

Structure of Monoclinic Sulphur–Selenium Se_3S_5

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(Received 6 July 1977; accepted 21 November 1977)

Abstract. Se_3S_5 , monoclinic, $P2/c$ or Pc , $a = 8.564$ (5), $b = 13.354$ (9), $c = 9.368$ (7) Å, $\beta = 124.32$ (5)°, $Z = 4$, $D_m = 2.925$ (7) g cm⁻³ (measured by flotation in a mixture of methyl iodide and methylene iodide). The structure was refined by full-matrix least squares to $R_2 = 0.054$. It is isostructural with monoclinic sulphur, $\text{S}_8(\gamma)$, with two distinct eight-membered rings in the crown configuration. Various disordered models have been investigated, but it has not been possible to establish whether the structure consists of distinct Se_3S_5 rings or a mixture of $\text{Se}_n\text{S}_{8-n}$ molecules.

Introduction. Equal molar amounts of finely powdered S and Se were sealed in an evacuated glass tube and thoroughly mixed by shaking. The tube was then heated to 450°C for 5.5 h. On cooling, a black mass with metallic appearance was produced. About 8 g of this material was broken into small fragments and extracted with 280 ml of benzene using a Soxhlet apparatus. After a few hours a reddish-yellow solution was obtained, which upon standing overnight produced reddish-orange crystals. These crystals were picked off and washed with a small amount of benzene and ether, and were dried over phosphoric oxide. The crystals were analyzed for Se using hydrazine hydrate, and found to contain 58.45% Se (calc. for Se_3S_5 , 59.64%). The compound melts at 118°C and decomposes above 119°C.

Intensity data were taken from a crystal ground into a sphere of radius 0.14 mm. 1206 reflections in one quadrant (hkl and $h\bar{k}l$) were collected on a Syntex P1 automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Reflections with negative intensities were rejected. The data were corrected for Lorentz, polarization and absorption effects ($\mu = 228.4$ cm⁻¹). Systematic absences were shown by precession photographs to be l odd for $h0l$, indicating space group $P2/c$ or Pc . The former was chosen following the choice of Watanabe (1974) for $\text{S}_8(\gamma)$, although a molecule of Se_2S_5 cannot have the required twofold axis. The trial structure was derived by direct methods using the XRAY 71 package of programs. The structure readily resolved to an R value

Table 1. Site population (% S) and positional parameters ($\times 10^4$) with e.s.d.'s in parentheses

	% S	x	y	z
A(1)	38	6585 (3)	3398 (1)	3273 (2)
A(2)	77	8164 (3)	5833 (2)	4727 (3)
A(3)	58	7515 (3)	4443 (1)	5455 (2)
A(4)	83	5814 (3)	6796 (2)	3852 (3)
B(1)	66	827 (3)	7952 (1)	1950 (3)
B(2)	55	2464 (3)	359 (2)	2123 (3)
B(3)	61	3178 (3)	8960 (2)	3542 (3)
B(4)	60	1520 (4)	1340 (2)	3323 (3)

of 0.14 with individual isotropic temperature factors and a composite scattering curve derived from those of S and Se (Cromer & Waber, 1965). Individual site populations were refined using the program *RFINE* (Finger, 1969). The results were used to compile composite scattering curves for each site and the structural parameters were further refined by using the full-matrix least-squares program *CUDLS* written locally by J. S. Stephens. The final value of R_2 $\{= [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}\}$ is 0.054 where $w = (0.5 - 0.0056F_o + 0.0009F_o^2 + 83.25\sigma/F_o^2)^{-1}$, with σ obtained from counting statistics. A parameter g for secondary-extinction correction (Larson, 1967) was also refined and has the value 6.73×10^{-7} . Positional parameters are shown in Table 1, with the site population corresponding to the percentage occupancy of S.‡

Discussion. The structure of the present compound appears to be the same as that reported briefly by Kawada, Matsumoto, Burzlafl & Hellner (1972). No atomic coordinates were given ($R = 0.223$) and the question of site occupancy was not pursued by these authors. The structure is isotypic with that of $\text{S}_8(\gamma)$ (Watanabe, 1974) with two crystallographically inequivalent molecules. Molecules *A* and *B* are identified with molecules 1 and 2 in $\text{S}_8(\gamma)$ on the basis of the deviation of the centres of the molecules by 0.13 and

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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 33211 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses*

Molecule <i>A</i>			
$A(1)-A(1')$	2.243 (3)	$A(1)-A(1')-A(3)$	105.7 (1)
$-A(3)$	2.219 (3)	$A(4)-A(2)-A(3)$	106.6 (1)
$A(2)-A(4)$	2.126 (3)	$A(1)-A(3)-A(2)$	105.8 (1)
$-A(3)$	2.156 (3)	$A(2)-A(4)-A(4')$	107.8 (1)
$A(4)-A(4')$	2.093 (3)		
Molecule <i>B</i>			
$B(1)-B(1')$	2.171 (5)	$B(1)-B(1')-B(3)$	105.9 (1)
$-B(3)$	2.169 (3)	$B(4)-B(2)-B(3)$	105.2 (1)
$B(2)-B(4)$	2.157 (3)	$B(1)-B(3)-B(2)$	106.3 (1)
$-B(3)$	2.171 (3)	$B(2)-B(4)-B(4')$	106.5 (1)
$B(4)-B(4')$	2.152 (4)		
Intermolecular interactions (<4.0 Å)			
$A(1)-B(1)$	3.769 (5)	$A(4)-B(4)$	3.404 (5)
$-B(4)$	3.894 (5)	$-B(3)$	3.577 (5)
$A(2)-B(1)$	3.571 (5)	$-B(1)$	3.696 (5)
$A(3)-B(1)$	3.777 (5)	$-B(1')$	3.901 (5)
$-B(1')$	3.970 (5)		

0.47 Å respectively from the glide plane. The comparable values for molecules 1 and 2 in $\text{S}_8(\gamma)$ are 0.14 and 0.49 Å respectively. The molecular centres may be considered to occupy the corners of two interpenetrating rectangular 'cages' so that each molecule of one kind is surrounded by eight molecules of the other kind. Each molecule is an eight-membered ring in the crown configuration. The plane of the ring contains the molecular twofold (pseudo) axis which coincides with the twofold axis of the space group and passes through two edges of the molecule. The orientation of the planes of these two rings with respect to the *a* axis differs slightly, being 28.2° for molecule *A* and 26.5° for molecule *B*.

The bond distances and angles are shown in Table 2. The average bond distance within a molecule is 2.166 (3) Å, intermediate between the values of 2.044 Å in $\text{S}_8(\gamma)$ and 2.318 Å in $\text{Se}_8(\alpha)$ (Cherin & Unger, 1966). An apparent bond length of 2.147 Å would be predicted for the composition Se_3S_5 . The individual bond lengths also reflect the composition of the sites. Molecule *A* shows much greater variation in composition among the four independent sites than does molecule *B*, with a correspondingly greater variation in interatomic distances. So the largest distance of 2.243 Å in molecule *A* is between sites occupied least by S (38%) while the shortest distance of 2.093 Å is between sites occupied most by S (83%). Fig. 1 shows the correlation between the average composition of adjacent sites and their apparent distances. The bond angle

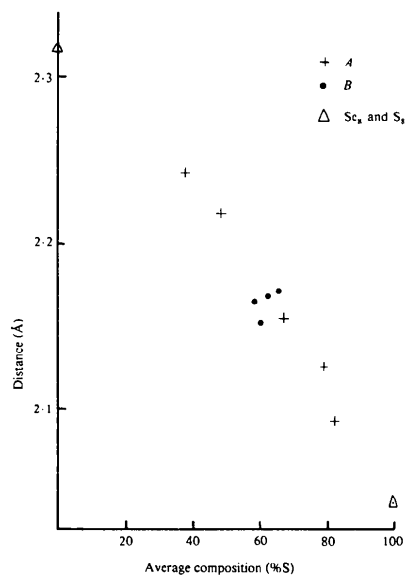


Fig. 1. Interatomic distances vs average site composition.

in the molecular average is about 1.5% smaller than that found in $\text{S}_8(\gamma)$ with the mean bond angle somewhat smaller in molecule *B* in both compounds. The shortest interaction between molecules is at 3.406 (5) Å, being smaller than that found in any of the allotropes of solid S.

Various disordered models have been tested. Among them were models with equal numbers of Se_2S_6 and Se_4S_4 rings, which have a true twofold axis, and models with spatially disordered rings of Se_3S_5 isomers. Unfortunately, no one model gives a definitely better fit to the intensity data than does any other. It is, therefore, not possible to state unequivocally whether the structure consists of a mixture of disordered $\text{Se}_n\text{S}_{8-n}$ rings, or whether each ring is a distinct Se_3S_5 molecule in one or more isomeric forms.

This work has been supported by the National Research Council of Canada through operating grants.

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