References

Coppens, S. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Sudarsanan, K. & Young, R. A. (1969). *Acta Cryst.* B**25**, 1534–1543.

Sudarsanan, K. & Young, R. A. (1972). *Acta Cryst.* B**28**, 3668–3670.

Sudarsanan, K., Young, R. A. & Donnay, J. D. H. (1973). *Acta Cryst.* B**29**, 808–814; 2649.

Wuensch, B. J. & Prewitt, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.

Acta Cryst. (1978). B**34**, 3064–3066

Scandium Hydrogenselenate Dihydrate

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(*Received* 5 *April* 1978; *accepted* 30 *May* 1978)

Abstract. $ScH(SeO_4)_2.2H_2O$, monoclinic, $C2/m$ (No. 12), $a = 8{\cdot}708$ (5), $b = 5{\cdot}632$ (4), $c = 9{\cdot}105$ (9) Å, $\beta = 101{\cdot}64$ (7)°, $V = 437{\cdot}3$ (6) Å^3, $Z = 2$, $D_x = 2{\cdot}79$ g cm^{-3}, μ(Mo $K\alpha$) = 91·0 cm^{-1}, $R = 0{\cdot}054$ for 1002 reflections. The structure consists of layers formed by ScO_6 octahedra and SeO_4 tetrahedra. The layers are connected together through water molecules by hydrogen bonds.

Introduction. Sc forms a very interesting series of compounds with selenium oxyacids. Some of these are normal salts [$Sc_2(SeO_4)_3.5H_2O$, Valkonen, Niinistö, Eriksson, Larsson & Skoglund, 1975; $Sc_2(SeO_4)_3$, Valkonen, 1978]. $(NH_4)_3Sc(SeO_4)_3$ is a complex compound (Valkonen & Niinistö, 1978) and $Sc(HSeO_3)_3$ (Valkonen & Leskelä, 1978) is an acid salt. In all these compounds Sc is six-coordinated to O atoms belonging to selenite or selenate groups or to the water of crystallization. For example, the structure of $(NH_4)_3Sc(SeO_4)_3$ consists of $Sc(SeO_4)_3^{3-}$ columns connected by hydrogen bonds, and the structure of $Sc_2(SeO_4)_3$ consists of a three-dimensional network. In this study the structure of the title compound is solved.

Crystals of the title compound suitable for X-ray analysis were grown by dissolving scandium oxide in a very concentrated solution of selenic acid and letting it evaporate at 50°C for about one week. The colorless prisms were approximately 0·3 × 0·2 × 0·2 mm.

The formula of the title compound can also be written as $Sc_2(SeO_4)_3H_2SeO_4.4H_2O$ with $Z = 1$. Scandium hydrogensulfate has been assigned the formula $Sc_2(SO_4)_3.3H_2SO_4$ (Komissarova, Shatskii & Moiseichenko, 1965; Wirth, 1914), but there is also evidence of another phase with the formula $Sc_2(SO_4)_3H_2SO_4.4H_2O$ (Trousil, 1938). The corresponding selenate has the formula $Sc_2(SeO_4)_3H_2SeO_4.4H_2O$ according to Trousil (1938). Bouissières, Gaume-Mahn, Henry la Blanchetais, Loriers & Trombe (1959), however, report only two molecules of water of crystallization.

Unit-cell parameters were determined and intensity data collected on a Syntex $P2_1$ (Fortran version) automatic four-circle single-crystal diffractometer with monochromatized Mo $K\alpha$ radiation. Unit-cell parameters were calculated by least-squares refinement of 20 reflections. Intensities of 1301 reflections were collected in the range $5 \leq 2\theta \leq 75°$ using the $\theta/2\theta$ technique and variable scan speed of 1–3° min^{-1}. The 1002 reflections with intensities greater than three times their standard deviations were used in the refinement. The unit cell was of the type C with no systematic absences (except those for type C). Therefore, space groups $C2$, Cm and $C2/m$ (Nos. 5, 8 and 12) were possible. An empirical absorption correction was made from the φ scan, after which Lorentz and polarization corrections were applied.

The structure was solved by direct methods with the computer program *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Refinement

Table 1. *Positional parameters* ($\times 10^4$) *for* $ScH(SeO_4)_2.2H_2O$

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

	x	y	z
Sc	0	0	0
Se	6023 (1)	0	8163 (1)
O(1)	4968 (5)	2375 (8)	8328 (5)
O(2)	6487 (9)	0	6505 (7)
O(3)	7598 (7)	0	9569 (7)
O(4)*	8726 (16)	902 (25)	4871 (16)

* With a population parameter of 0·5.

and plotting were carried out with the XRAY 76 program package (Stewart, 1976) and a Univac 1108 computer. The scattering factors were those of Cromer & Mann (1968) for neutral atoms. The final value of *R* was reached after block-diagonal matrix refinement with anisotropic temperature factors. H atom positions could not be determined from the difference Fourier map.

Discussion. Positional parameters for non-hydrogen atoms are listed in Table 1.* Sc atoms are surrounded by six O atoms belonging to six selenate groups (Figs. 1 and 2). Interatomic distances and angles are given in Table 2. Sc—O distances vary between 2·048 and 2·118 Å, in good agreement with distances for six-coordinated Sc (see Valkonen *et al.*, 1975; Valkonen & Niinistö, 1978; Valkonen & Leskelä, 1978; Valkonen, 1978). Since two of the opposite Sc—O distances are clearly shorter than the remaining four, the octahedron is tetragonally contracted.

Table 2. *Interatomic distances* (Å) *and angles* (°) *around* Sc *and* Se

Sc—O(1) (×4)	2·118 (4)
Sc—O(3) (×2)	2·048 (6)
O(3)—Sc—O(3′)	180·0
O(1)—Sc—O(1′)	180·0
O(1″)—Sc—O(1‴)	180·0
Range of O—Sc—O′	88·5 (2)–91·5 (2)
Se—O(1) (×2)	1·647 (4)
Se—O(2)	1·640 (7)
Se—O(3)	1·677 (6)
Range of O—Se—O′	108·4 (2)–112·8 (4)

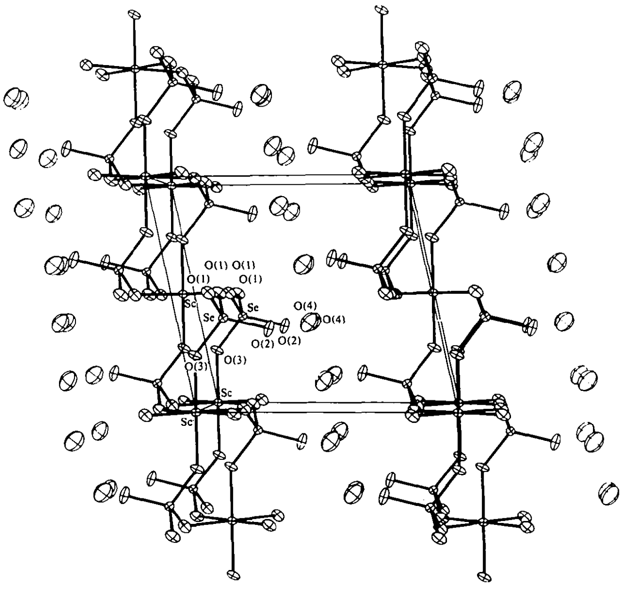

Fig. 1. Perspective view of the layer structure along the *b* axis. The *z* axis is horizontal.

In the selenate group Se is surrounded by four O atoms: O(2), O(3) and two O(1) atoms. O(1) is in the general eightfold position and O(2) and O(3) are in special fourfold positions. O(1) and O(3) are connected to Sc and the H atom of the hydrogenselenate must be bonded to O(2) (see Fig. 2). In the hydrogenselenites (*cf.* Valkonen & Leskelä, 1978), the Se—OH distance is longer than the Se—O distance, but the same elongation was not obvious in the present compound possibly due to the statistical distribution of H atoms.

According to thermal analyses the compound has two moles of water of crystallization which are expelled between 70 and 120°C. The low decomposition temperature indicates that the water molecules are loosely joined to the structure by hydrogen bonds, and this finding is confirmed by the crystal structure determination.

The O atom O(4), which belongs to the water of crystallization, is in the general eightfold position with the population parameter 0·5. Refinement without the atom O(4) yielded an *R* value of 7·1% and a peak in the difference Fourier map in the position 0·87, 0·08, 0·48. Refinement with a special position 0·87, 0, 0·48 for O(4) gave an *R* value of 6·0%, but the temperature factor U_{22} increased to over ten times its normal value.

It is also possible to refine the structure in the non-centrosymmetric space groups *C*2 or *Cm* (Nos. 5 and 8), calculating equivalent places for each atom; but in both cases two O atoms occur in fourfold positions with the population parameter 0·5, which is equivalent to the centrosymmetric space group *C*2/*m* (No. 12). There was no significant difference in the *R* values for centrosymmetric and non-centrosymmetric space groups.

The structure consists of layers formed by ScO_6 and SeO_4 polyhedra parallel to the *xy* plane. Each selenate group connects together three Sc atoms and each ScO_6

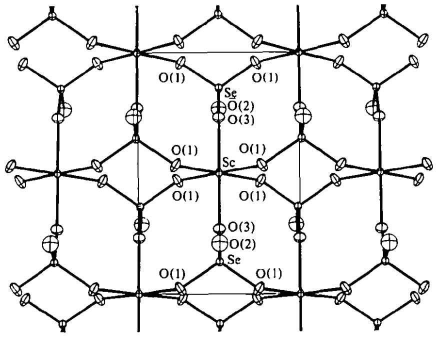

Fig. 2. Perspective view of the layer structure. The *y* axis is horizontal and the *x* axis is vertical.

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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 33662 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

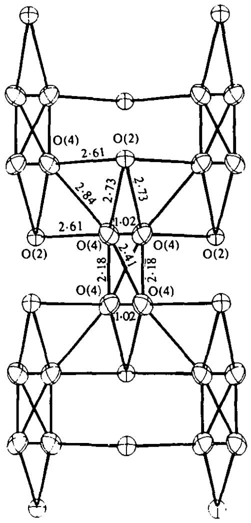

Fig. 3. All possible distances between the O(4) and O(2) atoms (Å). Standard deviations vary between 0·01 and 0·02 Å. All possible sites for O(4) are shown but only half of them are occupied. The y axis is horizontal and the x axis is vertical.

octahedron six selenate groups as shown in Fig. 2, and together they form the layer. Layers are connected together through O(2) and O(4) by hydrogen bonds.

There are two distances between O(2) and O(4), 2·61 and 2·73 Å. Probably the distance of 2·61 Å represents a hydrogen bond from Se—OH to H_2O fixing the position of O(4) nearer to the protonated selenate group.

The possible sites of the O atom O(4) form a rectangle, but only half of the sites are occupied. Oxygen atoms O(4) must be at opposite corners of the rectangle owing to the O(4)—O(4′) distances: 1·02 and 2·18 Å are too short, but the diagonal 2·41 Å is acceptable. Since there are two possible diagonals, there are two possible orientations for oxygen atoms O(4) (Fig. 3).

References

Bouissières, G., Gaume-Mahn, F., Henry la Blanchetais, Ch., Loriers, J. & Trombe, F. (1959). *Nouveau Traité de Chimie Minérale*. Vol. VII. *Scandium, Yttrium, Eléments des Terres Rares, Actinium*, Part 2, p. 935. Paris: Masson.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Komissarova, L. N., Shatskii, V. M. & Moiseichenko, G. I. (1965). *Russ. J. Inorg. Chem.* **10**, 407–411.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J.-P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Stewart, J. M. (1976). The XRAY system – version of 1976, Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Trousil, Z. (1938). *Collect. Czech. Chem. Commun.* **10**, 290–304.

Valkonen, J. (1978). *Acta Cryst.* B**34**, 1957–1959.

Valkonen, J. & Leskelä, M. (1978). *Acta Cryst.* B**34**, 1323–1326.

Valkonen, J. & Niinistö, L. (1978). *Acta Cryst.* B**34**, 266–268.

Valkonen, J., Niinistö, L., Eriksson, B., Larsson, L. O. & Skoglund, U. (1975). *Acta Chem. Scand. Ser. A*, **29**, 866–872.

Wirth, F. (1914). *Z. Anorg. Chem.* **87**, 9–12.

Acta Cryst. (1978). B**34**, 3066–3069

Tetrakis(dithioacetato)molybdenum(IV)

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(*Received* 13 *December* 1977; *accepted* 9 *May* 1978)

Abstract. $Mo(CH_3CS_2)_4$, monoclinic, $P2/c$; a = 9·616 (2), b = 8·706 (3), c = 12·539 (4) Å, β = 126·47 (2)°; Z = 2, D_m = 1·83, D_c = 1·81 g cm^{-3}. 1503 diffractometer data (Mo $K\alpha$ radiation) were used for solution and for refinement to an R value of 0·032. The structure consists of discrete $Mo(CH_3CS_2)_4$ molecules and the $[MoS_8]$ chromophore can be described as a triangular dodecahedron (isomer *mmmm*), significantly distorted toward a square antiprism (isomer *ssss*).

Introduction. A crystal of dimensions 0·25 × 0·8 × 0·6 mm was used to collect intensities on a Syntex $P2_1$ diffractometer, equipped with a graphite monochromator and a Mo X-ray tube ($K\alpha$, λ = 0·71073 Å). The lattice constants and the orientation matrix were