clusters. The monoanion has a slightly enlarged octahedron compared to the dianion, an indication that the electron removed in the oxidation is from a bonding orbital (although the increased charge on the tungsten core would be expected to expand it also). The W–Br(axial) bond is significantly shorter in the monoanion, presumably due to the electrostatic attraction of the negatively charged halide to the now more positively charged W_6 unit. The W–Br(facial) bonds are not significantly shorter in the monoanion despite the higher charge on the metals, possibly because the metal–bromide back-bonding inferred from the $W_6X_{14}^{2-}$ structures[5] and photophysics[8] is diminished in the oxidized metal core. The expected shortening of the metal–bromide(facial) bond upon metal–core oxidation may be compensated by the decrease in the interaction of filled metal orbitals with the empty Br 4d orbitals.

Acknowledgment. T.C.Z. and D.G.N. acknowledge graduate fellowships from the Sun Co. This work was supported by National Science Foundation Grants CHE84-19828 (H.B.G.), CHE82-11349 (USC SQUID Instrumentation Facility), and CHE82-19039 (Caltech X-ray Facility) and the Exxon Educational Foundation (W.P.S., B.S.).

Registry No. $(PPN)_2W_6Br_{14}$, 101955-15-1; W_6Cl_{12}, 12052-19-6; $(PPN)W_6Br_{14}$, 101955-18-4; $(TBA)W_6Cl_{14}$, 101955-24-2; $(TBA)W_6Cl_8Br_6$, 101955-26-4; $(TBA)W_6Br_8Cl_6$, 101955-22-0; $(TBA)_2W_6Cl_{14}$, 84648-02-2; $(TBA)_2W_6Cl_8Br_6$, 101955-16-2; $(TBA)_2W_6Br_8Cl_6$, 101955-20-8.

Supplementary Material Available: A table of anisotropic thermal parameters for refined atoms and electronic spectra of $W_6X_8Y_6^{2-}$ (5 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic Characterization of Dithiocarbamate Derivatives of Methyl-, Dimethyl-, and Trimethylgermane and Crystal Structure of Dimethylbis(*N*,*N*-dimethyldithiocarbamato)germanium

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Received July 18, 1985

Seven organogermanium derivatives of dithiocarbamic acid of the general formula $(CH_3)_nGeX_{4-n-m}[S_2CN(CH_3)_2]_m$ (where X = Cl, Br, I; $n = 1$–3, $m = 1, 2$) have been prepared either by the reaction of sodium *N*,*N*-dimethyldithiocarbamate with the appropriate halomethylgermane or in the case of partially substituted bromo and iodo derivatives by halide exchange reactions with bromotrimethylsilane and iodotrimethylsilane. The dithiocarbamates were characterized by vibrational and NMR spectroscopy and mass spectrometry. The ^{1}H and ^{13}C NMR spectra are consistent with the sulfur atoms undergoing rapid exchange in solution. The vibrational spectra of the halide-containing species suggest the presence of a relatively weak Ge–X bond consistent with the halide occupying the axial position in a distorted pseudo trigonal bipyramid. The crystal structure of $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ was determined and indicates that the germanium atom is at the center of a distorted octahedron, in contrast to the case of $(CH_3)_2GeCl[S_2CN(CH_3)_2]$, in which the geometry around the germanium atom is that of a distorted pseudo trigonal bipyramid. The compound crystallizes in the orthorhombic space group *Fdd*2 with unit cell parameters (21 ± 1 °C) $a = 25.05$ (3) Å, $b = 34.74$ (3) Å, $c = 6.896$ (6) Å, and $V = 6000$ (10) Å^3; $Z = 16$, ρ(obsd) = 1.53 g cm^{-3}, ρ(calcd) = 1.52 g cm^{-3}, and $R = 0.0283$ for 1107 observed reflections.

Introduction

The structural chemistry of organogermanium derivatives was reviewed in 1983,[1] and only five compounds were mentioned that contain a Ge–S bond. There have been many reports of dithiocarbamates of both transition metals[2–4] and main-group elements,[5] but we recently reported a preliminary note containing the first structure of an organogermanium dithiocarbamate.[6] In $(CH_3)_2GeCl[S_2CN(CH_3)_2]$ the dithiocarbamate group acts in an anisobidentate fashion[6] similar to that found for the tin analogue.[7] In view of the variety of structures found for other tin derivatives,[8] it was of interest to make a more extensive comparative study of the spectroscopic properties of other methylgermanium derivatives and to carry out structural determinations whenever appropriate crystals could be grown. Unfortunately, in only one case were we able to get crystals of the appropriate quality that did not decay rapidly during data collection.

Experimental Section

Starting Materials. Trichloromethylgermane (Alfa) was purified by trapping it out at −23 °C. The other halomethylgermanes (Alfa) were used as supplied as were bromo- and iodotrimethylsilane (Petrarch) and the sodium salt of dimethyldithiocarbamic acid (Kodak). Carbon di-

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sulfide was dried over phosphorus(V) oxide and distilled prior to use. All reactions were carried out on a vacuum line.

Preparation of Trimethyl(*N*,*N*-dimethyldithiocarbamato)germanium (1), $(CH_3)_3GeS_2CN(CH_3)_2$. The salt $(CH_3)_2NCS_2Na$ (0.514 g, 3.60 mmol) was dried for several hours before $(CH_3)_3GeBr$ (4.0 mmol) was distilled onto it at −196 °C followed by CS_2 (3 mL). The reaction vessel was allowed to warm up gradually and maintained at 0 °C with moderate stirring. After 4 h, solid NaBr was filtered off and the filtrate was slowly evaporated on the vacuum line. Needle-shaped white crystals were formed in the reaction vessel: yield 56%; mp 30 °C. Anal. Calcd for $C_6H_{15}NS_2Ge$: C, 30.29; H, 6.36; N, 5.89. Found: C, 30.18; H, 6.37; N, 6.19.

If the reaction was not carried out under water-free conditions, hydrolosis occurred with the formation of the salt $[Me_2NH_2]^+[S_2CN(CH_3)_2]^-$. The formation of the latter was confirmed when a structural study was initiated on the assumption that it was the desired product.[9]

Preparation of Chlorodimethyl(*N*,*N*-dimethyldithiocarbamato)germanium (2), $(CH_3)_2GeCl[S_2CN(CH_3)_2]$. The germane $(CH_3)_2GeCl_2$ (2.74 mmol) and CS_2 (4 mL) were distilled at −196 °C onto dry $(CH_3)_2NCS_2Na$ (0.392 g, 2.74 mmol). The vessel was warmed until the reactants had been mixed well by stirring and then maintained at −23 °C. After 2 h, solid NaCl was filtered off and the filtrate was allowed to evaporate gradually. The white crystals thus obtained were washed with cold *n*-hexane and dried: yield 50%; mp 56 °C. Anal. Calcd for $C_5H_{12}NS_2GeCl$: C, 23.25; H, 4.68; N, 5.42. Found: C, 23.11; H, 4.82; N, 5.84.

Preparation of Bromodimethyl(*N*,*N*-dimethyldithiocarbamato)germanium (3), $(CH_3)_2GeBr[S_2CN(CH_3)_2]$. Excess $(CH_3)_3SiBr$ (2.0 mmol) and CS_2 (3 mL) were added to $(CH_3)_2GeCl[S_2CN(CH_3)_2]$ (0.254 g, 1.77 mmol) by distillation into a trap held at liquid-N_2 temperature. The trap was warmed to 0 °C and maintained at this temperature for 12 h with occasional stirring. Finally, the mixture was allowed to evaporate and the product was dissolved in *n*-hexane and recrystallized in a refrigerator to obtain crystals of pure $(CH_3)_2GeBr[S_2CN(CH_3)_2]$: yield 33%; mp 84 °C. Anal. Calcd for $C_5H_{12}NS_2GeBr$: C, 19.83; H, 4.00; N, 4.63. Found: C, 19.75; H, 3.97; N, 4.67.

Preparation of Iododimethyl(*N*,*N*-dimethyldithiocarbamato)germanium (4), $(CH_3)_2GeI[S_2CN(CH_3)_2]$. Excess $(CH_3)_3SiI$ (1.9 mmol) and CS_2 (3.5 mL) were distilled onto freshly prepared $(CH_3)_2GeCl[S_2CN(CH_3)_2]$ held at −196 °C. The vessel was allowed to warm up, and the contents were stirred for 12 h at 0 °C. On evaporation, a slightly colored product was obtained, which was dissolved in a *n*-hexane/ether mixture and allowed to recrystallize in the refrigerator: yield 38%; mp 97 °C. Anal. Calcd for $C_5H_{12}NS_2GeI$: C, 17.17; H, 3.46; N, 4.01. found: C, 17.38; H, 3.52; N, 3.92.

Preparation of Dimethylbis(*N*,*N*-dimethyldithiocarbamato)germanium (5), $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$. The germane $(CH_3)_2GeCl_2$ (1.5 mmol) and CS_2 (3 mL) were distilled in sequence onto previously dried $(CH_3)_2NCS_2Na$ (0.520 g, 3.63 mmol) held at −196 °C. The reaction vessel was allowed to warm to 0 °C, and the contents were stirred vigorously for 12 h. The mixture was occasionally cooled (to ca. −10 °C) to slow down the reaction. Finally, the solid NaCl was removed by filtration and the filtrate was allowed to evaporate. The product thus obtained was recrystallized from CS_2 in the refrigerator to give white crystals: yield 51%; mp 174 °C. Anal. Calcd for $C_8H_{18}N_2S_4Ge$: C, 28.01; H, 5.29; N, 8.16. Found: C, 28.14; H, 5.38; N, 8.07.

Preparation of Dichloromethyl(*N*,*N*-dimethyldithiocarbamato)germanium (6), $CH_3GeCl_2[S_2CN(CH_3)_2]$. The germane CH_3GeCl_3 (2 mmol) and CS_2 (3 mL) were distilled onto previously dried $(CH_3)_2NCS_2Na$ (0.529 g, 3.69 mmol) held at −196 °C. The reaction vessel was then maintained in liquid-nitrogen fumes (ca. −20 °C) for 15 min. As soon as the color of the mixture started to change, it was filtered and the solvent was evaporated slowly while the vessel was kept cool. The transparent yellowish crystals thus obtained were immediately pumped on the vacuum line: yield 35%; mp 52 °C. Anal. Calcd for $C_4H_9NS_2GeCl_2$: C, 17.23; H, 3.26; N, 5.02. Found: C, 17.37; H, 3.61; N, 5.14.

Preparation of Dibromomethyl(*N*,*N*-dimethyldithiocarbamato)germanium (7), $CH_3GeBr_2[S_2CN(CH_3)_2]$. The germane CH_3GeCl_3 (3 mmol) and CS_2 (2 mL) were added in sequence to previously dried $(CH_3)_2NCS_2Na$ (0.558 g, 3.90 mmol) held at −196 °C. The reaction vessel was allowed to warm to −20 °C and the mixture moderately stirred. After 15 min, the mixture was filtered and the solvent was pumped off as rapidly as possible, prior to $(CH_3)_3SiBr$ (2 mmol) and CS_2 (1 mL) being distilled onto the crystalline residue. The mixture was left for 24 h at −23 °C. The solvent and excess $(CH_3)_3SiBr$ were then pumped off very slowly, while the vessel was kept cool (0 °C), and white fleecy crystals of $CH_3GeBr_2[S_2CN(CH_3)_2]$ were obtained: yield 30%; mp 60 °C. Anal. Calcd for $C_4H_9NS_2GeBr_2$: C, 13.07; H, 2.47; N, 3.81. Found: C, 13.11; H, 2.55; N, 3.87.

Attempts to prepare $CH_3GeI_2[S_2CN(CH_3)_2]$ by a similar exchange reaction with $(CH_3)_3SiI$ resulted in a mixture of products that could not be clearly identified.

Attempted Preparation of $CH_3GeCl[S_2CN(CN_3)_2]_2$ and $CH_3Ge[S_2CN(CH_3)_2]_3$. A larger excess of $(CH_3)_2NCS_2Na$ was used with CH_3GeCl_3 in an attempt to prepare the bis and tris derivatives. However, the only product that could be definitely identified was $CH_3GeCl_2[S_2CN(CH_3)_2]$.

Attempted Preparation of $Ge[S_2CN(CH_3)_2]_4$ and $GeCl_{4-x}[S_2CN(CH_3)_2]_x$. No reaction occurred between $GeCl_4$ and $(CH_3)_2NCS_2Na$ under the conditions described for the formation of $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$.

The microanalytical data were obtained from Guelph Chemical Laboratories of Guelph, Ontario. The melting points were determined on a Fisher-Johns melting point apparatus. The ^1H NMR spectra were recorded on Varian EM360 and Bruker WP80 instruments using tetramethylsilane as internal standard. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker CXP 100FT spectrometer with the central line of the $CDCl_3$ resonance (77.12 ppm) as reference. All ^1H NMR spectra were obtained in CS_2, and all $^{13}C\{^1H\}$ NMR spectra were obtained in $CDCl_3$ at room temperature unless otherwise mentioned. The infrared spectra were measured on a Perkin-Elmer 180 double-beam spectrophotometer or on a Nicolet 5DX FT spectrometer in CS_2 or CCl_4 and as Nujol mulls between CsI disks. The Raman spectra were recorded on a Spectra-Physics 700 spectrophotometer using the 4880-Å exciting line of an argon ion laser. The samples were crushed and sealed in small capillaries for Raman spectra. The electron-impact (70 eV) and field ionization mass spectra were recorded on a Varian GMAT-CH5 double-focusing mass spectrometer. The field ionization mode was used for the bromides and iodides because of their lack of volatility.

Crystallographic Measurements. Crystals of **5** are colorless prisms. A single crystal with approximate dimensions 0.12 × 0.27 × 0.38 mm was sealed in a thin-walled capillary and mounted along the largest dimension on a Syntex $P2_1$ four-circle diffractometer under the control of a Nova 1200 computer. The diffractometer, at a takeoff angle of 6.1°, was equipped with a molybdenum X-ray tube ($K\alpha$ $\lambda = 0.71069$ Å) and a highly oriented graphite monochromator ($2\theta_m = 12.2°$) and operated at 50 kV and 20 mA.

The crystal was optically centered in a random orientation. Determination of preliminary cell parameters and the orientation matrix was carried out as described in the Syntex $P2_1$ operation manual. Examination of the ω scans of several low-angle centered reflections showed no defects in the crystal; full peak width at half-height was less than 0.2°. The axial photographs, which were taken about each of the three chosen axes of the cell, displayed *m* symmetry and confirmed the orthorhombic system. A unique set of data in the shell defined by $15 < 2\theta < 30°$ was next collected at a fast scan rate (19.88° min^{-1}). A set of 15 strong reflections, widely separated in the reciprocal space, was chosen from these data and formed the basis for the determination of the accurate orientation matrix and cell parameters: $a = 25.05$ (3) Å, $b = 34.74$ (3) Å, $c = 6.896$ (6) Å, $V = 6000$ (10) Å^3, ρ(obsd) = 1.53 g cm^{-3}, ρ(calcd) = 1.52 g cm^{-3}, $Z = 16$, mol wt 343.1.

Intensity data were now collected in the range $4 < 2\theta < 50°$ via a θ(crystal)/2θ(counter) scan using bisecting geometry. The scan was from 2θ(Mo $K\alpha_1$(0.70926 Å)) − 1.0° to 2θ(Mo $K\alpha_2$(0.71354 Å)) + 1.0°. Backgrounds were measured both at the beginning and at the end of the scan, each for 25% of the time of the scan. The scan rate varied from 2.02 to 4.88° min^{-1}. As a general check on crystal stability as well as the electronic stability of the instrument, the intensities of three standard reflections were monitored after 50 reflections and were not found to vary significantly during data collection. A total of 1599 reflections ($+h$, $+k$,$+l$) were measured during which time the temperature remained 21 ± 1 °C. Systematic absences for hkl ($h + k$, $k + l$, $l + h \neq 2n$), $0kl$ ($k + l \neq 4n$), and $h0l$ ($l + h \neq 4n$) completely determine the space group $Fdd2(C_{2v}{}^{19}$, No. 43).

Data were corrected for Lorentz and polarization effects. (The *Lp* factor for a monochromator in the equatorial mode is given by

$$Lp = \frac{0.5}{\sin 2\theta}\left(\frac{1 + (\cos^2 2\theta_m)(\cos^2 2\theta)}{1 + \cos^2 2\theta_m} + \frac{1 + |\cos 2\theta_m| \cos^2 2\theta}{1 + |\cos 2\theta_m|}\right)$$

This equation assumes that the graphite monochromator crystal is 50% mosaic and 50% perfect.) An analytical absorption correction ($\mu = 24.71$ cm^{-1}) was also applied to data; the absorption coefficients ranged between 1.31 and 1.57.

The Ge atom position was obtained by a sharpened Patterson synthesis and has the expected twofold site symmetry. Refinement and subsequent

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Table I. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ with Standard Deviations in Parentheses

	x	y	z	U_{eq},[a] Å × 10^3
Ge	0.06076 (3)	0.41714 (2)	0.25000	42.3 (3)
S(1)	0.0584 (1)	0.4624 (1)	0.0120 (3)	59 (1)
S(2)	0.1146 (1)	0.4940 (1)	0.3547 (3)	66 (1)
S(3)	0.0103 (1)	0.3794 (1)	0.0505 (3)	55 (1)
S(4)	0.0364 (1)	0.3331 (1)	0.4010 (3)	66 (1)
N(1)	0.1003 (2)	0.5311 (1)	0.0239 (10)	48 (3)
N(2)	−0.0216 (2)	0.3091 (2)	0.1085 (10)	54 (4)
C(1)	0.1318 (2)	0.3972 (2)	0.2589 (15)	62 (4)
C(2)	0.0167 (3)	0.4305 (2)	0.4678 (12)	73 (5)
C(3)	0.0930 (3)	0.4999 (2)	0.1293 (10)	46 (4)
C(4)	0.0824 (3)	0.5361 (2)	−0.1728 (11)	61 (5)
C(5)	0.1290 (3)	0.5637 (2)	0.1056 (14)	69 (5)
C(6)	0.0064 (2)	0.3372 (2)	0.1873 (11)	43 (4)
C(7)	−0.0511 (3)	0.3141 (2)	−0.0688 (14)	79 (6)
C(8)	−0.0249 (3)	0.2719 (2)	0.1995 (14)	74 (6)

[a] U_{eq} is calculated from the refined anisotropic thermal parameters (deposited in the supplementary material) by $U_{eq} = {}^1/_3 \cdot \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table II. Interatomic Distances (Å) and Angles (deg) in $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$

Ge–S(1)	2.275 (2)	S(3)–C(6)	1.748 (7)
Ge–S(2)	3.078 (2)	S(4)–C(6)	1.661 (8)
Ge–S(3)	2.281 (2)	N(1)–C(3)	1.318 (8)
Ge–S(4)	3.158 (2)	N(1)–C(4)	1.440 (10)
Ge–C(1)	1.910 (6)	N(1)–C(5)	1.455 (8)
Ge–C(2)	1.921 (7)	N(2)–C(6)	1.318 (8)
S(1)–C(3)	1.759 (7)	N(2)–C(7)	1.439 (10)
S(2)–C(3)	1.658 (7)	N(2)–C(8)	1.439 (9)

S(1)–Ge–S(2)	65.2 (1)	Ge–S(3)–C(6)	100.8 (2)
S(1)–Ge–S(3)	87.0 (1)	Ge–S(4)–C(6)	73.5 (2)
S(2)–Ge–S(4)	144.0 (1)	S(1)–C(3)–S(2)	120.1 (4)
S(3)–Ge–S(4)	64.0 (1)	S(1)–C(3)–N(1)	115.0 (5)
S(1)–Ge–C(1)	107.4 (3)	S(2)–C(3)–N(1)	124.9 (5)
S(1)–Ge–C(2)	112.5 (2)	S(3)–C(6)–S(4)	121.6 (4)
S(2)–Ge–C(1)	84.2 (2)	S(3)–C(6)–N(2)	115.4 (6)
S(2)–Ge–C(2)	81.9 (2)	S(4)–C(6)–N(2)	123.0 (6)
S(3)–Ge–C(1)	109.1 (2)	C(3)–N(1)–C(4)	125.1 (6)
S(3)–Ge–C(2)	106.9 (2)	C(3)–N(1)–C(5)	119.8 (7)
S(4)–Ge–C(1)	80.4 (2)	C(4)–N(1)–C(5)	115.1 (6)
S(4)–Ge–C(2)	81.6 (2)	C(6)–N(2)–C(7)	122.3 (7)
C(1)–Ge–C(2)	126.7 (4)	C(6)–N(2)–C(8)	121.0 (7)
Ge–S(1)–C(3)	99.6 (3)	C(7)–N(2)–C(8)	116.7 (6)
Ge–S(2)–C(3)	75.1 (2)		

difference maps revealed the remaining atoms. The structure was refined by full-matrix least-squares methods. Complete anisotropic refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged at $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0283$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.0295$ based on 135 variables and 1107 unique "observed" reflections for which $I > 2\sigma(I)$ and the agreement factor between equivalent or multiply measured reflections is 0.01. Hydrogen atoms of methyl groups were included at the idealized positions (C–H = 0.95 Å, HCH = 109.5°) and were refined as rigid groups with isotropic thermal parameters 0.01 Å^2 greater than that of the corresponding carbon. A weighting scheme of the form $w = 1/[\sigma(F) + pF^2]$ was employed with a final p value of 0.0001. In the final cycle of refinement, the largest shift/error ratio was 0.03 and the final difference map had no features of chemical significance with the largest peak being 0.27 e Å^{-3}. No evidence of secondary extinction was found.

All calculations were performed on the IBM 3031 computer at the University of Windsor. The programs used during structural analysis include local versions of CHECK (check standard reflections),[10] PROC (data reduction),[10] SHELX (Fourier synthesis and structural refinement),[11] XANADU (crystallograhic calculations),[12] ORTEP (thermal ellipsoid plotting program),[13] and ABSORB (analytical absorption).[14] Scattering factors for all non-hydrogen atoms, including anomalous dispersion correcting terms ($\Delta f'$ and $\Delta f''$) for the Ge atom, were taken from ref 15, and scattering factors for hydrogen atoms were obtained from ref 16.

The final atomic corrdinates for non-H atoms are given in Table I, and important distances and angles, in Table II.

Despite many efforts, it was not possible to collect reasonable data for the other compounds, because of rapid decay of the crystals in the X-ray beam. We have no facilities for low-temperature work.

Results and Discussion

Trimethyl-, chlorodimethyl-, and dichloromethyl-, and dimethylbis(*N*,*N*-dimethyldithiocarbamato)germanium compounds were prepared by the reaction of a halomethylgermane with the sodium salt of dimethyldithiocarbamic acid. Bromodimethyl-, iododimethyl-, and dibromomethyl(*N*,*N*-dimethyldithiocarbamato)germanium compounds were prepared by halogen-exchange reactions with halotrimethylsilanes. All reactions were carried out on the vacuum line.

Reactions 1–6 were carried out at low temperatures (0 to −23

$$(CH_3)_3GeBr + NaS_2CN(CH_3)_2 \rightarrow \underset{\mathbf{1}}{(CH_3)_3GeS_2CN(CH_3)_2} + NaBr \quad (1)$$

$$(CH_3)_2GeCl_2 + NaS_2CN(CH_3)_2 \rightarrow \underset{\mathbf{2}}{(CH_3)_2GeCl[S_2CN(CH_3)_2]} + NaCl \quad (2)$$

$$(CH_3)_2GeCl[S_2CN(CH_3)_2] + (CH_3)_3SiX \rightarrow (CH_3)_2GeX[S_2CN(CH_3)_2] + (CH_3)_3SiCl \quad (3)$$
$$X = Br\ (\mathbf{3}),\ I\ (\mathbf{4})$$

$$(CH_3)_2GeCl_2 + 2NaS_2CN(CH_3)_2 \rightarrow \underset{\mathbf{5}}{(CH_3)_2Ge[S_2CN(CH_3)_2]_2} + 2NaCl \quad (4)$$

$$CH_3GeCl_3 + NaS_2CN(CH_3)_2 \rightarrow \underset{\mathbf{6}}{CH_3GeCl_2[S_2CN(CH_3)_2]} + NaCl \quad (5)$$

$$CH_3GeCl_2[S_2CN(CH_3)_2] + 2(CH_3)_3SiBr \rightarrow \underset{\mathbf{7}}{CH_3GeBr_2[S_2CN(CH_3)_2]} + 2(CH_3)_3SiCl \quad (6)$$

°C) with carbon disulfide as solvent. In reactions 1, 2, 4, and 5, the sodium halide was removed by filtration on the vacuum line. Gradual evaporation of the filtrate led to the formation of crystals of the desired products with final yields of ca. 50% for the pure products. In reactions 3 and 6, the solvent and chlorotrimethylsilane were distilled off and the product was dissolved in *n*-hexane and recrystallized in a refrigerator to give ca. 33% yield of pure product. The exchange obviously favors the formation of a Si–Cl bond. The analogous reaction to (6) using iodotrimethylsilane led to an intractable mixture. A possible side reaction, along with some exchange, could be coupling to give $[S_2CN(CH_3)_2]_2$. Even with an excess of the dithiocarbamate salt in reaction 5, there was no evidence of further substitution to form bis or tris derivatives. Also, under these conditions, no reaction was observed with tetrachlorogermane. The reduced reactivity as halogen atoms replace methyl groups is surprisingly marked although it has been noted that Ge–X bonds get appreciably stronger as the number of halogen substituents increases while, at the same time, the halogen atoms apparently carry a relatively smaller negative charge.[17]

All of the (*N*,*N*-dimethyldithiocarbamato)germanium compounds are air- and moisture-sensitive and therefore were stored

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Table III. Electron-Impact Mass Spectra of Compounds **1–5** and Field Ionization Mass Spectra of Compounds **6** and **7**[a]

1	**2**[b]	**3**[c]	**4**	**5**[b]	**6**[d]	**7**[d]	
						367 (5)	$CH_3GeBr_2[S_2CN(CH_3)_2]^{\bullet+}$
				344 (12)			$(CH_3)_2Ge[S_2CN(CH_3)_2]_2^{\bullet+}$
		303 (15)					$(CH_3)_2GeBr[S_2CN(CH_3)_2]^{\bullet+}$
						288 (100)	$CH_3GeBr[S_2CN(CH_3)_2]^+$
					279 (100)		$CH_3GeCl_2[S_2CN(CH_3)_2]^{\bullet+}$
	259 (5)						$(CH_3)_2GeCl[S_2CN(CH_3)_2]^{\bullet+}$
	244 (10)						$CH_3GeCl[S_2CN(CH_3)_2]^+$
239 (3)							$(CH_3)_3Ge[S_2CN(CH_3)_2]^{\bullet+}$
224 (15)	224 (5)	224 (100)	224 (100)	224 (30)			$(CH_3)_2Ge[S_2CN(CH_3)_2]^+$
	159 (10)						$CH_3GeCl_2^+$
	139 (12)						$(CH_3)_2GeCl^+$
137 (4)							$(CH_3)_2GeSH^+$
121 (83)	121 (28)	121 (<1)	121 (<1)	121 (19)	121 (56)	121 (67)	$(CH_3)_2NCS_2H^{\bullet+}$
118 (3)							$(CH_3)_2Ge(CH_2)^+$
	109 (5)						$GeCl^+$
88 (100)	88 (65)			88 (100)			$(CH_3)_2NCS^+$
		78 (18)	78 (<1)		78 (25)		$CS_2H_2^{\bullet+}$
76 (20)	76 (16)			76 (15)			$CS_2^{\bullet+}$
				56 (5)			$(CH_3)_2NC^+$
44 (69)	44 (100)			44 (47)			$CS^{\bullet+}$

[a] Data given in units of m/z; relative abundances of ions given in parentheses. [b] Non-germanium-containing peaks also seen at m/z 461 and 341. [c] Germanium cluster scan centered at m/z 382 presumed to correspond to $(CH_3)_2GeBr_2[S_2CN(CH_3)_2]^{\bullet+}$. [d] Very intense peak seen at m/z 208 presumed to correspond to $(CH_3)_2NCS_2SCN(CH_3)_2^{\bullet+}$.

Table IV. NMR Chemical Shifts (ppm)

	^1H		$^{13}C\{^1H\}$[c]		
compd[a]	Ge–CH_3	N–CH_3	Ge–CH	N–CH_3	C=S
$(CH_3)_3GeS_2CN(CH_3)_2$ (**1**)	0.67 (9 H)	3.37 (6 H)	3.2	44.4	196.9
$(CH_3)_2GeCl[S_2CN(CH_3)_2]$ (**2**)	1.42 (6 H)	3.42 (6 H)	14.8	43.2	195.9
$(CH_3)_2GeBr[S_2CN(CH_3)_2]$ (**3**)	1.47 (6 H)	3.33 (6 H)	16.5	44.3	197.1
$(CH_3)_2GeI[S_2CN(CH_3)_2]$ (**4**)	1.68 (6 H)	3.35 (6 H)	17.7	44.3	198.7
$(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ (**5**)	1.37 (6 H)	3.28 (12 H)	13.7	43.8	196.5[b]
$(CH_3)GeCl_2[S_2CN(CH_3)_2]$ (**6**)	1.84 (6 H)	3.37 (6 H)	24.7	45.1	193.3
$(CH_3)GeBr_2[S_2CN(CH_3)_2]$ (**7**)	2.12 (3 H)	3.37 (6 H)	27.6	44.9	193.3

[a] In ^1H NMR, the N–CH_3 peak of $(CH_3)_2NCS_2Na$ in D_2O appears at 3.78 ppm, and in the ^{13}C NMR, the N–CH_3 and C=S peaks appear at 47.7 and 210.5 ppm, respectively, downfield from $(CH_3)_3Si(CH_2)_2CO_2Na$. [b] In $CDCl_3/C_6D_6$. [c] In $CDCl_3$.

in sealed, evacuated vessels. They must be prepared under scrupulously water-free conditions; otherwise, no germanium-containing dithiocarbamate derivative is formed but the dimethylammonium salt of the dithiocarbamate can be detected. The formation of the salt was confirmed when a crystal structure determination was initiated on the assumption that a germane derivative had formed. However, the observed unit cell parameters, $a = 9.966$ (5) Å, $b = 7.681$ (5) Å, and $c = 12.168$ (7) Å and $\beta = 105.88$ (4)° in the space group $P2_1/c$, were essentially identical with those reported earlier[9] for the dimethylammonium salt. The chloro derivatives tend to sublime at temperatures close to ambient so that X-ray data collections were not possible because of loss of the crystals during collection. Currently, we do not have the facilities to carry out data collection at lower than ambient temperatures. All the (*N*,*N*-dimethyldithiocarbamato)germanium compounds are readily soluble in carbon disulfide and chloroform.

The mass spectra are reported in Table III. The classic germanium isotope pattern is evident in all clusters of peaks containing germanium, and equally well the absence of the pattern makes it clear which peaks correspond to ions not containing germanium. The electron-impact mass spectra are dominated by fragments from the dithiocarbamate group. In all cases, the molecular ion can be seen. For compound **1**, the $[M - CH_3]^+$ peak is the main germanium-containing fragment, as is typical of $(CH_3)_3GeX$ species,[18] while for compound **5**, the main germanium-containing feature corresponds to the $[M - S_2CN(CH_3)_2]^+$ fragment. For compound **2** the loss of CH_3, Cl, and $S_2CN(CH_3)_2$ all appear to be of comparable importance as dissociation pathways. The electron-impact mass spectra also show the presence of non-germanium-containing fragments at high molecular weight that must correspond to oligomers involving up to four units of the acid with loss of hydrogen and methyl groups. The field ionization spectra are, as expected, much simpler. Only for compound **4** is the molecular ion not seen, and in this case the $[M - I]^+$ ion totally dominates the spectrum.

The ^1H NMR and $^{13}C\{H\}$ NMR chemical shifts are presented in Table IV. The observation of a single N–CH_3 ^1H and ^{13}C NMR signal is consistent with the S positions averaging because C–N bond rotation will not be rapid at room temperature. The integrated ratios of peak heights are as expected. The values of the N–CH_3 and N–CH$_3$ chemical shifts are relatively insensitive to the nature of the methylgermanium moiety and show no obvious general trends. The value of the ^1H NMR chemical shift, 0.67 ppm, for the CH_3–Ge protons in **1** is close to that reported for $(CH_3)_3GeSCH_3$ at 0.51 ppm. However, that of **5** at 1.37 ppm is shifted considerably from that of $(CH_3)_2Ge(SCH_3)_2$ at 0.74 ppm.[20] The shift of approximately 0.7 ppm per dithiocarbamate group replacing a methyl group is close to that observed for the sequential replacement by a halogen atom as shown by $(CH_3)_3$-Ge–Cl (0.78) –Br (0.88) –I (0.98 ppm)[21] shifting to $(CH_3)_2Ge$–Cl_2 (1.18) –Br_2 (1.46) – I_2 (1.90 ppm).[22] In fact substitution by a dithiocarbamate group is similar to substitution by a bromine atom. Thus, the CH_3–Ge shift in **2** is 1.42 ppm compared to 1.34 ppm in $(CH_3)_2GeBrCl$ while in **3** it is 1.47 ppm compared to 1.46 ppm in $(CH_3)_2GeBr_2$ and in **4** it is 1.68 ppm compared to 1.65 ppm in $(CH_3)_2GeBrI$.[23] The same comparisons can be extended to the $CH_3GeX_2[S_2CN(CH_3)_2]$ compounds where the values are

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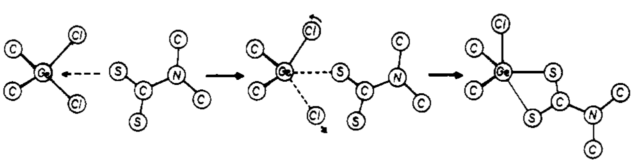
Table V. Selected Features and Their Assignments in the Vibrational Spectra (cm^{-1} (Relative Intensity)) of Compounds 1-7

1		2		3		4		5		6		7		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	assignment
1530 vs		1522 ms		1521 s, br	1520 (8)	1524 ms, br	1530 (7)	1485 m		1520 s	1548 (25)	1520 m	1541 (15)	ν(C-N(CH$_3$)$_2$)
1245 vs	1239 (18)	1226 ms	1227 (10)	1230 m	1228 (8)	1226 m	1222 (7)	1240 vs	1240 (10)	1237 ms	1242 (10)	1237 m	1226 (12)	ν(CS$_2$(asym)) or ν(C=S)
970 vs	984 (18)	978 s	981 (20)	980 m	984 (20)	974 ms	979 (15)	975 vs	987 (30)	972 m	981 (20)	971 ms	977 (25)	ν(CS$_2$(sym)) or ν(C-SGe)
601 m	602 (25)	622 m	622 (20)	621 m	627 (16)	627 m	627 (18)	625 m	623 (25)	611 m	615 (70)	601 m	602 (80)	ν(Ge-C(asym))
560 m	563 (100)	570 m	572 (100)	568 s	570 (80)	574 m	576 (85)	570 m	571 (100)	*a*	*a*	*a*	*a*	ν(Ge-C(sym))
435 m	432 (15)	418 m	424 (20)	414 m	424 (24)	424 w	426 (24)	430 m^b	429 (13)^b	417 ms	422 (10)	426 m	427 (10)	ν(Ge-SC)
								415 w	408 (30)					ν(GeS$_2$(sym))
										390 ms	382 (100)			ν(Ge-Cl)
		318 ms	310 (50)							330 m, br	300 (20)^c			ν(Ge-Cl(apex))
												267 m	271^d	ν(Ge-Br)
					202 (100)							232 m	220^d	ν(Ge-Br(apex))
							137 (100)							ν(Ge-I(apex))

^{a} Peaks are seen at 568 m, 568 (60) cm^{-1} for compound 6 and 563 m, 568 (50) cm^{-1} for compound 7 that are not assigned. See the discussion. ^{b} Correspond to ν(GeS$_2$(asym)). ^{c} Recorded in CS$_2$ solution as a broad, weak peak. ^{d} These bands are on the shoulder of the noise associated with the exciting line.

Scheme I



1.84 and 2.12 ppm, respectively, for X = Cl and Br, comparable to 1.74 and 2.02 ppm in CH_3GeCl_2Br and CH_3GeBr_3, respectively.[24] These comparisons can further be extended to the $^{13}C\{^1H\}$ NMR chemical shifts (Table IV) where again those of the dithiocarbamates can be compared to those of the bromine derivatives $(CH_3)_3GeBr$ (5.05), $(CH_3)_2GeBr_2$ (15.05), and CH_3GeBr_3 (20.37 ppm).[25] Attempts have been made to relate the values of the C=S chemical shifts to the nature of the bonding in dithiocarbamates. In $Ni[S_2CN(C_2H_5)_2]_2$ the ligands are bidentate and the C=S chemical shift is 206.4 ppm whereas in $Ir[S_2CN(C_2H_5)_2]_3(C_8H_8)$ there are one bidentate and two monodentate ligands and the chemical shifts are 205.0, 196.3, and 191.7 ppm.[26] The values obtained for these methylgermanium dithiocarbamates suggest that none should contain truly bidentate dithiocarbamate groups but that some of the values are high for monodentate linkages.

Selected features in the vibrational spectra of the methylgermanium dithiocarbamate derivatives, along with their assignments, are given in Table V.

The typical CH_3 modes, such as the CH_3-N and CH_3-Ge stretching vibrations in the 3000-2800-cm^{-1} region, the CH_3-Ge and CH_3-N rocking/wagging modes around 1130 cm^{-1}, and the distinctive CH_3-Ge rocking modes around 840 cm^{-1}, have not been included in the lists in the Table.

One obvious feature of the spectra is the similarity of the stretching bands arising form the dithiocarbamate group. The relatively high values for ν(C-N(CH$_3$)$_2$), ν(CS$_2$(asym)) or ν(C=S), and ν(CS$_2$(sym)) or ν(C-S-Ge) are all similar to those reported for analogous tin compounds.[27] This suggests that in none of the compounds is the dithiocarbamate group linked in a bidentate fashion.[28] It is also interesting to note that the asymmetric and symmetric Ge-C stretching vibrations give features in position and relative intensity that are very similar to those found in the halomethylgermanes.[29,30] In the $(CH_3)_2GeX_2$ (X = Cl, Br) species, the C-Ge-C angle is close to 120°,[31,32] so it is reasonable to assume that the same will be true for their dimethyldithiocarbamato derivatives. Further, as we found[6] for the Ge-Cl stretching vibrations in **2**, the values of ν(Ge-Br) and ν(Ge-I) are very much lower at 202 and 137 cm^{-1}, respectively, for the bromo- and iodo(dithiocarbamato)germanium compounds than is the case in $(CH_3)_2GeBr_2$ and $(CH_3)_2GeI_2$, where the average values are 279 and 231 cm^{-1}, respectively.[30,33] This suggests that all of these compounds (**2**-**4**) have the same structure containing a relatively long, pseudoaxial, Ge-X bond.

The vibrational spectra of **6** and **7** have an unexplained feature. In the Ge-C stretching region there should obviously be only *one* peak corresponding to the Ge-C stretch. The bands at 615 cm^{-1} (X = Cl) and 602 cm^{-1} (X = Br) clearly correspond to this

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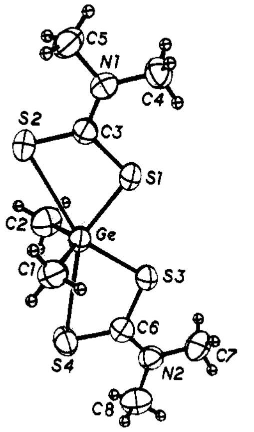
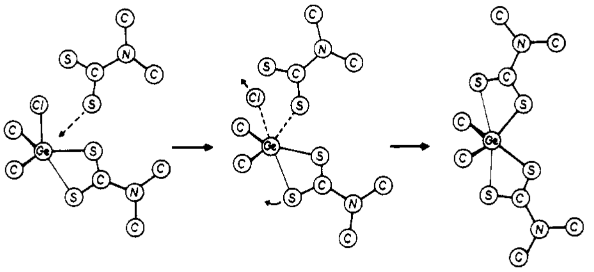


Figure 1. Structure of $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$. The thermal ellipsoids of the atoms are scaled to include 50% probability. H atoms are drawn arbitrarily small.

Scheme II



vibration in the Raman effect. However, the band at 568 cm^{-1} in both spectra defies simple explanation. There are no obvious impurities in terms of starting material, solvent, or other products that can account for this feature. The prominent band at 382 cm^{-1} (X = Cl) and 271 cm^{-1} (X = Br) suggests the presence of a normal Ge–X bond, as opposed to the unusually weak ones in compounds **2**–**4**. However, in both cases ill-defined shoulders around 300 and 220 cm^{-1}, respectively, suggest the possibility of the presence of a weak Ge–X bond, which would be indicative of the presence of both equatorial and axial Ge–X bonds.

In discussing the structure of compound **2**,[6] we pointed out that a good description was obtained by considering an attack of $(CH_3)_2NCS_2^-$ on $(CH_3)_2GeCl_2$ along the C_2 axis bisecting the Cl–Ge–Cl angle, which leaves one S atom attached in an equatorial position, wherein the two C atoms and the S atom form a plane (Scheme I). The remaining Cl atom is bent back to the axial position of a trigonal bipyramid, and the second S atom only partially occupies the vacant axial site. The structure of **5**, which is isomorphous with its tin analogue[34] and is displayed in Figure 1, can be conveniently considered as an extension of this model. Replacement of the Cl atom in **2** could result in the newly attached S atom taking up a position that is cis to the existing strongly bonded S atom, which could be forced to move in the plane away from the incoming atom (Scheme II). The new Ge–S bond would then be formed in a pseudotetrahedral position relative to the H_3C–Ge bonds with the existing Ge–S bond rotating to the other pseudotetrahedral position. The long Ge–S bonds would then have to take up the open positions to make an apparent six-coordinated structure. We have no other evidence that this is the mode of formation, but it does lead to a simple description of the structure. The four sulfur atoms form a plane that is slightly distorted with the sulfur atoms alternatively above and below their mean plane ($0.8512x - 0.3366y - 0.4028z = -4.2758$) by 0.080 (2) and 0.040 (2) Å, respectively. The Ge atom is positioned almost in the plane, and the plane bisects the C(1)–Ge–C(2) angle.

In the discussion of the NMR and vibrational spectra we have suggested that the $S_2CN(CH_3)_2$ group has a similar substituent effect as does a bromine atom. In the structural determination of $(CH_3)_2GeBr_2$ in the gas phase, the C–Ge–C angle was found to be 124 (7)°[32] compared to 126.7 (4)° in **5** while the average Ge–C bond lengths are 1.911 (12) and 1.915 (7) Å, respectively, in the two compounds. These values are remarkably similar given the difference in phases. Because four S atoms are accommodated in a plane, it is not surprising that the S–Ge–S bond angle is smaller than the Br–Ge–Br angle (87.0 (1) and 104 (2)°, respectively).

The description of the compound as pseudotetrahedral with two bonds occupying open positions seems more reasonable than a description based on a distorted octahedron, which is an alternative view. The C–Ge bonds would then be considered as trans, but the angle of 126.7 (4)° is a long way from 180°. The analogous Sn compound[34] has a similar structure but with a C–Sn–C angle of 136 (1)°, which is approximately halfway between the tetrahedral angle and linear. The similarity, in both relative intensity and position of the symmetric and asymmetric Ge–C stretch in **5** and $(CH_3)_2GeBr_2$, now seems reasonable as do the values of the chemical shifts. In other words, there is no evidence of the Ge- -S secondary bonding in the NMR or vibrational spectra. The anisobidentate ligand shows very similar features in **5** and **2** with the S–Ge- -S angle of 68.5 (1)° in the latter,[6] closing down to 65.2 (1) and 64.0 (1)° in the more crowded bis compound. The Ge–S bonds are 2.251 (1) and 2.896 (1) Å in the monosubstituted derivative[6] and average 2.278 (2) and 3.118 (2) Å in the bis compound, again reflecting the more crowded situation around the germanium atom in the latter compound. The two C–S bond distances in the mono derivatives are 1.690 (2) and 1.750 (2) Å,[6] which are comparable with the average values of 1.659 (8) and 1.753 (8) Å in the bis compound as are the average C–N and $N-CH_3$ distances of 1.318 (10) and 1.443 (10) Å.

Acknowledgment. We thank the NSERC-Strategic Grants Program—Industrial Materials and Processes for financial support.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom coordinates and isotropic thermal parameters, and mean planes data and a unit cell packing diagram (4 pages). Ordering information is given on any current masthead page.

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