Methyl- and Phenylgermanium Derivatives of Diethyldithiocarbamic Acid. The Crystal and Molecular Structure of Diphenylbis(*N*,*N*-diethyldithiocarbamato)-germanium

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Abstract

Methyl- and phenylgermanes were reacted with the sodium salt of *N*,*N*-diethyldithiocarbamic acid in carbon disulfide at low temperature under rigorous exclusion of moisture. Halogen-exchange reactions were carried out to prepare partially substituted bromo and iodo derivatives. The compounds were characterized by elemental analysis, infrared, Raman, proton and carbon-13 NMR spectroscopy and mass spectrometry. The spectroscopic results indicate monodentate or anisobidentate coordination of the diethyldithiocarbamate group. To confirm this assumption, the crystal structure of a representative compound, $(C_6H_5)_2Ge[SC(S)N(C_2H_5)_2]_2$, was determined by X-ray crystallography. The molecule crystallizes in the $C2/c$ space group with $a = 20.416(7)$, $b = 7.320(3)$, $c = 17.137(6)$ Å, $\beta = 90.06(3)°$, $V = 2561(2)$ Å^3, $Z = 4$, ρ(obs.) = 1.33 g cm^{-3}, ρ(calc.) = 1.36 g cm^{-3}. Using Mo Kα radiation (λ = 0.71069 Å), 1689 unique reflections were collected (21 ± 1) °C and the structure was refined to a final R value of 0.0377. The position of the phenyl and monodentate dithiocarbamate groups result in a distorted tetrahedral symmetry about germanium with a bonded Ge–S distance of 2.271(1) Å compared to a non-bonded Ge--S distance of 3.183 Å.

Introduction

Dithiocarbamate complexes have been extensively studied [1–7]. Much of the interest arises because the planar structure, which is unusual among sulfur-donor ligands, allows for delocalization of charge and a restriction to the rotation of the NR_2 group.

Dithiocarbamate groups normally act as bidentate groups [3–7]; typical examples being observed in $Co[SC(S)N(CH_3)_2]_2NO$ where the Co atom is at the center of a square pyramid [8], in $Cu_4[SC(S)N(C_2H_5)_2]_4$ where the dithiocarbamate group coordinates from the faces of the Cu_4-tetrahedron [9], and in $C_4H_9Sn[SC(S)N(C_2H_5)_2]$ where the geometry around the Sn atom is that of a pentagonal bipyramid [10]. Examples of monodentate dithiocarbamates are relatively scarce and when observed ususally occur among mixed ligand complexes such as $Ru[SC(S)N(C_2H_5)_2]_3NO$ [11] and $Pt[S(S)CN(C_4H_9\text{-}i)_2]_2[P(CH_3)_2(C_6H_5)]_2$ [12]. Structural changes are also brought about by variation of the alkyl group in the dithiocarbamate ligand. In $Zn(SC(S)N(CH_3)_2]_2$ [13], the dithiocarbamate groups are both bidentate and bridging, whereas in $Zn[SC(S)N(C_2H_5)_2]_2$ both of the dithiocarbamate groups are bidentate and the molecule is monomeric [14].

Previously, we reported the reactions of methylgermanium halides with the sodium salt of *N*,*N*-dimethyldithiocarbamic acid as well as on the structures of $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$ [15] and $(CH_3)_2Ge[SC(S)N(CH_3)_2]_2$ [16]. We now extend this study to the preparation of selected methyl- and phenylgermanium derivatives of *N*,*N*-diethyldithiocarbamic acid and report the crystal structure of $(C_6H_5)_2Ge[SC(S)N(C_2H_5)_2]_2$.

Experimental

General

$(CH_3)_3GeBr$, $(CH_3)_2GeCl_2$ and CH_3GeCl_3 were purchased from Alfa Inorganics, $(C_6H_5)_3GeBr$, $(C_6H_5)_2GeCl_2$ and $C_6H_5GeCl_3$ from Strem Chemicals and $(CH_3)_3SiBr$ and $(CH_3)_3SiI$ from Petrarch Chemicals and were used as obtained. $NaS_2CN(C_2H_5)_2$ was purchased from Aldrich Chemical Co. and was dried under vacuum prior to use. Fisher ACS grade CS_2 was dried over P_4O_{10} and then distilled. All the reactions were carried out under vacuum. It was imperative to avoid air and moisture to prevent formation of germanium oxides. The elemental analyses were performed by Guelph Chemical Labs, Guelph, Ontario and Galbraith Laboratories Inc., Knoxville, Tennessee. Density was measured by the flotation method (C_6H_6/CCl_4).

Spectra

The ^1H NMR spectra were recorded on a Varian EM360 spectrometer (60 MHz) in CS_2 or $CDCl_3$

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solutions using tetramethylsilane as internal standard. The $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker CXP100 FT spectrometer (22.64 MHz) in $CDCl_3$ solutions with a 2 s delay time and the chemical shifts were referenced to the central line of the $CDCl_3$ resonance at 77.12 ppm (1746 Hz). The infrared spectra were recorded on a Nicolet 5DX FT spectrometer as CsI pellets, Nujol mulls and CS_2 or CCl_4 solutions between CsI plates. The samples for Raman spectra were sealed in capillary tubes and the spectra recorded on a Spectra-Physics 700 using the 4880 Å exciting line or on a Spectra-Physics 164 using the 5145 Å exciting line of an argon ion laser. The mass spectra were recorded on a Varian GMAT CH5 double focusing spectrometer in the electron impact (EI) mode at 70 eV or in the field ionization (FI) mode. The melting points were determined on a Fisher-Johns apparatus, and the refractive indices were measured on a Bausch and Lomb refractometer and corrected to 25 °C.

X-ray Crystallographic Analysis

A prismatic crystal of **9** was sealed in a thin walled glass capillary and mounted and aligned on a Syntex $P2_1$ automated diffractometer, equipped with Mo Kα radiation ($\lambda(K\alpha) = 0.71069$ Å), a niobium filter and a scintillation counter. The unit cell dimensions were calculated from the setting angles of 15 reflections having $15° < 2\theta < 30°$ and data were collected following the procedure described previously [16]. The intensities of three monitor reflections measured after every 60 reflections did not change significantly during data collection. The systematic absences (hkl, $h + k = 2n + 1$, $h0l = 2n + 1$), indicate the space groups $C2/c$ or Cc. The former was used and later assumed correct because of successful refinement of the structure. The data were corrected for Lorentz and polarization effects and an analytical absorption correction was applied. Details of the X-ray data are given in Table I.

The position of the germanium atom was obtained from a sharpened Patterson synthesis with the germanium atom on the two-fold axis. The positions of the remaining non-hydrogen atoms were determined from a difference Fourier map. The structure was refined anisotropically by the full-matrix least-squares methods. The refinement converged to $R = 0.410$. Hydrogen atoms were included in subsequent refinements in ideal positions (C–H 0.95 Å and CCH or NCH 120 or 109.5°). Refinements gave final values of $R = 0.0377$ and $R_w = 0.0444$. The function $w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement and in the final cycles, a weighting scheme of the form $w = 1/[\sigma^2(F) + \rho F^2]$ was employed with a final ρ value of 0.004. No evidence of secondary extinction was found.

Sources of scattering factors and computer programs used have been given elsewhere [16]. The final atomic coordinates are given in Table II and important distances and angles in Table III.

TABLE I. Summary of Crystal Data, Intensity Collection and Structural Refinement for $(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$

Formula	$C_{22}H_{30}N_2S_4Ge$
Cell constants	20.416(7), 7.320(3), 17.137(6) Å, 90.06(3)°
Cell volume (Å^3)	2561(2)
Crystal system	monoclinic
Space group	$C2/c$
Molecular weight	522.6
Z, $F(000)$	4, 1088
ρ_c, ρ_o (g cm^{-3})	1.36, 1.33
Crystal dimensions (mm)	0.19 × 0.31 × 0.61
Absorption coefficient, μ (cm^{-1})	14.60
Min. absorption correction	1.311
Max. absorption correction	1.543
Temperature (°C)	21 ± 1
2θ angle (°)	4–50
Scan type	coupled 8 (crystal)/ 28 (counter)
Scan width	$K_{\alpha 1} - 1°$ to $K_{\alpha 2} + 1°$
Scan speed (° min^{-1})	variable, 2.02–4.88
Background time/scan time	0.5
Total reflections measured	2645 ($+h$, $+k$, $\pm l$)
Unique data used	1689 [$I > 3\sigma(I)$]
No. parameters (NP)	132
$R = (\Sigma\|\|F_o\| - \|F_c\|\|/\|F_o\|)$	0.0377
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.0444
$\Delta\rho_{max}$ (e Å^{-3})	0.6
Shift/e.s.d. (max)	0.1

Preparation of Trimethyl(N,N-diethyldithiocarbamato)germane (1), $(CH_3)_3Ge[SC(S)N(C_2H_5)_2]$

Bromotrimethylgermane, $(CH_3)_3GeBr$ (2 mmol) and CS_2 (2.5 ml) were distilled onto the previously dried salt, $(C_2H_5)_2NCS_2Na$ (0.457 g, 2.67 mmol). The vessel was warmed to melt the solvent and the mixture was stirred moderately while keeping the vessel cool (*ca.* −10 °C). The mixture was filtered and the solution was allowed to evaporate under vacuum to obtain pure $(CH_3)_3Ge[SC(S)N(C_2H_5)_2]$, as a clear liquid. Yield 63%, η 1.5628. *Anal.* Calc. for $C_8H_{19}NS_2Ge$: C, 36.13; H, 7.20; N, 5.27. Found: C, 35.80; H, 7.05; N, 5.22%.

Preparation of Chlorodimethyl(N,N-diethyldithiocarbamato)germane (2), $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Cl$

The germane, $(CH_3)_2GeCl_2$ (1.5 mmol) and CS_2 (3 ml) were condensed onto dry $(C_2H_5)_2NCS_2Na$ (0.530 g, 3.09 mmol) at −196 °C. The mixture was allowed to warm gradually to ambient temperature and was stirred for 4 h with occasional cooling to *ca.* −10 °C. NaCl and the unreacted carbamate salt were separated by filtration and the filtrate was

TABLE II. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-hydrogen Atoms of $(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$[a]

	x	y	z	U_{eq}[b] ($Å^2 \times 10^3$)
Ge	0.00000(0)	−0.14559(8)	0.25000(0)	32.8(3)
S(1)	0.06734(6)	0.08431(14)	0.28860(7)	45.3(6)
S(2)	0.12776(5)	−0.26214(14)	0.34422(6)	42.3(6)
N	0.1770(2)	0.0686(5)	0.3679(2)	40(2)
C(1)	0.1303(2)	−0.0356(5)	0.3376(2)	36(2)
C(2)	0.2293(2)	−0.0126(7)	0.4156(3)	57(3)
C(3)	0.2102(3)	−0.0287(8)	0.5002(3)	71(4)
C(4)	0.1799(2)	0.2682(5)	0.3575(3)	45(2)
C(5)	0.2238(3)	0.3211(7)	0.2918(4)	94(4)
C(11)	−0.0371(2)	−0.2736(6)	0.3378(2)	36(2)
C12)	−0.0406(2)	−0.1889(7)	0.4096(3)	55(3)
C(13)	−0.0641(3)	−0.2848(10)	0.4734(3)	72(3)
C(14)	−0.0830(2)	−0.4632(9)	0.4663(3)	70(4)
C(15)	−0.0805(2)	−0.5482(8)	0.3952(3)	66(3)
C(16)	−0.0577(2)	−0.4548(7)	0.3307(3)	52(3)

[a] e.s.d.s given in parentheses. [b] U_{eq} for the non-hydrogen atoms is calculated from the refined anisotropic thermal parameters, ($U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$).

TABLE III. Interatomic Distances (Å) and Angles (°) in $(C_6H_5)_2Ge[S_2CH(C_2H_5)_2]_2$[a]

Ge–S(1)	2.271(1)	S(1)–Ge–C(1)	111.8(1)
Ge–S(2)	3.183(1)	Ge–S(1)–C(1)	102.1(1)
Ge–C(11)	1.928(3)	S(1)–Ge–S(1′)	84.4(1)
S(1)–C(1)	1.768(3)	C(11)–Ge–C(11′)	121.8(1)
S(2)–C(1)	1.663(3)	C(1)–N–C(2)	120.4(3)
N–C(1)	1.326(4)	C(1)–N–C(4)	123.5(3)
N–C(2)	1.470(4)	C(2)–N–C(4)	116.0(3)
N–C(4)	1.473(4)	S(1)–C(1)–C(2)	120.3(2)
C(2)–C(3)	1.507(6)	S(1)–C(1)–N	115.0(3)
C(4)–C(5)	1.491(6)	S(2)–C(1)–N	124.7(3)
		N–C(2)–C(3)	112.2(3)
C(11)–C(12)	1.379(5)	Ge–C(11)–C(12)	119.9(3)
C(11)–C(16)	1.397(6)	Ge–C(11)–C(16)	120.8(3)
C(12)–C(13)	1.386(6)	C(12)–C(11)–C(16)	119.2(3)
C(13)–C(14)	1.367(8)	C(11)–C(12)–C(13)	119.6(4)
C(14)–C(15)	1.368(7)	C(12)–C(13)–C(14)	120.7(4)
C(15)–C(16)	1.381(5)	C(13)–C(14)–C(15)	120.2(4)
S(1)---S(2)	2.976	C(14)–C(15)–C(16)	120.0(5)
S(1)---S(1)′	3.050	C(11)–C(16)–C(15)	120.1(4)

[a] Symmetry equivalent position: $-x$, y, $0.5 - z$; e.s.d.s given in parentheses.

evaporated under vacuum. The solid residue thus obtained was dissolved in fresh CS_2 and recrystallized by slowly pumping off the solvent on the vacuum line. Yield 66%, melting point (m.p.) 51 °C. *Anal.* Calc. for $C_7H_{16}NS_2GeCl$: C, 29.36; H, 5.63; N, 4.89. Found: C, 29.39; H, 5.71; N, 4.77%.

Preparation of Bromodimethyl(N,N-diethyldithiocarbamato)germane (3), $(CH_3)_2Ge[SC(S)N(C_2H_5)]_2Br$

Excess $(CH_3)_3SiBr$ (2 mmol) and CS_2 (1 ml) were distilled onto freshly prepared $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Cl$ (0.271 g, 0.95 mmol). The solution was held at 0 °C and stirred for 3 h. The volatile reagents and solvent were slowly pumped off, and crystals of pure $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Br$ appeared. The product was washed with n-hexane and dried. Yield 47%, m.p. 86 °C. *Anal.* Calc. for $C_7H_{16}NS_2GeBr$: C, 25.41; H, 4.88; N, 4.24. Found: C, 25.14; H, 4.69; N, 4.17%.

Preparation of Iododimethyl(N,N-diethyldithiocarbamato)germane (4), $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]I$

Freshly prepared $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Cl$ (0.215 g, 0.75 mmol) was dissolved in $(CH_3)_3SiI$ (1.2 mmol) and CS_2 (1 ml) and allowed to react for 3 h with stirring at 0 °C. The volatile materials were slowly pumped off to obtain yellowish transparent crystals. The crystals were washed with cold n-hexane and dried under vacuum. Yield 55%, m.p. 96 °C. *Anal.* Calc. for $C_7H_{16}NS_2GeI$: C, 22.25; H, 4.27; N, 3.71. Found: C, 22.29; H, 4.14; N, 3.68%.

Alternatively, excess $(CH_3)_3SiI$ (1 mmol) and CS_2 (1 ml) were distilled onto freshly prepared $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Br$ (0.116 g, 0.50 mmol). The solution was stirred for 2 h at 0 °C and the volatile compounds were pumped off. The solid product was dissolved in fresh CS_2 and the solvent gradually evaporated under vacuum to obtain pure crystals of $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]I$. Yield 50%.

Attempted Preparation of Dimethylbis(N,N-diethyldithiocarbamato)germane, $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]_2$

Excess of the salt, $(C_2H_5)_2NCS_2Na$ was treated with $(CH_3)_2GeCl_2$ in CS_2. Only the monosubstituted product, $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Cl$ was obtained. Prolonged reaction times lead to the formation of mixtures which could not be identified.

Preparation of Dichloromethyl(N,N-diethyldithiocarbamato)germane (5), $CH_3Ge[SC(S)N(C_2H_5)_2]Cl_2$

The germane, CH_3GeCl_3 (2 mmol), and CS_2 (5 ml) were added at −196 °C to the dry crushed salt, $(C_2H_5)_2NCS_2Na$ (0.541 g, 3.15 mmol). The reaction vessel was maintained in liquid nitrogen fumes (*ca.* −20 °C) for 15 min to melt the CS_2 and CH_3GeCl_3. The mixture was stirred, and as soon as the color of the mixture started to turn yellowish it was immediately filtered. The solvent was slowly evaporated under vacuum while keeping the vessel cool (*ca.* −10 °C), and pale yellow crystals appeared. Yield 40%, m.p. 42 °C. *Anal.* Calc. for $C_6H_{13}NS_2GeCl_2$: C, 23.49; H, 4.27; N, 4.57. Found: C, 23.26; H, 4.34; N, 4.39%.

Preparation of Dibromomethyl(N,N-diethyldithiocarbamato)germane (6), $CH_3Ge[SC(S)N(C_2H_5)_2]Br_2$

Excess $(CH_3)_3SiBr$ (1.5 mmol) and CS_2 (1 ml) were added to freshly prepared $CH_3Ge[SC(S)N(C_2H_5)_2]Cl_2$ (0.250 g, 0.81 mmol). The solution was stirred for 2 h at *ca.* −20 °C. The volatile materials were slowly pumped off and yellow crystals appeared. The crystals were washed with cold n-hexane and dried. Yield 36%, m.p. 62 °C. *Anal.* Calc. for $C_6H_{13}NS_2GeBr_2$: C, 18.21; H, 3.31; N, 3.54. Found: C, 18.43; H, 3.40; N, 3.69%.

Attempts to prepare $CH_3Ge[SC(S)N(C_2H_5)_2]I_2$ by an exchange reaction with $(CH_3)_3SiI$ resulted in a mixture which could not be identified.

Preparation of Methyltris(N,N-diethyldithiocarbamato)germane (7), $CH_3Ge[SC(S)N(C_2H_5)_2]_3$

The germane, CH_3GeCl_3 (1 mmol) and the solvent, CS_2 (2.5 ml) were added to dry powdered $(C_2H_5)_2NCS_2Na$ (0.535 g, 3.12 mmol). The vessel was warmed to ambient temperature, and the color of the mixture turned yellow. The reaction mixture was stirred for 5 h before it was filtered. The filtrate on evaporation gave a yellow microcrystalline product, which was washed with cold ligroin and dried. Yield 52%, m.p. 94 °C. *Anal.* Calc. for $C_{16}H_{33}N_3S_6Ge$: C, 36.10; H, 6.25; N, 7.89. Found: C, 34.23; H, 6.92; N, 8.18%.

Preparation of Triphenyl(N,N-diethyldithiocarbamato)germane (8), $(C_6H_5)_3GeSC(S)N(C_2H_5)_2$

The dry salt, $(C_2H_5)_2NCS_2Na$ (0.511 g, 2.98 mmol) and $(C_6H_5)_3GeCl$ (0.441 g, 1.30 mmol) were mixed together and the reaction vessel was evacuated. The solvent, CS_2 (3 ml), was distilled into the vessel and the contents were stirred at 0 °C for 10 h. The solid materials were separated by filtration and the solvent was pumped off immediately. The viscous product thus obtained was dissolved in fresh CS_2 and on slow evaporation of the solvent white crystals appeared. Yield 60%, m.p. 128 °C. *Anal.* Calc. for $C_{23}H_{25}NS_2Ge$: C, 61.10; H, 5.57; N, 3.10. Found: C, 60.98; H, 5.40; N, 3.04%.

Preparation of Diphenylbis(N,N-diethyldithiocarbamato)germane (9), $(C_6H_5)_2Ge[SC(S)N(C_2H_5)_2]_2$

The germane, $(C_6H_5)_2GeCl_2$ (0.332 g, 1.12 mmol) was dissolved in CS_2 (3 ml) and the solution added to dry $(C_2H_5)_2NCS_2Na$ (0.507 g, 2.96 mmol) under a nitrogen atmosphere. The reaction mixture was immediately frozen by liquid nitrogen (−196 °C) and the reaction vessel evacuated. The contents were allowed to warm to ambient temperature and were stirred moderately for 4 h. The mixture was filtered, and the filtrate on evaporation yielded a solid product, which was recrystallized from CS_2 and n-hexane. Yield 72%, m.p. 144 °C. *Anal.* Calc. for $C_{22}H_{30}N_2S_4Ge$: C, 50.49; H, 5.78; N, 5.35. Found: C, 50.79; H, 5.66; N, 5.38%.

Results and Discussion

The syntheses of the compounds **1**–**9** are represented by

$$R_nGeX_{4-n} + m\,{}^{-}S_2CN(C_2H_5)_2 \longrightarrow R_nGe[S_2CN(C_2H_5)]_mX_{4-n} + mX^-$$

$$R_pGe[S_2CN(C_2H_5)_2]Cl_{3-p} \xrightarrow[\text{or } (CH_3)_3SiI]{(CH_3)_3SiBr} R_pGe[S_2CN(C_2H_5)_2]X_{3-p}$$

$R = CH_3; C_6H_5; X = Cl, Br, I; n, m = 1–3; p = 1, 2$

The compounds are susceptible to moisture and air, particularly those that are partially substituted. They dissolve readily in CS_2, CCl_4 and $CHCl_3$ and on heating have a tendency to sublime. Scrambling

TABLE IV. ^1H NMR Data of *N,N*-Diethyldithiocarbamic Acid Derivatives of Methyl and Phenylgermanes[a]

Compound		Chemical shifts δ (ppm)[b]		
		Ge–CH_3/C_6H_5	N–CH_2	CH_3
$(CH_3)_3Ge[S_2CN(C_2H_5)_2]$	(1)	0.65(9H)	3.80(4H, q)	1.22(6H, t)
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl$	(2)	1.34(6H)	3.72(4H, q)	1.28(6H, t)
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br$	(3)	1.50(6H)	3.75(4H, q)	1.30(6H, t)
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]I$	(4)	1.72(6H)	3.76(4H, q)	1.29(6H, t)
$CH_3Ge[S_2CN(C_2H_5)_2]Cl_2$	(5)	1.88(3H)	3.78(4H, q)	1.29(6H, t)
$CH_3Ge[S_2CN(C_2H_5)_2]Br_2$	(6)	2.17(3H)	3.73(4H, q)	1.30(6H, t)
$CH_3Ge[S_2CN(C_2H_5)_2]_3$	(7)	1.93(3H)	3.73(12H, q)	1.30(18H, t)
$(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]$	(8)	7.0 – 7.6(15H)	3.75(4H, q)	1.20(6H, t)
$(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$	(9)	7.1 – 7.9(10H)	3.68(8H, q)	1.15(12H, t)

[a] For $NaS_2CN(C_2H_5)_2$ in D_2O the N–CH_2 and CH_3 signals appear at 4.03(q, J = 7 Hz) and 1.22(t, J = 7 Hz), respectively, q = quartet, t = triplet. [b] All spectra were recorded in CS_2.

TABLE V. ^{13}C NMR Data of *N,N*-Diethyldithiocarbamic Acid Derivatives of Methyl and Phenylgermanes[a]

Compound		Chemical shifts δ (ppm)[b]			
		Ge–*C*H$_3$/*C*$_6$H$_5$	N–*C*H$_2$	*C*H$_3$	*C*=S
$(CH_3)_3Ge[S_2CN(C_2H_5)_2]$	(1)	3.3	48.5	12.2	195.0
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl$	(2)	15.9	49.0	12.2	194.2
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br$	(3)	17.2	49.1	12.0	195.0
$(CH_3)_2($ S(2) $C_2H_5)_2]I$	(4)	18.6	49.3	12.4	196.7
$CH_3Ge[S_2CN(C_2H_5)_2]Cl_2$	(5)	25.8	50.0	12.1	190.2
$CH_3Ge[S_2CN(C_2H_5)_2]Br_2$	(6)	28.6	49.9	12.1	191.3
$CH_3Ge[S_2CN(C_2H_5)_2]_3$	(7)	24.4	49.3	11.9	192.6
$(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]$	(8)	128.3, 129.5, 134, 135.0, 136.2	48.9	12.6	192.0
$(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$	(9)	128.1, 129.4, 134.2, 136.6, 138.1	48.7	12.5	193.0

[a] For $NaS_2CN(C_2H_5)_2$ in D_2O the N–*C*H$_2$, *C*H$_3$ and *C*=S peaks appear at 49.3, 12.3 and 207.3 ppm respectively in reference to dioxane (67.4 ppm). [b] All spectra were run in $CDCl_3$.

equilibria between halosilanes and halogermanes have been investigated [17]. However, in the exchange reactions involving dithiocarbamate compounds no mixed halogen species were observed.

NMR Spectra

The ^1H and $^{13}C\{^1H\}$ NMR data are presented in Tables IV and V. The ^1H NMR spectra show a quartet and a triplet assignable to the $N–C_2H_5$ group, and a singlet arising from the $Ge–CH_3$ group in the methylgermanes or two sets of multiplets arising from the $Ge–C_6H_5$ resonances in the phenylgermanes. The equivalence of the $N–C_2H_5$ groups may be the result of the rapid averaging of sulfur positions in solution as has been observed for tin and titanium dithiocarbamates [18]. The chemical shifts of the $N–C_2H_5$ group remain unchanged for all the compounds, but the $Ge–CH_3$ signals vary between 2.17–0.65 ppm. As was found with *N,N*-dimethyldithiocarbamatogermane derivatives, the chemical shifts follow trends noted for the corresponding bromomethylgermanes [16]. Thus they suggest a qualitative measure of the electronegativity of the dithiocarbamate group as being close to that of bromine. Similar trends are also observed in the $^{13}C\{^1H\}$ NMR spectra where the $Ge–CH_3$ signals reported herein can be compared with those of the methyl (*N,N*-dimethyldithiocarbamatogermanes) [16] and bromomethylgermanes [19]. The *C*=S resonances occur in the 190 ppm region which is again similar to those for the *N,N*-dimethyldithiocarbamatogermanes and $As[SC(S)N(C_2H_5)_2]_3$ in which the dithiocarbamate group was found to be anisobidentate in the solid state [16, 20, 21].

IR and Raman Spectra

The distinctive infrared and Raman frequencies in the 1600–150 cm^{-1} region are summarized in Table VI. The evidence of mode of attachment of the dithiocarbamate group is supposed to lie in the positions of ν(C=N) and ν(C=S) [22]. A high value for the ν(C=N) stretch close to 1600 cm^{-1} and a

TABLE VI. Major Vibrational Bands of Compounds 1–9

	ν(C–N)		ν(CS_2)asym		ν(CS_2)sym		ν(Ge–C)asym		ν(Ge–C)sym[a]		ν(Ge–S)		ν(Ge–X)	
	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
1	1519w		1267s	1263(12)	990m		605m	599(13)	567m	562(100)	436m	420(27)		
2	1511m	1501(46)	1275m	1270(36)	1012m,br	1007(21)	638s	630(25)	578s	579(100)	412s,br	439(62)	293vs,br	287(29)
3	1518s	1509(36)	1276m	1272(34)	1011m,br	1002(16)	637m	629(21)	575s	575(100)	407s	439(57)		165(14)
4	1525s	1520(30)	1277m	1274(42)	1002m	1005(9)	635w	630(22)	570m	573(100)	402m	444(64)		138(34)
5	1525s	1524(55)	1282m	1280(64)	1003m	1005(17)				609(92)	409sh		390s[b] 310s	380(100) 310(48)
6	1533s	1526(41)	1284m	1277(59)	1001m	1007(19)			610m	606(100)	404s		288m,br[b]	280(50) 205(48)
7	1517vs	1533(70)	1263m	1281(60)	988m	985(42)		608(58)	565w	566(100)	426w	408(86)		
8	1487s		1268s			1027(18)	see footnote c				433sh	420(21)		
9	1489s	1482(43)	1268s	1262(38)	1011s,br	1018(39)					415m,br	437(79)		

[a] 5–7, a second ν(Ge–C) vibration is caused by equational isomers around 570 cm^{-1}. [b] ν(Ge–X) band. [c] For $C_6H_5–M$ species there are six metal–carbon vibrations, of which four occur in the mid-infrared region (*ca.* 1090, 695, 460, 330 cm^{-1}).

sharp single band around 990 cm^{-1} is indicative of a bidentate dithiocarbamate group. However, for these compounds **1**–**9**, ν(C=N) is *ca.* 1522 cm^{-1} or lower so that a monodentate dithiocarbamate is strongly suggested. The ν(Ge–C) asymmetric and symmetric vibrations in the 635–560 cm^{-1} region are very similar to those of the parent germanes. For example, in the infrared spectra of $(CH_3)_3GeBr$, the ν(Ge–C) asymmetric and symmetric stretches appear at 612 and 572 cm^{-1} compared to 605 and 567 cm^{-1} for **1** and those of $(CH_3)_2GeBr_2$ appear at 633 and 588 cm^{-1} compared to 637 and 575 cm^{-1} for **3**. This suggests that the Ge–C bonds hardly differ in relative positions and strengths from those in the bromomethylgermanes [23]. The ν(Ge–S) vibrations occur in the expected 435–400 cm^{-1} region. However, the ν(Ge–X) stretching vibrations are considerably shifted towards the far infrared region. For example, ν(Ge–Cl) in **2** is observed at 293 cm^{-1} compared to that of $(CH_3)_3GeCl$ at 399 cm^{-1} [24]. This strongly suggests that the structure of **2** is similar to that of $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$, which can be described as having the Ge atom at the center of a distorted trigonal bipyramid with the two C atoms of the methyl groups and one of the S atoms occupying the equatorial positions [15]. The Cl atom then occupies one axial position where it is a longer and weaker bond compared to a typical 'tetrahedral' Ge–Cl bond [25]. Similarly, for compounds **3** and **4**, the Ge–Br and Ge–I bonds presumably occupy the same axial position because ν(Ge–Br) and ν(Ge–I) are at 165 and 138 cm^{-1}, respectively, compared to 265 and 228 cm^{-1}, respectively, in $(CH_3)_3GeBr$ [23] and $(CH_3)_3GeI$ [26]. Compounds **5** and **6** both show two peaks assignable to ν(Ge–Cl) at *ca.* 380 and 310 cm^{-1} and ν(Ge–Br) at *ca.* 280 and 205 cm^{-1}. These could be ascribed to asymmetric and symmetric modes of Ge–X bonds of intermediate strength. However, they could equally well be indicative of one Ge–X bond of similar strength to most Ge–X bonds and the other indicative of a weak, axial-type, Ge–X bond. This is at least consistent with the structures of **5** and **6** being similar to **2** and **3** but with a halogen atom replacing one of the equatorial CH_3 groups. The Ge–C stretches in **5** and **6** are seen at 609 and 606 cm^{-1} which is typical of normal Ge–C bonds as seen in CH_3GeBr_3 (612 cm^{-1}) [23]. Unfortunately, we were unable to prepare crystals of sufficient quality to attempt structure determinations.

Mass Spectra

The mass spectra data are given in Table VII. The germanium isotope pattern is evident in all clusters containing germanium and hence discernible from other fragments. The molecular ion is observed for most of the compounds and the fragmentation patterns are reminiscent of the parent germanes. The free acid peaks, which are present in all of the compounds, are also observed in dithiocarbamate esters and dialkylammonium salts. The abundance of free acid and its oligomers indicate that the dithiocarbamate groups are not strongly held and the germanium–sulfur link is relatively weak.

TABLE VII. Mass Spectra Data of Compounds **1**–**9**

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	
						533(<1)			$CH_3Ge[S_2CN(C_2H_5)_2]_3^{\cdot+}$
						518(<1)			$Ge[S_2CN(C_2H_5)_2]_3^{+}$
							453(25.2)		$(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]^{\cdot+}$
					395(42.8)				$CH_3Ge[S_2CN(C_2H_5)_2]Br_2^{\cdot+}$
								376(<1)	$(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]^{+}$
			358(4.1)						$(CH_3)_2GeI_2^{\cdot+}$
		331(4.6)							$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br^{\cdot+}$
					316(87.4)				$CH_3Ge[S_2CN(C_2H_5)_2]Br^{+}$
				307(100)					$CH_3Ge[S_2CN(C_2H_5)_2]Cl_2^{\cdot+}$
		296(3.8)						296(<1)	$[(C_2H_5)_2NCS_2]_2^{\cdot+}$
	287(100)								$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl^{\cdot+}$
267(21.7)									$(CH_3)_3Ge[S_2CN(C_2H_5)_2]^{\cdot+}$
				264(5.6)					$[(C_2H_5)_2NCS]_2S^{\cdot+}$
252(97.2)	252(8.9)	252(100)	252(100)						$(CH_3)_2Ge[S_2CN(C_2H_5)_2]^{+}$
149(40.0)	149(1.8)	149(4.1)	149(7.4)	149(20.9)	149(100)	149(56.4)	149(4.6)	149(81.0)	$(C_2H_5)_2NCS_2H^{\cdot+}$
					120(14.3)		120(4.9)		$C_2H_5NCS_2H^{+}$
									$(CH_3)_3Ge^{+}$
119(37.0)									$(C_2H_5)_2NCS^{+}$
116(100.0)				73(6.0)	73(23.3)	73(21.1)	73(100)	73(100)	$(C_2H_5)_2NH^{\cdot+}$

[a] Compound **1** was a recorded in EI mode. All others were recorded in FI mode. [b] Relative abundances are given in parentheses.

TABLE VIII. Metal–Sulfur (non-bonded), Carbon–Sulfur (double and single bond) and Carbon–Nitrogen (double bond) Distances in some Monodentate Dithiocarbamate Complexes

Compound	M--S	C=S	C–S	C=N	Reference
$Au[S_2CN(C_2H_5)_2]_3$	3.097, 3.182[a]	1.66(2), 1.66(2)	1.78(2), 1.76(2)	1.34(2), 1.32(2)	28
$Pt[S_2CN(C_2H_5)_2]_2P(C_6H_5)_3$	3.457(5)	1.685(19)	1.771(17)	1.331(14)	29
$W[S_2CN(CH_3)_2](C_5H_5)(CO)_3$	3.908(1)	1.676(3)	1.769(3)	1.341(3)	30
$Mo[S_2CN(C_2H_5)_2][HB\{(CH_3)_2C_3N_2H\}_3]$	3.820(2), 3.834(2)[b]	1.667(6), 1.678(5)	1.753(5), 1.752(5)	1.33(1), 1.33(1)	31
$Pt[S_2CN(C_4H_9)_2][P(CH_3)_2(C_6H_5)]_2$	3.392(3)[c]	1.692(8)	1.734(6)	1.349(9)	12
$Sn[S_2CN(CH_3)_2]_4$	3.439(6), 3.643(6)	1.69(2), 1.67(2)	1.74(2), 1.71(2)	1.30(2), 1.40(2)	32
$Ge[S_2CN(C_2H_5)_2]_2(C_6H_5)_2$	3.183(1)[c]	1.663(3)	1.768(3)	1.326(4)	this work

[a] Calculated from atomic positions. [b] The values are for two independent molecules. [c] The second monodentate dithiocarbamate group is related by symmetry.

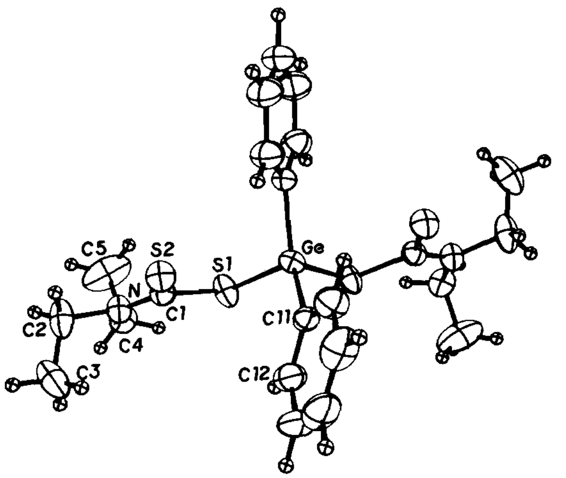

Fig. 1. Structure and labelling scheme for $(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$ (50% probability for thermal ellipsoids). Hydrogen atoms are drawn aribitrarily small. The unlabelled atoms are related to the labelled ones by a twofold axis passing through germanium.

Molecular Structure of $(C_6H_5)_2Ge[SC(S)N(C_2H_5)_2]_2$ (9)

Diphenylbis(*N*,*N*-diethyldithiocarbamato)germane (9) crystallizes as discrete molecules in the space group *C*2/*c*. The ORTEP diagram of the asymmetric unit in Fig. 1 indicates that both dithiocarbamate groups are monodentate unlike other germanium dithiocarbamates. The geometry about germanium is essentially that of a distorted tetrahedron with the distortion being similar to those found in a simple molecule like $(CH_3)_2GeBr_2$. Thus the C–Ge–C bond angle of 121.8(2)° is similar to that of 124(7)° in $(CH_3)_2GeBr_2$ and the Ge–C bond length of 1.928(3) Å is also close to the value of 1.91(1) Å in $(CH_3)_2GeBr_2$ [27].

The Ge–S bond length is 2.271(1) Å, which is slightly longer than the sum of the covalent radii and also slightly longer than that observed in $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$ [15]. The non-bonding Ge---S distance is 3.183(1) Å, which is considerably longer than in $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$ where a distance of 2.896(1) was assumed to indicate a weak secondary interaction and indicate an anisobidentate linkage. The large difference in the lengths of the C=S (1.663(3) Å) and C–S (1.768(3) Å) bonds also support the concept that the ligand is monodentate. Further, the long C=N bond of 1.326(4) Å is typical of those reported for monodentate dithiocarbamate groups (see Table VIII).

The contrast between the structure of 9 and its tin analogue, $(C_6H_5)_2Sn[S_2CN(C_2H_5)_2]_2$ [33] is of particular interest because many Ge and Sn analogues [34, 35] have been found to be isomorphous and isostructural such as $(CH_3)_2M[S_2CN(CH_3)_2]Cl$ and $(CH_3)_2M[S_2CN(CH_3)_2]_2$. In $(C_6H_5)_2Sn[S_2CN(C_2H_5)_2]_2$, both of the dithiocarbamate groups are bidentate with a *cis*-octahedral arrangement about tin and with the dithiocarbamate mean planes perpendicular to one another. In 9, by contrast, even if the non-bonded S atoms are taken into account, the arrangement is not close to octahedral geometry and the dithiocarbamate groups are pseudo-coplanar.

Supplementary Material

Tables of anisotropic thermal parameters, fractional coordinates and thermal parameters of hydrogen atoms, unit cell packing diagram and calculated and observed structure factors are available from the authors on request.

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