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Structure of Heptaammonium Hydrogendecavanadotetraselenite Nonahydrate

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Abstract. $(NH_4)_7[HSe_4V_{10}O_{37}].9H_2O$, $M_r = 1706{\cdot}64$, tetragonal, $I\bar{4}2m$, $a = 20{\cdot}829\,(3)$, $c = 21{\cdot}580\,(3)$ Å, $U = 9362\,(2)$ Å^3, $Z = 8$, $D_x = 2{\cdot}42$, $D_m = 2{\cdot}46$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 5{\cdot}04$ mm^{-1}, $F(000) = 6640$, $T = 293$ K, final $R = 0{\cdot}071$ for 2108 independent reflections with $F \geq 2{\cdot}5\sigma(F)$. The $[Se_4V_{10}O_{37}]^{8-}$ anion has an entirely novel structure consisting of an α-*B*-SeV_9 type derivative form of the Keggin structure to which three suspended SeO_3 trigonal pyramids and one capping VO_5 trigonal bipyramid are attached. The capping V atom elongates its neighboring V—V distances to distort the SeV_9 skeleton from C_{3v} symmetry. The V—O bond distances vary from 1·55 to 2·39 Å according to the coordination number of the O atom, whereas the Se—O distances deviate only from 1·69 to 1·75 Å. This is the first crystal structure study of a heteropolyvanadate which has heteroatoms with unshared electron pairs.

Introduction. The chemistry of heteropolyvanadates is not as developed as those of molybdates and tungstates. Structural studies of vanadates containing heteroatoms of main-group elements have been restricted to the case of arsenic and phosphorus in their highest oxidation states: $[H_4As_6V_4O_{30}]^{4-}$ (Durif & Averbuch-Pouchot, 1979) and $[HPV_{14}O_{42}]^{8-}$ (Kato, Kobayashi & Sasaki, 1982). Polyvanadoselenites were first prepared by Prandtl & Lustig (1905). They claimed there were three types of vanadoselenites: red, orange and yellow series. Red and yellow compounds had Se/V ratios of 5/12 and 2/2 respectively, and the ratios of the orange compounds varied from 4/6 to 12/6. However no further investigations have been attempted. We prepared an ammonium salt of the red series. X-ray structure analysis revealed the anion has an Se/V ratio of 4/10 and forms a novel framework.

Experimental. 0·3 g NH_4VO_3 dissolved in 40 ml hot water, 2·0 g SeO_2 and 2·5 ml aqueous ammonia added, followed by acetic acid to adjust the pH to *ca* 5; the solution was kept at 278 K for 8 h and deep-red orthogonal single crystals were obtained. Elemental analysis for $(NH_4)_7[HSe_4V_{10}O_{37}].9H_2O$ found (calc.): Se 18·57 (18·52), V 28·77 (29·84), H 2·72 (2·75), N 5·65 (5·74). The space group was determined by analysis of the three-dimensional Patterson function. D_m by flotation. Crystal 0·13 × 0·13 × 0·15 mm mounted on a Rigaku AFC-5R diffractometer on an RU-1000 X-ray generator (50 kV, 1000 mA) at the High Intensity X-Ray Facilities, Engineering Research Institute, Faculty of Engineering, The University of Tokyo: Mo $K\alpha$ radiation monochromated by a graphite plate: lattice constants obtained by least squares from 16 reflections ($17 < \theta < 18°$); 3829 reflections ($30 \geq h \geq k \geq 0$, $30 \geq l \geq 0$, $2 < \theta < 30°$), of which 2108 independent reflections with $F \geq 2{\cdot}5\sigma(F)$ were used for the structure determination and refinement; ω–2θ scan mode; scan speed 6° min^{-1} (ω); Lorentz–polarization corrections; absorption correction (empirical correction using ψ scans with four reflections, transmission factors 1·0041–1·0723); three standard reflections monitored every 100 reflections varied within ±2%.

Se atoms were located by direct method using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). From succeeding Fourier syntheses V and O atoms in the polyanion were found. Atomic positions for water and ammonium groups were obtained from subsequent difference Fourier syntheses. The structure was refined by least-squares methods (on *F*) in the *UNICS*III system (Sakurai & Kobayashi, 1979). The complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final refinement with anisotropic temperature factors for all atoms converged at $R = 0{\cdot}071$ and $wR = 0{\cdot}090$, $S = 2{\cdot}76$, $(\Delta/\sigma)_{\max} = 0{\cdot}2$, final $\Delta\rho$ excursions $\leq 1{\cdot}7$ e Å^{-3}. The weighting scheme employed was $w^{-1} = \sigma^2(F_o) + 0{\cdot}0004|F_o|^2$. All the calculations were carried out on the HITAC M682H and S-810 computers at the Computer Centre of the University of Tokyo. Final atomic parameters are given in Table 1.* In the course of refinement, the capping V atom was found to be disordered over three pits, site *A* on the mirror plane and site *B* off the mirror plane (Fig. 1*b*). Their multiplicities were calculated by full-matrix least squares, and turned out to be 0·34 and 0·16, respectively. Strictly speaking, this disorder

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44001 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates* ($\times 10^4$), *thermal parameters* ($Å^2$) *and multiplicities*

$$B_{\text{eq}} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}	Multiplicity
Se(1)	2122 (2)	2122	3074 (1)	1·2	0·5
Se(2)	2752 (1)	716 (1)	1938 (1)	2·2	1·0
Se(3)	3415 (2)	3415	2481 (1)	1·7	0·5
V(4)	1624 (2)	521 (2)	2928 (2)	2·7	1·0
V(5)	1198 (4)	1198	4258 (2)	2·6	0·5
V(6)	3288 (2)	906 (2)	3285 (2)	2·3	1·0
V(7)	2822 (2)	1578 (2)	4585 (2)	2·3	1·0
V(8)	3732 (2)	2384 (2)	3526 (2)	2·3	1·0
V(*A*)	2991 (5)	2991	4483 (3)	1·9	0·34
V(*B*)	2266 (11)	454 (9)	3988 (10)	1·4	0·16
O*c*(1445)	1571 (12)	1571	3294 (8)	1·5	0·5
O*c*(1678)	2739 (6)	1870 (7)	3519 (6)	1·7	1·0
O*e*(44)	815 (14)	815	2667 (10)	2·4	0·5
O*e*(45*B*)	1347 (7)	427 (8)	3732 (7)	2·6	1·0
O*e*(67*B*)	3258 (8)	937 (7)	4144 (6)	2·8	1·0
O*e*(68)	3940 (7)	1604 (7)	3323 (7)	2·1	1·0
O*e*(78*A*)	3509 (7)	2196 (7)	4366 (7)	2·4	1·0
O*v*(46*B*)	2521 (7)	521 (7)	3216 (7)	2·1	1·0
O*v*(57*B*)	2055 (7)	1162 (7)	4511 (7)	2·1	1·0
O*v*(77*A*)	2373 (13)	2373	4765 (8)	1·7	0·5
O*v*(88*A*)	3200 (13)	3200	3729 (9)	1·9	0·5
O*j*(24)	2002 (7)	917 (8)	2171 (7)	3·0	1·0
O*j*(26)	3207 (8)	1189 (8)	2421 (6)	2·9	1·0
O*j*(38)	3506 (7)	2609 (6)	2697 (6)	1·8	1·0
O*t*(2)	2804 (8)	1155 (8)	1294 (6)	3·1	1·0
O*t*(3)	3329 (13)	3329	1701 (9)	2·8	0·5
O*t*(4)	1574 (10)	−207 (8)	2743 (10)	4·7	1·0
O*t*(5)	834 (15)	834	4778 (11)	3·1	0·5
O*t*(6)	3767 (7)	296 (8)	3211 (7)	3·2	1·0
O*t*(7)	3039 (8)	1419 (8)	5288 (7)	3·4	1·0
O*t*(8)	4405 (7)	2703 (8)	3627 (7)	2·7	1·0
O*t*(*A*)	3363 (22)	3363	5058 (14)	6·1	1·0
N(1)	5000	0	2500	6·3	0·25
N(2)	5000	5000	3018 (27)	5·7	0·25
N(3)	2478 (20)	2478	1138 (11)	2·3	0·5
N(4)	4186 (27)	4186	1123 (13)	5·0	0·5
N(5)	4071 (9)	1954 (11)	1643 (10)	3·5	1·0
N(6)	2253 (12)	−391 (13)	4270 (12)	4·5	0·84
O(aq1)	1090 (29)	1090	1139 (12)	13·0	0·5
O(aq2)	4098 (14)	152 (12)	1491 (26)	20·1	1·0
O*t*(*B*)†	2484	−282	4365		0·16

† Not included in the refinement.

causes some displacements in the positions of the other atoms, but no significant effects were detected in the difference Fourier synthesis except for site *B*. A difference Fourier peak of 1·0 e $Å^{-3}$ was found for this site, which was assigned to the terminal O atom bound to V(*B*), O*t*(*B*), with 0·16 occupancy. However it was not included in the refinement. Therefore the occupancy of N(6) was fixed at 0·84 and the occupancies of other atoms were fixed at unity. Accordingly, the atomic positions obtained here are the overlap images of three disordered positions, and the position of the proton indicated by the elemental analysis was therefore not determined. Only two independent water of crystallization molecules were located, partly because of their zeolitic properties and partly because the disorder of the capping site causes the disorder of ammonium and water groups. This gave rise to the rather high values of *R* and *wR*.

Discussion. According to the notation of Pope (1983), the $[Se_4V_{10}O_{37}]^{8-}$ anion has an α-*B*-SeV$_9$ skeleton, in which three V_3O_{13} units consisting of three edge-shared VO_6 octahedra are connected to each other by sharing two vertices (O*v*) to form C_{3v} symmetry. This skeleton can be derived from the Keggin structure by removing one V_3O_{13} unit. One remaining V atom is attached to one of three pits of this skeleton (Fig. 1*b*) forming a VO_5 trigonal bipyramid, just in the same manner as the 'capping' VO_5 units in the 'bicapped Keggin' structure of the $[PV_{14}O_{42}]^{9-}$ anion (Kato, Kobayashi & Sasaki, 1982). The capping site is orientationally disordered around the above-mentioned pseudo-threefold axis. One Se atom is coordinated by three O atoms (O*c*) which are shared by three V atoms of each V_3O_{13} unit. The other three, also forming trigonal pyramids, are suspended from this skeleton by sharing two O atoms (O*j*) with two V_3O_{13} units, and the remaining O atoms are left unshared (Fig. 1*a*). This is the first example of a heteroatom with both an unshared electron pair and a terminal O atom. In the $[AsW_8O_{30}As^{*}OH]^{7-}$ anion (Leyrie, Tézé & Hervé, 1985), the As* atom has a

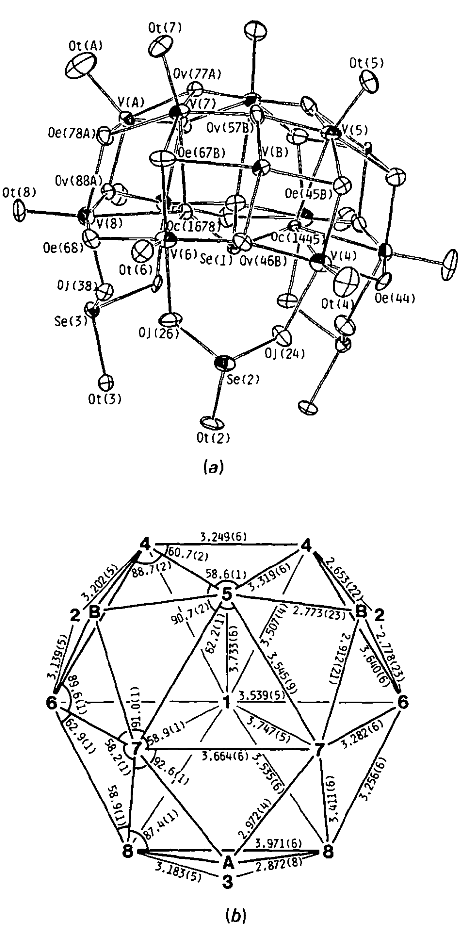

Fig. 1. (*a*) *ORTEP* (Johnson, 1976) view of the anion. The thermal ellipsoids are scaled to enclose 30% probability. (*b*) The skeleton made by Se and V atoms projected down to the plane made by atoms Se(2) and Se(3). Interatomic distances (Å) and angles (°) are shown with their e.s.d.'s in parentheses. The crystallographic mirror plane is normal to this plane and runs through Se(1), V(5) and V(*A*).

similar coordination to this suspended Se atom, having a lone pair of electrons and a terminal OH group. Whereas the As*—OH distance (1·861 Å) is significantly longer than the other As*—O distances (1·766 Å), as for the suspended Se atoms, Se—O*t* distances (1·67, 1·70 Å) are comparable with Se—O*j* distances (1·69, 1·72, 1·75 Å). Kato *et al.* (1982) mentioned that capping VO^{3+} units reduced the otherwise high negative charge of the $[PV_{14}O_{42}]^{9-}$ anion and stabilize it. These capping VO^{3+} and suspended SeO^{2+} units play similar roles.

As shown in Table 1, O atoms in the anion are simply classified into five groups: O*c* coordinated to three V atoms and the central Se atom; O*e* shared by two V atoms in the same V_3O_{13} unit; O*v* bridging two V atoms of the different units; O*j* bridging the skeleton and suspended Se atoms; O*t* bonded to only one metal atom. The parentheses following each O atom denote the metal atoms to which it coordinates.

Fig. 1(*b*) shows the skeleton formed by the Se and V atoms. It illustrates the effect of the capping V atom on its adjacent V—V distances. Distances between V atoms within the V_3O_{13} units vary from 3·249 to 3·411 Å, and between the V_3O_{13} units from 3·545 to 3·971 Å. These deviations are closely related to the occupancies and the positions of the capping V atoms. High occupancy and close proximity to the capping V atom elongate the V—V distances. Selected metal—O bond distances in the anion are listed in Table 2. Although the capping V atom is also expected to elongate its neighboring V—O distances, this effect is not clear because of the deviations of the individual V—O distances. V—O*e* distances near site *A* vary from 1·91 to 1·98 Å, near site *B* from 1·84 to 1·99 Å, and elsewhere from 1·74 to 1·99 Å. V—O*v* distances near site *A* deviate from 1·94 to 2·08 Å, and near site *B* from 1·79 to 1·97 Å. For Se—O bonds, no significant correlation was detected between the Se—O distances and the coordination numbers of O atoms; 1·67 and 1·70 Å for O*t*'s, 1·69–1·75 Å for O*j*'s, and 1·69 Å for O*c*'s. For the $[Se_2Mo_5O_{21}]^{4-}$ anion (Ichida, Fukushima & Sasaki, 1986), Se—O distances are 1·669–1·686 Å for O atoms bridging one Se and one Mo atom, and 1·686–1·732 Å for O atoms bridging one Se and two Mo atoms. Hydrogen bonds in the crystal are shown in Fig. 2. Neighboring anions are related to each other by twofold

Table 2. *Bond distances* (Å) *in the anion with e.s.d.'s in parentheses*

Se(1)	O*c*(1445)	1·69 (2)
	O*c*(1678)	1·69 (1)
Se(2)	O*j*(24)	1·69 (1)
	O*j*(26)	1·72 (2)
	O*t*(2)	1·67 (1)
Se(3)	O*j*(38)	1·75 (1)
	O*t*(3)	1·70 (2)
V(4)	O*c*(1445)	2·33 (1)
	O*e*(45*B*)	1·84 (2)
	O*e*(44)	1·88 (3)
	O*v*(46*B*)	1·97 (2)
	O*j*(24)	1·99 (2)
	O*t*(4)	1·57 (2)
V(5)	O*c*(1445)	2·35 (2)
	O*e*(45*B*)	1·99 (2)
	O*v*(57*B*)	1·87 (2)
	O*t*(5)	1·55 (2)
V(6)	O*c*(1678)	2·37 (1)
	O*e*(67*B*)	1·86 (1)
	O*e*(68)	1·99 (2)
	O*v*(46*B*)	1·79 (2)
	O*j*(26)	1·96 (1)
	O*t*(6)	1·62 (2)
V(7)	O*c*(1678)	2·39 (1)
	O*e*(67*B*)	1·87 (2)
	O*e*(78*A*)	1·98 (2)
	O*v*(57*B*)	1·82 (2)
	O*v*(77*A*)	1·94 (1)
	O*t*(7)	1·62 (2)
V(8)	O*c*(1678)	2·33 (1)
	O*e*(68)	1·74 (2)
	O*e*(78*A*)	1·91 (2)
	O*v*(88*A*)	2·08 (2)
	O*j*(38)	1·91 (1)
	O*t*(8)	1·57 (2)
V(*A*)	O*e*(78*A*)	1·99 (2)
	O*v*(77*A*)	1·92 (2)
	O*v*(88*A*)	1·74 (2)
	O*t*(*A*)	1·66 (3)
V(*B*)	O*e*(45*B*)	1·99 (3)
	O*e*(67*B*)	2·32 (3)
	O*v*(46*B*)	1·75 (3)
	O*v*(57*B*)	1·91 (2)

Table 3. *Interactions within* 3·1 Å *outside the polyanion with e.s.d.'s in parentheses*

N(1)	O(aq2)	2·89 (5)
	O*t*(6)	3·05 (1)
N(2)	O*e*(44^{i})	2·82 (4)
N(3)	O*t*(3)	2·79 (3)
	O*t*(2)	2·86 (4)
	O*v*(77*A*^{ii})	3·00 (3)
N(4)	O*t*(3)	2·82 (4)
	O*e*(45*B*^{i})	2·83 (5)
	O*t*(5^{ii})	2·90 (4)
N(5)	N(6^{iii})	2·80 (3)
	O*j*(38)	2·90 (3)
	O*j*(26)	2·93 (3)
	O*t*(6^{iii})	2·98 (3)
	O*t*(7^{iv})	3·10 (3)
N(6)	V(*B*)	1·86 (3)
	O*e*(45*B*)	2·80 (3)
	N(5^{v})	2·80 (3)
	O*t*(7^{vi})	2·86 (3)
	O*v*(46*B*)	3·02 (3)
O(aq1)	O*t*(*A*^{ii})	2·84 (4)
	O*j*(24)	2·95 (5)
O(aq2)	N(1)	2·89 (5)
	O*e*(68^{v})	2·94 (3)

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

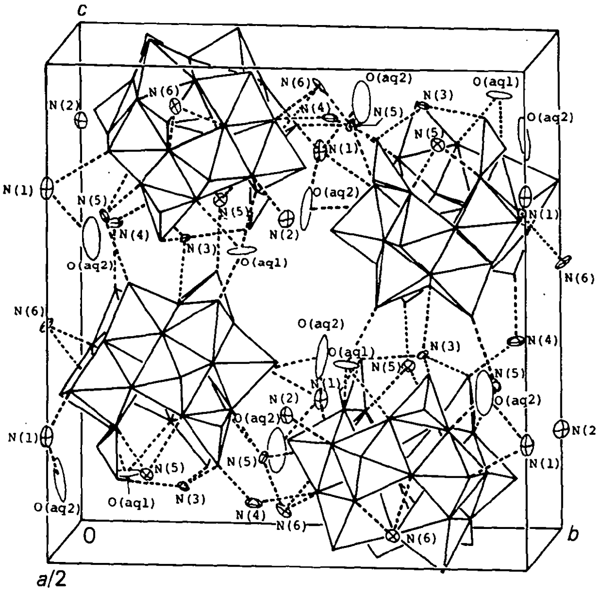

Fig. 2. The packing diagram. Only half of the cell ($0 \leq x \leq a/2$) is shown for clarity. The anions are represented in polyhedra forms. Thermal ellipsoids for water and ammonium groups are scaled to enclose 30% probability. Hydrogen bonds ≤3·1 Å are shown by dotted lines.

screw axes and connected to each other by hydrogen bonds through ammonium or water groups (Table 3). Of the six independent ammonium cations, N(3) has an exceptionally small temperature factor. It is coordinated by the three terminal O atoms bound to Se atoms.

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$Sc_5Re_8Si_{12}$, a New Orthorhombic Structure Type Related to $Sc_3Re_2Si_4$ and $Hf_2Ru_3Si_4$

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Abstract. $Sc_5Re_8Si_{12}$, $M_r = 2051·4$, orthorhombic, $oS100$, $Amm2$, $a = 14·475$ (4), $b = 19·66$ (1), $c = 5·237$ (2) Å, $V = 1490$ (1) Å^3, $Z = 4$, $D_x = 9·14$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 713$ cm^{-1}, $F(000) = 3492$, $T = 293$ K, $wR = 0·062$ for 2269 contributing reflections. The nearly face-centered structure is characterized by infinite parallel columns of face-joined Si-centered square antiprisms and infinite parallel columns of face-joined Re-centered deformed octahedra arranged in two structural slabs similar to those found in $Hf_2Ru_3Si_4$ and $Sc_3Re_2Si_4$. With respect to $Hf_2Ru_3Si_4$ or $Sc_3Re_2Si_4$ these two slabs are shifted in such a way that one is now the mirror image of the other; furthermore they are separated by additional atoms arranged in a plane and with composition $ScRe_2Si_4$. The $Sc_5Re_8Si_{12}$ structure is a correction of the previously published model of $ScRe_2Si_3$ in which four Sc atoms are missing in the unit cell.

Introduction. The phase diagram Sc–Re–Si has been investigated by Pecharskii (1979; cited by Rogl, 1984), who found five ternary phases: $Sc_2Re_3Si_4$, tetragonal, an ordered substitution variant of the Zr_5Si_4 type (Pecharskii, Bodak & Gladyshevskii, 1978); $Sc_3Re_2Si_3$, monoclinic, a new type (Pecharskii, Bodak & Gladyshevskii, 1979) for which a reinvestigation of the structure has shown that there are more Si atoms present, the true composition being $Sc_3Re_2Si_4$ (Chabot & Parthé, 1985); $ScRe_2Si_3$, orthorhombic, a new type (Pecharskii, Bodak & Gladyshevskii, 1979); '$ScReSi_2$' and '$Sc_8Re_3Si_9$' of unknown structures.

The structure model proposed for orthorhombic $ScRe_2Si_3$ attracted our attention because it contains holes which are not expected for this kind of compound. We decided thus to reinvestigate the composition and crystal structure of this phase.

Experimental. Samples of nominal compositions $Sc_4Re_9Si_{12}$, $Sc_5Re_8Si_{12}$, $Sc_4Re_8Si_{13}$ and $ScRe_2Si_3$ were prepared by arc melting under argon from Sc(99·99%), Re(99·99%) and Si(99·999%). Samples were X-ray powder analyzed both in their as-cast state and also after annealing (1070 K/7 d) and remelting, using a levitation technique to favor the crystal growth by slow cooling. None of the samples examined was single phase. Laue diffraction photographs showed a systematic splitting of the diffraction spots for most crystals selected. Good-quality single crystals were found in the $Sc_4Re_9Si_{12}$ as-cast sample only. The microchemical analysis of the majority phase of this sample was found, however, to be $Sc_{5.00(1)}Re_{7.85(1)}Si_{12.08(1)}$. The chemical analysis was performed on a Camebax MBX microprobe at 15 kV. The sample was analyzed simultaneously for Sc $K\alpha$, Re $M\beta$ and Si $K\alpha$ by wavelength dispersion and with $Sc_3Re_2Si_4$ (Chabot & Parthé, 1985) as standard. A single crystal of

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