

## Alkali scandium arsenates. I. The framework structures of $\text{KSc}(\text{HAsO}_4)_2$ and $\text{RbScAs}_2\text{O}_7$

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The crystal structures of hydrothermally synthesized potassium scandium hydrogen arsenate(V),  $\text{KSc}(\text{HAsO}_4)_2$ , (I), and rubidium scandium diarsenate(V),  $\text{RbScAs}_2\text{O}_7$ , (II), were determined from single-crystal X-ray diffraction data collected at room temperature. Compound (I) represents a new microporous structure type, designated MCV-3, which is characterized by a three-dimensional framework of corner-sharing alternating  $\text{ScO}_6$  octahedra and  $\text{HAsO}_4$  tetrahedra. Intersecting tunnels parallel to [101] and [110] host eight-coordinate K atoms. There is one hydrogen bond of medium strength [ $\text{O}\cdots\text{O} = 2.7153(18) \text{ \AA}$ ]. Compound (II) is the first reported diarsenate with a  $\text{KAlP}_2\text{O}_7$ -type structure and is isotopic with at least 27  $A^1M^{\text{III}}$  diphosphates. The average Sc—O bond lengths in (I) and (II) are 2.09 (2) and 2.09 (3)  $\text{ \AA}$ , respectively. The K and Sc atoms in (I) lie on an inversion centre and a twofold axis, respectively. All atoms in (II) are in general positions.

### Comment

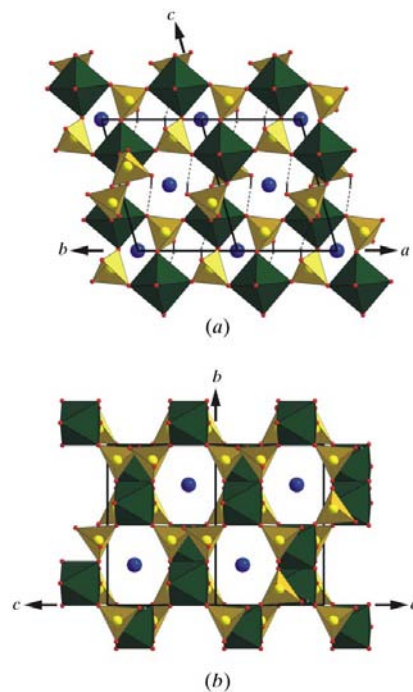
Because of interest in the crystal chemical behaviour of  $\text{Sc}^{\text{III}}$  cations in oxy salts, and for comparison with the behaviour of trivalent cations with similar ionic radii (e.g.  $\text{V}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$  and  $\text{Ga}^{\text{III}}$ ), we have recently started to investigate the crystallography and topology of metal scandium arsenates. The present contribution reports the crystal structures of two hydrothermally synthesized alkali scandium arsenates,  $\text{KSc}(\text{HAsO}_4)_2$ , (I), and  $\text{RbScAs}_2\text{O}_7$ , (II). A second contribution (Schwendtner & Kolitsch, 2004) will be devoted to the crystal structures of the triclinic and monoclinic modifications of  $\text{CsSc}(\text{HAsO}_4)_2$  and a brief overview of compounds  $A^1M^{\text{III}}(\text{HXO}_4)_2$  ( $A^1$  is a monovalent cation,  $M^{\text{III}}$  is a trivalent cation and  $X = \text{P}$  or  $\text{As}$ ).

Compound (I) is monoclinic ( $C2/c$ ) and represents a new microporous framework structure type, designated MCV-3 (MCV stands for Mineralogy and Crystallography Vienna). The asymmetric unit contains one K, one Sc, one As, four O and one H atom, of which only the K and Sc atoms occupy

special positions (the K atom lies on an inversion centre and the Sc atom on a twofold axis). Slightly distorted  $\text{ScO}_6$  octahedra are corner-linked to  $\text{AsO}_4$  tetrahedra and form a three-dimensional framework with slightly contorted, hexagonally shaped, tunnels parallel to [101] and narrower, more irregularly shaped, tunnels parallel to [110]; these tunnels host the eight-coordinate K atoms (Figs. 1–3). The larger tunnels have a size of about  $2.67 \times 2.74 \text{ \AA}$ , based on the  $\text{O}^{2-}$  ionic radius (1.35  $\text{ \AA}$ ; Shannon, 1976). The H atom is bonded to the ‘free’ corner of the  $\text{AsO}_4$  tetrahedron and is involved in a moderately strong hydrogen bond [ $\text{O4—H}\cdots\text{O2}(x, 1 - y, \frac{1}{2} + z)$ ] which extends roughly perpendicular to the (101) plane, i.e. parallel to the larger tunnels (Fig. 1a). As is typical of protonated  $\text{AsO}_4$  tetrahedra, the As—OH bond is distinctly elongated in comparison with the three remaining As—O bonds (Ferraris, 1970; Ferraris & Ivaldi, 1984). The mean As—O bond length in the protonated arsenate group (1.683  $\text{ \AA}$ ; Table 1) nearly coincides with the grand mean length in arsenates (1.682  $\text{ \AA}$ ; Baur, 1981). The mean Sc—O bond length in the  $\text{ScO}_6$  octahedron (2.090  $\text{ \AA}$ ) is slightly smaller than the grand mean value in oxidic compounds (2.105  $\text{ \AA}$ ; Baur, 1981).

Bond-valence sums for all atoms were calculated using the bond-valence parameters of Brese & O’Keeffe (1991); these values are 1.01 (for the K atom), 5.04 (As), 3.13 (Sc), 2.19 (O1), 1.82 (O2), 1.97 (O3) and 1.21 valence units (v.u.) (O4), and thus are all reasonably close to ideal valences. The slightly underbonded O2 atom is an acceptor of a hydrogen bond (see above).

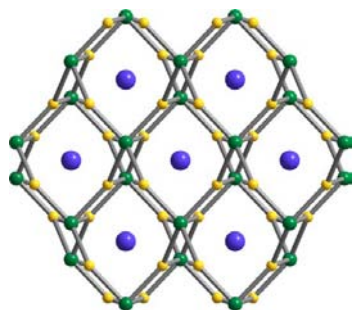
$\text{RbScAs}_2\text{O}_7$ , (II), is monoclinic ( $P2_1/c$ ) and isotopic with  $\text{KAlP}_2\text{O}_7$  (Ng & Calvo, 1973). The asymmetric unit contains



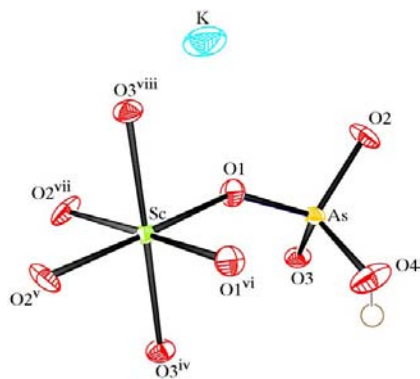
**Figure 1**  
A view of the framework structure of microporous (I) along (a) [110] and (b) [101]. Protonated  $\text{AsO}_4$  tetrahedra are corner-linked to slightly distorted  $\text{ScO}_6$  octahedra. The tunnels host eight-coordinate K atoms (dark spheres). The unit cell is outlined and the hydrogen bonding is shown in (a).

one Rb, one Sc, two As and seven O atoms, all of which occupy general positions. The atomic arrangement is based on a three-dimensional framework of corner-linked ScO<sub>6</sub> octahedra and As<sub>2</sub>O<sub>7</sub> groups. The charge-balancing Rb<sup>+</sup> cations are located in distorted six-sided tunnels parallel to [001] (Figs. 4 and 5). The shortest distance between two neighbouring Rb<sup>+</sup> cations in a single tunnel is 4.629 (1) Å. The irregular coordination environment of the Rb atoms consists of ten O ligands within 3.5 Å [an 11th, non-bonding, O-atom neighbour is located at a distance of 3.749 (2) Å]. The ScO<sub>6</sub> octahedron is distorted, with deviations of up to 8.70 (7)° from ideal geometry. The mean Sc–O bond length (2.090 Å) is, similarly to the situation in (I), slightly smaller than the mean value in oxidic compounds (2.105 Å; Baur, 1981). The mean As–O bond lengths in the two non-equivalent AsO<sub>4</sub> tetrahedra ( $\langle \text{As1–O} \rangle = 1.681$  Å and  $\langle \text{As2–O} \rangle = 1.684$  Å) forming the As<sub>2</sub>O<sub>7</sub> group are also close to the expected value (1.682 Å; Baur, 1981).

The As<sub>2</sub>O<sub>7</sub> diarsenate group shows a nearly staggered conformation, with an As1–O<sub>7(bridge)</sub>–As2 angle of 119.62 (10)°. The bridging angle is in good agreement with reviewed data for other diarsenates (the mean As–O<sub>bridge</sub>–As angle is 125.08°; Effenberger & Pertlik, 1993). The bridging O7 atom is very weakly bonded to the Rb atom (Table 3). The conformation of the As<sub>2</sub>O<sub>7</sub> diarsenate group in (II) appears unusual because compounds with isolated X<sub>2</sub>O<sub>7</sub> groups (X =



**Figure 2**  
A simplified view along [101] of the connectivity and the K-filled tunnels in the microporous framework structure of (I). The lines shown connect the centres of the tetrahedral and octahedral units (As and Sc).

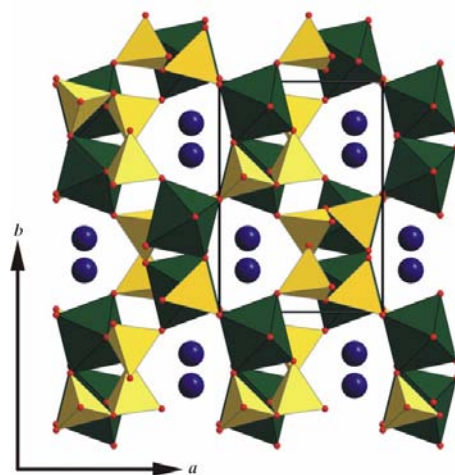


**Figure 3**  
The connectivity in (I), shown with displacement ellipsoids at the 70% probability level. The H atom is shown as a small sphere of arbitrary radius. [Symmetry codes: (iv)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (v)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (vi)  $-x, y, \frac{1}{2} - z$ ; (vii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (viii)  $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ]

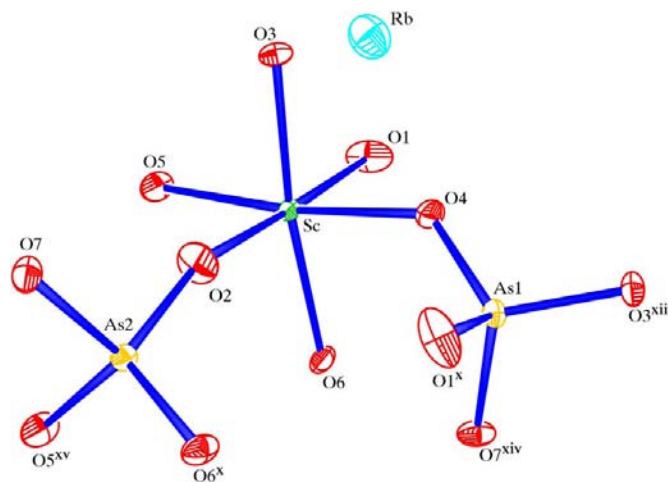
Si, P, S, As, Cr, Ge and V) in general show either a staggered conformation, with a bridging X–O<sub>bridge</sub>–X angle of greater than 140° (up to 180°), or an eclipsed conformation, with an X–O–X angle of less than 140°, where the O<sub>bridge</sub> atom belongs to the coordination sphere of at least one cation (Clark & Morley, 1976).

Bond-valence sums for all atoms were calculated using the bond-valence parameters of Brese & O’Keeffe (1991). For the metal atoms, these values are 0.93 (for the Rb atom), 5.09 (As1), 5.03 (As2) and 3.14 v.u. (Sc). The bond-valence sums of the O atoms are 2.07 (O1), 1.96 (O2), 2.10 (O3), 2.07 (O4), 1.95 (O5), 1.94 (O6) and 2.10 v.u. (O7). All these values are close to ideal valences.

Compound (II) is the first diarsenate reported to crystallize in the monoclinic (*P*<sub>2</sub>/*c*) structure type originally described by Ng & Calvo (1973) for KAlP<sub>2</sub>O<sub>7</sub>. Subsequent to their work, a surprisingly large number of other diphosphates,



**Figure 4**  
The framework structure of (II), projected down [001]. As<sub>2</sub>O<sub>7</sub> diarsenate groups (with a nearly staggered conformation) are corner-linked to slightly distorted ScO<sub>6</sub> octahedra. Ten-coordinate Rb atoms are located in tunnels running parallel to [001]. The unit cell is outlined.



**Figure 5**  
The connectivity in (II), shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (x)  $x, -\frac{3}{2} - y, z - \frac{1}{2}$ ; (xiii)  $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (xiv)  $x, -\frac{3}{2} - y, \frac{1}{2} + z$ ; (xv)  $1 - x, -2 - y, 1 - z$ .]

$A^1M^{III}X_2O_7$  ( $A^1 = H_3O, Na, K, NH_4, Rb, Cs, In$  and  $Tl, M^{III} = Al, Sc, Ti, V, Cr, Fe, Ga, Mo, In, Y$  and  $Yb$ , and  $X = P$  and  $As$ ) have also been reported to adopt this apparently fairly flexible structure type. In fact,  $KAIP_2O_7$ -type compounds form the largest group among the known structure types of  $A^1M^{III}P_2O_7$  compounds [at least seven types exist if  $A^1 = Li$  is included (Vitiš *et al.*, 2000)].

The following list of 27 diphosphates isotypic with  $KAIP_2O_7$  is based on a careful search in both crystallographic and literature databases and is thought to be complete (no previous such compilation exists):  $RbAlP_2O_7$  (Belkouch *et al.*, 1995),  $KScP_2O_7$  and  $(NH_4)ScP_2O_7$  (Kanep *et al.*, 1987),  $\beta$ - $NaTiP_2O_7$  (Leclaire *et al.*, 1988),  $KTiP_2O_7$ ,  $RbTiP_2O_7$  and  $CsTiP_2O_7$  (Wang & Hwu, 1991; Huang & Ibers, 2000; Zatovs'kyi *et al.*, 2000),  $(H_3O)VP_2O_7$  (El Badraoui *et al.*, 1996),  $NaVP_2O_7$  (Wang *et al.*, 1989),  $KVP_2O_7$  (Benhamada *et al.*, 1991),  $RbVP_2O_7$  (Flörke, 1990),  $(NH_4)VP_2O_7$  (Trommer *et al.*, 1998),  $CsVP_2O_7$  (Wang & Lii, 1989),  $KCrP_2O_7$  (Gentil *et al.*, 1997),  $Rb(Ni_{0.35}Cr_{0.30}Ti_{0.35})P_2O_7$  (Yakubovich *et al.*, 1995),  $CsCrP_2O_7$  (Linde & Gorbunova, 1982),  $TiCrP_2O_7$  (Bensch & Koy, 1995),  $NaFeP_2O_7$ -I (Gamondés *et al.*, 1971),  $KFeP_2O_7$  (Gamondés *et al.*, 1971; Riou *et al.*, 1988; Genkina & Timofeeva, 1989),  $RbFeP_2O_7$  and  $CsFeP_2O_7$  (Millet & Mentzen, 1991; Dvoncova & Lii, 1993),  $KGaP_2O_7$  (Genkina & Timofeeva, 1989),  $KMoP_2O_7$  (Chen *et al.*, 1989; Leclaire *et al.*, 1989),  $RbMoP_2O_7$  (Riou *et al.*, 1989),  $CsMoP_2O_7$  (Lii & Haushalter, 1987),  $In^IIn^{III}P_2O_7$  (Thauern & Glaum, 2003),  $RbYP_2O_7$  (Akrim *et al.*, 1993),  $CsYP_2O_7$  (Akrim *et al.*, 1994) and  $CsYbP_2O_7$  (Jansen *et al.*, 1991). In addition,  $Rb, Cs$  and  $Tl$  diphosphate members, with  $M^{III} = Gd, Tb, Dy, Ho, Y, Er, Tm$  and  $Yb$ , also have  $KAIP_2O_7$ -type structures according to X-ray powder diffraction and spectroscopic evidence (Khay & Ennaciri, 2001; Khay, Ennaciri & Harcharras, 2001; Khay, Ennaciri & Rulmont, 2001; Anisimova *et al.*, 1993a,b). Most of the above compounds were prepared at temperatures higher than 573 K by solid-state reactions or crystallization from the melt. It was not recognized in all cases that the specific compound adopts a structure type originally described for  $KAIP_2O_7$  (Ng & Calvo, 1973).

Compound (II) appears to be the first reported diarsenate with a  $KAIP_2O_7$ -type structure. A few other  $A^1M^{III}As_2O_7$  compounds are known at present, but they all crystallize in other structure types [e.g. monoclinic ( $P2_1/c$ )  $NaAlAs_2O_7$  (Driss & Jouini, 1994), triclinic ( $P\bar{1}$ )  $RbAlAs_2O_7$  and  $KAlAs_2O_7$  (Boughzala *et al.*, 1993; Boughzala & Jouini, 1995), and monoclinic ( $C2/c$ )  $NaInAs_2O_7$  (Belam *et al.*, 1997)], although they show connectivities similar to those in  $KAIP_2O_7$ -type compounds. It appears that  $RbScAs_2O_7$  crystallizes in the  $KAIP_2O_7$  structure type because of a 'suitable' relation between the ionic radii of the cations involved. All of the cations in (II) are slightly larger than those in  $KAIP_2O_7$ , and therefore the polyhedral framework in (II) is able to simply expand without any strain. Work in progress indicates that  $(NH_4)ScAs_2O_7$  also has a  $KAIP_2O_7$ -type structure. This result is not too surprising considering that the ionic radius of the  $NH_4^+$  cation is similar to that of the  $Rb^+$  cation (e.g. Khan & Baur, 1972).

Measured X-ray powder diffraction patterns (Cu  $K\alpha$  radiation) of (I) and (II) show good agreement with the respective calculated patterns.

## Experimental

Compounds (I) and (II) were prepared hydrothermally (in Teflon-lined stainless steel bombs at 493 K for 7 d, with slow furnace cooling) from a mixture of  $Sc_2O_3$ , arsenic acid hydrate, oxalic acid dihydrate, and  $KOH$  and  $Rb_2CO_3$ , respectively, with a volume ratio of approximately 1:1:1:1. The Teflon containers were then filled with distilled water to about one-third of their inner volume. The pH values of the starting and final solutions were approximately 1. Compound (I) formed small colourless tabular crystals (yield ca 98%), while compound (II) formed small colourless pseudo-disphenoidal crystals (yield ca 95%). Crystals of (I) and (II) are stable in air. Compound (I) also crystallized as small colourless pseudo-disphenoidal, often twinned (by non-merohedry), crystals from a hydrothermally reacted mixture of  $Sc_2O_3$ , arsenic acid hydrate and  $KOH$  (at 493 K for 7 d, with slow furnace cooling; yield 100%), the final pH of the reacted solution being about 2–3.

## Compound (I)

### Crystal data

$KSc(HAsO_4)_2$   
 $M_r = 363.92$   
 Monoclinic,  $C2/c$   
 $a = 8.349$  (2) Å  
 $b = 10.590$  (2) Å  
 $c = 9.189$  (2) Å  
 $\beta = 109.37$  (3)°  
 $V = 766.5$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 3.154$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 1459 reflections  
 $\theta = 2.0$ – $32.6$ °  
 $\mu = 10.08$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Irregular fragment, colourless  
 $0.16 \times 0.13 \times 0.10$  mm

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 ( $HKL$  SCALEPACK;  
 Otwinowski & Minor, 1997)  
 $T_{min} = 0.295, T_{max} = 0.432$   
 2720 measured reflections  
 1392 independent reflections

1352 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.009$   
 $\theta_{max} = 32.6$ °  
 $h = -12 \rightarrow 12$   
 $k = -16 \rightarrow 16$   
 $l = -13 \rightarrow 13$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.014$   
 $wR(F^2) = 0.039$   
 $S = 1.16$   
 1392 reflections  
 62 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.016P)^2 + 1.3P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 1.16$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.42$  e Å<sup>-3</sup>  
 Extinction correction:  $SHELXL97$   
 Extinction coefficient: 0.0025 (2)

**Table 1**

Selected interatomic distances (Å) for (I).

K—O1 <sup>i</sup>	2.6792 (12)	Sc—O2 <sup>v</sup>	2.1134 (11)
K—O3 <sup>ii</sup>	2.8382 (12)	As—O1	1.6618 (11)
K—O4 <sup>iii</sup>	3.0120 (16)	As—O3	1.6688 (12)
K—O2	3.3085 (13)	As—O2	1.6724 (10)
Sc—O1	2.0623 (11)	As—O4	1.7272 (12)
Sc—O3 <sup>iv</sup>	2.0956 (11)		

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

**Table 2**

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

D—H...A	D—H	H...A	D...A	D—H...A
O4—H...O2 <sup>ix</sup>	0.73 (3)	2.01 (3)	2.7153 (18)	161 (3)

Symmetry code: (ix)  $x, 1 - y, \frac{1}{2} + z$ .

**Compound (II)**

*Crystal data*

RbScAs<sub>2</sub>O<sub>7</sub>  $D_x = 3.717 \text{ Mg m}^{-3}$   
 $M_r = 392.27$  Mo  $K\alpha$  radiation  
 Monoclinic,  $P2_1/c$  Cell parameters from 2668 reflections  
 $a = 7.837 (2) \text{ \AA}$   $\theta = 2.0\text{--}32.6^\circ$   
 $b = 10.625 (2) \text{ \AA}$   $\mu = 17.31 \text{ mm}^{-1}$   
 $c = 8.778 (2) \text{ \AA}$   $T = 293 (2) \text{ K}$   
 $\beta = 106.45 (3)^\circ$  Irregular fragment, colourless  
 $V = 701.0 (3) \text{ \AA}^3$   $0.08 \times 0.07 \times 0.05 \text{ mm}$   
 $Z = 4$

*Data collection*

Nonius KappaCCD diffractometer 2544 independent reflections  
 $\varphi$  and  $\omega$  scans 2152 reflections with  $I > 2\sigma(I)$   
 Absorption correction: multi-scan  $R_{int} = 0.019$   
 (HKL SCALEPACK);  $\theta_{max} = 32.6^\circ$   
 Otwinowski & Minor, 1997)  $h = -11 \rightarrow 11$   
 $T_{min} = 0.338, T_{max} = 0.478$   $k = -16 \rightarrow 16$   
 4967 measured reflections  $l = -13 \rightarrow 13$

*Refinement*

Refinement on  $F^2$   $w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 0.77P]$   
 $R[F^2 > 2\sigma(F^2)] = 0.023$  where  $P = (F_o^2 + 2F_c^2)/3$   
 $wR(F^2) = 0.054$   $(\Delta/\sigma)_{max} = 0.001$   
 $S = 1.05$   $\Delta\rho_{max} = 0.83 \text{ e \AA}^{-3}$   
 2544 reflections  $\Delta\rho_{min} = -1.07 \text{ e \AA}^{-3}$   
 101 parameters Extinction correction: SHELXL97  
 Extinction coefficient: 0.0018 (3)

**Table 3**

Selected geometric parameters (Å, °) for (II).

Rb—O3	2.9093 (19)	Sc—O3	2.0986 (18)
Rb—O4 <sup>x</sup>	2.925 (2)	Sc—O4	2.1029 (19)
Rb—O6 <sup>xi</sup>	2.982 (2)	Sc—O5	2.1083 (19)
Rb—O4	3.140 (2)	Sc—O6	2.1148 (18)
Rb—O3 <sup>xiii</sup>	3.155 (2)	As1—O1 <sup>x</sup>	1.6366 (19)
Rb—O5 <sup>xii</sup>	3.277 (2)	As1—O3 <sup>xiii</sup>	1.6619 (17)
Rb—O5 <sup>xiii</sup>	3.296 (2)	As1—O4	1.6688 (19)
Rb—O2 <sup>xii</sup>	3.308 (2)	As1—O7 <sup>xiv</sup>	1.7564 (17)
Rb—O7 <sup>xii</sup>	3.423 (2)	As2—O2	1.651 (2)
Rb—O1 <sup>x</sup>	3.455 (3)	As2—O5 <sup>xv</sup>	1.6619 (19)
Sc—O1	2.035 (2)	As2—O6 <sup>x</sup>	1.6670 (18)
Sc—O2	2.081 (2)	As2—O7	1.7578 (18)

As1<sup>x</sup>—O7—As2 119.62 (10)

Symmetry codes: (x)  $x, -\frac{3}{2} - y, z - \frac{1}{2}$ ; (xi)  $1 + x, y, z$ ; (xii)  $2 - x, -2 - y, 1 - z$ ; (xiii)  $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (xiv)  $x, -\frac{3}{2} - y, \frac{1}{2} + z$ ; (xv)  $1 - x, -2 - y, 1 - z$ .

For comparison purposes, the atomic coordinates of isotypic CsVP<sub>2</sub>O<sub>7</sub> (Wang & Lii, 1989) were used as starting parameters in the final refinement of (II). The H atom in (I) was refined freely (for the O—H distance, see Table 2).

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: SHELXS97

(Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Berndt, 1999) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1052). Services for accessing these data are described at the back of the journal.

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