

## REGULAR STRUCTURAL PAPERS

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## A Redetermination of Monoclinic $\gamma$ -Sulfur

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### Abstract

The structure of  $\gamma$ -sulfur ( $P2/c$ ) has been redetermined from diffractometer data. The conformation of the  $S_8$  ring is the same as for  $\alpha$ - and  $\beta$ -sulfur, but the range of S—S distances is greater [2.035(2)–2.060(2) Å].

### Comment

The only complete structural analysis of  $\gamma$ -sulfur was performed using photographic data (Watanabe, 1974). We recently obtained good quality crystals of  $\gamma$ -sulfur as a by-product in the synthesis of bis(dialkylthiophosphoryl) disulfides. The refined structure is reported in the same space group and setting as that of the original paper,  $P2/c$  (Watanabe, 1974). Although there is qualitative agreement between the two structures, the improved data in the present study allow a closer examination of the molecular geometry.

The asymmetric unit is composed of two half  $S_8$  units, the molecules having twofold crystallographic symmetry. It is striking that there is a much greater variation in the S—S bond distances in  $\gamma$ -sulfur [2.035(2)–2.060(2) Å] compared to  $\alpha$ -sulfur [2.0384(7)–2.0489(6) Å (Rettig & Trotter, 1987)] and the ordered molecule in  $\beta$ -sulfur [2.040(2)–2.050(2) Å (Templeton, Templeton & Zalkin, 1976; Goldsmith & Strouse, 1977)]. However, the range of valence angles is about the same in all cases [ $\alpha$  107.39(2)–108.99(2),  $\beta$  106.5(1)–108.2(1),  $\gamma$  107.1(1)–108.6(1)°]. The range of torsion angles for the  $\gamma$  form is smaller than for the other two forms [ $\alpha$  95.27(4)–100.81(3),  $\beta$  96.5(1)–101.1(1),  $\gamma$  98.0(1)–99.9(1)°].

In the present study, all of the thermal parameters are fairly high for atoms as heavy as S, and atom S8 is noticeably anisotropic, as was also reported by Watanabe (1974). This observation, coupled with the rather wide range of S—S distances, led us to examine the possibility of either disorder or an incorrect choice of space group. A twofold disorder for the three atoms with the highest anisotropy refined correctly but with no improvement in the fit. Although a slightly better refinement ( $R = 0.035$  versus  $R = 0.036$ ) was obtained in space group  $Pc$ , the

number of high correlation coefficients and no reduction in the thermal parameters suggested that  $P2/c$  is indeed the best choice of space group.

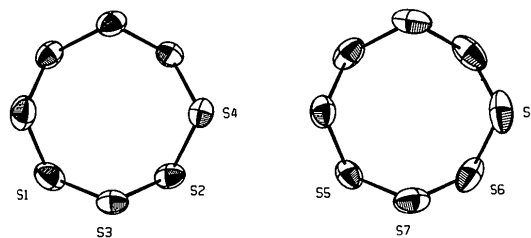


Fig. 1. Two independent  $S_8$  rings showing the difference in thermal motion. Probability ellipsoids are drawn at 50%.

### Experimental

#### Crystal data

$S_8$   
 $M_r = 256.51$   
 Monoclinic  
 $P2/c$   
 $a = 8.455$  (3) Å  
 $b = 13.052$  (2) Å  
 $c = 9.267$  (3) Å  
 $\beta = 124.89$  (3)°  
 $V = 838.8$  (9) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 2.03$  Mg m<sup>-3</sup>

#### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $3\theta/\theta$  scans ( $\omega/\theta$  motor coupling ratio 1:0.33)  
 Absorption correction: refined empirical (Walker & Stuart, 1983)  
 $T_{\min} = 0.7652$ ,  $T_{\max} = 1.0998$   
 1845 measured reflections  
 1727 independent reflections

#### Refinement

Refinement on  $F$   
 Final  $R = 0.036$   
 $wR = 0.041$   
 $S = 1.222$   
 939 reflections  
 74 parameters  
 $w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0011F_o^4]$   
 $(\Delta/\sigma)_{\max} = 0.004$   
 $\Delta\rho_{\max} = 0.3117$  e Å<sup>-3</sup>

#### Mo $K\alpha$ radiation

$\lambda = 0.71073$  Å  
 Cell parameters from 25 reflections  
 $\theta = 12$ – $14$ °  
 $\mu = 1.955$  mm<sup>-1</sup>  
 $T = 294$  K  
 Needle  
 $0.32 \times 0.14 \times 0.12$  mm  
 Pale yellow  
 Crystal source: crystallized from ethanol

#### 939 observed reflections

[ $I > 3.0\sigma(I)$ ]  
 $R_{\text{int}} = 0.046$   
 $\theta_{\max} = 25.99$ °  
 $h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 16$   
 $l = -10 \rightarrow 9$   
 3 standard reflections  
 frequency: 50 min  
 intensity variation: –1.12%

$\Delta\rho_{\min} = -0.3842$  e Å<sup>-3</sup>

Extinction correction: isotropic (Zachariasen, 1963)

Extinction coefficient:  $0.56 \times 10^{-6}$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: CAD-4 (Enraf-Nonius, 1977). Cell refinement: CAD-4 (Enraf-Nonius, 1977). Data reduction: *MolEN* (Fair, 1990). Program(s) used to refine structure: *LSFM MolEN* (Fair, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF MolEN* (Fair, 1990).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
S1	0.6485 (2)	0.3457 (1)	0.3247 (2)	0.0671 (7)
S2	0.8110 (1)	0.5792 (1)	0.4708 (1)	0.0522 (6)
S3	0.7446 (2)	0.4430 (1)	0.5319 (1)	0.0534 (6)
S4	0.5836 (2)	0.6768 (1)	0.3840 (1)	0.0511 (5)
S5	0.0799 (2)	0.7979 (1)	0.1993 (2)	0.0614 (6)
S6	0.2427 (2)	1.0310 (1)	0.2201 (2)	0.0787 (7)
S7	0.3074 (2)	0.8938 (1)	0.3501 (2)	0.0640 (7)
S8	0.1483 (2)	1.1271 (1)	0.3294 (2)	0.0744 (7)

Table 2. Anisotropic thermal parameters ( $\text{\AA}^2$ )

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S1	0.0797 (6)	0.0562 (8)	0.0675 (6)	0.0211 (6)	0.0413 (4)	0.0063 (6)
S2	0.0365 (4)	0.0697 (8)	0.0559 (5)	-0.0037 (5)	0.0239 (3)	0.0058 (6)
S3	0.0530 (5)	0.0669 (9)	0.0430 (4)	0.0066 (6)	0.0249 (3)	0.0133 (5)
S4	0.0536 (4)	0.0487 (7)	0.0511 (5)	-0.0067 (5)	0.0317 (3)	-0.0092 (5)
S5	0.0754 (6)	0.0472 (7)	0.0651 (5)	0.0031 (6)	0.0438 (4)	-0.0095 (5)
S6	0.0760 (5)	0.088 (1)	0.0731 (5)	-0.0369 (6)	0.0533 (3)	-0.0208 (6)
S7	0.0421 (5)	0.093 (1)	0.0674 (7)	0.0069 (7)	0.0246 (4)	-0.0128 (7)
S8	0.1215 (8)	0.0496 (8)	0.0682 (6)	-0.0331 (7)	0.0571 (5)	-0.0219 (6)

Table 3. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—S1	2.060 (2)	S5—S5	2.039 (3)
S1—S3	2.043 (2)	S5—S7	2.035 (2)
S2—S3	2.040 (2)	S6—S7	2.051 (2)
S2—S4	2.049 (2)	S6—S8	2.040 (3)
S4—S4	2.037 (1)	S8—S8	2.058 (2)
S1—S1—S3	107.9 (1)	S5—S5—S7	107.38 (9)
S3—S2—S4	107.78 (9)	S7—S6—S8	107.1 (1)
S1—S3—S2	107.75 (9)	S5—S7—S6	107.71 (7)
S2—S4—S4	108.62 (9)	S6—S8—S8	107.95 (8)
S1'—S1—S3—S2	-99.1 (1)	S5'—S5—S7—S6	-99.9 (1)
S3—S1—S1'—S3'	98.5 (1)	S7—S5—S5'—S7'	99.8 (1)
S4—S2—S3—S1	99.2 (1)	S8—S6—S7—S5	99.2 (1)
S3—S2—S4—S4'	-98.4 (1)	S7—S6—S8—S8'	-98.6 (1)
S2—S4—S4'—S2'	98.0 (1)	S6—S8—S8'—S6'	99.5 (1)

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). Starting coordinates and atom numbering were taken from Watanabe (1974).

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55547 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1021]

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## Synthesis and Structures of the Quaternary Sulfides $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$ and $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$

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## Abstract

The new quaternary compounds  $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$  and  $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$  have been synthesized.  $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$  has a hexagonal structure and  $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$  has both hexagonal and trigonal phases. The two compounds have similar structures to that of  $\text{CdI}_2$ , with double close-packed sulfur layers and transition-metal and main-group atoms disordered over the octahedral sites inside the double layers. These layers are separated by potassium ions that occupy trigonal prismatic sites.

## Comment

Two new quaternary sulfides,  $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$  and  $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$ , have been synthesized as part of a continuing effort to explore the synthesis and properties of new complex chalcogenides (Lu & Ibers, 1991a,b; Mansuetto, Keane & Ibers, 1992; Wu & Ibers, 1992). Trichet & Rouxel (1977) studied the analogous system  $\text{Na}_x\text{Zr}_{1-x}\text{In}_x\text{S}_2$  with X-ray powder diffraction techniques and complex impedance measurements. Three different phases, all good ionic conductors, were found in the composition range  $0 < x < 1$ . The intercalated compounds  $\text{A}_x\text{ZrS}_2$  (Cousseau, Trichet & Rouxel, 1973; Rouxel, Cousseau & Trichet, 1971) and  $\text{A}_x\text{SnS}_2$  (Le Blanc, Danot & Rouxel, 1969) ( $A = \text{Li, Na, K}$ ) show similar structural features. Their structures have generally been postulated from cell constants obtained from powder samples.