

Dimethylgermanium Glycyl-L-methionate

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(Received 24 November 1988; accepted 27 February 1989)

Abstract. (Glycyl-L-methioninato)dimethylgermanium, $[\text{Ge}(\text{C}_7\text{H}_{12}\text{N}_2\text{O}_3\text{S})(\text{CH}_3)_2]$, $M_r = 306.90$, orthorhombic, $P2_12_12_1$, $a = 9.599$ (5), $b = 11.428$ (6), $c = 12.282$ (10) Å, $V = 1347$ (1) Å³, $Z = 4$, $D_x = 1.513$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.4$ mm⁻¹, $F(000) = 632$, $T = 291$ (1) K. Final $R = 0.033$ for 2020 unique observed [$F \geq 4.0\sigma(F)$] diffractometer data. The polyhedron around Ge is a distorted trigonal bipyramid formed by two CH₃ groups in equatorial positions and the tridentate glycylmethioninate ligand, the latter having a nearly planar skeleton. The equatorial Ge—N_{peptide} bond is short: 1.889 (4) Å. The axial bond angle O_{carboxylate}—Ge—N_{amino} is 161.8 (1)°. Short intermolecular N—O distances between N_{amino} and O(=C)_{peptide} as well as O(=C)_{carboxylate} indicate the presence of hydrogen bonds.

Introduction. A general structural feature of diorganotin derivatives of dipeptides, e.g. diphenyltin glycyglycinate, Ph₂SnGlyGly (Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977), or dimethyltin glycylmethionate, Me₂SnGlyMet (Preut, Mundus, Huber & Barbieri, 1986), is the presence of intermolecular hydrogen bonds. In contrast, the intermolecular distances observed in Me₂GeGlyGly (Vornefeld, Huber, Preut & Brunner, 1989), which shows a trigonal bipyramidal environment of the central atom analogous to that of the diorganotin derivatives cited above, excluded the possibility of hydrogen bonds. This unexpected result induced further studies and we report here on the structure of Me₂GeGlyMet which actually exhibits hydrogen bonding.

Experimental. Prepared from Me₂GeBr₂ and glycyl-L-methionine in toluene in the presence of Et₃N (molar ratio 1:1:2). The colorless product was freed from [Et₃NH]Br by extraction with warm CHCl₃. Single crystals were obtained from methanol after adding petroleum ether (40–60 °C) and diethyl ether. Crystal size: 0.13 × 0.16 × 0.22 mm. $\omega/2\theta$ scan. Scan speed: 1.0–3.3° min⁻¹ in θ . CAD-4 diffractometer (Enraf–Nonius), graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 25 reflexions up to $2\theta = 23.0^\circ$; six standard reflexions

recorded every 2.5 h, only random deviations; 4969 reflexions measured, $1.5 \leq \theta \leq 26.0^\circ$, $0 \leq h \leq 12$, $-14 \leq k \leq 14$, $-15 \leq l \leq 7$; after averaging ($R_{\text{int}} = 0.018$) 2645 unique ($+h, \pm k, +l$) reflexions, 2020 with $F \geq 4.0\sigma(F)$, Lorentz-polarization correction and absorption correction via ψ scans, max./min. transmission 1.00/0.91; systematic absences ($h00$) $h = 2n + 1$, ($0k0$) $k = 2n + 1$, ($00l$) $l = 2n + 1$ conform to space group $P2_12_12_1$; structure solution via direct methods, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C—H 1.08 Å); refinement on F with 2020 reflexions and 146 refined parameters, $w = 1.24/[\sigma^2(F) + 0.001F^2]$, $S = 0.91$, $R = 0.033$, $wR = 0.035$, $(\Delta/\sigma)_{\text{max}} = 0.032$, no extinction correction; largest peak in final ΔF map ± 0.5 (2) e Å⁻³; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); the enantiomeric structure gave $R = 0.051$ and $wR = 0.055$ and was rejected; programs: Enraf–Nonius SDP-Plus (Frenz, 1985) for data reduction; SCHAKAL (Keller, 1987), SHELX76 (Sheldrick, 1976), PARST (Nardelli, 1982), SHELXTL-Plus (Sheldrick, 1987).

Discussion. A molecule of the title compound is shown in Fig. 1 and a stereoscopic view of the unit cell in Fig. 2. Atomic parameters are given in Table 1, bond lengths and angles in Table 2.* The polyhedron around Ge in Me₂GeGly-L-Met corresponds to that found in Me₂SnGlyMet (Preut *et al.*, 1986) and other diorganotin derivatives of dipeptides, such as Ph₂SnGlyGly (Huber *et al.*, 1977) or (cyclo-C₆H₁₁)₂SnGlyAla (Vornefeld, Huber, Preut & von Angerer, 1988). It is a distorted trigonal bipyramid with peptide nitrogen N(1) and the two C(CH₃) atoms in the equatorial, and O(1) of the unidentate

* Lists of H-atom coordinates, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51990 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

carboxylate group and amino nitrogen N(2) in the apical positions. The short Ge—N(1) distance of 1.889 (4) Å is virtually the same as in Me₂GeGlyGly [1.888 (4) Å; Vornefeld, Huber, Preut & Brunner (1989)]. It is shorter than that found in *trans*-bis(3,3-dimethyl-1-butynyl)hemiporphyracinegermanium in which Ge is six-coordinated [1.956 (2) Å; Hiller, Strähle, Mitulla & Hanack (1980)]. Also the Ge←N_{amino} bond lengths in Me₂GeGlyGly and Me₂GeGly-L-Met [2.110 (5) and 2.103 (4) Å], respectively, are not significantly different. In organogermatranes which, like Me₂GeGlyGly and Me₂GeGly-L-Met, contain pentacoordinated Ge but tertiary N_{amino} and not primary N_{amino}, the Ge←N bonds appear to be generally longer [2.19 (3) to 2.24 (2) Å; Atovmyan, Bleidelis, Kemme & Shibaeva (1970); Kemme, Bleidelis, Shibaeva & Atovmyan (1973); Gurkova, Gusev, Segel'man, Alekseev, Gar & Khromova (1981)]. The Ge—O distance of 2.008 (3) Å compares with that in Me₂GeGlyGly, 2.025 (4) Å; both are appreciably longer than that in Ph₃GeOCOCF₃ [1.86 Å; Glidewell & Liles (1983)].

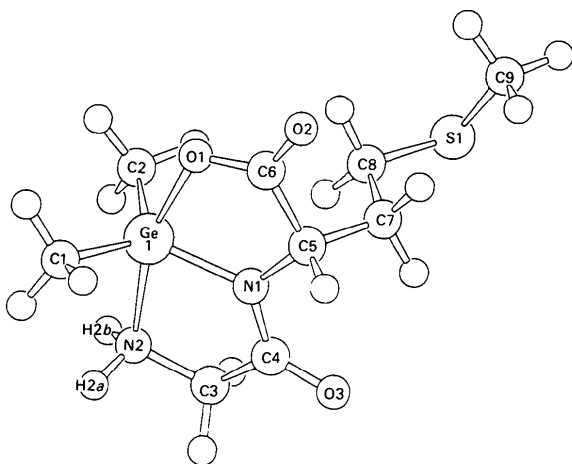


Fig. 1. General view of the molecule, showing the atom-numbering scheme.

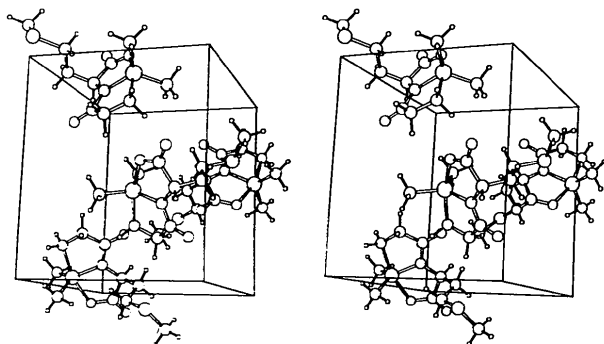


Fig. 2. Stereoscopic view of the unit cell (*a* horizontal, *b* vertical).

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ge(1)	0.3136 (5)	-0.05683 (4)	0.84697 (4)	40
S(1)	0.0050 (2)	0.0997 (1)	0.9870 (1)	68
N(1)	0.3530 (4)	-0.1223 (3)	0.8245 (3)	36
N(2)	0.5549 (5)	-0.2110 (3)	0.9388 (3)	43
O(1)	0.4528 (4)	0.0646 (3)	0.7460 (2)	47
O(2)	0.2703 (4)	0.1069 (3)	0.6417 (3)	51
O(3)	0.2051 (4)	-0.2740 (3)	0.8592 (3)	50
C(1)	0.6847 (6)	-0.0888 (6)	0.7509 (5)	63
C(2)	0.5550 (7)	0.0457 (5)	0.9682 (5)	65
C(3)	0.4208 (6)	-0.2671 (4)	0.9553 (4)	48
C(4)	0.3165 (5)	-0.2233 (4)	0.8736 (3)	39
C(5)	0.2557 (5)	-0.0624 (4)	0.7546 (3)	36
C(6)	0.3306 (5)	0.0448 (4)	0.7083 (3)	37
C(7)	0.1233 (5)	-0.0221 (4)	0.8116 (4)	47
C(8)	0.1545 (6)	0.0576 (5)	0.9100 (4)	56
C(9)	-0.0834 (8)	0.1918 (5)	0.8947 (6)	82

Table 2. Bond distances (Å) and angles (°)

N(1)—Ge(1)	1.889 (4)	C(3)—N(2)	1.453 (7)
N(2)—Ge(1)	2.103 (4)	C(6)—O(1)	1.282 (6)
O(1)—Ge(1)	2.008 (3)	C(6)—O(2)	1.228 (5)
C(1)—Ge(1)	1.921 (5)	C(4)—O(3)	1.229 (6)
C(2)—Ge(1)	1.908 (5)	C(4)—C(3)	1.503 (6)
C(8)—S(1)	1.785 (5)	C(6)—C(5)	1.530 (6)
C(9)—S(1)	1.764 (6)	C(7)—C(5)	1.522 (7)
C(4)—N(1)	1.348 (6)	C(8)—C(7)	1.543 (7)
C(5)—N(1)	1.440 (6)		
N(2)—Ge(1)—N(1)	81.0 (2)	C(3)—N(2)—Ge(1)	110.5 (3)
O(1)—Ge(1)—N(1)	81.0 (1)	C(6)—O(1)—Ge(1)	116.4 (3)
O(1)—Ge(1)—N(2)	161.8 (1)	C(4)—C(3)—N(2)	110.4 (4)
C(1)—Ge(1)—N(1)	122.0 (2)	O(3)—C(4)—N(1)	124.4 (4)
C(1)—Ge(1)—N(2)	95.0 (2)	C(3)—C(4)—N(1)	114.3 (4)
C(1)—Ge(1)—O(1)	92.3 (2)	C(3)—C(4)—O(3)	121.2 (4)
C(2)—Ge(1)—N(1)	117.7 (2)	C(6)—C(5)—N(1)	107.3 (4)
C(2)—Ge(1)—N(2)	94.8 (2)	C(7)—C(5)—N(1)	114.3 (4)
C(2)—Ge(1)—O(1)	95.8 (2)	C(7)—C(5)—C(6)	108.7 (4)
C(2)—Ge(1)—C(1)	120.3 (3)	O(2)—C(6)—O(1)	124.8 (4)
C(9)—S(1)—C(8)	101.9 (3)	C(5)—C(6)—O(1)	115.9 (4)
C(4)—N(1)—Ge(1)	120.6 (3)	C(5)—C(6)—O(2)	119.3 (4)
C(5)—N(1)—Ge(1)	119.1 (3)	C(8)—C(7)—C(5)	112.2 (4)
C(5)—N(1)—C(4)	120.3 (4)	C(7)—C(8)—S(1)	114.7 (4)

Short intermolecular N...O distances [N(2)...O(2)-(1-x, -1/2+y, 1.5-z): 2.851 (5), N(2)...O(3)(1/2+x, -1/2-y, 2-z): 2.875 (5) Å], which are markedly shorter than the sum of the van der Waals radii of 3.11 Å (Kitaigorodskii, 1979), indicate the presence of hydrogen bonds. In contrast, in Me₂GeGlyGly (Vornefeld, Huber, Preut & Brunner, 1989) no intermolecular interactions *via* hydrogen bonds exist. Taking the calculated positions of the two H atoms at N_{amino}, the two distances H(2b)...O(2) = 1.798 (5) and H(2a)...O(3) = 1.874 (5) Å and the angles N—H...O(2) 163.9 (4) and N—H...O(3) 152.4 (4)° result.

Financial assistance from the Deutsche Forschungsgemeinschaft and the Fonds der Chemi-

schen Industrie and a gift of chemicals from Degussa, Frankfurt, are gratefully acknowledged.

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Acta Cryst. (1989). **C45**, 1506–1509

Structure of Bis(dipropyldithiocarbamato)tellurium(II)

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(Received 30 August 1988; accepted 20 February 1989)

Abstract. Bis(dipropylcarbamodithioato-*S,S'*)-tellurium(II), [Te(C₇H₁₄NS₂)₂], $M_r = 480.28$, orthorhombic, *Pbca*, $a = 13.587(2)$, $b = 12.908(3)$, $c = 24.468(4)$ Å, $V = 4291.21$ Å³, $D_m = 1.50$, $D_x = 1.487$ Mg m⁻³, $Z = 8$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.639$ mm⁻¹, $F(000) = 1936$, $T = 293$ K, final $R = 0.048$, $wR = 0.047$ for 3969 unique reflections. The Te atom is coordinated to four S atoms forming an asymmetric planar complex with Te—S bond distances in the range 2.511(1)–2.853(1) Å. Molecules related by a centre of symmetry are bridged through one of the S atoms with a short intermolecular contact Te...S(1') = 3.499(1) Å. The dithiocarbamate parts of the two ligands are planar.

Introduction. Four sulfur-coordinated tellurium(II) complexes have been shown to prefer a planar configuration around the central Te atom. With mono-

dentate ligands such as thiourea and phenylene-thiourea, the complexes are square-planar (Rout, Seshasayee, Aravamudan & Sowrirajan, 1984; Anderson, 1971). The bonding in such square-planar complexes can be explained in terms of three-centre four-electron bonding (Fabiani, Spagna, Vaciago & Zambonelli, 1971; Foss, 1967, 1970). The same behaviour is also followed in most cases by Se^{II} complexes (Husebye & Helland-Madsen, 1970; Rout, Seshasayee, Radha & Aravamudan, 1983).

In all the dithiocarbamate complexes of Te^{II} the four S atoms in the molecule are bonded to the central Te atom in an asymmetric manner, having two short Te—S bonds and two long Te—S bonds. As part of our studies of divalent tellurium and selenium complexes of dithiocarbamate ligands the title compound was prepared and its crystal structure determined.