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Preparation and Characterization of Trimethylgermanium−Sulfur Compounds Derived from 2-Dithiocarbamoyl-3-dithiocarbonylthiopropionate. Crystal Structures of $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ and $Me_3GeO_2C(-CHNHC(S)SCH_2-)$

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Attempts to isolate organogermanium derivatives at three different sites in a ligand prepared from cysteine are reported. The formation of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ is established by NMR spectroscopy. This derivative undergoes CS_2 elimination followed by further decomposition and rearrangement to yield $Me_3GeO_2C(-CHNHC(S)SCH_2-)$. The crystal structures of $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ and the starting salt, $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ were determined. $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (**1**) crystallizes in the hexagonal space group ($P6_5$, No. 170) with the cell parameters $a = 10.305(4)$ Å, $b = 10.305(4)$ Å, $c = 23.740(5)$ Å, $V = 2183(1)$ Å^3, $Z = 6$, $R = 0.0553$, $R_w = 0.0438$. $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ (**4**) crystallizes in the orthorhombic space group ($P2_12_12_1$, No. 19) with the cell parameters $a = 10.463(6)$ Å, $b = 22.644(5)$ Å, $c = 10.241(5)$ Å, $V = 2426(1)$ Å^3, $Z = 4$, $R = 0.0571$, $R_w = 0.0472$. The immediate environment about Ge is that of tetrahedral with the orientation of the terminal C═O bond being toward germanium. The Ge- - -O distance of 3.02(1) Å is clearly less that the sum of the van der Waals radii of germanium and oxygen raising the possibility of a weak interaction. A plausible mechanism for the conversion of $Me_3GeCSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ into $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ is proposed.

Introduction

Extensive studies have been reported over the years on dithiocarbamate derivatives,[1−3] including several by ourselves on organogermanium derivatives.[4−6] By contrast, the chemistry of trithiocarbonates has received considerably less attention, possibly because of the relative ease with which their derivatives undergo carbon disulfide elimination.[7−9] Most of the reports on trithiocarbonates relate to transition metal derivatives and very little has appeared with regard to main group elements, especially with respect to structural and spectroscopic studies, other than two reports by us on organogermanium derivatives.[10,11] Reaction of CS_2 with cysteine in the presence of ammonia gives a dithiocarbamate-trithiocarbonate, which can be isolated as the ammonium salt, triammonium 2-dithiocarbamoyl-3-dithiocarbonylthiopropanoate.[9] This salt has the potential to produce interesting ligand chemistry because it contains three different sites in the same molecule which can bond to metal centers. As a preliminary to exploring the utility of this ligand, the preparation and characterization of the salt, including an X-ray structure, is presented in this paper along with an examination of the reactivity of the ligand toward trimethylgermane.

Experimental Section

Starting Materials. Me_3GeCl, Me_3GeBr, Me_3GeI, Ph_3GeCl, Ph_3GeBr, and Ph_2GeCl_2, were obtained from Aldrich and Strem Chemicals; all starting materials being used as supplied. All solvents were dried and distilled prior to use, and all reactions were carried out under anhydrous conditions. The preparation of the ammonium salt, $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (**1**), from cysteine was based on the method described in the literature.[12,13] Typically, cysteine (4.5 g, 37.2 mmol) was dissolved in distilled water (ca. 20 mL), followed by slow addition of ammonia solution (ca. 20 mL). After stirring for 1 h at room temperature, CS_2 (ca. 10 mL) was added slowly, and stirring was continued for another 1 h before previously ice-cooled anhydrous ethanol (ca. 200 mL) was added. Yellow crystals of $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (**1**) (ca. 9.0 g, 27.8 mmol, yield 75%) slowly came out of the solution on standing. IR (cm^{-1}) main features: 3400 mw vbr, 1660 ms, 1554 vs, 1274 vs, 1236 s, 1178 s, 1098 ms, 994 vs, 924 s. ^{1}H NMR (D_2O referenced to DSS) for $S_2CSCH_aH_bCH_x(NH_nCS_2)CO_2$: δ 3.82 [$J_{ab} = 14.1$, $J_{ax} = 3.9$ Hz] (H_a); 3.74 [$J_{ba} = 14.1$, $J_{bx} = 9.2$ Hz] (H_b); 4.95 [$J_{ax} = 3.9$, $J_{bx} = 9.2$ Hz] (H_x); 4.89 [broad] (NH_n).

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^{13}C NMR (D_2O referenced to DSS) for $S_2CSCH_2CH(NHCS_2)CO_2$: δ 43.71 (CH_2); 63.52 (CH); 177.95 (CO_2); 212.62 (S_2CN); 246.71 (S_2CS). The corresponding data for L-cysteine for comparison. ^{1}H NMR (D_2O referenced to DSS): δ for $HCSCH_aH_bCH_x(NH_2)CO_2H$; 3.08 [$J_{ab} = 15.0$, $J_{ax} = 4.0$ Hz] (H_a); 3.00 [$J_{ba} = 15.0$, $J_{bx} = 5.7$ Hz] (H_b); 3.97 [$J_{ax} = 4.0$, $J_{bx} = 4.0$ Hz] (H_x); 4.89 [broad] (NH_n). ^{13}C NMR (D_2O referenced to DSS): δ for $HCSCH_2CH_x(NH_2)CO_2H$; 25.48 (CH_2); 56.58 (CH_x); 173.18 (CO_2).

Preparation of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (2). Typically, Me_3GeCl (0.5 mL, 4.05 mmol) or Me_3GeBr or Me_3GeI and CS_2 (ca. 15 mL) were distilled into a flask held at −196 °C into which the salt (**1**) (0.60 g, 1.86 mmol) had been previously charged. The mixture was stirred for 4 h before the unreacted salt and any ammonium salt formed was filtered off. Solvent was pumped off the filtrate to give a liquid product, $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**2**) (0.65 g, 1.05 mmol, yield 78%). ^{1}H NMR ($CDCl_3$) for $(CH_3)_3GeS_2CSCH_aH_bCH_x[NH_nCS_2Ge(CH_3)_3]CO_2Ge(CH_3)_3$: δ 0.72 (s) [$(CH_3)_3GeS_2CS$]; 0.71 (s) [$(CH_3)_3GeS_2CN$]; 0.61 (s) [$(CH_3)_3GeO_2C$]; 4.11 [$J_{ab} = 13.9$, $J_{ax} = 8.2$ Hz] (H_a); 3.91 [$J_{ba} = 13.9$, $J_{bx} = 8.3$ Hz] (H_b); 5.28 [$J_{ax} = 8.2$, $J_{bx} = 8.3$, $J_{nx} = 6.9$ Hz] (H_x); 7.90 [doublet, $J_{nx} = 6.9$ Hz] (NH_n). ^{13}C NMR ($CHCl_3$) for $(CH_3)_3GeS_2CSCH_2CH(NHCS_2Ge(CH_3)_3)CO_2Ge(CH_3)_3$: δ 2.82 [$(CH_3)_3GeS_2CS$]; 2.82 [$(CH_3)_3GeS_2CN$]; 1.92 [$(CH_3)_3GeO_2C$]; 39.98 (CH_2); 58.64 (CH); 171.39 (CO_2); 197.93 (S_2CN); 225.06 (S_2CS).

Decomposition Products of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (2). The decomposition of **2** was monitored by NMR spectroscopy leading to the identification of an intermediate product $Me_3GeSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**3**) and the isolatable final product $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ (**4**). ^{1}H NMR ($CDCl_3$) for $(CH_3)_3GeSCH_aH_bCH_x[NH_nCS_2Ge(CH_3)_3]CO_2Ge(CH_3)_3$ **(3)**: δ 0.49 (s) [$(CH_3)_3GeCS$]; 0.74 (s) [$(CH_3)_3GeS_2CN$]; 0.63 (s) [$(CH_3)_3GeO_2C$]; 3.23 [$J_{ab} = 13.0$, $J_{ax} = 7.5$ Hz] (H_a); 3.07 [$J_{ba} = 13.0$, $J_{bx} = 6.7$ Hz] (H_b); 5.16 [$J_{ax} = 7.5$, $J_{bx} = 6.7$, $J_{nx} = 6.3$ Hz] (H_x); 8.02 [doublet, $J_{nx} = 6.3$ Hz] (NH_n). ^{13}C NMR ($CHCl_3$) for $(CH_3)_3GeSCH_2CH(NHCS_2Ge(CH_3)_3)CO_2Ge(CH_3)_3$ **(3)**: δ 1.76 [$(CH_3)_3GeS$]; 2.87 [$(CH_3)_3GeS_2CN$]; 2.02 [$(CH_3)_3GeO_2C$]; 28.08 (CH_2); 60.68 (CH); 171.87 (CO_2); 197.27 (S_2CN). ^{1}H NMR ($CDCl_3$) for $(CH_3)_3GeO_2C(-CHNHC(S)SCH_2-)$ (**4**): δ 0.64 (s) [$(CH_3)_3GeO_2C$]; 3.76 [$J_{ab} = 11.3$, $J_{ax} = 8.2$ Hz] (H_a); 3.71 [$J_{ba} = 11.3$, $J_{bx} = 8.2$ Hz] (H_b); 4.74 [$J_{ax} = J_{bx} = 8.2$ Hz] (H_x); 8.02 [broad] (NH_n). ^{13}C NMR ($CHCl_3$) for $(CH_3)_3GeO_2C(\text{-}CHNHC(S)SCH_2-)$ (**4**): δ 1.98 [$(CH_3)_3GeO_2C$]; 35.83 (CH_2); 64.92 (CH); 170.51 (CO_2); 200.98 (S_2CN). The identification of **4** was confirmed by X-ray crystallography.

Attempted Preparations of Other Organogermane Derivatives, Such as $Ph_3GeS_2CSCH_2CH(NHCS_2GePh_3)CO_2GePh_3$ and $Ph_2XGeS_2CSCH_2CH(NHCS_2GePh_2X)CO_2GePh_2X$ (X = Cl, Br). Substitution of Me_3GeX (X = Cl, Br, I) by Ph_2GeCl_2, Ph_3GeCl, or Ph_3GeBr as starting materials resulted in no reaction taking place, even though several solvents, various temperatures, and longer reaction times were attempted.

Physical Measurements. The infrared spectra were recorded on a Nicolet 5DX FT spectrometer as KBr pellets or oils smeared between KBr windows in the region 4000−400 cm^{-1}, and far-infrared spectra on a Bomem DA3 infrared spectrometer between polyethylene films as oils or Nujol mulls. The Raman spectra were recorded on samples in sealed glass capillaries on a JEOL-XY Raman spectrometer using the 5145 Å exciting line of an argon ion laser. The ^{1}H and ^{13}C{H} NMR spectra were recorded on a Bruker 300 FT/NMR spectrometer at 300.133 and 75.471 MHz, respectively, in $CDCl_3$ using Me_4Si as internal standard. All NMR spectra were run at ambient temperature and under standard operating conditions. The melting points were determined on a Fisher-Johns apparatus.

X-ray Crystallographic Analysis. A yellow needlelike crystal of **1** and a colorless block crystal of **4** were sealed on a glass fiber and in a glass capillary, respectively and mounted on a Rigaku AFC6S diffractometer, with graphite-monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $20.28 < 2\theta < 26.49°$ for **1** and $7.79 < 2\theta < 12.17°$ for **4** corresponded to primitive hexagonal and primitive orthorhombic cells, respectively for **1** and **4** whose dimensions are given in Table 1. Based on the systematic absences ($000l$, $l = 6n + 1$) for **1** and ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) for **4**, statistical analyses of intensity distribution, and the successful solution and refinement of the structure, the space groups were determined to be $P6_5$ (No. 170) and $P2_12_12_1$ (No. 19), for **1** and **4**, respectively.

Table 1. Crystallographic Data for $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (**1**) and $[Me_3GeO_2C(-CHNHC(S)SCH_2-)]_2$ (**4**)

	1	**4**
fw, g mol^{-1}	324.51	559.79
a, Å	10.305(4)	10.463(6)
b, Å	10.305(4)	22.644(5)
c, Å	23.740(5)	10.241(5)
α, deg	90.000	90.000
β, deg	90.000	90.000
γ, deg	120.00	90.000
V, Å^3	2183(1)	2426(1)
space group	$P6_5$	$P2_12_12_1$
Z	6	4
ρ_{calcd}, g cm^{-3}	1.48	1.53
T, °C	23	23
μ, cm^{-1}	7.98	28.40
R^a	0.0555	0.0571
$R_w{}^b$	0.0438	0.0472

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

The data were collected at a temperature of 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.0°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.31 and 0.32°, for **1** and **4**, respectively, with a takeoff angle of 6.0°. Scans of $(1.68 + 0.30 \tan\theta)°$ (**1**) and $(1.42 + 0.30 \tan\theta)°$ (**4**) were made at speeds of 32.0 and 16.0°/min (in ω) for **1** and **4**, respectively. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of four scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, and the crystal-to-detector distance was 285 mm.

Totals of 862 (**1**) and 2471 (**4**) reflections were collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficients for Mo Kα are 7.9 and 28.4 cm^{-1} for **1** and **4**, respectively. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.70 to 1.00 (**1**) and from 0.57 to 1.00 (**4**). The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods.[14] The sulfur atoms in **1** and the germanium atoms in **4** were refined anisotropically while the rest were refined isotropically. Hydrogen atoms, with the exception of H(13) in **4** which was located in the difference Fourier map, were included in their idealized position with C−H or N−H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement[15] was based on 495 (**1**) and 840 (**4**) observed reflections ($I > 3.00\ \sigma(I)$) and 88 (**1**) and 115 (**4**) variable parameters and converged (largest parameter shift was 0.001 times its esd) with weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0553$ (**1**) and 0.0571 (**4**), and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2} = 0.0438$ (**1**) and 0.0472 (**4**). The structures were inverted to ensure that the final refinement was carried out on the correct enantiomer.

The standard deviation of an observation of unit weight[16] was 2.03 (**1**) and 1.77 (**4**). The weighting scheme was based on counting statistics

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(15) Least-squares: Function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o{}^2(F_o{}^2)$, $\sigma^2(F_o{}^2) = [S^2(C + R^2B) + (pF_o{}^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, Lp = Lorentz−polarization factor, and p = p factor.

Table 2. Final Fractional Coordinates and *B*(eq) for Non-Hydrogen Atoms of $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2$ (**1**) with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	*B*(eq)
S(1)	0.3239(4)	0.3209(3)	0.0440	2.9(1)
S(2)	0.0073(4)	0.2565(4)	0.0406	4.5(2)
S(3)	0.0584(3)	0.0079(3)	0.0439(2)	3.0(1)
S(4)	0.0809(4)	−0.3238(4)	−0.1148(2)	3.8(2)
S(5)	0.3911(4)	−0.0532(3)	−0.1088(2)	3.5(1)
O(1)	0.3987(8)	−0.1866(8)	0.0397(4)	2.7(2)
O(2)	0.5427(8)	0.0622(8)	0.0457(4)	3.0(2)
N(1)	0.193(1)	−0.1541(9)	−0.0255(4)	1.9(2)
N(2)	0.293(1)	−0.428(1)	−0.0344(5)	3.0(2)
N(3)	0.294(1)	0.580(1)	0.1300(5)	3.2(2)
N(4)	0.711(1)	−0.075(1)	0.0917(5)	3.5(2)
C(1)	0.136(1)	0.202(1)	0.0436(7)	2.9(2)
C(2)	0.208(1)	−0.026(1)	0.0631(6)	2.8(2)
C(3)	0.296(1)	−0.032(1)	0.0095(5)	1.5(2)
C(4)	0.221(1)	−0.171(1)	−0.0780(5)	2.0(2)
C(5)	0.422(1)	−0.056(1)	0.0330(5)	1.8(2)

and included a factor ($p = 0.002$ and 0.009 for **1** and **4**, respectively) to downweight the intense reflections. Plots of $w\Sigma(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and −0.31 e/A^3, respectively, for **1** and to 0.53 and −0.49 e/Å^3, respectively, for **4**.

Neutral-atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_c;[18] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[19] All calculations were performed using the TEXSAN[20] crystallographic software package of Molecular Structure Corp.

The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables 2 and 3, and important distances and bond angles are given in Tables4 and 5. ORTEP diagrams of **1** and **4** are given in Figures 1 and 2. Additional crystallographic data are available as Supporting Information.

Results and Discussion

The salt triammonium 2-dithiocarbamoyl-3-dithiocarbonylthiopropanoate, $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (**1**), is prepared in good yield by a method based on that described in the literature,[12,13] involving the reaction of cysteine with an ammonia solution and carbon disulfide, in accord with eq 1.

$$HSCH_2CH(NH_2)CO_2H + 3NH_3{\cdot}H_2O + 2CS_2 \rightarrow [NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2] \quad (1)$$

The subsequent reaction of a trimethylgermanium halide with **1** results in the formation of a compound, $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**2**), in which all of the potential sites are occupied by trimethylgermane in accord with eq 2.

$$3Me_3GeX + [NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2] \rightarrow Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3 + 3NH_4X \quad (2)$$

Table 3. Atomic Coordinates and *B*(eq) of Non-Hydrogen Atoms for $[Me_3GeO_2C(-CHNHC(S)SCH_2-)]_2$ (**4**)

atom	*x*	*y*	*z*	*B*(eq)
Ge(1)	0.0928(3)	0.5216(1)	0.1038(3)	3.9(1)
Ge(2)	0.1284(3)	0.7633(1)	−0.3671(3)	4.4(2)
S(1)	−0.4030(7)	0.4531(3)	0.2127(7)	4.5(2)
S(2)	−0.5634(7)	0.5607(3)	0.2166(8)	5.8(2)
S(3)	−0.3709(7)	0.7718(3)	−0.1654(7)	4.5(2)
S(4)	−0.4815(6)	0.6512(3)	−0.1451(8)	4.9(2)
O(1)	−0.068(1)	0.4929(6)	0.057(1)	3.4(4)
O(2)	−0.162(2)	0.5787(8)	0.050(2)	4.3(4)
O(3)	0.034(1)	0.7513(7)	−0.219(2)	4.4(4)
O(4)	−0.116(2)	0.6960(7)	−0.312(2)	6.5(5)
N(1)	−0.400(2)	0.5297(8)	0.029(2)	3.6(4)
N(2)	−0.247(2)	0.6832(8)	−0.082(2)	2.5(4)
C(1)	0.180(2)	0.450(1)	0.110(3)	4.8(6)
C(2)	0.070(3)	0.558(1)	0.274(3)	5.7(7)
C(3)	0.141(2)	0.578(1)	−0.035(2)	5.2(7)
C(4)	−0.166(2)	0.528(1)	0.043(2)	4.2(6)
C(5)	−0.288(2)	0.492(1)	−0.002(3)	5.0(7)
C(6)	−0.455(2)	0.520(1)	0.142(2)	3.2(5)
C(7)	−0.312(2)	0.435(1)	0.078(2)	4.1(6)
C(8)	0.158(3)	0.688(1)	−0.441(3)	6.9(8)
C(9)	0.279(3)	0.799(1)	−0.293(3)	8(1)
C(10)	0.028(3)	0.816(1)	−0.481(3)	6.9(8)
C(11)	−0.077(2)	0.722(1)	−0.216(2)	3.0(5)
C(12)	−0.145(2)	0.727(1)	−0.092(2)	3.6(6)
C(13)	−0.362(2)	0.6960(9)	−0.123(2)	2.8(5)
C(14)	−0.222(3)	0.786(1)	−0.087(3)	5.9(8)

Table 4. Important Interatomic Distances (Å) and Angles (deg) for $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (**1**)[a]

S(1)−C(1)	1.70(2)	S(2)−C(1)	1.67(2)
S(3)−C(1)	1.75(2)	S(3)−C(2)	1.81(2)
S(4)−C(4)	1.75(1)	S(5)−C(4)	1.72(2)
O(1)−C(5)	1.26(2)	O(2)−C(5)	1.27(1)
N(1)−C(3)	1.44(2)	N(1)−C(4)	1.31(2)
C(2)−C(3)	1.58(2)	C(3)−C(5)	1.54(2)
S(1)- - -N^{I}(2)	3.33(1)	S(1)- - -N(3)	3.49(1)
S(2)- - -N^{II}(4)	3.47(1)	S(3)- - -N(4)	3.43(1)
S(4)- - -N^{III}(4)	3.23(2)	S(4)- - -N^{IV}(4)	3.37(1)
S(4)- - -N(2)	3.45(1)	S(5)- - -N^{V}(3)	3.40(2)
O(1)- - -N(2)	2.79(2)	O(1)- - -N^{VI}(3)	2.99(2)
O(1)- - -N(4)	3.09(2)	O(2)- - -N^{VII}(3)	2.91(3)
O(2)- - -N^{VIII}(2)	2.94(2)	O(2)- - -N(4)	2.94(2)
S(1)−C(1)−S(2)	125(1)	S(1)−C(1)−S(3)	122(1)
S(2)−C(1)−S(3)	113.5(9)	C(1)−S(3)−C(2)	106.3(7)
S(3)−C(2)−C(3)	111(1)	C(2)−C(3)−C(5)	105(1)
C(2)−C(3)−N(1)	108(1)	C(2)−C(5)−N(1)	113(1)
C(3)−N(1)−C(4)	123(1)	N(1)−C(4)−S(4)	117(1)
N(1)−C(4)−S(5)	122(1)	S(4)−C(4)−S(5)	121(1)
C(3)−C(5)−O(1)	120(1)	C(3)−C(5)−O(2)	116(1)
O(1)−C(5)−O(2)	113(1)		

[a] Numbers in parentheses refer to estimated standard deviations in the least-significant digits. [b] Symmetry equivalent positions: $^{I}x, 1 + y, z$; $^{II}x - 1, y, z$; $^{III}-y, x - y - 1, ^2/_3 + z - 1$; $^{IV}x - y - 1, x - 1, ^5/_6 + z - 1$; $^{V}1 - y, x - y, ^2/_3 + z - 1$; $^{VI}x, y - 1, z$; $^{VII}1 + x - y, x, ^5/_6 + z - 1$; $^{VIII}1 + y, 1 - x + y, ^1/_6 + z$.

This reaction takes place readily whether trimethylgermanium chloride, bromide or iodide are used as starting materials, whether CS_2 or CH_2Cl_2 are used as solvents or whether the reaction is run at room temperature or at −78 °C. However, substitution of Me_3GeX (X = Cl, Br, I) by Ph_2GeCl_2, Ph_3GeCl, or Ph_3GeBr as starting materials, surprisingly, did not result in any reaction taking place even though several solvents, various temperatures, and longer reaction times were attempted.

As with most trithiocarbonate compounds,[9] $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**2**) is sensitive to air and moisture. It also readily undergoes CS_2 elimination from the S_2CS site, as was found for the analogous trithiocarbonate derivatives,[10,11] to give $Me_3GeSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**3**)

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(16) Standard deviation of an observation of unit weight: $[\Sigma w(|F_o| - |F_c|)^2/N_o - N_v)^{1/2}$, where N_o = number of observations, and N_v = number of variables.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(18) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(19) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(20) *TEXSAN−TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

Table 5. Important Interatomic Distances (Å) and Angles (deg) for $[Me_3GeO_2C(-CHNHC(S)SCH_2H-)]_2$ (**4**)[a]

Ge(1)−O(1)	1.87(1)	Ge(2)−O(3)	1.83(2)
Ge(1)−C(1)	1.85(2)	Ge(2)−C(8)	1.89(3)
Ge(1)−C(2)	1.94(3)	Ge(2)−C(9)	1.93(3)
Ge(1)−C(3)	1.97(3)	Ge(2)−C(10)	1.97(3)
O(1)−C(4)	1.30(3)	O(3)−C(11)	1.34(2)
O(2)−C(4)	1.15(3)	O(4)−C(11)	1.22(2)
C(4)−C(5)	1.58(3)	C(11)−C(12)	1.46(3)
N(1)−C(5)	1.48(3)	N(2)−C(12)	1.46(3)
N(1)−C(6)	1.31(2)	N(2)−C(13)	1.31(2)
S(2)−C(6)	1.65(2)	S(4)−C(13)	1.63(2)
S(1)−C(6)	1.77(2)	S(3)−C(13)	1.77(2)
S(1)−C(7)	1.73(3)	S(3)−C(14)	1.79(3)
C(5)−C(7)	1.55(3)	C(12)−C(14)	1.56(3)
Ge(1)- - -O(2)	3.01(3)	Ge(1)- - -O(2)	3.03(3)
N(2)- - -O(2)	2.87(2)		
O(1)−Ge(1)−C(1)	98.6(9)	O(3)−Ge(1)−C(8)	107(1)
O(1)−Ge(1)−C(2)	105.5(9)	O(3)−Ge(1)−C(9)	100(1)
O(1)−Ge(1)−C(3)	105.6(9)	O(3)−Ge(1)−C(10)	107.3(9)
C(1)−Ge(1)−C(2)	114(1)	C(8)−Ge(2)−C(9)	114(1)
C(2)−Ge(1)−C(3)	114(1)	C(9)−Ge(2)−C(10)	113(1)
C(1)−Ge(1)−C(3)	117(1)	C(8)−Ge(2)−C(10)	114(1)
Ge(1)−O(1)−C(4)	122(2)	Ge(2)−O(3)−C(11)	124(2)
O(1)−C(4)−O(2)	125(3)	O(3)−C(11)−O(4)	121(2)
O(1)−C(4)−C(5)	111(2)	O(3)−C(11)−C(12)	114(2)
O(2)−C(4)−C(5)	124(2)	O(4)−C(11)−C(12)	125(2)
N(1)−C(5)−C(4)	106(2)	N(2)−C(12)−C(11)	112(2)
N(1)−C(5)−C(7)	104(2)	N(2)−C(12)−C(14)	1024(2)
S(1)−C(6)−N(1)	112(2)	S(3)−C(13)−N(2)	110(2)
S(1)−C(6)−S(2)	120(1)	S(3)−C(13)−S(2)	122(1)
S(2)−C(6)−N(1)	128(2)	S(4)−C(13)−N(2)	128(2)
C(5)−N(1)−C(6)	116(2)	C(12)−N(2)−C(13)	120(2)
C(4)−C(5)−C(7)	114(2)	C(11)−C(12)−C(14)	110(2)

[a] Numbers in parentheses refer to estimated standard deviations in the least-significant digits.

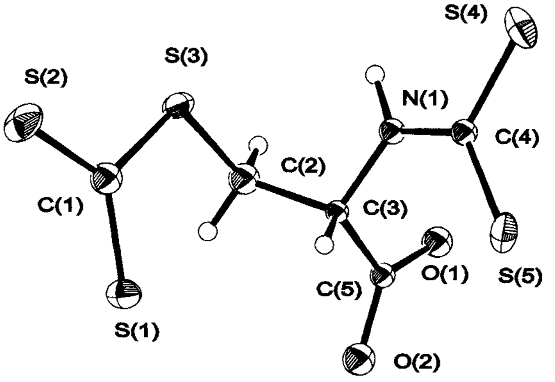

Figure 1. ORTEP plot of the anion of the molecule $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (**1**). The atoms are drawn with 30% probability ellipsoids and spheres.

in accord with eq 3.

$$Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3 \rightarrow Me_3GeSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3 + CS_2 \quad (3)$$

The CS_2 elimination can be followed over time by ^1H and ^{13}C NMR spectra. In the ^{13}C NMR spectrum, the peaks attributable to CS_2 and to the intermediate decomposition product **3** appear and increase in intensity, as those attributable to the original compound **2** decrease, until they totally disappear after several hours at room temperature. Compound **3** undergoes further decomposition, which is clearly more complicated and not only involves CS_2 elimination from the $NHCS_2$ site but also rearrangements that lead to a variety of unidentifiable dissociation products. Fortunately, one of these is obtained as colorless crystals which resulted in its identification by X-ray structural investigation as 4-(trimethylgermyl)oxycarbonylthiazolidin-2-thione, $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ (**4**), whose melting point is 98 °C. A reasonable mechanism to this product is presented in Figure 3.

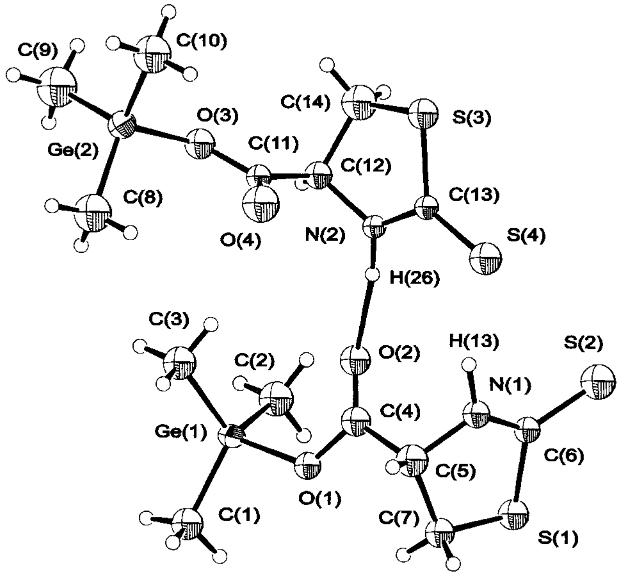

Figure 2. ORTEP plot of the molecule $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ (**4**). The atoms are drawn with 30% probability ellipsoids and spheres.

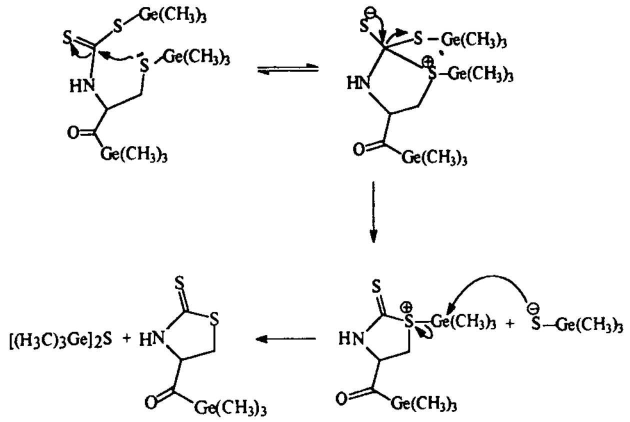

Figure 3. Reasonable mechanism for the decomposition of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**2**) to $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ (**4**).

Molecular Structures of $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$ (1) and $Me_3GeO_2C(-CHNHC(S)SCH_2-)$ (4). Triammonium 2-dithiocarbamoyl-3-dithiocarbonylthiopropanoate (**1**) crystallizes in the space group *P*6_5 (No. 170). The ORTEP diagram (Figure 1) shows, along with Table 4, that the ammonium cations are, as expected, associated with the three obvious sites in the anion, S_2CS, S_2CN, and CO_2. Thus the closest S- - -NH_4 distances are 3.33(1) and 3.58(1) Å for S(1)- - -NH_4 and S(2)- - -NH_4, respectively, in the S_2CS site, and 3.23 and 3.40(2) Å for S(4)- - -NH_4 and S(5)- - -NH_4, respectively, in the S_2CNH site. These distances are comparable to the average K- - -S distance (3.4(1) Å) in KS_2COEt.[21] The closest O- - -N distances at the CO_2 site are 2.79(2) and 2.94(2) Å for O(1)- - -NH_4 and O(2)- - -NH_4, respectively. All S- - -N distances less than 3.5 and all O- - -N distances less than 3.1 Å are listed in Table 4. Unfortunately, the limited amount of data makes the resolution such that hydrogen atoms on the ammonium ions could not be detected. However, these distances

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(21) Mazzi, F.; Tachini, C. *Z. Kristallogr.* **1963**, *118*, 378.

are comparable with N- - -O distances for N−H- - -O hydrogen bonds being typically in the range 2.8−3.0 Å.[22]

Within the S_2CSC moiety in **1**, the average C−S(terminal) distances of 1.685(21) Å can be compared with the value of 1.628(8) for the C═S(terminal) bonds in $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$10 and $Me_2Ge[S_2CSEt]_2$,[11] where the bond is presumably close to having a bond order of 2. This is consistent with the π-bond delocalization resulting in bond orders for C(1)−S(1) and C(1)−S(2) of approximately 1.5. The average $S_2C(1)-S(3)$ bond length of 1.75(2) Å is essentially identical to the corresponding bonds in $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ and $Me_2Ge[S_2CSEt]_2$ (av 1.75(2) Å) as is the $S_2C(2)-S(3)$ bond length of 1.81(2) Å. Thus in this salt, **1**, or in the trithiocarbonate derivatives, the π-bond delocalization extends to the S_2C-SC bonds but probably not to the S_2CS-C bonds. Within the S_2CNHC moiety in **1**, the average C−S(terminal) distances of 1.735(21) Å is considerably longer than in the S_2CS group suggesting that there is competition from greater π-bond participation in the C−N bond which is relatively short, 1.31(2) Å. Further the C(3)−N(1)-C(4) angle of 123(1)° is indicative of a planar nitrogen atom. Within the O_2CS moiety in **1**, the average C−O(terminal) distance of 1.265(7) Å is larger than the value of 1.19(2) for the C═O(terminal) bonds in $Ph_3Ge[SCO_2Me]$, $Ph_3Ge[SCO_2(i\text{-}Pr)]$, and $Ph_2Ge[SCO_2(i\text{-}Pr)]_2$,[11] where the bond is presumably close to having a bond order of 2. As with the terminal CS_2 groups, this is consistent with the π-bond delocalization resulting in bond orders for C(5)−O(1) and C(5)−O(2) of approximately 1.5. The terminal C−S and C−O bond lengths in **1** can also be compared to those in the salt, KS_2COEt, which average 1.68(5) for the former and 1.35(6) for the latter.

4-(Trimethylgermyl)oxycarbonylthiazolidin-2-thione (**4**) crystallizes in the space group $P2_12_12_1$ (No. 19). The ORTEP diagram in Figure 2 and Table 5 indicate that the immediate environment about germanium is that of a distorted tetrahedron. In trithiocarbonates and monothiocarbonates,[11] the average values of the C−Ge−C angles were larger (e.g. 110.8(4)° in $Ph_3Ge[SCO_2Me]$) than the S−Ge−C angles (108(6)°) and one of the S−Ge−C angles was considerably smaller (100.4(3)°) than the other two. The same general pattern is noted for **4** except that the presence of a Ge−O rather than a Ge−S bond results in larger C−Ge−C angles, an average of 114(1)° for the two independent molecules in the asymmetric unit, a smaller O−Ge−C angle (av 99.3(10)°) essentially the same as in $Ph_3Ge[SCO_2R]$ derivatives and therefore the other two O−Ge−C angles smaller (av 106.4(9)°) than in $Ph_3Ge[SCO_2Me]$ (111.8(15)°) and $Ph_3Ge[SCO_2(i\text{-}Pr)]$ (110.7(27)°). The average Ge−C bond length of 1.93(5) Å is comparable to values typical of those in dithiocarbamates such as 1.927(2) Å in $Me_2GeCl[S_2CNMe_2]$,[4] trithiocarbonates such as 1.94(1) Å in $Me_2Ge[S_2CSEt]_2$,[11] and monothiocarbonates, 1.931(9)−1.950(9) Å in $Ph_3Ge[SCO_2Me]$ and 1.93(1) to 1.94(1) Å in $Ph_3Ge[SCO_2(i\text{-}Pr)]$.[11] The average Ge−O bond length of 1.85(3) Å is between that found in $Ph_3COGePh_3$ (1.945 Å)[23] and $Ph_3GeOGePh_3$ (av 1.76 Å),[24] is longer than in typical germanates (1.74−1.78 Å),[25] but is shorter than the sum of the covalent radii of 1.96 Å.[26]

The terminal C═O bond length of 1.19(5) Å is essentially the same as in the monothiocarbonates $Ph_3Ge[SCO_2R]$ and close to the expected value for a C═O double bond. Similarly, the orientation is such that the Ge- - -O nonbonding distance of 3.02(1) Å is slightly shorter than those in $Ph_3Ge[SCO_2Me]$ and $Ph_3Ge[SCO_2(i\text{-}Pr)]$ and less than the sum of the van der Waals radii of 3.47 Å. However, the intramolecular interactions, if any, must be extremely weak. By contrast, the two independent molecules in the asymmetric unit of **4** are related by the presence of a hydrogen bond between N(2) and O(2) which are separated by 2.87(2) Å, which is typical of the distance of an N−H- - -O hydrogen bond. The thermal parameters of O(2) and N(2) are smaller than those of O(4) and N(1), which is also consistent with hydrogen bonding between the former. Unfortunately, it was not possible to detect the hydrogen atom attached to N(2) in the difference Fourier map, although the hydrogen atom attached to N(1), which is not hydrogen bonded, was detected, so H(26) is set in an idealized position. As with the dithiocarbonates, the GeO−C bond length is, as expected, longer (av 1.32(4) Å) than the C═O, but still considerably shorter that the sum of the covalent radii of C and O of 1.51 Å. The degree of π character is also indicated by the Ge−O−C bond angle of 123(1)°.

The angles within the ring system range from 118(3)° for C−N−C, emphasising the essentially trigonal planar environment about N, to 92(1)° for C−S−C, emphasizing the tendency of R_2S compounds to have angles closer to 90°. The three angles involving a carbon center range from 103(1)° for N−C−C to 111(1)° for N−C−S, with S−C−C falling in the middle at 107(1)°. The angles about the carbon atom in the NC(S)S group add up to 360°, as expected for the planar carbon atom, with S−C═S and N−C═S having values of 121(1) and 128(1)°, respectively, which suggests less delocalization of the π-bond into the former than the latter. The terminal C═S bond length of 1.64(3) Å in **4** is comparable to that in the trithiocarbonates, $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$[10] and $Me_2Ge[S_2CEt]_2$, 1.63(1) Å.[11] The average C−SC and S−CS bond lengths of 1.77(3) Å in **4** are apparently slightly shorter than those of the C−SC bond in the trithiocarbonates (av 1.82(1) Å) but slightly longer than the S−CS bond in these trithiocarbonates (av 1.74(2) Å) as well as in dithiocarbamates such as $Me_2Ge[S_2CNMe_2]_2$ and $Me_2GeCl[S_2CNMe_2]$ (av 1.75(1) Å).[5,4] The CN−C and S_2C-N bond lengths of 1.47(2) and 1.31(1) Å, respectively are essentially the same as in the dithiocarbamates $Me_2Ge[S_2CNMe_2]_2$ and $Me_2GeCl[S_2CNMe_2]$ (1.45(1) and 1.32(1) Å, respectively), indicating that in this dithiocarbamate fraction which is part of a ring system, the π-electron delocalization in the S_2CN group is essentially the same as in those attached to germanium.

Nuclear Magnetic Resonance Spectra. In the ^1H NMR spectrum of L-cysteine, $HSCH_aH_bCH_x(NH_2)(CO_2H)$, in D_2O, the protons attached to carbon display patterns typical of ABX systems. The first of the two bands of peaks, which is attributable to $CH_x(NH_2)$, is seen at 3.97 ppm (X of ABX with $J_{ax} = 4.0$ and $J_{bx} = 5.7$ Hz) while in the second band, which is attributable to SCH_aH_b, H_a is seen at 3.08 ppm (A of ABX, $J_{ab} = 15$, $J_{ax} = 4.0$ Hz) and H_b at 3.00 ppm (B of ABX, $J_{ab} = 15$, $J_{bx} = 5.7$ Hz). The coupling constants were obtained by simulation using the program "PANIC". With this as a basis, the ^1H NMR spectrum in D_2O of the salt, $[NH_4]_3[S_2CSCH_aH_bCH_x(NHCS_2)CO_2]$ (**1**), similarly shows characteristics of an ABX system with the band attributable to CH_x at 4.95 ppm (X of ABX with $J_{ax} = 3.9$ Hz, $J_{bx} = 9.2$ Hz) and that attributable to CH_aH_b has H_a at 3.82 ppm (A of ABX, $J_{ab} = 14.1$, $J_{ax} = 3.9$ Hz) and H_b at 3.75 ppm (B of ABX, $J_{ba} = 14.1$, $J_{bx} = 9.2$ Hz).

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In the ^{13}C NMR spectrum of the salt, the chemical shifts for SCH_aH_b and CH_x are 43.71 and 63.52 ppm, respectively, compared to 25.48 and 56.58 ppm for the corresponding L-cysteine. The chemical shifts of 246.71 ppm for S_2CS, 212.62 ppm for S_2CN, and 177.95 ppm for $CHCO_2$ compare well with those of the corresponding simpler salts, KS_2CSR (ca. 248.0 ppm), NaS_2CNR_2 (ca. 210.0 ppm), and KO_2COR (ca. 180.0 ppm) (R = alkyl groups). The salt is relatively stable in the solid state at room temperature, as is demonstrated by the fact that an adequate X-ray structure determination was achieved. However, in D_2O solution, it is clear that carbon disulfide elimination takes place. Thus, when the sample is left in an NMR tube at room temperature, a peak at 192.7 ppm attributable to CS_2 emerges in the ^{13}C NMR spectrum after ca. 24 h. This peak gradually increases in intensity while there is a corresponding decline in the intensity of the signal at 246.71 ppm attributable to S_2CS. After ca. 1 week, the peak attributable to S_2CS totally disappears, while the intensities of the remaining peaks, other than that of the CS_2, stay constant. The loss of CS_2 clearly results in the formation of the salt $[NH_4]_3[SCH_2CH(NHCS_2)CO_2]$.

The ^{1}H NMR spectrum of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ **(2)** recorded immediately after the sample was made, confirms that the compound contains three trimethylgermane groups in different environments, and that it is over 98% pure relative to any hydrogen-containing impurities. Further, all peaks have the expected intensity ratios and fine structure. Thus, the chemical shift of $(CH_3)_3Ge{-}S_2CS$ is 0.72 ppm in the identical position to those in the related trithiocarbonate derivatives, $(CH_3)_3GeS_2CSR$ (R = Et, *i*-Pr),[10] that of $(CH_3)_3Ge{-}S_2CN$ is 0.71 ppm, which is very close to the values of 0.67 and 0.65 ppm which were observed in the dithiocarbamates, $(CH_3)_3GeS_2CN(CH_3)_2$ and $(CH_3)_3GeS_2CN(C_2H_5)_2$, respectively[5,6] and that of $(CH_3)_3GeO_2C{-}$ is 0.61 ppm. It is interesting to compare these values with those of the simple halides, Me_3GeF (0.51 ppm), Me_3GeCl (0.78 ppm), and Me_3GeBr (0.88 ppm). This suggests that the effective group electronegativity of the $O_2C{-}$ group is greater than those of the $S_2CN{-}$ and $S_2CS{-}$ groups but the difference is less than the difference in electronegativity between fluorine and chlorine. As for the other hydrogen atoms in the molecule, the chemical shifts for H_a, H_b, and H_x in $Me_3GeS_2C{-}SCH_aH_bCH_x(NH_n){-}$ show a similar ABX pattern as in L-cysteine with H_a at 4.11 ppm (A of ABX, $J_{ab} = 13.9$, $J_{ax} = 8.2$ Hz) and H_b at 3.91 ppm (B of ABX, $J_{ab} = 13.9$, $J_{bx} = 8.3$ Hz). The chemical shift for H_x is a band at 5.28 ppm, consisting of eight peaks, arising from four peaks (X of ABX) being further coupled with H_n ($J_{ax} = 8.2$, $J_{bx} = 8.3$, $J_{xn} = 6.9$ Hz). The chemical shift for the hydrogen atom attached to nitrogen, H_n, is a doublet, arising from coupling with H_x, at 7.90 ppm (d, $J_{nx} = 6.9$ Hz).

In the ^{13}C NMR spectra, the chemical shifts are 225.06 ppm for S_2CS, 197.93 ppm for S_2CN, and 171.39 ppm for O_2C, respectively, which are correspondingly comparable to 226.0 ppm in Me_3GeS_2CSEt[10] and 197.0 ppm in $Me_3GeS_2CNMe_2$.[6] The sample dissolved in $CDCl_3$ was kept in the NMR tube at room temperature for approximately 1 h, before the spectrum began to change as a result of the onset of CS_2 elimination to initially give $Me_3GeSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**3**). The changes continued for up to 24 h to eventually yield $(CH_3)_3GeO_2C({-}CH_xCH_aH_bSC(S)NH_n{-})$ (**4**) along with unidentifiable products.

Table 6. Selected Features and Their Assignments in the Infrared Spectrum of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**2**)[a,b]

$(CH_3)_3Ge{-}S_2CS{-}$		$(CH_3)_3Ge{-}S_2CNH{-}$		$(CH_3)_3Ge{-}O_2C{-}$	
site	assignment	site	assignment	site	assignment
1066 s	$\nu(S_2CS)_a$	3361 mw	$\nu(N{-}H)$	1693 s	$\nu(C{=}O)$
1044 s	$\nu(S_2CS)_b$	1518 m	$\nu(C{-}N)$	1044 ms	$\nu(C{-}O)$
838 vs	$\rho(Ge{-}CH_3)$	1238 vs	$\nu(CS_2)$asym	838 s	$\rho(Ge{-}CH_3)$
809 s	$\nu(S_2CS)_c$	983 s	$\nu(CS_2)$sym	663 s	$\nu(Ge{-}O)$
609 s	$\nu(Ge{-}C)_{asym}$	838 vs	$\rho(Ge{-}CH_3)$	630 s, sh	$\nu(Ge{-}C)_{asym}$
568 s	$\nu(Ge{-}C)_{sym}$	610 s, sh	$\nu(Ge{-}C)$asym	575 s, sh	$\nu(Ge{-}C)_{sym}$
507 vw	$\nu(S_2CS)_d$	568 s, sh	$\nu(Ge{-}C)$sym		
396 m	$\nu(Ge{-}S)$	402 s	$\nu(Ge{-}S)$		

[a] s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very. [b] Run neat between KBr plates.

In the ^{1}H NMR spectrum $Me_3GeSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**3**), the chemical shifts for CH_3, H_a and H_b in $(CH_3)_3Ge{-}S{-}CH_aH_b$ are all shifted toward TMS relative to the original compound **2**. As mentioned above, shifts toward TMS of the CH_3 chemical shift usually indicate that Ge is attached to a more electronegative element so this suggests that the overall electronegativity of the S_2CSR group is less than that of the S group. Not surprisingly, given the similarity of the two compounds, the chemical shifts for the other hydrogen atoms in **3** are very close to those in **2**. In the ^{13}C NMR spectrum of **3** a peak at 192.7 ppm attributable to CS_2 appears and increases in intensity along with the gradual decrease and eventual disappearance of a peak at 225.06 ppm attributable to S_2CS in **2**. A peak at 28.08 ppm attributable to SCH_aH_b in **3** has a shift of approximately 12 ppm toward TMS relative to the one at 39.98 ppm attributable to $S_2CSCH_aH_b$ in **2**. The remaining carbon atoms have essentially the same chemical shifts in both compounds, as expected.

In the ^{1}H NMR spectrum of $(CH_3)_3GeO_2C({-}CH_xCH_aH_bSC(S)NH_n{-})$ (**4**), the chemical shift for $(CH_3)_3GeO_2C$ at 0.64 ppm is comparable to the values of 0.61 ppm in **2** and 0.63 ppm in **3**. The remaining protons attached to carbon are assigned as follows; a triplet at 4.74 ppm with $J_{ax} = J_{bx} = 8.2$ Hz for H_x (X of ABX); a band with H_a at 3.76 ppm (A of ABX, $J_{ab} = 11.23$, $J_{ax} = 8.2$ Hz) and H_b at 3.71 ppm (B of ABX, $J_{ba} = 11.23$, $J_{bx} = 8.2$ Hz) for H_a and H_b. The peak attributable to NH_n is seen as a broad peak at 7.50 ppm. In the ^{13}C NMR spectrum, the peak due to Me_3GeO_2C is at 170.51 ppm, close to those in **2** and **3**, while that of S_2CN is at 200.98 ppm, shifted only 3 ppm downfield from its position in **2** and **3**. Finally, because the starting material leading to **1**−**4** was L-cysteine, there is no reason to expect the formation of more than one enantiomer and no signals were observed indicative of the presence of a mixture of diastereomers.

Vibrational Spectra of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (2) and $Me_3GeO_2C({-}CHNHC(S)SCH_2{-})$ (4). Characteristic features in the infrared spectrum of **2** are presented in Table 6, and those in the infrared and Raman spectra of **4** are in Table 7. Because of the relative ease of decomposition of **2**, attempts to record a Raman spectrum of reasonable quality failed. The assignments of the relevant peaks related to the presence of the S_2CS and S_2CN moieties in the infrared spectrum of $Me_3GeS_2CSCH_2CH(NHCS_2GeMe_3)CO_2GeMe_3$ (**35**) are made on the basis of assignments reported for the thioxanthates[10,11] and related dithiocarbamate species,[4−6] along with comparisons with spectra of the triammonium salt.

For the $Me_3Ge{-}O_2C{-}$ site, a strong band due to the C=O vibration, observed at 1600 cm^{-1} in the salt **1** is shifted to higher frequency at 1693 cm^{-1} for **2** and 1699 cm^{-1} for **4**, suggesting that the ligand is essentially monodentate in both cases with germanium bonded to just one of the oxygen atoms of the O_2C group. There are, of course, three different Me_3Ge environments in **2**. However, the more intense CH_3 deformation mode for

Table 7. Selected Features and Their Assignments in the Vibrational Spectrum of $Me_3GeO_2C(-CHNHC(S)SCH_2H-)$ (**4**)[a,b]

IR[c]	Raman[d]	assignment
3404 w		ν(N−H)
1699 s	1705 (3)	ν(C=O)
1627 s		δ(N−H)
1494 s	1495 (2)	ν(C−N)
1357 s		$\delta(CH_3)_3)$
1247 s	1252 (7)	$\nu(CS_2)_{asym}$
1045 s	1033 (30)	ν(C−O)
977 w	980 (2)	$\nu(CS_2)_{sym}$
830 ms		$\rho(Ge-CH_3)$
660 s	676 (25)	ν(Ge−O)
630 s	638 (30)	$\nu(Ge-C)_{asym}$
574 mw	582 (100)	$\nu(Ge-C)_{sym}$

[a] Parentheses denote relative intensities in the Raman effect. [b] s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very. [c] Run neat between KBr plates. [d] Run neat in sealed capillaries.

Me_3GeX compounds is normally seen in the same region of the spectrum regardless of the nature of X and this appears to be the case here also. However, the Ge−C stretching vibrations, do appear to differ slightly in **2** according to whether germanium is attached to the S_2CS, S_2CN, or O_2C groups. It has been generally observed that the Ge−C stretching vibrations shift to a higher wavenumber if germanium is attached to a more electronegative entity. This is illustrated by the spectra of Me_3GeBr and Me_2GeBr_2,[27] where the Ge−C asymmetric and symmetric stretching modes are at 612 and 572 cm^{-1}, respectively, for the former compared to 633 and 588 cm^{-1} for the latter, so that despite the considerable increase in mass, there is an increase in wavenumber as a result of the methyl group being replaced by the more electronegative bromine atom. The relative values of the chemical shifts in the ^1H NMR spectra suggested that the SCSN moiety could be slightly more electronegative than S_2CS, but both are clearly less so than O_2C. The assignments of the asymmetric and symmetric Ge−C stretches are therefore made to 630 and 575 cm^{-1}, respectively, for $(CH_3)_3GeO_2C-$ and to 610 and 568 cm^{-1} and to 609 and 568 cm^{-1} for $(CH_3)_3GeS_2CN-$ and $(CH_3)GeS_2CS-$, respectively, the latter being essentially the same as those reported for the trithiocarbonates, Me_3GeS_2CSR (R = Et, *i*-Pr, *n*-Pr, *n*-Bu).[10] The Ge−S stretching vibrations for a variety of dithiocarbamates[4−6] range from 400 to 435 cm^{-1}, whereas those in the trithiocarbonates[10,11] range from 394 to 398 cm^{-1}. Thus, it is reasonable to assign the Ge−S stretching modes at 396 cm^{-1} for $Ge-SCS_2$ and at 402 cm^{-1} for Ge−SCSN. The Ge−O stretching mode is observed at higher wavenumber than Ge−S mode, at 663 cm^{-1} for **2** and 660 cm^{-1} for **4**, which are very close to the values reported for $(CH_3)_3Ge-OCH_3$.[28]

Conclusion

In view of our success in forming a wide range of organogermanium mono- and trithiocarbonate derivatives as well as dithiocarbamates, the lack of reactivity of the potential ligand, $[NH_4]_3[S_2CSCH_2CH(NHCS_2)CO_2]$, toward a variety of organogermanium halides was disappointing. The presence of the three potentially active sites in the anion are clearly seen in the X-ray structure of the salt, yet only for trimethylgermanium halides did we observe the expected reaction, which was immediately followed by CS_2 elimination and rearrangement to a heterocyclic derivative.

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Supporting Information Available: Tables S1−S5 listing experimental details, anisotropic thermal parameters of non-hydrogen atoms, and final fractional coordinates and thermal parameters for hydrogen atoms (4 pages). Ordering information is given on any current masthead page. Structure factor tables may be obtained directly from the authors.

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