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Redetermination of tetrakis(trimethylstannyl)germane

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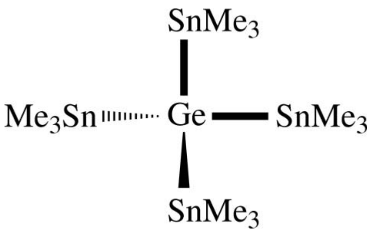
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(Sn–C) = 0.008 Å; R factor = 0.049; wR factor = 0.105; data-to-parameter ratio = 36.7.

Redetermination of the structure of the title compound, [Ge(SnMe$_3$)$_4$] or [GeSn$_4$(CH$_3$)$_{12}$], previously refined from powder diffraction data only [Dinnebier, Bernatowicz, Helluy, Sebald, Wunschel, Fitch & van Smaalen *et al.* (2002). *Acta Cryst*. B**58**, 52–61], confirms that four bulky trimethylstannyl ligands surround the central Ge atom (site symmetry 1) in a tetrahedral coordination.

Related literature

For related literature, see: Dinnebier *et al.* (2002); Wrackmeyer & Bernatowicz (1999); Chizmeshya *et al.* (2003).



Experimental

Crystal data

[GeSn$_4$(CH$_3$)$_{12}$]
M_r = 727.76
Triclinic, $P\bar{1}$
a = 9.1666 (7) Å
b = 9.9521 (7) Å
c = 14.5400 (14) Å
α = 90.033 (2)°
β = 90.546 (1)°
γ = 111.736 (1)°
V = 1232.06 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 5.19 mm^{-1}
T = 298 (2) K
0.22 × 0.22 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min}$ = 0.317, $T_{\max}$ = 0.460
12284 measured reflections
5646 independent reflections
4466 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.085

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.105
S = 1.01
5646 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.09 e Å^{-3}
$\Delta\rho_{\min}$ = −1.01 e Å^{-3}

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We express our gratitude to the National Science Foundation for their contribution toward the purchase of the single-crystal instrumentation used in this study through Award #CHE-9808440.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2036).

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S1. Comment

The structure of the Ge[Sn(CH$_3$)$_3$]$_4$ cluster has been previously determined by powder X-ray diffraction and magic angle spinning NMR spectroscopy (Dinnebier *et al.*, 2002). Here, we have developed a new synthetic route to form Ge[Sn(CH$_3$)$_3$]$_4$ in high yields (80–90%) and, for the first time, adequately sized crystals suitable for a single-crystal structure determination. The long-term objective is to use this bonding information to understand structural trends in recently developed $Ge_{1-x}Sn_x$ and $Ge_{1-x-y}Sn_xSi_y$ semiconductor alloys, including unusual deviations from Vegard's Law (Chizmeshya *et al.*, 2003). Various tetrahedral cluster compounds with the general formula A(BH$_3$)$_4$ (where {A, B}= {Si, Ge, Sn}) are potentially viable low-temperature CVD precursors of Group IV alloys with highly metastable compositions and structures that cannot be obtained by conventional growth routes.

The central Ge atom is tetrahedrally coordinated with four Me$_3$Sn ligands. The average Ge—Sn distance of 2.5934 (8) Å agrees well with the predicted value of 2.5680 Å for a Ge(SnH$_3$)$_4$ analogue (Chizmeshya *et al.*, 2003). In the previous structure determination using powder data, estimated standard deviations for bond lengths and angles are given as 0.04 Å and 0.1°, respectively. In the current determination, an improvement in precision for the structure can be seen in the Ge—Sn core bond lengths, which range from 2.5912 (7) to 2.5953 (8) Å, and bond angles, which range from 107.59 (3) to 111.09 (3) °.

S2. Experimental

After addition of GeH$_4$ (0.1 g; 1.3 mmol) to Me$_3$SnNMe$_2$ (1.0 g; 5 mmol) at -196 °C, the mixture was warmed to room temperature and stirred for 24 h. The volatiles were identified as HNMe$_2$ and small amounts of GeH$_4$ by gas phase IR spectroscopy and were removed at room temperature *in vacuo*.

GeH$_4$ + 4 Me$_3$SnNMe$_2$ => Ge[Sn(CH$_3$)$_3$]$_4$ + 4 HNMe$_2$

The white solid was recrystallized from a saturated toluene solution at -20 °C and the purity was confirmed by matching the IR spectrum, powder XRD pattern, 1H NMR spectrum, and melting point with the published data (Dinnebier *et al.*, 2002; Wrackmeyer & Bernatowicz, 1999). This represents a simpler alternative than the multistepped reaction, hydrolysis, and separation procedure required with the reaction of Me$_3$SnLi and GeCl$_4$ in tetrahydrofuran. Larger crystals, suitable for single-crystal XRD, were grown by subliming the pure powder in a sealed quartz tube held at 100 °C on one end and room temperature on the other. In contrast, sublimation at 135 °C *in vacuo* yields only microcrystalline powders.

S3. Refinement

H atoms were positioned geometrically and refined using a riding model, with C–H = 0.96 Å and U_{iso}(H) = 1.5 times U_{eq}(C).

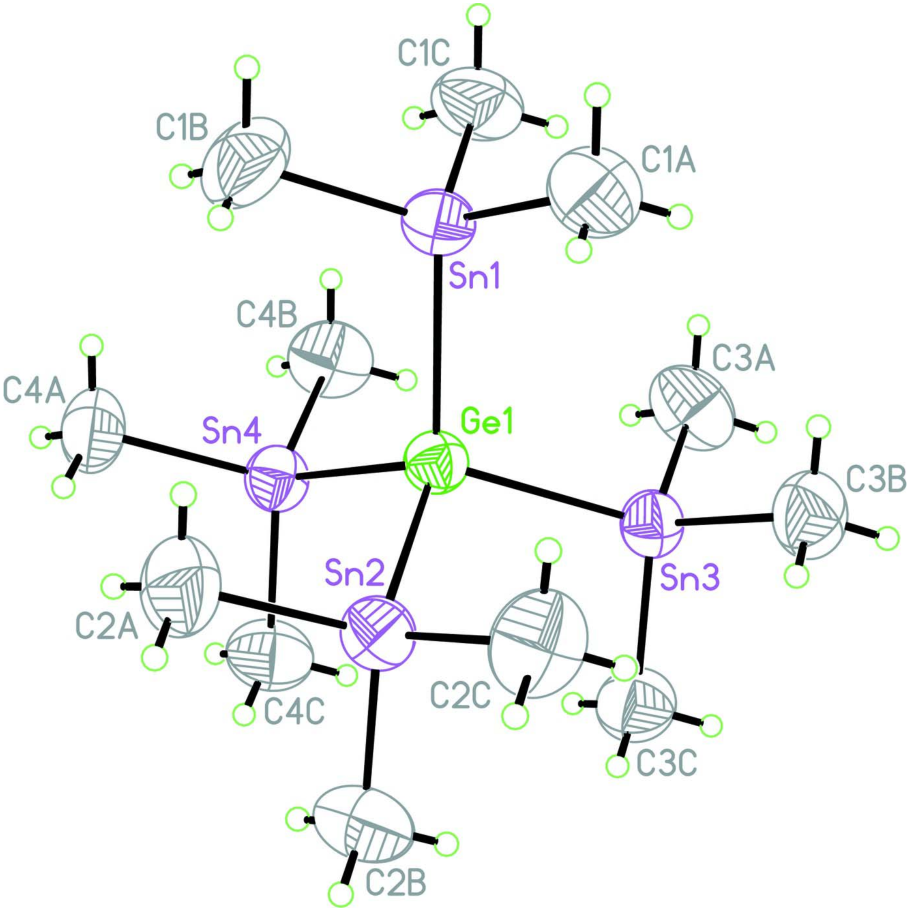

Figure 1

Structure of Ge[Sn(CH$_3$)$_3$]$_4$. (Ellipsoids are drawn at the 50% probability level.)

tetrakis(trimethylstannyl)germane

Crystal data

[GeSn$_4$(CH$_3$)$_{12}$]
M_r = 727.76
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 9.1666 (7) Å
b = 9.9521 (7) Å
c = 14.5400 (14) Å
α = 90.033 (2)°
β = 90.546 (1)°
γ = 111.736 (1)°
V = 1232.06 (17) Å^3

Z = 2
F(000) = 680
D_x = 1.962 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6668 reflections
θ = 2.2–27.5°
μ = 5.19 mm^{-1}
T = 298 K
Block, colorless
0.22 × 0.22 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scan

Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.317, T_{max} = 0.460
12284 measured reflections
5646 independent reflections
4466 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.085$
$\theta_{\rm max} = 27.6°$, $\theta_{\rm min} = 2.2°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.105$
$S = 1.01$
5646 reflections
154 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.09$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.01$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Ge1	0.75863 (7)	0.73542 (6)	0.75103 (5)	0.04589 (16)
Sn1	0.76633 (5)	0.47736 (5)	0.75113 (4)	0.05566 (14)
Sn2	0.67526 (5)	0.79813 (5)	0.91050 (3)	0.05480 (14)
Sn3	0.55868 (5)	0.75649 (5)	0.63013 (3)	0.05205 (13)
Sn4	1.03424 (5)	0.92048 (5)	0.70999 (3)	0.05197 (13)
C1A	0.5374 (9)	0.3234 (8)	0.7776 (6)	0.084 (2)
H1AA	0.5400	0.2278	0.7776	0.125*
H1AB	0.4659	0.3296	0.7306	0.125*
H1AC	0.5030	0.3432	0.8364	0.125*
C1B	0.9275 (9)	0.4584 (9)	0.8546 (7)	0.092 (3)
H1BA	0.9284	0.3623	0.8534	0.138*
H1BB	0.8949	0.4776	0.9141	0.138*
H1BC	1.0311	0.5270	0.8424	0.138*
C1C	0.8419 (9)	0.4301 (9)	0.6205 (6)	0.084 (2)
H1CA	0.8442	0.3344	0.6214	0.126*
H1CB	0.9451	0.4990	0.6080	0.126*
H1CC	0.7702	0.4355	0.5734	0.126*
C2A	0.8272 (9)	0.7754 (10)	1.0181 (6)	0.088 (3)
H2AA	0.7939	0.7992	1.0762	0.132*
H2AB	0.9332	0.8395	1.0067	0.132*
H2AC	0.8224	0.6774	1.0194	0.132*
C2B	0.6866 (10)	1.0148 (8)	0.9115 (6)	0.087 (2)

H2BA	0.6556	1.0371	0.9707	0.131*
H2BB	0.6172	1.0264	0.8651	0.131*
H2BC	0.7922	1.0790	0.8993	0.131*
C2C	0.4400 (9)	0.6608 (10)	0.9404 (6)	0.088 (3)
H2CA	0.4116	0.6858	0.9996	0.132*
H2CB	0.4321	0.5619	0.9409	0.132*
H2CC	0.3703	0.6730	0.8943	0.132*
C3A	0.6191 (9)	0.7151 (9)	0.4940 (5)	0.085 (2)
H3AA	0.5431	0.7236	0.4509	0.128*
H3AB	0.6202	0.6191	0.4909	0.128*
H3AC	0.7212	0.7840	0.4792	0.128*
C3B	0.3259 (8)	0.6064 (8)	0.6589 (6)	0.076 (2)
H3BA	0.2539	0.6160	0.6134	0.115*
H3BB	0.2952	0.6266	0.7187	0.115*
H3BC	0.3247	0.5095	0.6575	0.115*
C3C	0.5645 (8)	0.9736 (8)	0.6319 (6)	0.075 (2)
H3CA	0.4909	0.9828	0.5874	0.112*
H3CB	0.6683	1.0393	0.6172	0.112*
H3CC	0.5371	0.9959	0.6920	0.112*
C4A	1.2038 (8)	0.9083 (9)	0.8092 (6)	0.081 (2)
H4AA	1.3058	0.9769	0.7938	0.121*
H4AB	1.2058	0.8125	0.8088	0.121*
H4AC	1.1756	0.9299	0.8693	0.121*
C4B	1.0969 (8)	0.8697 (9)	0.5750 (5)	0.078 (2)
H4BA	1.1990	0.9379	0.5593	0.117*
H4BB	1.0210	0.8748	0.5306	0.117*
H4BC	1.0986	0.7738	0.5752	0.117*
C4C	1.0413 (9)	1.1383 (7)	0.7095 (6)	0.080 (2)
H4CA	1.1451	1.2033	0.6940	0.120*
H4CB	1.0148	1.1625	0.7693	0.120*
H4CC	0.9674	1.1468	0.6648	0.120*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ge1	0.0459 (3)	0.0435 (3)	0.0477 (4)	0.0158 (3)	0.0020 (3)	0.0011 (3)
Sn1	0.0596 (3)	0.0444 (2)	0.0628 (3)	0.0192 (2)	−0.0006 (2)	0.0007 (2)
Sn2	0.0586 (3)	0.0588 (3)	0.0469 (3)	0.0216 (2)	0.0030 (2)	0.0002 (2)
Sn3	0.0501 (2)	0.0549 (3)	0.0501 (3)	0.0183 (2)	−0.00229 (19)	−0.0012 (2)
Sn4	0.0469 (2)	0.0507 (3)	0.0549 (3)	0.01392 (19)	0.00327 (19)	0.0024 (2)
C1A	0.079 (5)	0.058 (4)	0.102 (7)	0.012 (4)	0.009 (5)	0.015 (4)
C1B	0.086 (6)	0.081 (6)	0.119 (8)	0.042 (5)	−0.015 (5)	0.022 (5)
C1C	0.098 (6)	0.080 (5)	0.080 (6)	0.039 (5)	0.011 (5)	−0.021 (4)
C2A	0.091 (6)	0.110 (7)	0.068 (6)	0.045 (5)	−0.023 (4)	−0.006 (5)
C2B	0.120 (7)	0.072 (5)	0.076 (6)	0.041 (5)	0.003 (5)	−0.012 (4)
C2C	0.071 (5)	0.105 (7)	0.082 (6)	0.025 (5)	0.022 (4)	0.018 (5)
C3A	0.102 (6)	0.091 (6)	0.051 (5)	0.022 (5)	0.010 (4)	−0.011 (4)
C3B	0.055 (4)	0.082 (5)	0.084 (6)	0.016 (4)	0.006 (4)	−0.003 (4)

C3C	0.080 (5)	0.060 (4)	0.086 (6)	0.028 (4)	0.000 (4)	0.009 (4)
C4A	0.063 (4)	0.102 (6)	0.080 (6)	0.035 (4)	−0.020 (4)	−0.016 (5)
C4B	0.079 (5)	0.084 (5)	0.069 (5)	0.026 (4)	0.029 (4)	0.006 (4)
C4C	0.094 (6)	0.049 (4)	0.094 (7)	0.022 (4)	0.009 (5)	0.009 (4)

Geometric parameters (Å, º)

Ge1—Sn4	2.5912 (7)	Sn2—C2C	2.132 (7)
Ge1—Sn3	2.5917 (8)	Sn2—C2A	2.152 (7)
Ge1—Sn1	2.5952 (7)	Sn3—C3A	2.141 (7)
Ge1—Sn2	2.5953 (8)	Sn3—C3C	2.141 (7)
Sn1—C1A	2.130 (7)	Sn3—C3B	2.148 (7)
Sn1—C1C	2.139 (8)	Sn4—C4C	2.145 (7)
Sn1—C1B	2.156 (7)	Sn4—C4A	2.147 (7)
Sn2—C2B	2.120 (8)	Sn4—C4B	2.162 (7)
Sn4—Ge1—Sn3	108.29 (3)	C2B—Sn2—Ge1	110.0 (2)
Sn4—Ge1—Sn1	109.08 (3)	C2C—Sn2—Ge1	110.9 (3)
Sn3—Ge1—Sn1	111.09 (3)	C2A—Sn2—Ge1	111.2 (2)
Sn4—Ge1—Sn2	109.91 (3)	C3A—Sn3—C3C	107.0 (3)
Sn3—Ge1—Sn2	107.59 (3)	C3A—Sn3—C3B	108.5 (3)
Sn1—Ge1—Sn2	110.83 (3)	C3C—Sn3—C3B	110.3 (3)
C1A—Sn1—C1C	108.9 (3)	C3A—Sn3—Ge1	111.5 (2)
C1A—Sn1—C1B	109.3 (3)	C3C—Sn3—Ge1	108.7 (2)
C1C—Sn1—C1B	108.0 (3)	C3B—Sn3—Ge1	110.9 (2)
C1A—Sn1—Ge1	109.4 (2)	C4C—Sn4—C4A	108.0 (3)
C1C—Sn1—Ge1	110.3 (2)	C4C—Sn4—C4B	108.7 (3)
C1B—Sn1—Ge1	111.0 (2)	C4A—Sn4—C4B	109.4 (3)
C2B—Sn2—C2C	107.9 (3)	C4C—Sn4—Ge1	112.1 (2)
C2B—Sn2—C2A	108.2 (3)	C4A—Sn4—Ge1	109.6 (2)
C2C—Sn2—C2A	108.6 (3)	C4B—Sn4—Ge1	109.0 (2)