonated AsO_4 tetrahedra are corner-linked to slightly distorted ScO_6 octahedra. A system of intersecting tunnels hosts the charge-balancing Cs^+ cations (dark spheres). The unit cell is outlined, and the hydrogen bonding is shown in (*b*) (dashed lines).

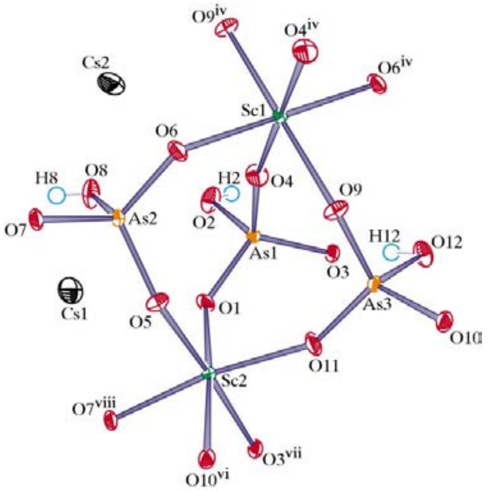


Figure 2
The connectivity in (I), shown with displacement ellipsoids at the 50% probability level. The H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (iv) $-x, 1-y, 1-z$; (vi) $-x, 1-y, -z$; (vii) $1-x, 1-y, -z$; (viii) $-x, 2-y, -z$.]

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length in arsenate compounds (1.682 Å; Baur, 1981). The As—OH bonds are distinctly elongated in comparison with the As—O bonds (Table 1), as is typical of protonated AsO_4 tetrahedra (Ferraris, 1970; Ferraris & Ivaldi, 1984).

The two Cs atoms have coordination numbers of 12 (Cs1) and 11 (Cs2) within 3.9 Å, and show average Cs—O bond lengths of 3.40 and 3.42 Å, respectively. Bond-valence sums for all atoms were calculated using the bond-valence parameters of Brese & O'Keeffe (1991). The values obtained [1.07 (Cs1), 0.95 (Cs2), 3.03 (Sc1), 3.13 (Sc2), 5.08 (As1), 4.98 (As2), 5.05 (As3), 2.12 (O1), 1.32 (O2), 1.95 (O3), 1.98 (O4), 1.96 (O5), 1.90 (O6), 1.86 (O7), 1.30 (O8), 1.78 (O9), 1.84 (O10), 1.94 (O11) and 1.26 (O12) valence units (v.u.)] are all reasonably close to the expected ideal valences, and confirm that O3, O8 and O12 represent hydroxyl groups. The two most underbonded O atoms (O9 and O10) are acceptors of two of the three strong to medium-strong hydrogen bonds (Table 2), which reinforce the framework along different vectors rougly parallel to the *ab* plane. The compound is isotypic with $(NH_4)Fe^{III}(HPO_4)_2$ and several other acid phosphates (see overview below for details).

Compound (II) is monoclinic (space group $P2_1/c$) and the asymmetric unit contains one Cs, one Sc, two As, eight O and two H atoms. Similar to what was observed for (I), the crystal structure is characterized by a three-dimensional negatively charged $[Sc(HAsO_4)_2]^-$ framework built of ScO_6 octahedra sharing corners with $HAsO_4$ tetrahedra (Figs. 3 and 4). The ScO_6 octahedron shares each of its six vertices with adjacent $HAsO_4$ tetrahedra, while each $HAsO_4$ tetrahedron shares three (unprotonated) vertices in the construction of the framework. The charge-balancing Cs^+ cations are located in tunnels which run parallel to the *a* axis (Fig. 3). These tunnels are defined by the stacking of 24-membered rings, which are constructed from corner-linkage of six ScO_6 octahedra and six $HAsO_4$ tetrahedra.

The average Sc—O bond length is 2.094 Å, very similar to that in (I). In $KSc(HAsO_4)_2$ and $RbScAs_2O_7$ (Schwendtner & Kolitsch, 2004), the corresponding values are negligibly smaller (2.090 Å). It is worth noting that all these values are consistently smaller than the reported mean Sc—O bond length in oxidic compounds (2.105 Å; Baur, 1981). The two protonated arsenate groups have average As—O bond lengths (1.680 for As1 and 1.683 Å for As2) which agree well with the mean length in arsenate compounds (1.682 Å; Baur, 1981). As in (I), the As—OH bonds are distinctly elongated in comparison with the As—O bonds (Table 3). The Cs atom is coordinated by 13 O atoms within 3.8 Å, and shows an average Cs—O bond length of 3.42 Å, similar to the situation in (I). Bond-valence sums for all atoms were calculated using the bond-valence parameters of Brese & O'Keeffe (1991). They amount to 1.05 (Cs), 3.11 (Sc), 5.07 (As1), 5.05 (As2), 1.79 (O1), 1.91 (O2), 2.03 (O3), 1.36 (O4), 2.02 (O5), 1.81 (O6), 2.07 (O7) and 1.28 (O8) v.u., and confirm that O4 and O8 belong to hydroxyl groups. The three somewhat underbonded O ligands (O1, O2 and O6) are all acceptors of three strong to weak hydrogen bonds (Table 4). The strongest of these bonds reinforces the framework roughly along the *c* axis. The compound is isotypic with $(H_3O)Fe^{III}(HPO_4)_2$ and some other acid phosphates (see overview below for details).

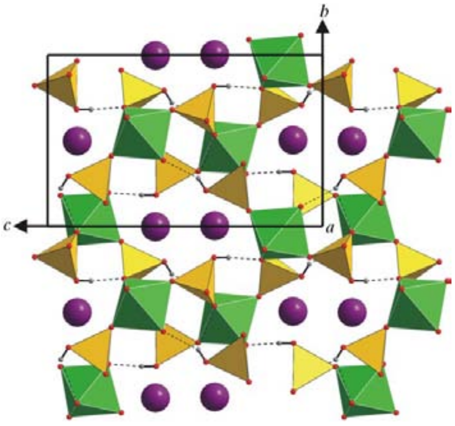

Figure 3
The framework structure of (II) projected down [100]. Protonated AsO_4 tetrahedra are corner-linked to slightly distorted ScO_6 octahedra. Tunnels parallel to [100] host the charge-balancing Cs^+ cations (dark spheres). The unit cell is outlined and the hydrogen bonding is indicated by dashed lines.

At present, six different structure types are known to exist for compounds with the general formula $A^IM^{III}(HXO_4)_2$ (A^I is a monovalent cation, M^{III} is a trivalent cation, and X is P or As). These types comprise one triclinic type, four monoclinic types and one rhombohedral type, and these will now be discussed.

The triclinic type (space group $P\overline{1}$) was originally described for $(NH_4)Fe^{III}(HPO_4)_2$ by Yakubovich (1993). (Note that, for reasons which were not given, this author chose an *I*-centered triclinic cell for the description of the structure.) As early as 1959, Smith & Brown (1959) had prepared the compounds $A^IM^{III}(HPO_4)_2$ (A^I is NH_4 or K, and M^{III} is Al or Fe) and studied $KFe^{III}(HPO_4)_2$ by single-crystal X-ray film methods. The non-standard primitive triclinic cell they found for this phase can be transformed into a standard cell with $a = 7.20$ Å, $b = 8.76$ Å and $c = 9.49$ Å, and $\alpha = 64.58°$, $\beta = 69.82°$ and $\gamma = 70.13°$, which clearly indicates that $KFe^{III}(HPO_4)_2$ also adopts this structure type. Crystals of the other three members were too small to be studied by single-crystal methods (Smith &

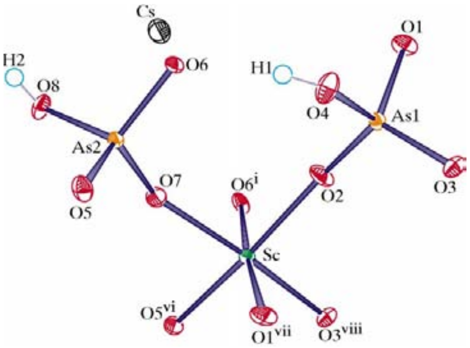

Figure 4
The connectivity in (II), shown with displacement ellipsoids at the 50% probability level. The H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vii) $1 + x, y, z$; (viii) $1 - x, -y, -z$.]

Brown, 1959). The unindexed X-ray powder diffraction pattern of $(NH_4)Fe^{III}(HPO_4)_2$ listed in the ICDD powder diffraction file (ICDD-PDF; No. 44-736; ICDD, 2003) is fairly similar to the theoretical pattern calculated from the crystal-structure data given by Yakubovich (1993). The structure types of the Al analogues $A^IAl(HPO_4)_2$ (A^I is NH_4 or K) appear uncertain, although the unindexed X-ray powder diffraction patterns for $(NH_4)Al^{III}(HPO_4)_2$ (ICDD-PDF No. 44-755) and $(NH_4)Al^{III}(HPO_4)_2{\cdot}xH_2O$ (ICDD-PDF No. 44-726) suggest that at least the ammonium member may also be isotypic with its Fe^{III} analogue [no published pattern exists for $KAl^{III}(HPO_4)_2$]. Subsequently, the triclinic type was also found for the acid phosphates α-$RbV^{III}(HPO_4)_2$ (Lii & Wu, 1994; Haushalter *et al.*, 1995), α-$RbFe^{III}(HPO_4)_2$ (Lii & Wu, 1994), α-$(NH_4)(Al_{0.64}Ga_{0.36})(HPO_4)_2$ (Stalder & Wilkinson, 1998) and α-$(NH_4)V^{III}(HPO_4)_2$ (Bircsak & Harrison, 1998). α-$CsSc(HAsO_4)_2$, (I), is the first acid arsenate crystallizing with this structure type. Note that the prefix α is nowadays commonly added to chemical formulae in order to distinguish individual phases from their monoclinic β dimorphs (see below).

The first monoclinic type (space group $P2_1/c$; $a \sim 5$ Å, $b \sim 9$ Å and $c \sim 14$ Å, and $\beta \sim 95°$) was originally determined for $(H_3O)Fe^{III}(HPO_4)_2$ (Vencato *et al.*, 1989). Later, isotypic β-$RbV^{III}(HPO_4)_2$ and β-$(NH_4)V^{III}(HPO_4)_2$ (Haushalter *et al.*, 1995), $CsIn(HPO_4)_2$ (ICDD-PDF No. 53-1111) and $RbSc(HPO_4)_2$ (Bartu & Wildner, 2004) were reported. The prefix β is now commonly added to chemical formulae in order to distinguish these phases from their triclinic α dimorphs (see above). Note that the X-ray powder data listed for $RbSc(HPO_4)_2$ in ICDD-PDF No. 53-1110 are indexed with the wrong $P2_1/m$ space group. A detailed comparison of this type and the above triclinic type is provided by Haushalter *et al.* (1995). β-$CsSc(HAsO_4)_2$, (II), is the first acid arsenate adopting this structure type. A structurally similar arsenate is $PbFe(AsO_4)(AsO_3OH)$ (Effenberger *et al.*, 1996), which is monoclinic (space group $P2_1/n$) and has roughly comparable unit-cell parameters ($a = 4.85$ Å, $b = 8.48$ Å and c 15.56 Å, and $\beta = 92.8°$).

The second monoclinic type also has space-group symmetry $P2_1/c$, but completely different cell parameters ($a \sim 10$ Å, $b \sim 8$ Å and $c \sim 10$ Å, and $\beta \sim 116°$). It was recently described for three indium acid phosphates $A^IIn(HPO_4)_2$ (A^I is K, Rb and NH_4) by Filaretov *et al.* (2002). No arsenate member is presently known. The third monoclinic type (space group $C2/c$) is shown by $KSc(HAsO_4)_2$ and was reported in Part I of our series on alkali scandium arsenates (Schwendtner & Kolitsch, 2004). No phosphate member is known at present. The fourth monoclinic type (space group Cc) is represented by $NaSc(HPO_4)_2$ (Bartu & Wildner, 2004), the only member known. This type is unique among the six recognized structure types because it is the only one showing a non-centrosymmetric atomic arrangement. The sixth type and the only one having a symmetry higher than monoclinic is represented by $RbFe^{III}(HPO_4)_2$ (Lii & Wu, 1994), which is rhombohedral (space group $R\bar{3}c$) and exhibits a rather long c axis ($\sim$53 Å).

All these six different structure types have one feature in common: they are characterized by three-dimensional frameworks built of strictly alternating $M^{III}O_6$ octahedra and HXO_4 tetrahedra. The A^I cations occupy voids and (often intersecting) tunnels within the frameworks. The OH groups of the HXO_4 tetrahedra always point towards void areas in the polyhedral arrangement. However, the connectivities of the tetrahedral and octahedral units in each structure type are quite distinct.

The hydrogen bonding in these compounds is also of interest. Haushalter *et al.* (1995) observed that the hydrogen bonds provided by the HPO_4 groups are very strong in the case of (monoclinic) β-$RbV^{III}(HPO_4)_2$ ($O\cdots O = 2.41$ Å, no s.u. given) and β-$(NH_4)V^{III}(HPO_4)_2$ ($O\cdots O = 2.50$–3.00 Å, no s.u. given), but weak in the case of (triclinic) α-$RbV^{III}(HPO_4)_2$. In contrast, the hydrogen bonds in α-$(NH_4)V^{III}(HPO_4)_2$ (Bircsak & Harrison, 1998) were fairly strong [$O\cdots O = 2.574\ (2)$–$2.742\ (3)$ Å]. The present results also do not confirm the scheme observed by Haushalter *et al.* (1995). In fact, α-$CsSc(HAsO_4)_2$ shows slightly stronger hydrogen bonds [$O\cdots O = 2.623\ (3)$–$2.784\ (4)$ Å; Table 2] than β-$CsSc(HAsO_4)_2$ [$O\cdots O = 2.691\ (7)$–$3.199\ (7)$ Å; Table 4]. Thus, the details of the hydrogen bonding seem to be determined by the interplay between the polyhedra involved in the respective structures and cannot be predicted, although it appears that increasing the size of the polyhedra and/or of the A^I cations results in an overall weakening of the hydrogen bonds.

It is worth noting that structure types one and two (α and β compounds) show a strong tendency to co-crystallize in the same experimental run. This behaviour was observed for dimorphous $RbV^{III}(HPO_4)_2$ (Haushalter *et al.*, 1995), $(NH_4)V^{III}(HPO_4)_2$ (Bircsak & Harrison, 1998) and $CsSc(HAsO_4)_2$ (present work, see *Experimental*). Apparently, the lattice energies of both modifications are very similar.

Experimental

A mixture of Sc_2O_3, arsenic acid, Cs_2CO_3 (volume ratio *ca* 1:1:1) and distilled water was treated hydrothermally in a Teflon-lined steel autoclave (493 K, 7 d, initial and final pH $\sim$2). The reaction products were compounds (I) and (II). Compound (I) formed small colourless rhomb-shaped plate-like crystals (yield *ca* 2%). Compound (II) crystallized as small colourless prisms which were invariably twinned by non-merohedry (yield *ca* 98%). The twinning was often recognizable from re-entrant angles, but the twin law was not determined.

Compound (I)

Crystal data

$CsSc(HAsO_4)_2$
$M_r = 457.73$
Triclinic, $P\bar{1}$
$a = 7.520\ (2)$ Å
$b = 9.390\ (2)$ Å
$c = 10.050\ (2)$ Å
$\alpha = 65.48\ (3)°$
$\beta = 70.66\ (3)°$
$\gamma = 70.10\ (3)°$
$V = 592.0\ (3)$ Å^3
$Z = 3$

$D_x = 3.852$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4259 reflections
$\theta = 2.0$–$32.6°$
$\mu = 13.81$ mm^{-1}
$T = 293\ (2)$ K
Tabular, colourless
$0.08 \times 0.06 \times 0.03$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ψ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.405$, $T_{\max} = 0.682$
8447 measured reflections
4302 independent reflections
3839 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 32.6^\circ$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.057$
$S = 1.05$
4302 reflections
179 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 0.84P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.62$ e Å^{-3}
$\Delta\rho_{\min} = -1.55$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0055 (3)

Table 1
Selected interatomic distances (Å) for (I).

Cs1—O1	2.984 (2)	Sc1—O9	2.1478 (19)
Cs1—O8	3.231 (3)	Sc2—O5	2.045 (2)
Cs1—O2	3.388 (3)	Sc2—O11	2.049 (2)
Cs1—O7$^{\rm i}$	3.436 (2)	Sc2—O1	2.0631 (19)
Cs1—O5$^{\rm i}$	3.645 (2)	Sc2—O10$^{\rm vi}$	2.119 (2)
Cs1—O12$^{\rm ii}$	3.720 (2)	Sc2—O3$^{\rm vii}$	2.1319 (19)
Cs2—O3$^{\rm iii}$	3.014 (2)	Sc2—O7$^{\rm viii}$	2.142 (2)
Cs2—O8	3.127 (2)	As1—O4	1.6566 (19)
Cs2—O2	3.144 (2)	As1—O1	1.6587 (19)
Cs2—O12$^{\rm ii}$	3.164 (2)	As1—O3	1.6753 (18)
Cs2—O6$^{\rm i}$	3.294 (2)	As1—O2	1.729 (2)
Cs2—O9$^{\rm iv}$	3.478 (2)	As2—O5	1.6599 (18)
Cs2—O7$^{\rm v}$	3.542 (2)	As2—O6	1.666 (2)
Cs2—O10$^{\rm iv}$	3.553 (2)	As2—O7	1.6825 (18)
Cs2—O7$^{\rm i}$	3.659 (2)	As2—O8	1.740 (2)
Cs2—O4	3.785 (2)	As3—O11	1.653 (2)
Cs2—O4$^{\rm iii}$	3.820 (3)	As3—O10	1.6672 (18)
Sc1—O4	2.051 (2)	As3—O9	1.6755 (19)
Sc1—O6	2.113 (2)	As3—O12	1.732 (2)

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O9$^{\rm i}$	0.83 (4)	1.96 (4)	2.784 (3)	173 (3)
O8—H8$\cdots$O10$^{\rm ii}$	0.64 (5)	1.98 (5)	2.623 (3)	174 (6)
O12—H12$\cdots$O3	0.87 (4)	1.87 (4)	2.739 (3)	175 (4)

Symmetry codes: (i) $1+x, y, z$; (ii) $x, 1+y, z$.

Compound (II)

Crystal data

$CsSc(HAsO_4)_2$
$M_r = 457.73$
Monoclinic, $P2_1/c$
$a = 5.546$ (1) Å
$b = 9.375$ (2) Å
$c = 15.034$ (3) Å
$\beta = 95.16$ (3)°
$V = 778.5$ (3) Å^3
$Z = 4$
$D_x = 3.905$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2410 reflections
$\theta = 2.0$–30.0°
$\mu = 14.00$ mm^{-1}
$T = 293$ (2) K
Prismatic fragment, colourless
0.10 × 0.02 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ψ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.310$, $T_{\max} = 0.756$
4355 measured reflections
2240 independent reflections
1995 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 30.0^\circ$
$h = -7 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.085$
$S = 1.18$
2240 reflections
118 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 16P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.76$ e Å^{-3}
$\Delta\rho_{\min} = -1.11$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00322 (19)

Table 3
Selected interatomic distances (Å) for (II).

Cs—O5$^{\rm i}$	3.068 (5)	Sc—O7	2.074 (5)
Cs—O3$^{\rm ii}$	3.116 (5)	Sc—O5$^{\rm vi}$	2.089 (5)
Cs—O7$^{\rm iii}$	3.144 (5)	Sc—O1$^{\rm vii}$	2.092 (5)
Cs—O4$^{\rm i}$	3.203 (5)	Sc—O3$^{\rm viii}$	2.095 (5)
Cs—O4$^{\rm iv}$	3.341 (6)	Sc—O6$^{\rm i}$	2.150 (4)
Cs—O8$^{\rm v}$	3.385 (5)	As1—O3	1.653 (4)
Cs—O8	3.396 (5)	As1—O2	1.657 (5)
Cs—O8$^{\rm iii}$	3.413 (5)	As1—O1	1.685 (4)
Cs—O6	3.554 (5)	As1—O4	1.726 (5)
Cs—O4$^{\rm ii}$	3.603 (5)	As2—O7	1.654 (5)
Cs—O7	3.749 (5)	As2—O5	1.663 (5)
Cs—O6$^{\rm i}$	3.763 (5)	As2—O6	1.671 (4)
Cs—O1$^{\rm iv}$	3.777 (5)	As2—O8	1.742 (5)
Sc—O2	2.062 (5)		

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

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H1$\cdots$O6	0.79 (14)	1.90 (14)	2.691 (7)	170 (14)
O8—H2$\cdots$O1$^{\rm i}$	0.80 (10)	2.36 (9)	2.974 (7)	135 (8)
O8—H2$\cdots$O2$^{\rm ii}$	0.80 (10)	2.64 (9)	3.199 (7)	129 (8)

Symmetry codes: (i) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The crystal fragment of (II) used for the data collection was partially twinned by non-merohedry (estimated twin ratio > 4:1). A total of 41 reflections most strongly affected by the twinning were omitted in the final refinement steps. For comparison purposes, the atomic coordinates of isotypic α-$(NH_4)V^{III}(HPO_4)_2$ (Bircsak & Harrison, 1998) and $(H_3O)Fe^{III}(HPO_4)_2$ (Vencato *et al.*, 1989) were used as starting parameters in the final refinements of (I) and (II), respectively. However, the Sc atom in (II) had to be moved to a symmetry-equivalent position in order to obtain a properly connected set of atoms. The H atoms in both (I) and (II) were freely refined. The highest electron-density peak in (I), 1.62 e Å^{-3}, is at a distance of 0.63 Å from the Cs2 and the deepest hole, −1.55 e Å^{-3}, is at a distance of 0.59 Å from the same site. The highest electron-density peak in (II), 2.76 e Å^{-3}, is at a distance of 1.75 Å from the O4 site and the deepest hole, −1.11 e Å^{-3}, is at a distance of 0.69 Å from the Cs site.

For both compounds, data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1053). Services for accessing these data are described at the back of the journal.

References

Bartu, P. & Wildner, M. (2004). Personal communication.

Baur, W. H. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 31–52. New York: Academic Press.

Bircsak, Z. & Harrison, W. T. A. (1998). *Acta Cryst.* C**54**, 1195–1197.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Version 2.1b. Crystal Impact GbR, Bonn, Germany.

Effenberger, H., Hejny, C. & Pertlik, F. (1996). *Monatsh. Chem.* **127**, 127–133.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Ferraris, G. (1970). *Rend. Soc. Ital. Mineral. Petrol.* **26**, 589–598. (In Italian.)

Ferraris, G. & Ivaldi, G. (1984). *Acta Cryst.* B**40**, 1–6.

Filaretov, A. A., Zhizhin, M. G., Olenev, A. V., Gurkin, A. A., Bobylev, A. P., Lazoryak, B. I., Danilov, V. P. & Komissarova, L. N. (2002). *Zh. Neorg. Khim.* **47**, 1930–1946. (In Russian.)

Haushalter, R. C., Wang, Z., Thompson, M. E. & Zubieta, J. (1995). *Inorg. Chim. Acta*, **232**, 83–89.

ICDD (2003). Powder Diffraction File. PDF-2. International Centre for Diffraction Data, 12 Campus Boulevard, Newtown Square, PA 19073-3273, USA.

Lii, K.-H. & Wu, L.-S. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1577–1580.

Ng, H. N. & Calvo, C. (1973). *Can. J. Chem.* **51**, 2613–2620.

Nonius (2003). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Schwendtner, K. & Kolitsch, U. (2004). *Acta Cryst.* C**60**, i79–i83.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Smith, J. P. & Brown, W. E. (1959). *Am. Mineral.* **44**, 138–142.

Stalder, S. M. & Wilkinson, A. P. (1998). *J. Mater. Chem.* **8**, 261–263.

Vencato, I., Mattievich, E., Moreira, L. de F. & Mascarenhas, Y. P. (1989). *Acta Cryst.* C**45**, 367–371.

Yakubovich, O. V. (1993). *Kristallografiya*, **38**, 43–48. (In Russian.)