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Synthesis, Characterization, and Structure of $Me_2ClGe(S_2CNMe_2)$

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Organostannane and organosilane derivatives of dithiocarbamate are well-known.[1-6] By contrast, analogous germanium compounds have not been studied extensively. We report the synthesis of chlorodimethyl(*N,N'*-dimethyldithiocarbamato)germane, its characterization by ^1H and ^{13}C NMR, infrared and Raman spectroscopy, and mass spectrometry, and its single-crystal X-ray structure determination.

Experimental Section

$Me_2ClGe(S_2CNMe_2)$ was synthesized by stirring an equimolar mixture of Me_2GeCl_2 and Me_2NCS_2Na (typically 3.0 mmol) in a CS_2 solution (typically 10.0 mmol) at −23 °C for 2 h on a standard vacuum line. After NaCl was filtered off, $Me_2ClGe(S_2CNMe_2)$ (in ca. 50% yield) was crystallized by slow evaporation of the solvent. Anal. Calcd for $C_5H_{12}ClGeNS_2$: C, 23.25; H, 4.68; N, 5.42. Found: C, 23.11; H, 4.82; N, 5.84. The ^1H NMR spectrum was recorded in carbon disulfide solution with tetramethylsilane as internal standard and the ^{13}C NMR spectrum in $CDCl_3$ solution on JEOL C60-HL and Bruker CPX 100 (FT model) spectrometers, respectively. The infrared spectrum was recorded as a Nujol mull between CsI plates on a Perkin-Elmer 180 spectrometer and the Raman spectrum as a solid on a Spectra-Physics 700 spectrometer using the argon ion laser exciting line at 488.0 nm. The mass spectrum was recorded on a Varian GMAT-CH_5 spectrometer operating at 70 eV and shows the parent ion peak as a typical Ge-containing cluster centered at m/z 259 as well as the following: $(M - CH_3)^+$ at 244, $(M - Cl)^+$ at 224, $(Me_2NCSSH)^{+\cdot}$ at 121.

The crystal used for X-ray analysis was sealed in a capillary tube, and data were collected on a Syntex $P2_1$ diffractometer. Details concerning collection and reduction of data and sources of scattering factors and computer programs used have been previously reported.[7] Unit cell dimensions were determined from 15 reflections having $15 < 2\theta < 30°$. Three intensity standards were measured after 50 reflections, and no significant decay of the data was observed. Lorentz, polarization, and analytical absorption corrections were applied to the data that contained systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), consistent with space group $P2_1/c$. The structure was solved by sharpened Patterson synthesis and refined by full-matrix least-squares methods to $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.0319$ and $R_{wF} = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2 = 0.0382$. The quantity minimized was $(|F_o| - |F_c|)^2$ with the final weighting scheme of $1/[\sigma^2(F) + 0.005F^2]$. Hydrocarbon atoms were included at the idealized positions (C–H = 0.95 Å; H–C–H = 109.5°). Details of X-ray data and refinement parameters are summarized in Table I, and the final atomic coordinates for non-hydrogen atoms are given in Table II.

Results and Discussion

Chlorodimethyl (*N,N'*-dimethyldithiocarbamato)germane was synthesized by the reaction

$$(CH_3)_2GeCl_2 + (CH_3)_2NCS_2Na = (CH_3)_2ClGe[S_2CN(CH_3)_2] + NaCl$$

Table I. Crystallographic Data

a, Å	12.682 (4)
b, Å	7.532 (3)
c, Å	12.085 (4)
β, deg	109.88 (2)
V, Å^3	1085 (1)
cryst syst	monoclinic
space group	$P2_1/c$
mol wt	258.3
Z	4
ρ_{calcd}, g cm^{-3}	1.58
ρ_{obsd}, g cm^{-3}	1.56 (flotation, benzene/CCl_4)
cryst dimens, mm	0.08 × 0.23 × 0.30
radiation	Mo Kα = 0.710 69 Å
monochromator	highly oriented graphite
temp, °C	21
abs coeff (μ), cm^{-1}	32.71
min abs cor	1.589
max abs cor	3.721
2θ angle, deg	4–50
scan type	coupled θ(crystal)/2θ(counter)
scan width	Kα_1 − 1 to Kα_2 + 1
scan speed, deg min^{-1}	variable, 2.02–4.88
bkgd time/scan time	0.5
total reflcns measd	2267 ($+h,+k,\pm l$)
no. of unique data used	1299 [$I > 3\sigma(I)$]
no. of parameters (NP)	91
R	0.0319
R_{wF}	0.0382

Table II. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $Me_2ClGe(S_2CNMe_2)$ with Standard Deviations in Parentheses

	x	y	z	U_{eq},[a] Å^2 × 10^3
Ge	0.31361 (1)	0.09202 (6)	0.34074 (4)	51.5 (3)
Cl	0.3503 (1)	−0.0777 (2)	0.5029 (1)	73 (1)
S(1)	0.1851 (1)	0.2725 (2)	0.1255 (1)	58 (1)
S(2)	0.1279 (1)	0.0522 (1)	0.2986 (1)	47 (1)
N	−0.0220 (3)	0.1659 (4)	0.1018 (3)	30 (2)
C(1)	0.3812 (5)	−0.0470 (8)	0.2486 (5)	81 (4)
C(2)	0.3741 (4)	0.3177 (7)	0.4073 (5)	70 (3)
C(3)	0.0857 (3)	0.1661 (5)	0.1644 (3)	40 (2)
C(4)	−0.0645 (4)	0.2563 (6)	−0.0119 (3)	52 (2)
C(5)	−0.1058 (4)	0.0765 (6)	0.1391 (5)	56 (2)

[a] U_{eq} for the non-hydrogen atoms is calculated from the refined anisotropic thermal parameters ($U_{eq} = {}^1/_3\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*a_i \cdot a_j$).

Table III. Bond Distances (Å) and Angles (deg)

Distances			
Ge–Cl	2.251 (1)	S(1)–C(3)	1.690 (2)
Ge–S(1)	2.896 (1)	S(2)–C(3)	1.750 (2)
Ge–S(2)	2.254 (1)	N–C(3)	1.317 (2)
Ge–C(1)	1.929 (2)	N–C(4)	1.463 (2)
Ge–C(2)	1.925 (2)	N–C(5)	1.453 (3)
Angles			
Cl–Ge–S(1)	159.2 (1)	C(1)–Ge–C(2)	121.9 (1)
Cl–Ge–S(2)	90.7 (1)	Ge–S(1)–C(3)	76.9 (1)
S(1)–Ge–S(2)	68.5 (1)	Ge–S(2)–C(3)	96.4 (1)
Cl–Ge–C(1)	101.2 (1)	C(3)–N–C(4)	121.2 (2)
S(1)–Ge–C(1)	87.8 (1)	C(3)–N–C(5)	123.2 (2)
S(2)–Ge–C(1)	115.6 (1)	C(4)–N–C(5)	115.6 (2)
Cl–Ge–C(2)	101.7 (1)	S(1)–C(3)–N	124.5 (1)
S(1)–Ge–C(2)	89.1 (1)	S(2)–C(3)–N	117.6 (1)
S(2)–Ge–C(2)	116.7 (1)	S(1)–C(3)–S(2)	117.9 (2)

Its ^1H NMR spectrum in CS_2 solution shows two singlets of equal intensity readily assignable to $\delta(Ge{-}CH_3)$ at 1.42 and $\delta(N{-}CH_3)$ at 3.42 by comparison with related molecules.[2,8] Similarly, the ^{13}C NMR spectrum shows peaks attributable to $\delta(Ge{-}CH_3)$ at 14.8, $\delta(N{-}CH_3)$ at 43.2, and $\delta(C{=}S)$ at

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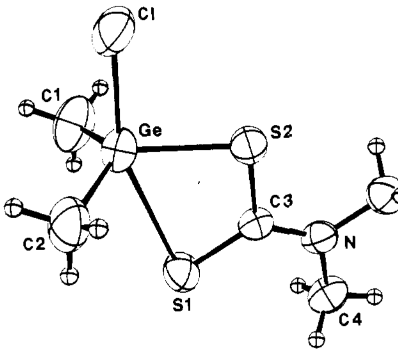

Figure 1. Structure and labeling scheme for $Me_2ClGe(S_2CNMe_2)$ (50% probability for thermal ellipsoids). Hydrogen atoms are drawn arbitrarily small. Bond distances and angles are complied in Table III.

195.6 relative to tetramethylsilane.[9,10] The vibrational spectra show the following features (cm^{-1}): $\nu(CS)_2$ (asymmetric and symmetric) at 1168 and 1002;[1,2,11] $\nu(GeC_2)$ (asymmetric and symmetric) at 635 (627 Raman) and 581 (574 Raman);[8,12] ν(GeS) at 418 (423 Raman).[13] Thus, a monodentate ligand is suggested with a pseudotetrahedral arrangement about germanium. The only peak attributable to ν(GeCl) is at 315 cm^{-1} (310 Raman), which suggests a relatively weak Ge–Cl bond as found for the axial Ge–Cl bond in the trigonal-bipyramidal structure of $Cl_4Ge{\cdot}NMe_3$.[12,14,15] These apparently conflicting pieces of information indicated the need for a structural determination (Figure 1).

The Ge atom in $Me_2ClGe(S_2CNMe_2)$ is essentially 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. The Cl atom clearly occupies one axial position while the second S atom of the dithiocarbamate ligand occupies the second axial site but at a distance much greater than expected for a normal covalent Ge–S bond, forming an angle of 159.2 (1)° rather than 180° with the Ge–Cl bond.

The Ge–C bond lengths (1.929 (2), 1.925 (2) Å) are typical of all methylgermanes and remarkably close to those found in Me_2GeCl_2 (1.928 (6) Å).[16] Similarly, the peaks assigned to the GeC_2 stretches are close to those assigned for Me_2GeCl_2 (634, 592 cm^{-1}).[12] The Ge–S bond in the equatorial plane is of a length (2.254 (1) Å) expected from the sum of the covalent radii of Ge and S (2.25 Å),[17] and the value of ν(GeS) is close to that expected for a normal Ge–S bond.[13] By contrast, the Ge–Cl bond (2.251 (1) Å) is appreciably longer than it is in Me_2GeCl_2 (2.143 (4) Å)[16] but remarkably close to the length of the axial Ge–Cl bond in $Cl_4Ge{\cdot}NMe_3$ (2.24 (1) Å).[14] The assignment of GeCl to 315 cm^{-1} is therefore reasonable and consistent with the presence of a weaker Ge–Cl bond. Furthermore, the Ge–S distance (2.896 (1) Å) for the second S atom is so long that a second peak in the Ge–S stretching region cannot be expected.

The C–Ge–C angle is hardly changed (121 (4)–121.9 (1)°) when one of the Cl atoms in Me_2GeCl_2 is substituted by the dithiocarbamate ligand. If the reaction originates by a nucleophilic attack by a S atom along the C_2 axis bisecting the Cl–Ge–Cl angle in Me_2GeCl_2, then this equatorial S atom virtually remains at its attacking position, the CH_3 groups are unaffected, the remaining Cl atom is bent back to the axial position of a trigonal bipyramid, and the vacant site on the opposite side is partly occupied by the second S atom. Presumbly, with a monodentate attachment, the S and Cl atoms would simply rearrange to a pseudotetrahedral arrangement. However, the molecule is apparently "frozen" in this intermediate structure to give anisobidentate coordination. The structure is similar to that of $Me_2ClSn(S_2CNMe_2)$,[3] although the C–Sn–C angle is considerably larger (128 (2)°) and the axial Cl–Sn–S angle smaller (154.5 (4)°) than the corresponding angles in the Ge analogue. Both distortions seem surprising because a closer adherence to 120 and 180° angles might be anticipated on the larger Sn atom.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Interligand Frontier Orbital Contacts in Phenanthroline Chelates

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The idea of intermolecular contacts as a basis for phase transitions in solids is relatively unexplored. Recent interest in cooperative intersystem crossing in Fe(II) chelates containing phenanthroline as a ligand[1] and in solid-state racemization of phenanthroline-containing chelates[2] has prompted our study of a frontier orbital basis for interligand contacts in such materials. We report here a striking correspondence between the stereochemistry of the cation packing in $Fe(phen)_3I_2{\cdot}2H_2O$ and the π HOMO/LUMO topologies of the phenanthroline molecule.

Using literature values[3] of the bond distances and bond angles of the coordinated phenanthroline molecule, we have carried out a full valence electron INDO calculation to determine the ligand π HOMO and π LUMO topologies. Both perspective and contour plots of the wave probability functions ($\psi^*\psi$) are shown in Figure 1.[4] These functions are readily identifiable as π and π^* types for the ethylene linkage that bridges the two pyridyl rings of phenanthroline (adjacent closed contour regions have opposite signs of ψ). Clearly there is also well-developed delocalization of the HOMO and LUMO

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