0,050.* Auf eine Extinktionskorrektur wurde verzichtet, da bei einer Verfeinerung ohne die drei stärksten Reflexe 400, 002 und 402 die Lageparameter innerhalb der Fehlergrenzen blieben und nur der R-Wert von 0,039 auf 0,029 sank, während die Temperaturfaktoren geringfügig anstiegen. Die Lageparameter und anisotropen Temperaturfaktoren der Verfeinerung mit allen Reflexen ($F_o > 3\sigma$) sind Tabelle 1 zu entnehmen. Abstände und Winkel sind in Fig. 1 eingetragen.

Diskussion. Das zunehmende Interesse, das Germanium(II)-sulfid bei physikalisch-technischen Untersuchungen findet (Schulz, 1975; Gregora, Velický & Závetová, 1976; Hulliger, 1977), liess es wünschenswert erscheinen, die Struktur mit den inzwischen verbesserten Untersuchungsmethoden zu verfeinern.

Wie aus Fig. 1 ersichtlich, verlaufen in der GeS-Elementarzelle zwei GeS-Schichten parallel zu (100). Sie gehen gemäss der Raumgruppe *Pnam* durch die Gleitspiegelebene *a* symmetrisch auseinander hervor. Im Vergleich zur NaCl-Struktur, aus der Zachariasen (1932) die GeS-Struktur herleitete, sind die Schichten stark gewellt wie in den isotypen IV–VI-Strukturen GeSe, SnS und SnSe (Dutta & Jeffrey, 1965). Die Oktaederkoordination der Kationen des NaCl-Typs ist beim GeS zu einer 3+3-Koordination verzerrt, wobei die drei längeren Ge–S-Abstände höchstens noch als sehr schwache Ge–S-Bindungen betrachtet werden können.

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*Die Liste der Strukturfaktoren ist bei der British Library Lending Division (Supplementary Publication No. SUP 33234: 4 pp.) hinterlegt. Kopien sind erhältlich durch: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Auf die anisotropen Temperaturfaktoren würde sich eine Extinktionskorrektur auswirken. Deshalb kann nur mit Vorbehalt gesagt werden, dass die thermischen Schwingungen des Schwefelatoms innerhalb der Fehlergrenzen isotrop sind. Die mittleren Schwingungsamplituden betragen 0,097 (7), 0,095 (6) und 0,098 (6) Å. Dagegen ist die Schwingung von Germanium deutlich anisotrop mit den mittleren Schwingungsamplituden von 0,112 (3) Å ‖ [001] und 0,081 (4) bzw. 0,085 (3) Å in der (001)-Ebene.

Wir danken Herrn Professor Dr Liebau für hilfreiche Diskussionen, Frau I. Pallas für die Bereitstellung und Anpassung von Rechenprogrammen, dem Rechenzentrum der Universität Kiel für die zur Verfügung gestellte Rechenzeit und Frau S. Melzer für die Durchführung technischer Arbeiten.

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Scandium Hydrogenselenite

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Abstract. $Sc(HSeO_3)_3$, monoclinic, Cc (No. 9), $a = 11 \cdot 130$ (2), $b = 9 \cdot 506$ (4), $c = 7 \cdot 598$ (2) Å, $\beta = 97 \cdot 59$ (2)°, $V = 796 \cdot 97$ Å^3, $Z = 4$, $D_x = 3 \cdot 58$ g cm^{-3}, μ(Mo $K\alpha$) $= 145 \cdot 3$ cm^{-1}, $R = 0 \cdot 031$ for 1109 reflections. The structure consists of octahedrally coordinated Sc atoms linked together by SeO_3 groups.

Introduction. $Sc(HSeO_3)_3$ was first prepared by Nilson (1880). Its powder diffraction data and thermal behaviour were recently recorded by Znamenskaya & Komissarova (1973). The present structure analysis is part of a systematic investigation of rare-earth sulphates, selenates and selenites in our laboratory.

Crystals suitable for X-ray analysis were obtained by two different methods. The first involved slow evaporation at room temperature of a solution containing 200 mg Sc_2O_3, 25 ml HNO_3 (65%), and 10 ml of a solution prepared from 50 wt% SeO_2 and 50 wt% H_2O. In the course of about two weeks, well developed colourless prisms of $Sc(HSeO_3)_3$ formed. The second method involved the precipitation of scandium selenite as described by Immonen, Koskenlinna, Niinistö & Pakkanen (1976). After 200 mg of the precipitate, 1 g SeO_2, and 20 ml H_2O had been kept in a steel reactor at 160°C for about two weeks, colourless prisms formed as above.

For recording the X-ray data a Syntex $P2_1$ (Fortran version) automatic four-circle diffractometer employing graphite-monochromatized Mo $K\alpha$ radiation was used. The cell parameters were determined by a least-squares fit to the setting for the four angles of 18 reflections. The intensities of 1297 independent reflections up to a 2θ of 60° were measured and those 1109 with $I > 3\sigma(I)$ were considered significant. The $\theta/2\theta$ scan technique was used and the scan speed was 2° min^{-1}. The net intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections were made on the basis of the φ-scan data. The systematic absences in the original intensity data indicated the space group Cc (No. 9) or $C2/c$ (No. 15). Only space group Cc gave the solution.

The positions of the Se and Sc atoms were obtained by direct methods using the program *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Only the 200 E values larger than 1·2 were used. Refinement was carried out with the XRAY 76 system (Stewart, 1976). The scattering factors were those of

Table 1. *Positional parameters* ($\times 10^4$) *for* $Sc(HSeO_3)_3$

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

	x	y	z
Se(1)	7209 (0)	9039 (0)	7770 (0)
Se(2)	335 (1)	1110 (1)	664 (1)
Se(3)	8644 (1)	5548 (1)	2845 (1)
Sc(1)	52 (2)	2502 (2)	4699 (2)
O(1)	6782 (8)	8174 (10)	5828 (12)
O(2)	8632 (8)	8557 (10)	8230 (11)
O(3)	7493 (9)	724 (10)	6919 (14)
O(4)	1008 (8)	1905 (9)	2521 (10)
O(5)	541 (8)	9382 (8)	1163 (10)
O(6)	1508 (9)	1388 (10)	9366 (12)
O(7)	9765 (8)	4469 (9)	3551 (12)
O(8)	9325 (9)	6832 (9)	1883 (13)
O(9)	8561 (10)	6363 (10)	4949 (11)

Table 2. *Bond lengths* (Å) *and angles* (°) *in the* SeO_3 *groups*

Estimated standard deviations are given in parentheses.

Se(1)–O(1)	1·701 (9)	O(1)–Se(1)–O(2)	101·6 (4)
Se(1)–O(2)	1·641 (9)	O(1)–Se(1)–O(3)	99·4 (4)
Se(1)–O(3)	1·772 (10)	O(2)–Se(1)–O(3)	96·7 (4)
Se(2)–O(4)	1·686 (8)	O(4)–Se(2)–O(5)	102·4 (4)
Se(2)–O(5)	1·695 (8)	O(4)–Se(2)–O(6)	97·0 (4)
Se(2)–O(6)	1·757 (10)	O(5)–Se(2)–O(6)	100·6 (4)
Se(3)–O(7)	1·649 (9)	O(7)–Se(3)–O(8)	103·4 (4)
Se(3)–O(8)	1·657 (10)	O(7)–Se(3)–O(9)	96·0 (4)
Se(3)–O(9)	1·790 (9)	O(8)–Se(3)–O(9)	99·0 (4)

Table 3. *Bond lengths* (Å) *in the* Sc *octahedra*

Estimated standard deviations are given in parentheses.

Sc–O(1)	2·102 (9)	Sc–O(5)	2·140 (8)
Sc–O(2)	2·071 (9)	Sc–O(7)	2·070 (9)
Sc–O(4)	2·158 (9)	Sc–O(8)	2·041 (10)

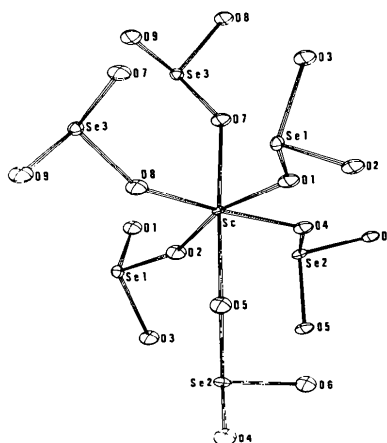| O(1)–Sc–O(4)	82·8 (4)	O(4)–Sc–O(7)	88·8 (4)
O(2)–Sc–O(4)	82·9 (4)	O(2)–Sc–O(7)	98·5 (4)
O(1)–Sc–O(5)	83·5 (4)	O(5)–Sc–O(8)	86·4 (4)
O(2)–Sc–O(5)	89·8 (4)	O(7)–Sc–O(8)	90·4 (4)
O(4)–Sc–O(5)	93·5 (4)	O(1)–Sc–O(8)	90·8 (4)
O(1)–Sc–O(7)	88·8 (4)	O(2)–Sc–O(8)	103·5 (4)

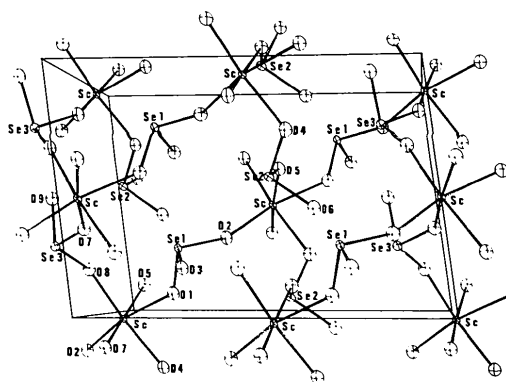Fig. 1. The coordination around Sc.

Fig. 2. Contents of the unit cell. The a axis is horizontal and the c axis vertical.

Table 4. *A comparison of* Se—O *and* Se—OH *distances in selenous acid and in some compounds containing hydrogenselenite*

Compound		Se—O distance (Å)	Se—OH distance (Å)	Reference
H_2SeO_3	ND*	1·643	1·735–1·743	Larsen, Lehmann & Søtofte (1971)
$NH_4H_3(SeO_3)_2$	XD	1·652–1·676	1·737–1·757	Tellgren, Ahmad & Liminga (1972)
$NH_4H_3(SeO_3)_2$	ND	1·651–1·671	1·746–1·752	Tellgren & Liminga (1974a)
$LiH_3(SeO_3)_2$	XD	1·65–1·68	1·76–1·77	Mohana Rao & Viswamitra (1971)
$LiH_3(SeO_3)_2$	ND	1·653–1·691	1·720–1·765	Tellgren & Liminga (1972)
$NaH_3(SeO_3)_2$	XD	1·706	1·778–1·780	Vijayan (1968)
$NaH_3(SeO_3)_2$	ND	1·702–1·718		Chomnilpan, Tellgren & Liminga (1977)
$KH_3(SeO_3)_2$	XD	1·669	1·707–1·730	Hansen, Hazell & Rasmussen (1969)
$KH_3(SeO_3)_2$	ND	1·662	1·713–1·731	Lehmann & Larsen (1971)
$RbH_3(SeO_3)_2$	XD	1·640–1·683	1·739–1·757	Tellgren, Ahmad & Liminga (1973)
$RbH_3(SeO_3)_2$	ND	1·644–1·682	1·737–1·745	Tellgren & Liminga (1977)
$CsH_3(SeO_3)_2$	XD	1·683–1·735		Tellgren & Liminga (1974b)
$NaHSeO_3$	XD	1·70–1·72	1·82	Chou, Hu & Yu (1963)
$PrH_3(SeO_3)_2(Se_2O_5)$	XD	1·624–1·656	1·766–1·805	Koskenlinna & Valkonen (1977a)
$MnH(SeO_3)(Se_2O_5)$	XD	1·662–1·700	1·776	Koskenlinna & Valkonen (1977b)
$Sc(HSeO_3)_3$	XD	1·641–1·701	1·757–1·790	Present work

* ND = Neutron diffraction; XD = X-ray diffraction.

Cromer & Mann (1968) for neutral atoms. After refinement of the positions of the Sc and Se atoms the value of R was 0·133. The positional parameters of all the O atoms were obtained from the difference Fourier map. The structure was then refined with isotropic temperature factors to an R value of 0·044. After block-diagonal refinement with anisotropic temperature factors the value of R reduced to 0·031.* H atoms could not be found from the difference Fourier map.

Discussion. Positional parameters for the nonhydrogen atoms are given in Table 1. Bond lengths and angles in SeO_3 groups are in Table 2. The Sc atom is octahedrally coordinated by O atoms belonging to six selenite groups (Fig. 1). The ScO_6 octahedron is distorted. The Sc—O distances vary between 2·041 and 2·158 Å (Table 3): these are in good agreement with distances for six-coordinated Sc: $Sc(OH)C_3H_2O_4.2H_2O$ 2·048–2·119 Å (Hansson, 1973), $Sc(C_5H_7O_2)_3$ 2·061–2·082 Å (Anderson, Neuman & Melson, 1973), $Sc(C_7H_5O_2)_3$ 2·102 Å (Anderson, Neuman & Melson, 1974), $Sc_2(SeO_4)_3.5H_2O$ 2·002–2·176 Å (Valkonen, Niinistö, Eriksson, Larsson & Skoglund, 1975) and $(NH_4)_3Sc(SeO_4)_3$ 2·007–2·185 Å (Valkonen & Niinistö, 1978).

Se forms the apex of a trigonal pyramid with O atoms at the corners of the base triangle. The distances between Se and O are normal compared with other hydrogenselenites (Table 4). Two O atoms [O(1) and

O(2), O(4) and O(5), O(7) and O(8)] from each selenite group are coordinated to Sc atoms, and one O [O(3), O(6) and O(9)] is bonded to H. The average Se—O distance (1·672 Å) is clearly shorter than the average Se—OH distance (1·773 Å), as in other hydrogenselenites (Table 4).

The unit-cell packing is shown in Fig. 2. The structure consists of ScO_6 octahedra linked into a three-dimensional network by SeO_3 groups.

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α-Tetraphosphorus Tetrasulphide

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Abstract. P_4S_4, monoclinic, $C2/c$, $a = 9\cdot771$ (8), $b = 9\cdot047$ (7), $c = 8\cdot746$ (6) Å, $\beta = 102\cdot67$ (6)°, $U = 754\cdot3$ Å³, $Z = 4$, $D_x = 2\cdot22$ g cm⁻³, μ (Mo $K\alpha$) = $18\cdot4$ cm⁻¹. The structure was determined by direct methods and refined to an R of $0\cdot035$ for 1121 unique diffractometer data. A crystallographic twofold axis passes through two of the S atoms, and the molecule possesses $\bar{4}2m$ (D_{2d}) symmetry within experimental error. Mean bond lengths and angles are: P—P, $2\cdot350$ (1); P—S, $2\cdot108$ (2) Å; P—P—S, $100\cdot4$ (1); S—P—S, $95\cdot1$ (1); P—S—P, $98\cdot9$ (1)°. Librational corrections increase both these bonds by $0\cdot010$ Å.

Introduction. The single-line ³¹P NMR spectrum of α-P_4S_4 indicates a highly symmetrical structure, and is consistent with either the realgar structure (a square of S atoms bisecting a tetrahedron of As atoms in As_4S_4) or the inverted realgar structure adopted by S_4N_4, Se_4N_4 and Te_4N_4. Although α-P_4S_4 was first reported recently by Griffin, Minshall & Sheldrick (1976), a theoretical study by Gleiter (1970) had predicted a D_{2d} realgar structure with long P—P bonds compared with those found in other phosphorus sulphides.

A single crystal was prepared by slow cooling of a saturated solution in *o*-dichlorobenzene, and sealed in a Lindemann-glass capillary tube. 2524 reflexions were measured with a Syntex $P2_1$ four-circle diffractometer, Mo $K\alpha$ radiation and a graphite monochromator. After application of Lp and absorption corrections, equivalent reflexions were merged to give 1121 unique reflexions with $F > 4\sigma(F)$ based on counting statistics. Cell dimensions were obtained from diffractometer measurements of 15 reflexions. The full structure was located by multisolution Σ_2 sign expansion, and refined by full-matrix least squares with anisotropic atoms, complex neutral-atom scattering factors, and the weighting scheme $w = 1/[\sigma^2(F) + 0\cdot000119F^2]$ to a final R' ($=\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$) of $0\cdot029$; the corresponding unweighted R was $0\cdot035$. A final difference electron density synthesis did not show any features greater than $0\cdot5$ e Å⁻³, and an analysis of variance in terms of $|F_o|$ and $\sin\theta$ did not show any systematic trends. Atomic coordinates are given in Table 1, and

Table 1. *Fractional coordinates* (×10⁴)

	x	y	z
P(1)	−17 (1)	2024 (3)	5666 (6)
P(2)	1501 (3)	3861 (5)	8700 (9)
S(1)	0	5380 (6)	7500
S(2)	0	508 (6)	7500
S(3)	1960 (3)	2945 (4)	6657 (7)