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Silicon Disulphide and Silicon Diselenide: A Reinvestigation

By Johannes Peters and Bernt Krebs

Anorganisch-Chemisches Institut der Universität Münster, Correnssstrasse, D-4400 Münster, Federal Republic of Germany

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Abstract. SiS_2 and $SiSe_2$ are orthorhombic and isostructural, *Ibam*, with $a = 9{\cdot}583$ (3), $b = 5{\cdot}614$ (2), $c = 5{\cdot}547$ (2) Å, $V = 298{\cdot}4$ Å^3, $Z = 4$, $D_x = 2{\cdot}052$ Mg m^{-3} at 293 K, $a = 9{\cdot}545$ (3), $b = 5{\cdot}564$ (2), $c = 5{\cdot}552$ (2) Å, $V = 294{\cdot}9$ Å^3, $D_x = 2{\cdot}077$ Mg m^{-3} at 138 K for SiS_2, and $a = 9{\cdot}669$ (3), $b = 5{\cdot}998$ (2), $c = 5{\cdot}851$ (2) Å, $V = 339{\cdot}3$ Å^3, $Z = 4$, $D_x = 3{\cdot}640$ Mg m^{-3} at 293 K, $a = 9{\cdot}619$ (3), $b = 5{\cdot}989$ (2), $c = 5{\cdot}851$ (2) Å, $V = 337{\cdot}1$ Å^3, $D_x = 3{\cdot}665$ Mg m^{-3} at 138 K for $SiSe_2$. The refinements at 138 K (SiS_2) and 293 K ($SiSe_2$) confirm the known structure types with some significant changes in cell dimensions and atomic coordinates. Final R factors for SiS_2 ($SiSe_2$) are 0·041 (0·018) for 200 (253) observed reflexions. Within the chains of edge-sharing SiS_4 ($SiSe_4$) tetrahedra, the SiS (SiSe) bond lengths are 2·133 (1) Å [2·275 (1) Å], the S–Si–S (Se–Si–Se) bond angles in the planar four-membered Si_2S_2 (Si_2Se_2) rings are 98·8 (1)° [100·0 (1)°].

Introduction. A more precise knowledge of the structures of SiS_2 (Zintl & Loosen, 1935; Büssem, Fischer & Gruner, 1935) and $SiSe_2$ (Weiss & Weiss, 1952) is highly desirable to give reliable structure data for comparison of bond properties with other Si–S and Si–Se compounds. Crystal structures are now available for analogous four-membered Si_2S_2 rings in $Si_2S_2Cl_4$ and $Si_2S_2Br_4$ (Peters, Mandt, Meyring & Krebs, 1981) and for similar Ge_2S_2, Ge_2Se_2 and Sn_2S_2 rings in $Ge_2S_6^{4-}$, $Sn_2S_6^{4-}$ (Krebs, Pohl & Schiwy, 1972; Eulenberger, 1978), high-temperature GeS_2, $GeSe_2$ (Dittmar & Schäfer, 1975, 1976), and in $Ge_2Se_6^{4-}$ (Krebs & Müller, 1982).

SiS_2 was obtained by reacting Al_2S_3 with SiO_2 at 1570 K in a dry N_2 stream, fibrous colourless single crystals being prepared in a sealed quartz-glass tube at 1420 K. Space-group extinctions (hkl: $h + k + l \neq 2n$, $h0l$: h, $l \neq 2n$, $0kl$: k, $l \neq 2n$) confirmed the space groups given earlier. Unit-cell dimensions were determined at 138 and 293 K by least-squares refinement from diffractometer measurements of 20 reflexions. A complete set of 235 unique intensity data were collected at 138 K in the range up to $2\theta = 60°$ on a 0·03 × 0·05 × 0·36 mm needle-shaped crystal. The crystal was sealed in a capillary and mounted along the needle axis [001]. All measurements were made with a Syntex $P2_1$ diffractometer, using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å, 2θ–θ scan technique, intensity-dependent scan speed between 2 and 15° min^{-1}, scan range in 2θ: 2·0° + α_1–α_2 separation, parallel graphite monochromator). Data reduction was done by Lorentz and polarization corrections; no absorption ($\mu = 1{\cdot}79$ mm^{-1}) or extinction corrections were necessary. 200 reflexions were accepted as being statistically above background on the basis that $I > 1{\cdot}96\sigma(I)$ and were used in the refinements. The coordinates given by Zintl & Loosen (1935) were transformed into a standard setting and the full-matrix least-squares refinement [*SHELX* program system: Sheldrick (1976)] gave final R values of $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0{\cdot}041$ (all 235 data: 0·044), $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}037$. The weighting scheme was based on counting statistics. Form factors for the elements were used as given in *International Tables for X-ray Crystallography* (1974).

Needle-shaped colourless single crystals of $SiSe_2$ were prepared from the elements in a sealed quartz-glass tube at 1170 K for 12 d. 271 independent X-ray diffraction data up to $2\theta = 60°$ were collected on a 0·04 × 0·036 × 0·28 mm crystal at 293 K, 253 of which were significantly above background. Details of the unit cell and intensity measurements and of the refinement were as for SiS_2. An absorption correction was included in the data reduction ($\mu = 23{\cdot}4$ mm^{-1}), the smallest transmission factors being 0·28. The final residuals after anisotropic refinement were $R_1 = 0{\cdot}018$ (for all 271 data: 0·022), $R_2 = 0{\cdot}020$.

Final atomic coordinates and anisotropic temperature factors for both crystal structures are given in Table 1. Table 2 shows the interatomic distances and bond angles.* In Fig. 1 the unit cell with atomic designations and thermal ellipsoids for the $SiSe_2$ room-temperature structure is given.

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36555 (5 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. SiS_2 *at* 138 K *and* $SiSe_2$ *at* 293 K: *fractional atomic coordinates and anisotropic temperature factor coefficients* (Å^2) *with e.s.d.'s*

The anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*)]$.

		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}
SiS_2	Si	0·0	0·0	0·25	0·0187 (10)	0·0220 (11)	0·0128 (8)	0·0
	S	0·11820 (14)	0·2088 (3)	0·0	0·0214 (7)	0·0234 (8)	0·0147 (6)	−0·0055 (6)
$SiSe_2$	Si	0·0	0·0	0·25	0·0332 (5)	0·0314 (5)	0·0176 (4)	0·0
	Se	0·12342 (3)	0·21163 (6)	0·0	0·0397 (2)	0·0388 (2)	0·0241 (2)	−0·0110 (1)

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s*

SiS_2		$SiSe_2$	
Si—S	2·133 (1)	Si—Se	2·275 (1)
$Si\cdots Si^{i}$	2·776 (1)	$Si\cdots Si^{i}$	2·926 (1)
$S\cdots S^{i}$	3·239 (2)*	$Se\cdots Se^{i}$	3·484 (1)*
$S\cdots S^{ii}$	3·577 (2)*	$Se\cdots Se^{ii}$	3·776 (1)*
$S\cdots S^{iii}$	3·620 (2)*	$Se\cdots Se^{iii}$	3·873 (1)*
$S\cdots S^{iv}$	3·774 (2)	$Se\cdots Se^{iv}$	3·842 (1)
$S\cdots S^{v}$	3·752 (2)	$Se\cdots Se^{v}$	3·871 (1)
$S\cdots S^{vi}$	4·268 (2)	$Se\cdots Se^{vi}$	4·530 (1)
$S\cdots S^{vii}$	3·950 (2)	$Se\cdots Se^{vii}$	4·203 (1)
$S—Si—S^{i}$	98·8 (1)	$Se—Si—Se^{i}$	100·0 (1)
$S—Si—S^{ii}$	114·0 (1)	$Se—Si—Se^{ii}$	112·2 (1)
$S^{i}—Si—S^{ii}$	116·1 (1)	$Se^{i}—Si—Se^{ii}$	116·7 (1)
$Si—S—Si^{i}$	81·2 (1)	$Si—Se—Si^{i}$	80·0 (1)

Symmetry code

(i)	$-x, -y, -z$	(v)	$\frac{1}{2}-x, \pm\frac{1}{2}+y, 0$
(ii)	$-x, y, \pm\frac{1}{2}$	(vi)	$x, 1-y, \pm\frac{1}{2}$
(iii)	$x, -y, \pm\frac{1}{2}$	(vii)	$-x, 1-y, 0$
(iv)	$\frac{1}{2}-x, \frac{1}{2}-y, \pm\frac{1}{2}$		

* Edges of the tetrahedra.

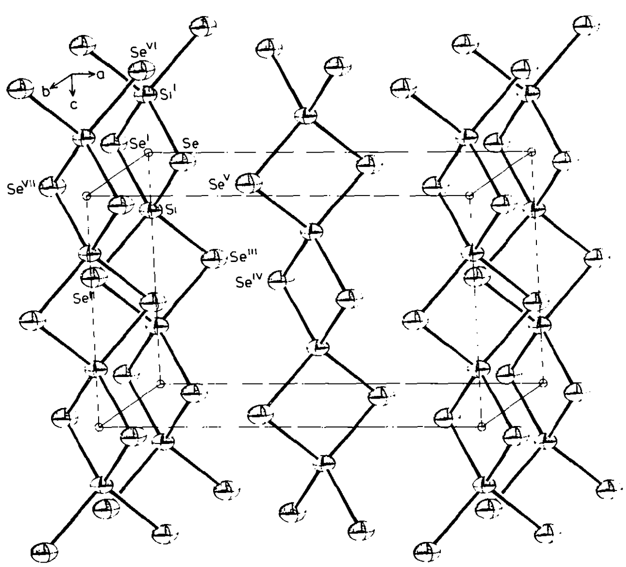

Fig. 1. Unit cell of $SiSe_2$ with 50% probability thermal ellipsoids at 293 K.

Discussion. The room-temperature unit-cell dimensions differ by a maximum of 0·04 Å from the early film values given for SiS_2 by Zintl & Loosen (1935) and Büssem, Fischer & Gruner (1935); the deviation from the reported $SiSe_2$ data (Weiss & Weiss, 1952; Hillel & Cueilleron, 1971) is in some cases as large as 0·09 Å. This is partly due to the difficulties in the earlier investigations in obtaining good quality single crystals and in indexing the powder diagrams because of the approximate relationship $a \simeq \sqrt{3}b \simeq \sqrt{3}c$. Comparison of the cell dimensions for the two temperatures shows that the covalent bond system within the polymeric chain is reflected in the constant lengths of the **c** edges. This also shows that no significant difference is to be expected for low- and room-temperature bond lengths (apart from possible librational corrections).

The two isotypic structures contain chains of distorted edge-sharing SiS_4 and $SiSe_4$ tetrahedra running parallel to **c**. Comparison of the observed Si—S distances to the mean value of about 2·12–2·14 Å in a large number of 'unstrained' Si—S compounds [see, for example, Mandt & Krebs (1976); Krebs & Mandt (1977); to this class belongs the quartz-like high-pressure modification of SiS_2: Prewitt & Young (1965)] shows that the angular strain imposed on the tetrahedra by their edge sharing by no means results in a bond lengthening. Similar observations are made in $Si_2S_2Br_4$ [Si—S 2·114 (8) Å], $Si_2S_2Cl_4$ [Si—S 2·114 (1) Å] (Peters, Mandt, Meyring & Krebs, 1981) and in the polymeric systems of high-temperature GeS_2 [Ge—S 2·223 (5) Å] and $GeSe_2$ [Ge—Se 2·361 (5) Å] (Dittmar & Schäfer, 1975, 1976), This is, however, in contrast to the dimeric anions $Ge_2S_6^{4-}$ (Krebs, Pohl & Schiwy, 1972; Eulenberger, 1978) and $Ge_2Se_6^{4-}$ (Krebs & Müller, 1982) where the Ge—S [2·272 (2) and 2·274 (3) Å] and Ge—Se [2·417 (2) Å] bonds in the four-membered rings are significantly longer (with a corresponding shortening of the negatively charged terminal ones).

The S—Si—S and Se—Si—Se bond angles within the Si_2S_2 and Si_2Se_2 rings in SiS_2 and $SiSe_2$ (Table 2), as in $Si_2S_2Cl_4$ [99·8 (1)°] and $Si_2S_2Br_4$ [99·2 (4)°], are closer to the ideal tetrahedral angle than the corresponding angles in high-temperature GeS_2 [97·9 (1)°], $Ge_2S_6^{4-}$ [93·9 (2)° and 95·0 (2)°] and $GeSe_2$

[99·6 (1)°] and $Ge_2Se_6^{4-}$ [95·4 (1)°]. Among the nonbonding S···S and Se···Se distances the common edges of the tetrahedra are, as expected, by far the shortest. It is, however, remarkable that in $SiSe_2$ the clear distinction between the shorter Se···Se distances within the edges of the tetrahedra and the much longer ones outside the tetrahedra gets partly lost, the interchain distances $Se\cdots Se^{iv}$ and $Se\cdots Se^{v}$ being of the same order as the intratetrahedral distances.

The thermal parameters (Table 1) for $SiSe_2$ are roughly twice as large as those for SiS_2 in accordance with the higher temperature for the measurements. The significantly smaller values of U_{33} compared to U_{11} and U_{22} for both SiS_2 and $SiSe_2$ indicate, as expected, librational motion of the quasi-rigid $(SiS_2)_n$ and $(SiSe_2)_n$ chains around [001] rather than translational motion parallel to this direction.

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Structure of 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3;2,3-di-μ-chloro-*triangulo*-triosmium

BY FREDERICK W. B. EINSTEIN, TERRY JONES AND KENNETH G. TYERS

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

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Abstract. $Os_3Cl_2(CO)_{10}$, $[(\mu\text{-}Cl)_2Os_3(CO)_{10}]$, M_r = 921·61, orthorhombic, *Pbca*, a = 25·580 (8), b = 22·832 (6), c = 12·036 (3) Å, V = 7029·5 Å^3, Z = 16, D_c = 3·483, D_m = 3·25 Mg m^{-3}, μ(Mo $K\alpha$) = 21·7 mm^{-1}. The structure was solved by direct methods and refined by block-diagonal least squares to a final R value of 0·041 for 2838 independent reflections, $I > 2·3\sigma(I)$. There are two crystallographically independent molecules with similar geometry in the asymmetric unit. The triosmium core defines an isosceles triangle with the dibridged non-bonding, osmium–osmium vector being 3·233 (2) Å, compared to the non-bridged bond distance of 2·852 (2) Å (av.).

Introduction. A yellow crystal, 0·25 × 0·30 × 0·22 mm, was obtained by recrystallization from hexane and used for the diffraction studies.

Weissenberg and precession photographs taken with Cu $K\alpha$ radiation showed the crystal to be orthorhombic and systematic absences $0kl$: $k = 2n + 1$, $h0l$: $l = 2n + 1$, $hk0$: $h = 2n + 1$, uniquely defined the space group as *Pbca*.

Data were collected on a Picker FACS-1 automated four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda K\alpha_1$ = 0·7093 Å) using a graphite monochromator and a scintillation counter with pulse-height discrimination. Cell dimensions were obtained from a least-squares refinement of 26 accurately centered reflexions with 2θ > 23°. Intensity data were collected using a scan rate of 2° min^{-1}, a symmetrical scan width of (1·2 + 0·692 × tan θ)° and background counts of 10% of the total scan time at each scan limit. Peak-profile analyses were performed on all reflections (Grant & Gabe, 1978). Two standards were measured after every 70 reflec-

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