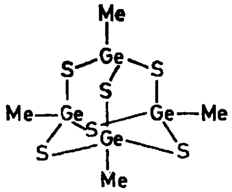
Molecular and Crystal Structures of Tetra(methylgermanium) Hexasulphide

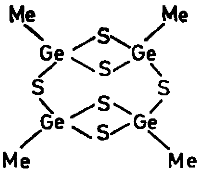
By **Robert H. Benno** and **Charles J. Fritchie, jun.**,* Richardson Chemical Laboratories, Tulane University, New Orleans, Louisiana 70118, U.S.A.

The title compound has been shown by *X*-ray crystallographic methods to have an adamantane-type structure. Mean distances and angles are Ge–S 2·218(3), Ge–C 1·922(10) Å, S–Ge–S 111·8(3), Ge–S–Ge 104·6(2), and S–Ge–C 107·0(3)°. Crystals are monoclinic, space group $C2/c$, with a = 9·422(5), b = 16·779(8), c = 10·708(5) Å, β = 107·94(3)°, and Z = 4. Molecular symmetry C_2 is required. Refinement of 738 independent counter measured reflections gave R 5·2%.

THE versatility of sulphur as a bridging ligand and the importance of sulphur–metal (iron) complexes in enzyme systems [1] have led us to investigate the crystal structure of the organogermanium complex $(MeGe)_4S_6$.[2] Sulphur is capable of sharing two electrons with two other atoms (as in H_2S) or sharing four electrons with three other atoms {as in $[EtSFe(NO)_2]_2$,[3] $[EtSFe(CO)_3]_2$,[4] and $S_2Ni_3(C_5H_5)_3$}.[5] Both ' adamantane ' (I) and ' open cage ' (II) structures which have been suggested [2] for $(MeGe)_4S_6$ involve the former type of bonding.



(I)



(II)

EXPERIMENTAL

A single crystal, bounded by {110} and having a diamond cross-section with major diagonal (b^*) 0·3, minor diagonal (a^*) 0·2, and length 0·6 mm, was mounted on [001]. Precession (Mo-K_α) and Weissenberg (Cu-K_α radiation) photographs were used to obtain preliminary unit-cell and space-group data. Refined unit-cell parameters were obtained by a least-squares fit to $\sin^2 \theta$ values determined by use of a Picker four-circle diffractometer and Mo-K_α radiation.

Crystal Data.—$C_4H_{12}Ge_4S_6$, M = 542·9, Monoclinic, a = 9·422(5), b = 16·779(8), c = 10·708(5) Å, β = 107·94(3)°,

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[1] W. D. Phillips, E. Knight, jun., and D. C. Blomstrom, in ' Non-Heme Iron Proteins,' ed. A. San Pietro, Antioch Press, Yellow Springs, Ohio, 1965, pp. 69—85.

[2] K. Moedritzer, *Inorg. Chem.*, 1967, **6**, 1248.

[3] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, 1958, **11**, 599.

[4] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, **2**, 328.

[5] L. F. Dahl, V. A. Uchtman, and H. Varenkamp, *J. Amer. Chem. Soc.*, 1968, **90**, 3272.

$U = 1611(1)$ Å^3, $F(000) = 1136$, $Z = 4$, $D_c = 2{\cdot}239(2)$. Space group $C2/c$ from systematic absences.[6a] Mo-K_α radiation $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 85{\cdot}28$ cm^{-1}. Since the general position of space group $C2/c$ is eight-fold, the molecule is required to have either $C2$ or C_i symmetry. The former was found to be the case.

Intensity data were measured by use of zirconium-filtered Mo-K_α radiation on a Picker card-controlled four-circle diffractometer fitted with a pulse-height analyser and a scintillation counter. Reflections with $3° < 2\theta < 40°$ were scanned in the 2θ mode at 1° min^{-1}, using a scan range of 2°. On each side of the scan range a 20 s background count was recorded. A standard reflection was measured *ca.* every 2 h, but showed no significant changes.

A total of 738 reflections was scanned, constituting the independent quadrant of reciprocal space within the given 2θ limits. A standard deviation, σ_I, was estimated for each reflection on the basis of standard counting statistics in peak and background readings and of scale factor uncertainty. Any reflection for which $I < 2\sigma_I$ was considered to be unobserved and assigned $I = 2\sigma_I$ for further computations. Structure magnitudes were derived by use of Lorentz and polarization factors. The standard deviation in F, σ_F, was derived by the propagation-of-error equation $\sigma_F = \sigma_I/(2|F_o| \,.\, L \,.\, P)$, where L and P are Lorentz and polarization factors. Unobserved reflections were included in least-squares calculations only if $|F_c| > |F_o|$. Twenty-two were included in the final calculation. Reflection $2,0,\bar{6}$ for which $F_o = 371$ and $F_c = -486$, was given zero weight.

Structure Analysis.—A trial structure consisting of the four germanium and six sulphur atoms was obtained from the three-dimensional Patterson function. With sulphur and germanium atoms input isotropically, an initial R of 28·6% was obtained after a single least-squares cycle. A Fourier difference map was used to locate the carbon atoms. Least-squares refinement with germanium, sulphur, and carbon anisotropic yielded R 5·4%. Hydrogen atoms were located in additional general plane difference maps, but were input in idealized positions in which the hydrogens of the methyl groups were constrained to have tetrahedral symmetry with the rotation of the methyl groups fixed by difference maps.

Convergence was reached at 5·2% after the hydrogens were input with an isotropic B of 3 and only the non-hydrogen atoms refined. The weight used for each reflection in the final least-squares calculations was $1/\sigma_F{}^2$. Scattering factors were taken from ref. 6(*b*), and were corrected for the complex effects of dispersion. The least-squares refinement program BLSA, modified from the block-diagonal form of UCLALSI (Gantzel, Sparks, and Trueblood), was used to minimize the quantity: $\Sigma w||F_o| - |F_c||^2$ by means of a block-diagonal matrix with a 9×9 block for each atom. Other programs used were FOUR and GENMAP for Fourier summation (C. J. Fritchie, jun.), GSET4 for goniometer orientation (C. T. Prewitt), ORTEP for plotting Figures (C. K. Johnson), CELL for determining unit-cell constants (B. L. Trus), and MGEOM for determining standard deviations (J. T. Mague). Calculations were performed on an IBM 7044 computer at the Tulane Computer Laboratory.

Final atomic parameters are listed in Tables 1 and 2. Observed and final calculated structure factors are noted in Supplementary Publication No SUP 20609 (2 pp., 1 microfiche).*

TABLE 1

Final atomic parameters, with standard deviations in parentheses *

Atom	10^4x	10^4y	10^4z
Ge(1)	1(1)	−1796(7)	858(1)
Ge(2)	1948(1)	−315(7)	3037(1)
S(3)	2073(3)	−1068(2)	1369(3)
S(4)	2049(3)	−1054(2)	4781(2)
S(5)	0 †	484(2)	1/4 †
S(6)	0 †	−2604(2)	1/4 †
C(7)	3660(11)	360(8)	3481(10)
C(8)	14(13)	−2456(7)	−622(11)
H(9)	184	−2130	−1347
H(10)	−930	−2735	−971
H(11)	850	−2857	−387
H(12)	4608	41	3655
H(13)	3654	721	2896
H(14)	3784	634	4308

* Hydrogen atoms are in idealized positions. † These parameters are fixed by symmetry.

TABLE 2

Anisotropic thermal parameters (× 10^4),* with standard deviations in parentheses

Atom	B_{11}	B_{22} ‡	B_{33}	B_{12}	B_{13}	B_{23}
Ge(1)	165(2)	138(4)	69(1)	4(1)	115(2)	−5(1)
Ge(2)	123(1)	169(4)	69(1)	−7(1)	80(2)	4(1)
S(3)	151(4)	253(12)	79(3)	6(4)	130(5)	−3(3)
S(4)	151(4)	253(12)	57(3)	2(4)	70(5)	15(3)
S(5)	137(5)	128(14)	84(4)	0 †	86(7)	0 †
S(6)	242(7)	87(14)	86(4)	0 †	149(8)	0 †
C(7)	417(16)	490(60)	55(11)	−25(17)	75(20)	20(15)
C(8)	241(18)	210(40)	99(11)	−3(17)	177(21)	−25(14)

All hydrogens are assigned an isotropic thermal parameter of B 3·0 Å^2.

* The thermal expression has the form: $[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl]$. † These parameters are fixed by symmetry. ‡ (×10^5).

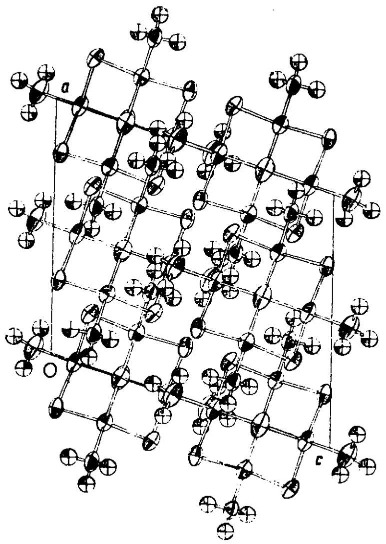

FIGURE 1 The unit cell viewed down the *b* axis

DISCUSSION

Molecular Configuration.—The crystal structure is illustrated in Figures 1 and 2. The molecule has the

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full-size copies).

[6] 'International Tables for *X*-Ray Crystallography,' vol. I, 3rd edn., 1969, Kynoch Press, Birmingham, (*a*) p. 101; (*b*) pp. 202—245.

adamantane-type structure, shown in stereoscopic view in Figure 3. Every germanium atom is bonded to three sulphur atoms and one carbon atom which are located at the corners of a slightly distorted tetrahedron. The mean Ge–S bond length [2·218(3) Å] (see Table 3) agrees within 2σ with that reported[7] for GeS_2 (2·19 Å) and is also essentially in agreement with the sum of the covalent radii[8] (2·25 Å). (Throughout this paper, standard deviations estimated by use of the least-squares normal equations are quoted for individual measures; the larger of the above or the root-mean-square deviation is quoted for each mean.) Our bond angle for Ge–S–Ge [104·6(2)°, see Table 4] agrees with Zachariasen's Ge–S–Ge angles (98, 104, and 107°), as well as the value of 104·5(1)° for the Si–S–Si angle in $(MeSi)_4S_6$,[9] which is isomorphous with $(MeGe)_4S_6$. Zachariasen reported no values for the S–Ge–S bond angle, but our mean value of 111·8(3)° is identical to the corresponding angle S–Si–S of 111·8(1)° in the silicon analogue.[9] Deviations from the tetrahedral value in the R–S–R bonding angle (where R is any group bound to sulphur) are common and are probably

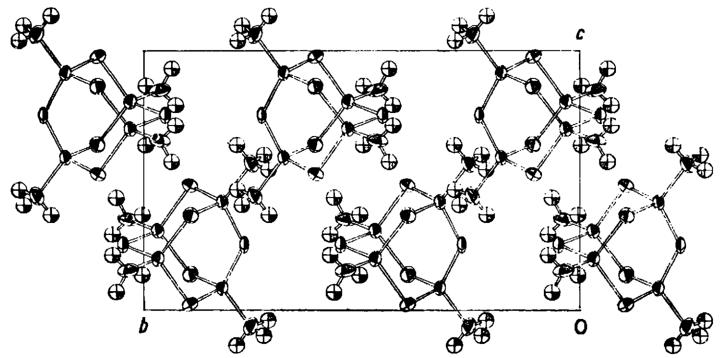

FIGURE 2 The unit cell viewed down the *a* axis

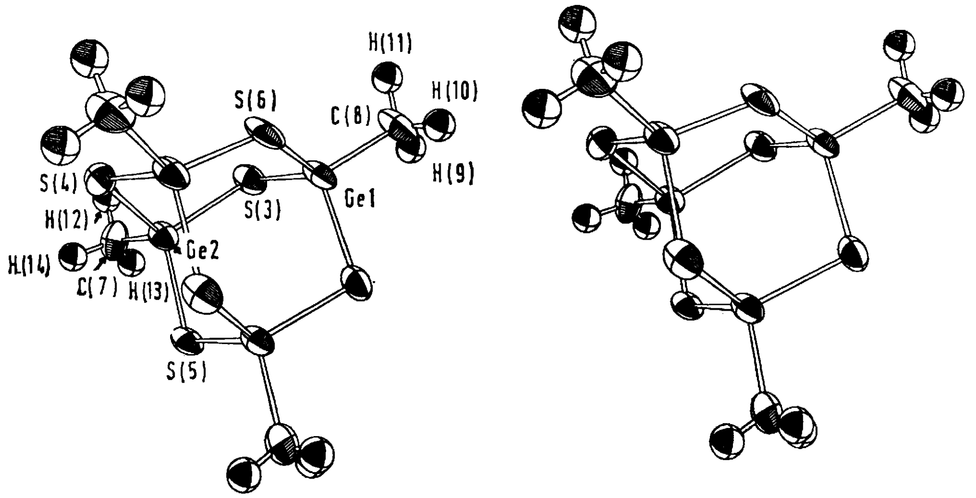

FIGURE 3 Stereoscopic view of one molecule showing the atom numbering system used; S(5) and S(6) lie on a crystallographic two-fold axis

TABLE 3

Bond distances (Å) with standard deviations in parentheses

Ge(1)–S(3)	2·224(3)	Ge(2)–C(7)	1·907(11)
Ge(1)–S(6)	2·219(3)	C(7)–H(12)	1·01 *
Ge(1)–S(4′)	2·221(3)	C(7)–H(13)	0·87
Ge(2)–S(3)	2·219(3)	C(7)–H(14)	0·97
Ge(2)–S(4)	2·220(3)	C(8)–H(9)	1·00
Ge(2)–S(5)	2·202(3)	C(8)–H(10)	0·99
Ge(1)–C(8)	1·936(11)	C(8)–H(11)	1·00

* The hydrogen atoms are in idealized positions determined with the aid of difference-Fourier maps.

TABLE 4

Bond angles (°) with standard deviations in parentheses *

Angle	Value	Angle	Value
S(3)–Ge(1)–S(6)	110·8(1)	S(4′)–Ge(1)–C(8)	107·0(4)
S(3)–Ge(1)–S(4′)	112·5(1)	S(3)–Ge(2)–C(7)	106·8(3)
S(4′)–Ge(1)–S(6)	112·0(1)	S(4)–Ge(2)–C(7)	108·0(4)
S(3)–Ge(2)–S(4)	111·1(1)	S(5)–Ge(2)–C(7)	106·0(3)
S(3)–Ge(2)–S(5)	112·5(1)	Ge(1)–S(3)–Ge(2)	104·5(1)
S(4)–Ge(2)–S(5)	112·1(1)	Ge(1)–S(6)–Ge(1′)	104·8(1)
S(3)–Ge(1)–C(8)	106·8(4)	Ge(2)–S(4)–Ge(1′)	104·2(1)
S(6)–Ge(1)–C(8)	107·5(4)	Ge(2)–S(5)–Ge(2′)	105·0(1)

* Primed atoms are related to the corresponding unprimed ones by the molecular two-fold axis.

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[7] W. H. Zachariasen, *J. Chem. Phys.*, 1936, **4**, 618.

[8] L. Pauling and M. L. Huggins, *Z. Krist.*, 1934, **87**, 205.

[9] J. C. J. Bart and J. J. Daly, *Chem. Comm.*, 1968, 1207.

due to repulsion between the R groups and the lone pairs of electrons on the sulphur atom.

The mean Ge–C bond distance [1·922(10) Å] is in relatively good agreement with the Ge–C bond length of 1·98(3) Å found in tetramethylgermanium.[10] Our value for the S–Ge–C angle [107·0(3)°] is identical to the corresponding angle S–Si–C [107·0(2)°] in the Si analogue. The hydrogen atoms of the methyl groups have almost perfectly staggered configurations with respect to corresponding sulphur atoms on the adjacent germanium atoms. Such a staggered configuration is expected if intramolecular forces are the largest factor affecting the orientation of the methyl groups.

The structure of $(MeSn)_4S_6$ has also been determined;[11] it is isomorphous with both $(MeGe)_4S_6$ and $(MeSi)_4S_6$.

We thank Dr. Moedritzer for a sample of the crystals used.

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[10] L. O. Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036.

[11] H. J. Milledge, personal communication.