The Crystal Structure of Scandium Selenate Pentahydrate

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The crystal structure of $Sc_2(SeO_4)_3 \cdot 5H_2O$ has been determined by single crystal X-ray diffraction techniques. The compound crystallizes in the space group $P1$, with unit cell dimensions $a = 11.225(4)$, $b = 11.804(3)$, $c = 5.766(2)$ Å, $\alpha = 91.35(4)$, $\beta = 100.10(2)$ and $\gamma = 89.03(7)°$. There are two formula units in each cell. Partial solution of the structure was accomplished by direct methods; subsequent electron density calculations revealed the positions of all non-hydrogen atoms. The structure was refined by least-squares calculations to an R value of 0.084 for 1730 significant reflections. The scandium atoms are octahedrally coordinated by oxygen atoms belonging to selenate groups and to water molecules. The mean $Sc-O$ distances in scandium coordination polyhedra vary from 2.08 to 2.10 Å and mean $Se-O$ bond lengths in selenate groups from 1.61 to 1.64 Å.

Our work on scandium sulfates and selenate pentahydrates was initiated as part of an investigation into the structural chemistry of rare earth compounds. Crystal and IR data for these compounds have been given and discussed in a previous report.[1] We are now reporting the results of a three-dimensional X-ray characterization of scandium selenate pentahydrate.

EXPERIMENTAL

Measurement of crystal and intensity data. The crystal data of $Sc_2(SeO_4)_3 \cdot 5H_2O$ are summarized in Table 1.

Single crystal intensities were collected on a Philips PW 1100 diffractometer, with graphite monochromated $CuK\alpha$ radiation. A scintillation counter with pulse height discrimination was used to detect the radiation. The dimensions of the crystal were $0.14 \times 0.10 \times 0.08$ mm³. The $\theta - 2\theta$ scan technique was employed, with a scan range of 1.5° and a scan speed of 0.02°/s.

Table 1. Crystal data of scandium selenate pentahydrate.

Formula	$Sc_2(SeO_4)_3 \cdot 5H_2O$
Formula weight	608.88
Lattice constants	$a = 11.225(4)$ Å
	$b = 11.804(3)$ Å
	$c = 5.766(2)$ Å
	$\alpha = 91.35(4)°$
	$\beta = 100.10(2)°$
	$\gamma = 89.03(7)°$
Cell volume	$V = 751.8$ Å³
Measured density	$D_m = 2.67$ g cm⁻³
Calculated density	$D_x = 2.69$ g cm⁻³
Molecules per unit cell	$Z = 2$
Space group	$P1$

Three test reflections were measured hourly to check for possible decomposition or misalignment of the crystal in the X-ray beam, but none occurred during the data collection. The background intensities were calculated as averages of the intensities at each end of the scan interval. All reflections with $\theta < 60°$ were recorded and, of these, 1730 reflections were considered to be significant based on the criterion $\sigma(I_{net})/I_{net} < 0.25$. The net intensities were corrected for Lorentz and polarization factors as well as for absorption ($\mu = 170$ cm⁻¹).

Structure determination and refinement. All calculations were carried out using IBM 1800 and 360/75 computers in Stockholm and a UNIVAC 1108 computer in Helsinki; the crystallographic programs have been described elsewhere.[2,3]

Unit cell dimensions indicated the presence of two formula units in each cell, and thus it was not possible to solve the Patterson function owing to the large number of heavy atoms. E-Statistics did not give any clear indication of the presence or absence of a symmetry center. We attempted to solve the structure by direct methods using the symbolic addition

Table 2. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^2$). Standard deviations are given in parenthesis.

Atom	x	y	z	U
Sc(1)	4732(8)	7634(4)	4822(5)	0.50(6)
Sc(2)	4594(9)	2611(5)	4789(5)	0.64(6)
Sc(3)	8600(7)	34(3)	956(3)	0.71(8)
Sc(4)	626(6)	5129(3)	8677(3)	0.61(7)
Se(1)	6596(4)	2588(2)	2054(2)	0.57(4)
Se(2)	6000(4)	7639(2)	1888(2)	0.71(4)
Se(3)	3279(4)	7605(2)	7738(2)	0.55(4)
Se(4)	2651(4)	2607(2)	7561(2)	0.85(4)
Se(5)	1547(4)	74(2)	3928(2)	1.13(4)
Se(6)	7723(4)	5128(2)	5724(2)	0.77(4)
O(1)	6797(20)	2766(9)	3528(10)	0.01(26)
O(2)	4116(29)	2930(14)	1319(14)	2.15(35)
O(3)	6880(23)	1244(11)	1694(12)	0.94(29)
O(4)	8884(22)	3328(10)	1738(11)	0.32(27)
O(5)	6158(22)	8883(10)	1259(11)	0.15(27)
O(6)	8122(25)	6833(12)	1691(13)	1.48(32)
O(7)	3347(28)	7110(14)	1441(14)	2.63(36)
O(8)	6407(28)	7970(13)	3333(14)	2.22(34)
O(9)	969(30)	8339(14)	7928(16)	3.21(40)
O(10)	5783(24)	8139(12)	8374(13)	1.80(32)
O(11)	3138(29)	6412(14)	8406(15)	2.39(38)
O(12)	3232(26)	7497(13)	6331(13)	1.92(33)
O(13)	2527(32)	2628(16)	6112(16)	3.78(42)
O(14)	817(24)	1714(12)	7977(13)	1.58(31)
O(15)	5283(24)	2251(12)	8193(13)	1.29(32)
O(16)	2058(25)	3929(12)	7803(13)	1.42(32)
O(17)	2694(23)	1319(11)	3868(12)	0.16(27)
O(18)	910(22)	9628(10)	2496(11)	0.70(27)
O(19)	3783(28)	9280(14)	4592(14)	2.85(38)
O(20)	9141(20)	104(10)	4482(11)	0.25(27)
O(21)	9841(25)	5212(13)	4848(13)	1.74(32)
O(22)	8497(30)	5567(15)	7127(15)	3.47(40)
O(23)	6692(31)	3849(15)	5841(15)	2.32(39)
O(24)	5779(25)	5912(13)	5004(13)	2.20(33)
W(1)[a]	2733(26)	5009(13)	376(14)	2.14(35)
W(2)	8652(26)	6346(13)	9473(14)	1.70(32)
W(3)	8586(28)	3836(15)	9359(15)	3.09(39)
W(4)	904(23)	1290(11)	417(12)	1.31(31)
W(5)	442(25)	8779(12)	225(13)	1.62(32)
W(6)	6787(22)	237(10)	9106(11)	0.54(27)
W(7)	7052(24)	1418(11)	5792(11)	0.90(30)
W(8)	2249(28)	3775(14)	3735(14)	2.53(39)
W(9)	1473(21)	7072(10)	3832(11)	0.42(28)
W(10)	7821(27)	8423(13)	5818(14)	2.19(36)

[a] W indicates water oxygen atoms.

procedure [4] and, after several attempts, succeeded in finding a partial solution, giving the positions of four selenium and two scandium atoms. Refinement in the centric space group did not lead to further improvements and therefore the acentric case $P1$ was tested.

Calculations revealed that the six atoms found were almost symmetrically located in the cell with respect to each other. An electron density map phased on these six atoms yielded the positions of the remaining non-hydrogen atoms.

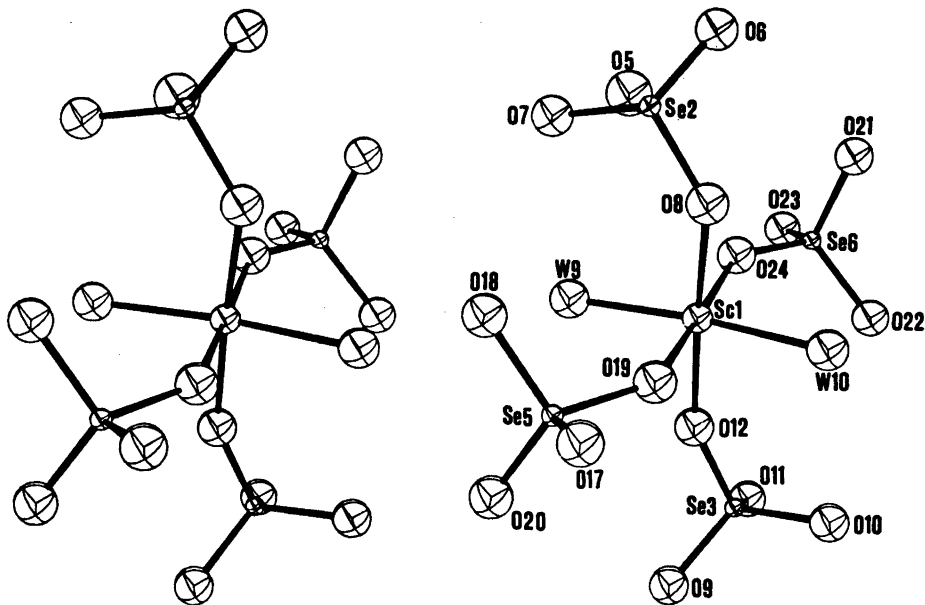Coordinates of the atoms were refined by the

Fig. 1. A stereoscopic view of the coordination about the Sc(1) atom.

method of block-diagonal least-squares calcula-tions with isotropic temperature factors. The scattering factors for the neutral atoms were used.[5] Corrections were made for anomalous dispersion but not for extinction. In the refine-ment the weighting scheme of Hughes [6] with $|F_{o,min}| = 5.0$ and $h = 4.0$ was used.

The final R value was 0.084 ($R = \sum ||F_o| - |F_c||/\sum |F_o|$). It was not possible to locate any of the hydrogen atoms from a difference Fourier

map calculated after the final refinement. The goal of this investigation, however, was to study the coordination of the non-hydrogen atoms and for this purpose the intensity data were quite satisfactory in spite of the rather high speed employed in data collection.

The positional and thermal parameters with their estimated standard deviations are given in Table 2. A listing of the observed and calculated structure factors is available from the authors upon request.
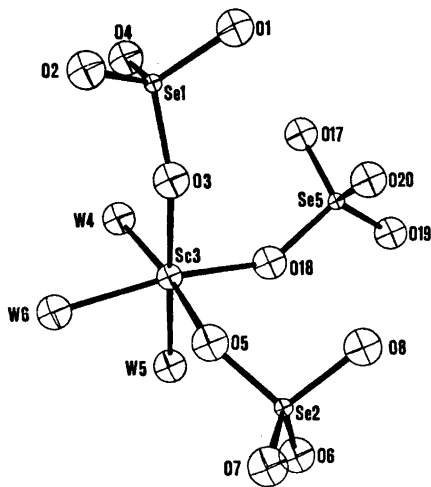

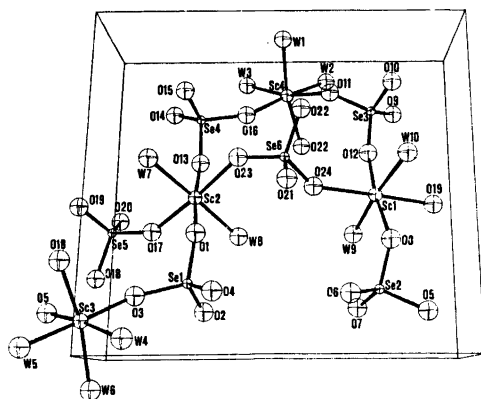*Fig. 2.* A perspective drawing showing the coordination about the Sc(3) atom.

Fig. 3. A perspective drawing of the structure of $Sc_2(SeO_4)_3.5H_2O$ showing the unit cell packing. The a axis is vertical, the b axis is horizontal and the c axis points into the paper.

Table 3. Bond lengths (Å) and selected angles (°) involving Sc.[a] Estimated standard deviations are given in parenthesis.

Sc(1) − O(8)	2.100(18)		Sc(2) − O(1)	2.065(14)
Sc(1) − O(19)	2.031(18)		Sc(2) − O(13)	2.062(21)
Sc(1) − O(12)	2.035(17)		Sc(2) − O(17)	2.045(14)
Sc(1) − O(24)	2.130(16)		Sc(2) − O(23)	2.114(18)
Sc(1) − W(9)	2.106(13)		Sc(2) − W(7)	2.176(14)
Sc(1) − W(10)	2.131(16)		Sc(2) − W(8)	2.141(17)
Sc(3) − O(3)	2.026(15)		Sc(4) − O(11)	2.127(17)
Sc(3) − O(18)	2.045(12)		Sc(4) − O(16)	2.009(16)
Sc(3) − O(5)	2.002(14)		Sc(4) − O(22)	2.012(17)
Sc(3) − W(4)	2.119(15)		Sc(4) − W(1)	2.078(15)
Sc(3) − W(5)	2.101(16)		Sc(4) − W(2)	2.153(16)
Sc(3) − W(6)	2.166(13)		Sc(4) − W(3)	2.120(18)

O(19) − Sc(1) − W(10)	80.7(6)		W(4) − Sc(3) − W(6)	82.8(5)
O(24) − Sc(1) − W(10)	99.3(6)		O(3) − Sc(3) − O(18)	96.7(5)
W(9) − Sc(1) − W(10)	172.2(6)		O(18) − Sc(3) − W(6)	165.4(6)
O(19) − Sc(1) − O(24)	177.9(7)		O(3) − Sc(3) − W(5)	178.7(5)
O(23) − Sc(2) − W(7)	84.5(6)		O(11) − Sc(4) − W(1)	82.8(6)
O(23) − Sc(2) − W(8)	96.1(7)		O(22) − Sc(4) − W(3)	101.5(7)
O(1) − Sc(2) − O(13)	173.8(7)		O(11) − Sc(4) − W(3)	166.7(6)
W(7) − Sc(2) − W(8)	177.5(7)		O(16) − Sc(4) − W(2)	172.5(6)

[a] Only the extreme angle values are listed for each coordination octahedron.

DESCRIPTION AND DISCUSSION OF STRUCTURE

The scandium atoms are octahedrally coordinated by oxygen atoms belonging to selenate groups and to water molecules. Scandium atoms Sc(1) and Sc(2) are coordinated by two water molecules while the remaining scandium atoms are coordinated by three; thus all water molecules are in the inner-coordination sphere of scandium atoms. Figs. 1 and 2 show the coordination about scandium atoms Sc(1) and Sc(3), respectively. The atomic numbering scheme adopted is indicated in these pictures and in Fig. 3 which shows the unit cell viewed down the c-axis.

The Sc − O distances vary between 2.00 Å and 2.17 Å, but there are not significant differences between the scandium atoms. The mean Sc − O values for Sc(1) − Sc(4) are 2.09, 2.10, 2.08, and 2.08 Å, respectively; the average of all Sc − O distances is 2.09 Å. This average is in good agreement with the bond lengths reported in recent literature for six-coordinated scandium,[7-9] but is slightly less than the value obtained by combining the suggested ionic radii (1.40 Å for O^{2-} and 0.745 Å for Sc^{3+}).[10,11]

It should be noted that the mean Sc − O-(water) distance (2.13 Å) is somewhat longer than the corresponding Sc − O(selenate) distance (2.05 Å); a similar pattern has been observed in several rare earth sulfates.[12-14] This difference leads to slightly more distorted coordination octahedra for Sc(3) and Sc(4), which are coordinated by three water oxygens, as compared to Sc(1) and Sc(2); cf. Table 3 for distances and angles.

In the selenate groups the average value of all Se − O bond lengths is 1.63 Å; cf. Table 4 for distances and angles involving selenium atoms. The mean values of Se − O distances for selenate groups Se(1) − Se(6) come within the estimated standard deviations from this value. However, the individual bond lengths in some selenate groups vary significantly; e.g. in the Se(6) group they range from 1.57 to 1.70 Å. The mean Se − O distances found in this study are comparable to the corresponding bond lengths observed in other selenates. Table 6 lists the selenates whose crystal structures are known, along with their average Se − O bond lengths. The overall average is 1.64 Å and the mean values for different selenate groups do not differ much from this value. A closer look at

Table 4. Bond lengths (Å) and angles (°) in SeO₄ groups. Estimated standard deviations are given in parenthesis.

Se(1)−O(1)	1.654(12)		Se(2)−O(5)	1.626(13)	
Se(1)−O(2)	1.578(16)		Se(2)−O(6)	1.614(15)	
Se(1)−O(3)	1.663(14)		Se(2)−O(7)	1.636(16)	
Se(1)−O(4)	1.652(13)		Se(2)−O(8)	1.650(16)	
Se(3)−O(9)	1.652(18)		Se(4)−O(13)	1.614(18)	
Se(3)−O(10)	1.613(14)		Se(4)−O(14)	1.599(15)	
Se(3)−O(11)	1.591(17)		Se(4)−O(15)	1.619(14)	
Se(3)−O(12)	1.581(15)		Se(4)−O(16)	1.643(15)	
Se(5)−O(17)	1.603(13)		Se(6)−O(21)	1.696(16)	
Se(5)−O(18)	1.676(12)		Se(6)−O(22)	1.649(17)	
Se(5)−O(19)	1.670(16)		Se(6)−O(23)	1.622(18)	
Se(5)−O(20)	1.618(13)		Se(6)−O(24)	1.571(14)	

O(1)−Se(1)−O(2)	112.5(7)	O(13)−Se(4)−O(14)	112.3(8)
O(1)−Se(1)−O(3)	112.8(6)	O(13)−Se(4)−O(15)	108.2(9)
O(1)−Se(1)−O(4)	102.9(6)	O(13)−Se(4)−O(16)	101.2(9)
O(2)−Se(1)−O(3)	104.5(7)	O(14)−Se(4)−O(15)	108.2(7)
O(2)−Se(1)−O(4)	115.8(7)	O(14)−Se(4)−O(16)	113.4(8)
O(3)−Se(1)−O(4)	108.6(7)	O(15)−Se(4)−O(16)	113.3(7)
O(5)−Se(2)−O(6)	112.6(7)	O(17)−Se(5)−O(18)	105.9(6)
O(5)−Se(2)−O(7)	108.3(7)	O(17)−Se(5)−O(19)	104.3(7)
O(5)−Se(2)−O(8)	101.1(7)	O(17)−Se(5)−O(20)	111.3(7)
O(6)−Se(2)−O(7)	115.2(8)	O(18)−Se(5)−O(19)	105.2(7)
O(6)−Se(2)−O(8)	107.9(8)	O(18)−Se(5)−O(20)	109.0(6)
O(7)−Se(2)−O(8)	110.8(8)	O(19)−Se(5)−O(20)	120.2(7)
O(9)−Se(3)−O(10)	114.6(8)	O(21)−Se(6)−O(22)	116.2(8)
O(9)−Se(3)−O(11)	107.9(9)	O(21)−Se(6)−O(23)	112.8(8)
O(9)−Se(3)−O(12)	108.0(8)	O(21)−Se(6)−O(24)	101.9(7)
O(10)−Se(3)−O(11)	103.7(7)	O(22)−Se(6)−O(23)	105.2(8)
O(10)−Se(3)−O(12)	109.6(8)	O(22)−Se(6)−O(24)	110.3(8)
O(11)−Se(3)−O(12)	113.1(8)	O(23)−Se(6)−O(24)	110.7(8)

Table 5. Additional distances less than 3.0 Å. Polyhedral edges are not included. Estimated standard deviations are given in parenthesis.

O(1)−W(7)	2.959(18)	O(13)−W(8)	2.952(25)
O(1)−W(8)	2.952(18)		
		O(14)−W(4)	2.768(20)
O(2)−W(1)	2.735(22)	O(14)−W(7)	2.994(18)
O(2)−W(4)	2.727(20)		
		O(15)−W(3)	2.807(21)
O(3)−W(4)	2.933(20)	O(15)−W(6)	2.675(19)
O(3)−O(5)	2.846(19)		
		O(16)−W(3)	2.879(24)
O(4)−W(8)	2.743(19)		
O(4)−W(3)	2.703(12)	O(17)−W(8)	2.915(21)
O(5)−W(5)	2.914(20)	O(18)−W(5)	2.721(19)
O(5)−W(6)	2.946(18)		
		O(19)−W(9)	2.696(20)
O(6)−W(9)	2.819(18)	O(19)−W(10)	2.697(22)
O(6)−W(2)	2.635(22)		

Table 5. Continued.

O(7) – W(1)	2.759(22)		O(20) – W(7)	2.609(20)
O(7) – W(5)	2.794(21)		O(20) – W(10)	2.645(20)
O(8) – W(10)	2.822(22)		O(21) – W(8)	2.675(24)
			O(21) – W(9)	2.685(20)
O(9) – W(5)	2.709(24)			
O(9) – W(10)	2.720(22)		O(22) – W(2)	2.790(24)
O(10) – W(2)	2.844(20)		O(23) – W(7)	2.885(22)
O(10) – W(6)	2.642(18)			
			O(24) – W(9)	2.952(19)
O(11) – W(1)	2.781(23)			
			W(1) – W(2)	2.887(21)
O(12) – W(9)	2.859(19)		W(1) – W(3)	2.807(21)
O(12) – W(10)	2.985(23)		W(2) – W(3)	2.968(23)
			W(4) – W(5)	2.978(20)
			W(4) – W(6)	2.835(17)
			W(5) – W(6)	2.853(18)

Table 6. Comparison of averaged Se – O distances (Å) found in selenate structures. Vibrationally corrected values are given in parenthesis.

Compound	Mean Se – O distance	E.s.d[a]	Reference
H_2SeO_4	1.61	n.a.	Bailey & Wells [15]
$[Al_2(OH)_2(H_2O)_8](SeO_4)_2.2H_2O$	1.62	n.a.	Johansson [16]
$MnSeO_4$	1.65	0.02	Fuess & Will [17]
$CoSeO_4$	1.64	0.05	Fuess & Will [17]
$NiSeO_4$	1.67	0.02	Fuess & Will [17]
$HgSeO_4$	1.64	0.07	Dorm [18]
$Cu(NH_3)_4SeO_4$	1.635 $(1.643)^b$	0.008	Morosin [19]
Na_2SeO_4	1.654	0.021	Kálmán & Cruickshank [20]
K_2SeO_4	(1.648)	0.016	Kálmán, Stephens & Cruickshank [21]
$NiSeO_4.6H_2O$	1.65	0.03	Fuess [22]
$Ce_2(SeO_4)_3.5H_2O$	1.65	0.03	Aslanov, Farag & Porai-Koshits [23]
	1.65	0.04	
	1.65	0.03	
$Na_2Cu(SeO_4)_2.2H_2O$	1.649	0.014	Pentavin & Philippot [24]
$K_2Co(SeO_4)_2.2H_2O$	1.634	0.007	Pentavin
	1.633	0.006	Philippot & Lindqvist [25,26]
$Sc_2(SeO_4)_3.5H_2O$	1.637	0.016	This work
	1.632	0.016	
	1.609	0.018	
	1.619	0.018	
	1.642	0.016	
	1.635	0.018	

[a] The e.s.d column lists the largest deviation in individual bond length (Å) in each crystallographically independent polyhedron. [b] From Ref. 20.

the structures, however, reveals in some cases rather large variations in the individual bond lengths within the same selenate group. For instance, in $CoSeO_4$ the shortest distance is 1.56 ± 0.02 Å while the longest one is 1.69 ± 0.03 Å;[17] a somewhat similar situation is found in H_2SeO_4.[15]

The scandium atoms are cross-linked in the structure by sharing their selenate ions with other scandium atoms, as can be seen in Fig. 3. Linkages approximately parallel to the *b*-axis are formed, joining the Sc(1) and Sc(2) atoms *via* Se(5) and Se(6) selenate groups into continuous chains. To these chains, Sc(3) atoms are linked by Se(1) and Se(2) groups and, on the opposite side, Sc(4) by Se(3) and Se(4) groups; thus a three-dimensional structure is formed. Not all selenate oxygen atoms, however, are bonded to scandium atoms, there are ten oxygen atoms which are exclusively bounded to selenium atoms (*cf.* Table 3).

The structure is further strengthened by hydrogen bonding, which may involve the water molecules and selenate oxygens. The listing of additional distances less than 3.0 Å in Table 5 also includes the possible hydrogen bonds.

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