out of the P_3 plane (Jones, 1980), while $[Au\{P(C_6H_5)_3\}_3][B_9H_{12}S]$ has Au–P 2·345, 2·384, 2·389 Å, P–Au–P 112·3, 121·5, 124·1°, the Au atom lies 0·2 Å out of the P_3 plane (Guggenberger, 1974). In contrast to all of these $[Au\{P(C_6H_5)_3\}_3(SCN)]$ displays four-coordinate geometry, with much longer Au–P distances (2·384, 2·401 and 2·413 Å), and a very much longer Au–S distance of 2·791 Å. The similarity in structure of the trigonal $[Au\{P(C_6H_5)_3\}_2(SCN)]$ and $[Au\{P(C_6H_5)_3\}_2Cl]$ in contrast to the linear $[Au\{P(cyclo\text{-}C_6H_{11})_3\}_2][SCN]$ suggests that the steric requirements of the phosphine are the determining factor in the structure.

Computer programs used included *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978).

We are grateful to the University of Puerto Rico Computing Service for generous grants of time on the IBM 370/148 computer, and to L. Bird for helpful discussions. Research was supported in part by grant RR-8102 from the Division of Research Resources, National Institutes of Health.

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Acta Cryst. (1982). B**38**, 1320–1323

The Structure of μ-Thio-bis[tribenzylgermanium(IV)]

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(*Received* 2 *November* 1981; *accepted* 2 *December* 1981)

Abstract. $C_{42}H_{42}Ge_2S$, monoclinic, $C2/c$, a = 25·448 (7), b = 9·344 (2), c = 17·304 (3) Å, β = 118·31 (2)°, U = 3622·6 Å^3, M_r = 724·04, D_c = 1·327 Mg m^{-3} for Z = 4, $F(000)$ = 1496, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 1·674 mm^{-1}; R = 0·0861 for 1512 reflections. The structure consists of molecules lying across the twofold axes of the unit cell: the GeSGe angle is 106·6 (2)° and the Ge–S distance 2·233 (4) Å.

Introduction. As part of a study of hexa-organo substituted triatomics, $X(R_3M)_2$, we have previously reported the structures of $O(Ph_3Ge)_2$ (Glidewell & Liles, 1978*a*) and $O[(PhCH_2)_3Ge]_2$ (Glidewell & Liles, 1979*a*). The structure of $S(Ph_3Ge)_2$ has also been reported (Krebs & Korte, 1979). $O(Ph_3Ge)_2$ and $O[(PhCH_2)_3Ge]_2$ both have very wide GeOGe angles, 135·2 (2) and 180·0 (0)° respectively: the former can be ascribed to a 'hard atom' contact between the Ge atoms (Glidewell & Liles, 1978*a*) and the latter can be accounted for in terms of a second-order Jahn–Teller effect (Glidewell, 1978*a*,*b*). To test whether a similar effect could be observed when the central O atom was replaced by an S atom – thus reducing the electronegativity difference between the central atom and the $(PhCH_2)_3Ge$ groups – we have determined the structure of $S[(PhCH_2)_3Ge]_2$.

$S[(PhCH_2)_3Ge]_2$ was prepared from $(PhCH_2)_3GeBr$ (Bauer & Burschkies, 1934) by the action of Na_2S in ethanol solution (Burschkies, 1935). Crystals suitable for X-ray examination were obtained from 60–80 petrol solution.

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Data were collected using a Stoe STADI-2 two-circle automatic diffractometer with graphite-crystal-monochromatized Mo $K\alpha$ radiation for a crystal of dimensions $0{\cdot}2 \times 0{\cdot}1 \times 0{\cdot}5$ mm mounted about **b**. The intensities of 1583 reflections in the quadrant $\pm h$, $+k$, $+l$ with $2 \leq \theta \leq 30°$, $k = 0$–11 ($0 \leq \mu \leq 24{\cdot}730°$) were measured using the ω–2θ scan mode. Each reflection was scanned using 140 steps of width $0{\cdot}01°$ (in ω) and a time of $1{\cdot}0$ s per step. Backgrounds were measured at each end of the scan for 70 s. Standard reflections were measured every 50 reflections and showed only small random deviations from their mean intensities. No corrections for absorption were made.

Systematic absences hkl $h + k = 2n + 1$, $h0l$ $l = 2n + 1$ showed the space group to be $C2/c$ (C_{2h}^6, No. 15) or Cc (C_s^4, No. 9).

The structure was solved using Patterson and difference syntheses in space group Cc and was refined, initially in Cc and subsequently in $C2/c$, using *SHELX* 76 (Sheldrick, 1976). The solution in Cc showed the molecule to have twofold symmetry; thus the refinement was completed in $C2/c$. Blocked-matrix least-squares refinement, such that the Ge and S atoms refined every cycle and each benzyl group refined once every three cycles, with anisotropic temperature factors for all non-H atoms, and with the H atoms in calculated positions (C—H = $1{\cdot}08$ Å) with common isotropic temperature factors for each phenyl and methylene group (210 parameters) converged in space group $C2/c$ to give R ($= \sum \Delta / \sum |F_o|$, $\Delta = ||F_o| - |F_c||$) of $0{\cdot}0861$ and R_G [$= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$] of $0{\cdot}0944$ for 1512 independent reflections with $F_o > 4\sigma(F_o)$. The reduction in R_G for a similar refinement in Cc was not significant at the 50% level (Hamilton, 1965). A final difference map showed no significant residual electron density. Complex neutral-atom scattering factors were used for all atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The final coordinates are given in Table 1. These, together with the full covariance matrix, were used to calculate the bond lengths and bond angles of the $(C_3Ge)_2S$ core of the molecule given in Table 2. Selected dihedral angles between planes, and torsional angles are given in Table 3. Fig. 1 shows the molecule and the atom-numbering scheme.*

Table 1. *Atomic fractional coordinates* ($\times 10^4$) *and the equivalent isotropic temperature parameters* (U_{iso}) ($\times 10^3$, Å^2)

U_{iso} is defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij}.

	x	y	z	U_{iso}
Ge	763 (1)	313 (2)	3340 (1)	38 (1)
S	0	1741 (6)	2500	46 (4)
C(1)	685 (9)	−238 (20)	4395 (11)	58 (13)
C(11)	690 (8)	1164 (18)	4926 (11)	37 (11)
C(12)	160 (8)	1827 (18)	4721 (10)	37 (11)
C(13)	145 (9)	2980 (20)	5193 (11)	54 (15)
C(14)	629 (11)	3491 (21)	5857 (13)	60 (16)
C(15)	1179 (11)	2863 (21)	6078 (11)	56 (15)
C(16)	1215 (9)	1680 (19)	5621 (12)	55 (13)
C(2)	795 (7)	−1423 (14)	2711 (9)	41 (10)
C(21)	1096 (6)	−2651 (15)	3346 (9)	35 (9)
C(22)	770 (7)	−3582 (18)	3601 (11)	51 (12)
C(23)	1074 (9)	−4636 (21)	4205 (11)	62 (13)
C(24)	1672 (8)	−4819 (21)	4596 (10)	59 (12)
C(25)	1984 (8)	−3930 (20)	4332 (13)	70 (14)
C(26)	1700 (7)	−2864 (19)	3721 (11)	53 (12)
C(3)	1483 (7)	1436 (19)	3676 (11)	58 (12)
C(31)	1647 (6)	1726 (17)	2952 (10)	38 (9)
C(32)	2051 (6)	819 (18)	2856 (11)	48 (11)
C(33)	2197 (7)	1093 (22)	2186 (11)	61 (13)
C(34)	1923 (8)	2176 (22)	1604 (11)	59 (13)
C(35)	1522 (8)	3047 (21)	1700 (12)	61 (14)
C(36)	1382 (8)	2804 (21)	2352 (12)	63 (14)

Table 2. *Geometry of the molecule (excluding the phenyl rings)*

The geometries of the phenyl rings have been deposited in a supplementary table. The superscript (I) refers to the symmetry position $\bar{x}, y, \frac{1}{2} - z$.

Bond distances (Å)

Ge···Ge^{I}	3·581 (3)	Ge–S	2·233 (4)		
Ge–C(1)	1·996 (23)	Ge–C(2)	1·977 (15)	Ge–C(3)	1·946 (18)
C(1)–C(11)	1·59 (3)	C(2)–C(21)	1·52 (2)	C(3)–C(31)	1·52 (3)

Bond angles (°)

Ge–S–Ge^{I}	106·6 (2)		
S–Ge–C(1)	108·5 (6)	C(1)–Ge–C(2)	109·9 (8)
S–Ge–C(2)	112·5 (4)	C(1)–Ge–C(3)	110·7 (8)
S–Ge–C(3)	106·1 (5)	C(2)–Ge–C(3)	109·1 (8)
Ge–C(1)–C(11)	110 (1)	Ge–C(2)–C(21)	111 (1)
Ge–C(3)–C(31)	116 (1)		

Table 3. *Selected dihedral angles between planes, and torsion angles* (°)

The equations of the least-squares planes and the distances of selected atoms from the planes have been deposited in a supplementary table. The superscript (I) refers to the symmetry position $\bar{x}, y, \frac{1}{2} - z$.

Dihedral angles between the planes of the phenyl C atoms C(ij) and C(kj)

i	k		i	k		i	k		i	k	
1	1	78·7 (3)	1	3	75·4 (4)	1	1^{I}	75·2 (2)	1	2^{I}	14·9 (9)
1	3^{I}	60·4 (3)	2	3	46·1 (5)	2	2^{I}	78·3 (3)	2	3^{I}	−85·4 (3)
3	3^{I}	75·5 (4)									

Dihedral angles between the planes of the phenyl C atoms C(ij) and the planes of the Ge–C(i)–C($i1$) groups

i =	1	2	3
	−88·2 (1)	88·7 (4)	83·3 (3)

Torsion angles. The torsion angle i–j–k–l is positive if when viewed in the direction $j \to k$, the projection of i–j has to be rotated clockwise to coincide with the projection of k–l.

C(1)–Ge–Ge^{I}–C(1)^{I}	−149·5 (8)	C(1)–Ge–Ge^{I}–C(2)^{I}	−40·6 (7)
C(1)–Ge–Ge^{I}–C(3)^{I}	69·5 (10)	C(2)–Ge–Ge^{I}–C(2)^{I}	68·2 (6)
C(2)–Ge–Ge^{I}–C(3)^{I}	178·4 (9)	C(3)–Ge–Ge^{I}–C(3)^{I}	71·5 (11)

* Lists of structure factors, anisotropic thermal parameters, geometries of the phenyl rings, least-squares planes and a figure showing unit-cell contents have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36582 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Structural comparisons of* $O(R_3M)_2$ *and* $S(R_3M)_2$ (R = Ph, $PhCH_2$; M = Si, Ge, Sn)

R, M =	Ph, Si	$PhCH_2$, Si	Ph, Ge	$PhCH_2$, Ge	Ph, Sn	$PhCH_2$, Sn
$\angle(MOM)$ (°)	180·0 (0)[a]	180·0 (0)[b]	135·2 (2)[c]	180·0 (0)[e]	137·3 (1)[g]	180·0 (0)[i]
$\angle(MSM)$ (°)	–	–	111·0 (1)[d]	106·6 (2)[f]	107·3 (2)[h]	–
$d(M-O)$ (Å)	1·616 (1)[a]	1·613 (4)[b]	1·767 (3)[c]	1·730 (1)[e]	1·955 (3)[g]	1·919 (0)[i]
$d(M-S)$ (Å)	–	–	2·235 (21)[d]	2·233 (4)[f]	2·411 (8)[h]	–

References: (*a*) Glidewell & Liles (1978*b*). (*b*) Glidewell & Liles (1981). (*c*) Glidewell & Liles (1978*a*). (*d*) Krebs & Korte (1979). (*e*) Glidewell & Liles (1979*a*). (*f*) This work. (*g*) Glidewell & Liles (1978*c*). (*h*) Glidewell & Liles (1982). (*i*) Glidewell & Liles (1979*b*).

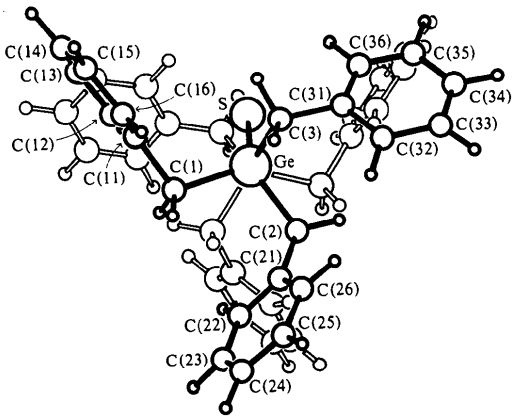

Fig. 1. The molecule showing the numbering scheme.

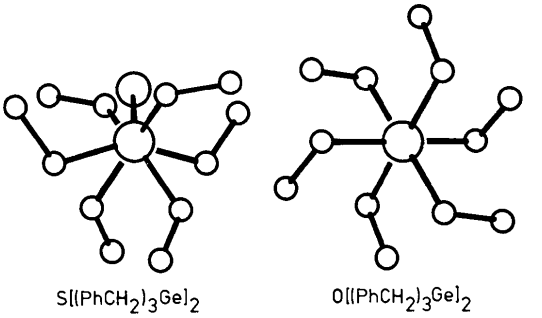

Fig. 2. Molecular-core conformations [phenyl carbons C(*i*2)–C(*i*6) omitted for clarity] in $X[(PhCH_2)_3Ge]_2$ (X = O, S), viewed along Ge···Ge direction.

Discussion. The structure consists of discrete molecules lying across the twofold axis. Both the GeSGe angle, 106·6 (2)°, and the GeS distance 2·233 (4) Å are very similar to those in the analogous phenyl compound $S(Ph_3Ge)_2$, 111·0 (1)° and 2·235 (21) Å (Krebs & Korte, 1979). In addition, the overall structural similarities between $S(Ph_3M)_2$ (M = Ge, Sn) and also between $S(R_3Ge)_2$ (R = Ph, $PhCH_2$) (Table 4) suggest that the skeletal geometry in $S[(PhCH_2)_3Sn]_2$ will be very similar to that found here for $S[(PhCH_2)_3Ge]_2$: however, the skeletal structures of $S(R_3Si)_2$ are unpredictable. The data in Table 4 indicate that none of the thio species so far investigated shows any sign of geometrical anomaly manifested in the MSM angle; nor does $Se(Ph_3Sn)_2$ (Krebs & Jacobson, 1979).

It is interesting to compare the conformations of $O[(PhCH_2)_3Ge]_2$ and $S[(PhCH_2)_3Ge]_2$: Table 3 contains a summary of the important inter-plane and torsion angles. The conformation in the thio compound viewed along the Ge···Ge vector (Fig. 1) shows an almost fully staggered $C_3Ge\cdots GeC_3$ arrangement, as indicated also by the several independent CGe···GeC torsion angles (Table 3). The phenyl-group conformation is such that pairs of phenyls, on Ge and Ge^{1}, are eclipsed despite the staggering of the GeC bonds, with the two eclipsed rings almost perpendicular to one another: the two independent interplane angles describing this are 78·3 (3) and −75·4 (4)°.

In contrast, the phenyl groups in the oxo compound, which has S_6 molecular symmetry, are staggered as are the GeC bonds also, but again pairs of adjacent phenyl groups are almost mutually perpendicular, interplane angle 86·4° (Glidewell & Liles, 1979*a*). Since the angles between the phenyl rings C(*ij*) and the adjacent plane Ge–C(*i*)–C(*ij*) are essentially the same in the thio compound (Table 3, mean value 86·7°) and in the oxo analogue, 84·3°, the differences in phenyl conformations arise entirely from rotations about the GeC bonds. If starting with the all-staggered conformation of $O[(PhCH_2)_3Ge]_2$, the three benzyl groups on one end of the molecule are simply rotated by 120° about their GeC bonds in the same sense and towards the benzyl groups at the other end, the conformation found for $S[(PhCH_2)_3Ge]_2$ is obtained. The conformations of the central molecular cores are shown for the two molecules in Fig. 2.

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Acta Cryst. (1982). B**38**, 1323–1324

Bis(2,2′:6′,2″-terpyridine)copper(II) Hexafluorophosphate

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(*Received* 23 *February* 1981; *accepted* 3 *December* 1981)

Abstract. $[Cu(C_{15}H_{11}N_3)_2](F_6P)_2$, $M_r = 820{\cdot}0$, tetragonal, $P\bar{4}2_1c$, $a = 8{\cdot}930$ (3), $c = 20{\cdot}623$ (5) Å, $V = 1644{\cdot}6$ Å^3, $Z = 2$, $D_m = D_c = 1{\cdot}66$ g cm^{-3}, $F(000) = 882$, μ(Mo $K\alpha$) = 8·97 cm^{-1}. The $[Cu(tpy)_2](F_6P)_2$ structure was solved by the Patterson method and refined to $R = 0{\cdot}048$ for 559 independent reflections. This structure consists of isolated $[M(tpy)]^{2+}$ groups and isolated $(F_6P)^-$ octahedra. It is compared with $[Cu(tpy)_2](NO_3)_2$.

Introduction. Crystal structures of various M^{2+} terpyridine complexes have recently been reported (Maslen, Raston & White, 1974; Allmann, Henke & Reinen, 1978), but so far no data are available for similar compounds with the $(F_6P)^-$ ligand.

$[Cu(tpy)_2](F_6P)_2$ was first synthesized by one of us (TR) starting from a 2,2′:6′,2″-terpyridine solution in hot water and a $CuCl_2.2H_2O$ solution. A KF_6P solution was added to the Cu–tpy chloride complex until a light-green precipitate appeared. This precipitate was washed with chloroform and crystallized from acetone to give green crystals, which were dried *in vacuo* over P_2O_5.

Elemental analysis: calculated for $[Cu(C_{15}H_{11}N_3)_2](F_6P)_2$: C 43·9, N 10·2, H 2·7, Cu 7·8%; experimental: C 44·1, N 10·4, H 2·8, Cu (determined by atomic absorption spectroscopy) 7·9%.

A crystal of $[Cu(tpy)_2](F_6P)_2$, 0·3 × 0·27 × 0·25 mm, was mounted on a Syntex $P2_1$ four-circle diffractometer. Graphite-monochromated Mo $K\alpha_1$ radiation ($\lambda = 0{\cdot}7107$ Å) was used. 720 reflections with $2\theta \leq 47°$ were collected. Of these, 559 with $I \geq 2{\cdot}5\sigma(I)$ were considered as observed. The relative

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