SHORT STRUCTURAL PAPERS

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Anhydrous Scandium Selenate

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Abstract. $Sc_2(SeO_4)_3$, monoclinic, $P2_1/c$ (No. 14), $a = 8{\cdot}899\,(2)$, $b = 9{\cdot}212\,(2)$, $c = 15{\cdot}179\,(3)$ Å, $\beta = 124{\cdot}83\,(2)°$, $V = 1021{\cdot}52$ Å^3, $Z = 4$, $D_x = 3{\cdot}37$ g cm^{-3}, μ(Mo $K\alpha$) = 119·7 cm^{-1}, $R = 0{\cdot}038$ for 1602 reflections. The structure consists of octahedrally coordinated Sc atoms linked together by SeO_4 tetrahedra.

Introduction. Structures of scandium selenites and selenates are being investigated in this laboratory. The scandium compounds $Sc_2(SeO_4)_3.5H_2O$ (Valkonen, Niinistö, Eriksson, Larsson & Skoglund, 1975), $(NH_4)_3Sc(SeO_4)_3$ (Valkonen & Niinistö, 1978) and $Sc(HSeO_3)_3$ (Valkonen & Leskelä, 1978) have already been solved, and the structure of $Na_3Sc(SO_4)_3.5H_2O$ has been determined elsewhere (Sizova, Voronkov & Belov, 1975). $Sc_2(SeO_4)_3$ was crystallized earlier by Crookes (1909) and Trousil (1938), and Bouissières, Gaume-Mahn, Henry la Blanchetais, Loriers & Trombe (1959) have reported it to be tetragonal but give no lattice parameters. The present communication describes the structure refinement of $Sc_2(SeO_4)_3$.

The compound was crystallized as follows: 200 mg Sc_2O_3 was dissolved in 3 cm^3 selenic acid (0·8 g cm^{-3}) and 10 cm^3 H_2O. Then 150 mg $LiOH.H_2O$ was added to increase the pH, since $Sc_2(SeO_4)_3$ does not crystallize in very acidic solution. Well developed colourless prisms of $Sc_2(SeO_4)_3$ were grown by keeping the solution covered with a watchglass and over a water bath for a few days. Ammonia and sodium hydroxide solutions could not be used owing to the precipitation of $(NH_4)_3Sc(SeO_4)_3$ and $Na_3Sc(SeO_4)_3.5H_2O$, respectively.

A computer-controlled Syntex $P2_1$ (Fortran version) four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation was utilized in the determination of unit-cell parameters and the collection of intensity data. The crystal size was 0·2 × 0·2 × 0·1 mm and temperature 298 K. Cell dimensions were calculated from diffractometer measurements of setting angles for 21 reflections. Intensity data were collected in The space group $P2_1/c$ (No. 14) was determined on the basis of systematic absences in the original intensity the interval $5° < 2\theta < 60°$ using the $\theta/2\theta$ technique and a scan speed of 2° min^{-1}. Of the 2144 unique reflections measured, 1602 had intensities $I > 3\sigma(I)$. data. Empirical absorption correction was from the φ scan, after which Lorentz and polarization corrections were applied.

The solution, refinement and plots were carried out with the XRAY 76 program package (Stewart, 1976) and a Univac 1108 computer. Scattering factors were taken from Cromer & Mann (1968). The Sc and Se atomic positions were determined by direct methods from the 211 E values larger than 1·2. The positions of two Sc and three Se atoms were then refined, and the subsequent difference Fourier map gave the positions of the O atoms. After refinement with isotropic temperature factors the value of R was 5·1%, and after block-diagonal-matrix refinement with anisotropic temperature factors the final value of R was 3·8%.

Table 1. *Positional parameters* ($\times 10^4$) *for* $Sc_2(SeO_4)_3$

The standard deviations of the last significant figures are given in parentheses.

	x	y	z
Se(1)	2451 (1)	8785 (1)	3491 (1)
Se(2)	4660 (1)	3844 (1)	3562 (1)
Se(3)	9580 (1)	7525 (1)	4944 (1)
Sc(1)	3680 (3)	5340 (2)	1166 (2)
Sc(2)	8688 (3)	327 (2)	1159 (2)
O(1)	3879 (10)	9199 (9)	3186 (6)
O(2)	3386 (11)	9107 (10)	4752 (6)
O(3)	2032 (11)	7058 (8)	3271 (7)
O(4)	9405 (11)	4765 (10)	2223 (6)
O(5)	3288 (11)	3915 (10)	3948 (7)
O(6)	4679 (11)	2207 (8)	3151 (6)
O(7)	3949 (12)	5000 (9)	2606 (6)
O(8)	3253 (12)	9264 (10)	448 (7)
O(9)	9661 (11)	6866 (9)	3966 (7)
O(10)	7631 (11)	8334 (9)	4441 (7)
O(11)	8788 (10)	1320 (9)	4357 (7)
O(12)	9821 (10)	8737 (9)	755 (6)

Table 2. *Bond lengths* (Å) *and angles* (°) *in* ScO_6 *octahedra*

Estimated standard deviations are given in parentheses.

Sc(1)–O(1)	2·086 (9)	O(2)–Sc(1)–O(6)	87·2 (4)
Sc(1)–O(2)	2·072 (10)	–O(7)	174·4 (4)
Sc(1)–O(6)	2·106 (8)	–O(10)	93·0 (4)
Sc(1)–O(7)	2·083 (11)	–O(11)	91·0 (4)
Sc(1)–O(10)	2·097 (8)	O(6)–Sc(1)–O(7)	88·5 (4)
Sc(1)–O(11)	2·069 (9)	–O(10)	172·5 (4)
O(1)–Sc(1)–O(2)	95·4 (4)	–O(11)	96·8 (3)
–O(6)	86·4 (3)	O(7)–Sc(1)–O(10)	91·7 (4)
–O(7)	88·0 (4)	–O(11)	85·9 (4)
–O(10)	86·1 (3)	O(10)–Sc(1)–O(11)	90·8 (13)
–O(11)	173·0 (4)		
Sc(2)–O(3)	2·082 (10)	O(4)–Sc(2)–O(5)	91·2 (4)
Sc(2)–O(4)	2·096 (7)	–O(8)	176·1 (4)
Sc(2)–O(5)	2·117 (10)	–O(9)	97·4 (4)
Sc(2)–O(8)	2·065 (8)	–O(12)	87·9 (4)
Sc(2)–O(9)	2·127 (11)	O(5)–Sc(2)–O(8)	85·6 (4)
Sc(2)–O(12)	2·060 (10)	–O(9)	171·3 (3)
O(3)–Sc(2)–O(4)	86·6 (4)	–O(12)	93·8 (4)
–O(5)	91·2 (4)	O(8)–Sc(2)–O(9)	85·8 (4)
–O(8)	95·9 (4)	–O(12)	90·0 (4)
–O(9)	85·3 (4)	O(9)–Sc(2)–O(12)	88·1 (4)
–O(12)	170·8 (3)		

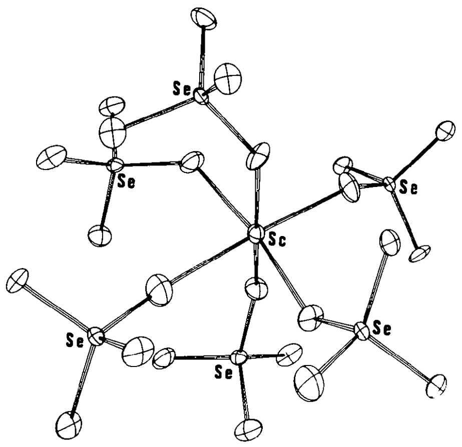

Fig. 1. The coordination around Sc.

Table 3. *A comparison of* Sc–O *distances and* O–Sc–O *angles in some scandium compounds*

Compound	Sc–O range (Å)	O–Sc–O range (°)
$Sc_2(SeO_4)_3.5H_2O$ (1)	2·002–2·176	80·7–101·5 165·4–177·9
$(NH_4)_3Sc(SeO_4)_3$ (2)	2·007–2·185	82·9–96·9 174·5–176·6
$Na_3Sc(SO_4)_3.2H_2O$ (3)	2·05–2·12	82·5–96·0
$Sc(HSeO_3)_3$ (4)	2·041–2·158	82·8–103·5 163·9–173·6
$Sc_2(SeO_4)_3$ (5)	2·060–2·127	85·3–97·4 170·8–176·1

References: (1) Valkonen *et al.* (1975). (2) Valkonen & Niinistö (1978). (3) Sizova, Voronkov & Belov (1975). (4) Valkonen & Leskelä (1978). (5) Present work.

Table 4. *Bond lengths* (Å) *and angles* (°) *in* SeO_4 *tetrahedra*

Estimated standard deviations are given in parentheses.

Se(1)–O(1)	1·626 (11)	O(1)–Se(1)–O(2)	109·6 (5)
–O(2)	1·620 (8)	–O(3)	107·3 (5)
–O(3)	1·625 (8)	–O(4)	109·6 (5)
–O(4)	1·635 (8)	O(2)–Se(1)–O(3)	108·9 (5)
		–O(4)	109·2 (5)
		O(3)–Se(1)–O(4)	112·1 (4)
Se(2)–O(5)	1·630 (12)	O(5)–Se(2)–O(6)	110·3 (5)
–O(6)	1·636 (8)	–O(7)	107·9 (5)
–O(7)	1·609 (9)	–O(8)	110·5 (5)
–O(8)	1·634 (8)	O(6)–Se(2)–O(7)	110·5 (5)
		–O(8)	108·4 (5)
		O(7)–Se(2)–O(8)	109·2 (5)
Se(3)–O(9)	1·644 (11)	O(9)–Se(3)–O(10)	109·3 (4)
–O(10)	1·622 (9)	–O(11)	110·5 (5)
–O(11)	1·615 (8)	–O(12)	111·5 (5)
–O(12)	1·616 (9)	O(10)–Se(3)–O(11)	109·0 (4)
		–O(12)	109·3 (5)
		O(11)–Se(3)–O(12)	107·2 (4)

Discussion. Positional parameters for the non-hydrogen atoms are given in Table 1.* Sc atoms are surrounded by six O atoms belonging to six SeO_4 groups (Fig. 1). The average Sc(1)–O distance is 2·085 Å, and the individual Sc(1)–O distances vary insignificantly between 2·069 and 2·106 Å (Table 2). The average Sc(2)–O distance is 2·091 Å, but the individual distances vary between 2·060 and 2·127 Å, and the Sc(2) octahedron appears to be distorted. The Sc(2)–O distances can be divided into two groups, four short and two longer distances on opposite sides of the octahedron, *i.e.* the octahedron is slightly tetragonally elongated. Distances between Sc and O are normal compared with other Sc compounds (Table 3).

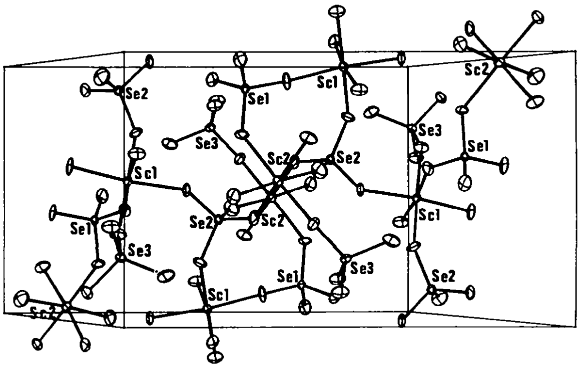

Fig. 2. Contents of the unit cell. *c* is horizontal, *b* vertical.

The O atoms of the SeO_4 groups are each connected to different Sc atoms. Because every O is bonded to Sc,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33275 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the variation in Se—O distances is small and SeO_4 groups are quite regular (Table 4). The average Se—O distance is 1·626 Å [Se(1)—O 1·627, Se(2)—O 1·627, Se(3)—O 1·624 Å], which is in good agreement with other selenate structures (Valkonen *et al.*, 1975).

As shown in Fig. 2, one unit cell is made up of 8 ScO_6 octahedra and 12 SeO_4 tetrahedra. These groups are linked through shared O atoms and together form a three-dimensional network.

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Neodymium Diarsenide: A Single-Crystal Structure Refinement[*]

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Abstract. $NdAs_2$, monoclinic, $P2_1/c$, $a = 4\cdot1081$ (2), $b = 6\cdot8201$ (2), $c = 10\cdot4431$ (3) Å, $\beta = 106\cdot718$ (3)°, $Z = 4$, $U = 280\cdot22$ Å^3, FW 294·1, $D_x = 6\cdot97$ g cm^{-3}, μ(Mo $K\alpha$) = 429 cm^{-1}, $F(000) = 504$. The model below was refined by full-matrix least squares with allowance for anomalous dispersion and extinction to $R_2 = 0\cdot054$ for 928 observed diffractometer data. The structure is of a new distinctive type. The Nd atoms form buckled 6^3 nets which are stacked along the short a axis giving a continuous three-dimensional Nd network with open hexagonal channels. Adjoining pairs of hexagons outline skew prisms which are centred by almost planar As_4 zigzag chains. These polyanions are centrosymmetric, with terminal and bridge As—As distances of 2·477 and 2·497 Å respectively; the As—As—As angle is 104·3°. The overall coordination numbers are 14, 16 and 12 for Nd, As(1) and As(2), respectively, with average As—As, Nd—As and Nd—Nd distances of 2·49, 3·18 and 4·09 Å respectively.

Introduction. Intensity data were collected on a computer-controlled Picker diffractometer using local programs [for details not given here see Wang, Gabe, Calvert & Taylor (1976)]. $NdAs_2$ crystals were grown on polycrystalline $NdAs_2$ (0·05 g) at 600°C in a tube of 7 ml volume containing iodine (0·03 g) and arsenic (0·05 g). Two fragments were studied, both protected by sealed capillaries. The larger, a lath-shaped fragment (0·04 × 0·06 × 0·2 mm) mounted along its length, was used to collect 2044 reflections with $2\theta < 65°$ by the θ–2θ scan technique (Mo $K\alpha$ radiation, graphite monochromator) with a scan range which was varied as (0·6 × 0·7 tan θ + 0·6)°; 91% of the reflections were taken as observed ($I > 2\sigma$; where σ is the standard deviation of the net count). The lattice parameters were derived from 68 reflections with $2\theta > 60°$ and agree well with those reported earlier (Ono, Despault, Calvert & Taylor, 1970). Two symmetry-equivalent sets ($hk\bar{l}$ + hkl, $\bar{h}\bar{k}\bar{l}$ + $\bar{h}\bar{k}l$) were collected, corrected for absorption (Wang, Gabe, Calvert & Taylor, 1976), Lorentz and polarization factors and then averaged to give 932 independent observed hkl; the discrepancy between the two sets ($\sum \Delta I/\sum I$) was 0·022 and transmission factors ranged from 0·09 to 0·21. The space group had been determined (Ono, Despault, Calvert & Taylor, 1970) as $P2_1/c$ and this was confirmed by precession photographs ($h0l$ observed for $l = 2n$ and $0k0$ for $k = 2n$). A trial structure was obtained by direct methods and these coordinates were refined by full-matrix least squares with allowance for anomalous dispersion and isotropic extinction correction (Larson, 1970) using the laboratory PDP-8 computer and local programs; the final values for R_1 and R_2 are 0·049 and 0·054 with

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