Crystal and Molecular Structure of Tetra-arsenic Pentasulphide

By **Harold J. Whitfield**, Division of Chemical Physics, C.S.I.R.O., P.O. Box 160, Clayton, Victoria, Australia 3168

The crystal structure of the title compound has been determined by three-dimensional single-crystal *X*-ray study from photographic data. Crystals are monoclinic, space group $P2_1/m$, with $Z = 2$ in a unit cell of dimensions $a = 7{\cdot}98$, $b = 8{\cdot}10$, $c = 7{\cdot}14$ (all $\pm0{\cdot}02$) Å, $\beta = 101{\cdot}0 \pm 0{\cdot}5°$. The structure is built of discrete As_4S_5 molecules of approximate C_{2v} symmetry with As–As 2·55 Å, and mean As–S 2·24 Å. The structure was solved by direct methods and least-squares refinement gave *R* 0·11 for 613 observed reflections.

DIMORPHITE, As_4S_3, is sparingly soluble in carbon disulphide. This solution reacts with a solution of sulphur in carbon disulphide to yield finely crystalline realgar, As_4S_4. Realgar is also produced if a solution of As_4S_3 in CS_2 is illuminated with light for a long period or treated with a dilute solution of I_2 in CS_2 at −78 °C, and slowly warmed to room temperature. Occasionally, if a solution of As_4S_3 in CS_2 is allowed to evaporate slowly to dryness, fine needle-like crystals are obtained. One of these crystals was subjected to single-crystal *X*-ray study and shown to consist of tetra-arsenic pentasulphide molecules. The results of this study are presented here.

EXPERIMENTAL

Crystal Data.—As_4S_5, Monoclinic, $a = 7{\cdot}98 \pm 0{\cdot}02$, $b = 8{\cdot}10 \pm 0{\cdot}02$, $c = 7{\cdot}14 \pm 0{\cdot}02$ Å, $\beta = 101{\cdot}0 \pm 0{\cdot}5°$, $U = 453{\cdot}0$ Å^3, $Z = 2$, space group $P2_1/m$ from systematic absences: $0k0$ for $k \neq 2n$.* Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 288$ cm^{-1}.

A needle-shaped crystal with dimensions 0·03 × 0·04 × 0·2 mm was mounted about its longest dimension (parallel to the *c* axis) and multiple-film equi-inclination Weissenberg data were obtained by use of Ni-filtered Cu-K_α radiation for layers $hk0$—5. All crystals observed were twinned, but it was possible to index reflections from each part of the twin separately as the reciprocal lattices of the two components of the twin had a common a^*b^* plane. In-

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* These absences are compatible [1] with space groups $P2_1$ and $P2_1/m$. A statistical test [2] suggested that the crystal is centrosymmetric and thus space group $P2_1/m$; this was confirmed by the subsequent satisfactory refinement.

[1] 'International Tables for *X*-Ray Crystallography,' vol. II, Kynoch Press, Birmingham, 1959.

[2] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

tensities were estimated visually by comparison with a calibrated series of spots, and Lorentz, polarization, and spot-extension corrections were applied, but not those for absorption or extinction.

Insufficient of the compound was isolated for normal chemical analysis and density determination. However the method of preparation, the colour of the crystals and their strong scattering power for *X*-rays suggested that they were an arsenic sulphide. Assuming the density is similar to that of known arsenic sulphides, the measured cell volume indicates a possible stoicheiometry of As_4S_5. Indeed, two molecules of As_4S_5 in a unit cell of volume 453·0 Å^3 gives D_c 3·37 g cm^{-3}, slightly less than that recorded for As_4S_3 (3·57),[3] As_4S_4 (3·59),[4] and As_2S_3 (3·48).[5]

TABLE 1

Positional and thermal parameters * with standard deviations in parentheses, and peak electron densities (ρ eA^{-3}) for the individual atoms of As_4S_5

	As(1)	As(2)	As(3)	S(1)	S(2)	S(3)
x	0·0217(7)	0·0505(6)	0·3912(4)	0·1853(11)	0·2318(10)	0·5414(15)
y	0·2500	0·2500	0·4890(5)	0·4649(11)	0·4629(11)	0·2500
z	0·8033(9)	0·4543(8)	0·7439(6)	0·9140(14)	0·4511(13)	0·7894(19)
β_{xx}	0·0080(8)	0·0084(8)	0·0082(5)	0·0079(12)	0·0089(12)	0·0062(18)
β_{yy}	0·0117(9)	0·0108(8)	0·0112(5)	0·0112(13)	0·0094(13)	0·0103(18)
β_{zz}	0·0136(16)	0·0086(15)	0·0149(10)	0·0147(26)	0·0100(26)	0·0150(36)
β_{xy}	0·0000	0·0000	−0·0011(5)	0·0003(11)	−0·0008(10)	0·0000
β_{xz}	0·0009(8)	−0·0028(8)	−0·0007(5)	0·0008(12)	−0·0004(12)	−0·0041(18)
β_{yz}	0·0000	0·0000	−0·0021(6)	−0·0033(14)	0·0019(13)	0·0000
ρ	60	60	62	28	28	26

* The temperature factor is given by $\exp - (\beta_{xx}h^2 + \beta_{yy}k^2 + \beta_{zz}l^2 + 2\beta_{xz}hl + 2\beta_{xy}hk + 2\beta_{yz}kl)$.

Assuming then that the unit cell contains eight arsenic and ten sulphur atoms, the observed structure factors were placed on an approximately absolute scale. The phases of 107 of the reflections with the highest unitary structure factors were determined directly by use of direct-method computer programs.[6] An electron-density map was constructed by use of the phases of these reflections and from this the approximate positions of eight heavy atoms in the unit cell were obtained. Placing arsenic atoms at these co-ordinates, the approximate phases of all the reflections were obtained. By use of Fourier and difference-Fourier syntheses, the positions of ten other light atoms in the unit cell were obtained. These were assumed to be sulphur atoms. The molecular entity of four arsenic and five sulphur atoms was found to be structurally reasonable. A least-squares refinement of the data using isotropic temperature factors with adjustment of the interlayer scale factors gave *R* 0·13 for 613 observed reflections. A further least-squares refinement with anisotropic temperature factors but no change of interlayer scale factors gave *R* 0·11.

A final Fourier synthesis based on all the observed reflections gave the electron-density peaks listed in Table 1 for the atoms in the asymmetric unit. A final difference electron-density map was almost featureless; the maximum electron density observed was 3 eÅ^{-3}.

RESULTS AND DISCUSSION

The positional and thermal parameters of the asymmetric unit are given in Table 1 together with the peak electron density determined from the final Fourier synthesis. Interatomic distances and bond angles are listed in Table 2, and observed and calculated structure factors are recorded in Supplementary Publication No. SUP 20720 (3 pp., 1 microfiche).* Figure 1 shows a perspective view of the molecule. The crystal consists of As_4S_5 molecules, with two arsenic atoms and one sulphur atom lying on a mirror plane in positions 2*e* and one arsenic and two sulphur atoms in general positions 4*f*. The plane As(3), As(3′), S(3) is normal to the crystallographic mirror plane through As(2), As(1), and S(3), and is a plane of symmetry of the molecule, so that the overall symmetry is C_{2v}.

TABLE 2

Distances and angles, with standard deviations in parentheses

(*a*) Distances (Å)

As(1)–As(2)	2·546(11)	As(3)–S(1)	2·230(11)
As(1)–S(1)	2·229(10)	As(3)–S(2)	2·241(11)
As(2)–S(2)	2·254(10)	As(3)–S(3)	2·268(8)

(*b*) Angles (°)

As(1)–S(1)–As(3)	108·5(5)	As(2)–As(1)–S(1)	101·0(3)
As(2)–S(2)–As(3)	108·3(4)	As(1)–As(2)–S(2)	100·8(3)
As(3)–S(3)–As(3′)	117·3(4)	S(1)–As(1)–S(1′)	102·7(4)
S(1)–As(3)–S(2)	98·8(3)	S(2)–As(2)–S(2′)	99·8(4)
S(1)–As(3)–S(3)	105·8(4)	S(2)–As(3)–S(3)	104·1(4)

(*c*) Non-bonded distances (Å)

As(1) · · · As(3)	3·620(9)	S(1) · · · S(2)	3·396(16)
As(2) · · · As(3)	3·643(9)	S(1) · · · S(1′)	3·482(15)
As(3) · · · As(3′)	3·870(9)	S(2) · · · S(2′)	3·449(16)
As(1) · · · S(2)	3·704(13)	S(1) · · · S(3)	3·586(16)
As(2) · · · S(1)	3·689(14)	S(2) · · · S(3)	3·555(15)

The shortest intermolecular contacts, indicated in Figure 2 by dotted lines are S(2) · · · As(1) 3·37 and S(2) · · · As(2) 3·39 Å. Molecules of As_4S_5 are thus linked by van der Waals forces into strings parallel to

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-sized copies.

[3] H. J. Whitfield, *J. Chem. Soc.* (*A*), 1970, 1800.

[4] T. Ito, N. Morimoto, and R. Sadanaga, *Acta Cryst.*, 1952, **5**, 775.

[5] M. J. Buerger, *Amer. Mineral.*, 1942, **27**, 301.

[6] Programs Sigma, Converge, and Fastan for solution by direct methods, M. M. Woolfson, G. Germain, and P. Main.

the *b* axis of the crystal. The next shortest As · · · S and S · · · S intermolecular contacts are 3·57 Å and 3·58 Å respectively which may be compared with the van der Waals radius sums of 3·85 and 3·70 Å.

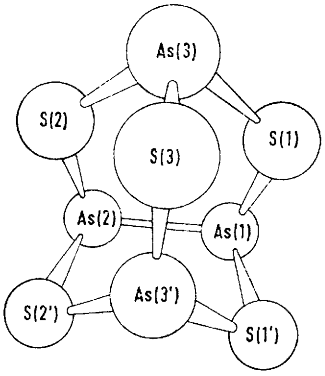

FIGURE 1 As_4S_5 molecule

The structure found here for As_4S_5 is that suggested by Lauer *et al.*[7] for a crystalline residue of composition As_4S_5 produced by the hydrolytic cleavage of the $As_4S_6^{2-}$ anion. This structure is quite different from those of P_4S_5[8] and P_4Se_5[9] which have an exocyclic sulphur and selenium atom respectively double-bonded to a five-valent phosphorus atom; the difference is readily rationalized in terms of the reluctance of arsenic, compared to phosphorus, to attain the five-valent state.

The As–As bond distance (2·55) is close to that in $As_4S_6^{2-}$ (2·58)[10] in α-As_4S_4 (2·59),[4] β-As_4S_4 (2·60),[11] and As_4Se_4 (2·56 Å).[12]

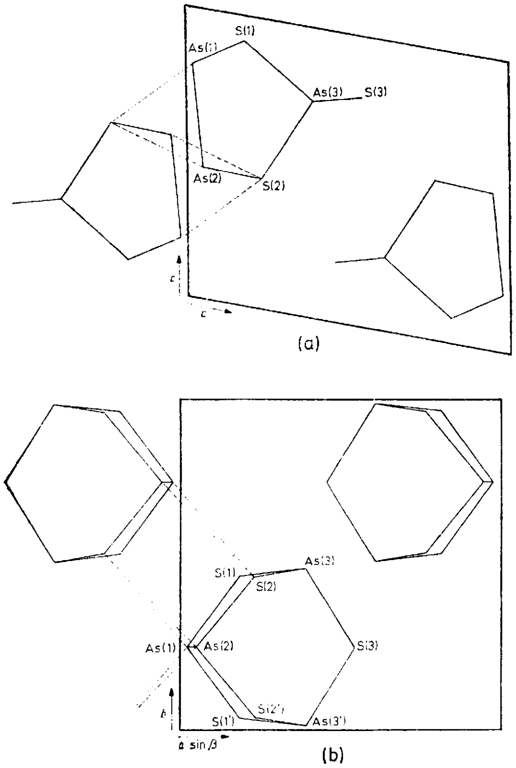

FIGURE 2 Projection of the unit cell along (a) 010 and (b) 001

[2/2909 *Received, 28th December*, 1972]

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[7] W. Lauer, M. Becke-Goehring, and K. Sommer, *Z. anorg. Chem.*, 1969, **371**, 193.

[8] S. Van Houten and E. H. Wiebenga, *Acta Cryst.*, 1957, **10**, 156.

[9] G. J. Penney and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1971, 245.

[10] E. J. Porter and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1971, 3130.

[11] H. J. Whitfield, to be published.

[12] T. J. Bastow and H. J. Whitfield, preceding paper.