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Synthesis and Characterization of *O*-Methyl and *O*-Ethyl Dithiocarbonate (Xanthate) Derivatives of Dimethyl- and Diphenylgermane. Crystal Structure of $Ph_2Ge[S_2COMe]_2$

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The *O*-alkyl dithiocarbonate (xanthate) derivatives of dimethyl- and diphenylgermane $Me_2Ge[S_2COMe]_2$, $Me_2Ge[S_2COEt]_2$, $Ph_2Ge[S_2COMe]_2$, and $Ph_2Ge[S_2COEt]_2$ have been prepared in 60–80% yields by reaction of the sodium salt of the dithiocarbonic (xanthic) acid with dichlorodimethyl- or dichlorodiphenylgermane. The compounds were characterized by elemental analysis and infrared, Raman, and ^1H and ^{13}C NMR spectroscopy. The crystal structure of $Ph_2Ge[S_2COMe]_2$ was determined. $Ph_2Ge[S_2COMe]_2$, which crystallizes as monoclinic in the space group $C2/c$ (C_{2h}^6, No. 15), has the cell parameters $a = 16.225$ (6) Å, $b = 6.897$ (2) Å, $c = 17.923$ (3) Å, $\beta = 96.94$ (2)°, $V = 1991$ (1) Å^3, $Z = 4$, $R = 0.0654$, and $R_w = 0.0674$. The environment about germanium is essentially that of a pseudotetrahedron with monodentate xanthate ligands resulting in a S–Ge–S angle of 93.4 (2)° and a C–Ge–C angle of 117.1 (3)°. In contrast with corresponding dithiocarbamate derivatives of germanium, the second sulfur atom is clearly not involved in a secondary interaction. If any such interaction exists, it is through the oxygen atom.

Introduction

These studies are essentially a continuation of those previously reported by us on other sulfur-containing groups attached to germanium, such as dithiophosphates[1-3] and *N*,*N*-dialkyldithiocarbamates.[4-6] *O*-Alkyl dithiocarbonates (xanthates) have been extensively used as ligands, particularly toward transition metals.[7,8] Studies of main-group element xanthates include structural studies on tin(II) and tin(IV) derivatives. In $Sn(S_2COEt)_4$, two of the ligands are monodentate and two are bidentate,[9] whereas only monodentate ligands are found for bis(*O*-ethyl xanthato)bis(quinolin-8-olato)tin(IV)[10] and bis(*O*-methyl dithiocarbonato)tin(II).[11] The environment about tin in the latter compound strongly resembles that about lead in analogous lead(II) compounds.[12,13]

Experimental Section

Materials. Dichlorodimethylgermane, degassed at −196 °C, and dichlorodiphenylgermane were obtained from Alfa Products. Sodium *O*-methyl dithiocarbonate and sodium *O*-ethyl dithiocarbonate were prepared by adding a slight excess of CS_2 into a mixture of equimolar amounts of NaOH and ROH, where R = Me and Et, in the manner described previously.[14]

Synthesis. The method is essentially that described earlier for the formation of various organogermanium organotin, and organolead xanthates, including the preparation of $Ph_2Ge[S_2COEt]_2$, by reaction of Ph_2GeBr_2 with potassium *O*-ethyl dithiocarbonate.[15]

Typically, degassed dichlorodimethylgermane (1 mmol) was distilled onto the previously dried and degassed sodium *O*-methyl dithiocarbonate (2 mmol) held at −196 °C. The solvent, CS_2 (5 mL), was distilled into the reaction vessel, which was then allowed to warm up to ambient temperature at which time stirring was initiated. After the mixture was stirred for 15 min, the vessel was surrounded by an ice bath and stirring was continued for 3 h. The reaction mixture was then filtered to remove NaCl and the filtrate slowly evaporated on the vacuum line to give solid $Me_2Ge[S_2COMe]_2$: yield 68%; mp 57 °C. Anal. Calcd for $C_6H_{12}O_2S_4Ge$: C, 22.73; H, 3.82. Found: C, 22.32; H, 4.08. Similarly obtained were the following compounds. $Me_2Ge[S_2COEt]_2$: yield 60%. Anal. Calcd for $C_8H_{16}O_2S_4Ge$: C, 27.85; H, 4.67. Found: C, 26.45; H, 5.10. $Ph_2Ge[S_2COMe]_2$: yield 77%; mp 90 °C. Anal. Calcd for $C_{16}H_{16}O_2S_4Ge$: C, 43.56; H, 3.66. Found: C, 43.83; H, 3.77. $Ph_2Ge[S_2COEt]_2$: yield 86%; mp 107 °C. Anal. Calcd for $C_{18}H_{20}O_2S_4Ge$: C, 46.08; H, 4.30. Found: C, 47.80; H, 4.48. Only for $Ph_2Ge[S_2COMe]_2$ was a single crystal of suitable size and quality obtained to allow for crystallographic studies. $Me_2Ge[S_2COEt]_2$ is a liquid at room temperature.

Table I. Crystallographic Data for $Ph_2Ge[S_2COMe]_2$

chem formula: $C_{16}H_{16}O_2S_4Ge$	fw: 441.15
$a = 16.225$ (6) Å	space group: $C2/c$ (No. 15)
$b = 6.897$ (2) Å	$T = 24$ °C
$c = 17.923$ (3) Å	$\lambda = 0.71069$ Å
$\beta = 96.94$ (2)°	$\rho_{obsd} = 1.44$ g cm^{-3}
$V = 1991$ (1) Å^3	$\rho_{calcd} = 1.47$ g cm^{-3}
$Z = 4$	$\mu = 18.75$ cm^{-1}
$R = 0.0654$	transm coeff = 0.73–0.86
$R_w = 0.0674$	

Table II. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $Ph_2Ge[S_2COMe]_2$ with Standard Deviations in Parentheses

atom	x	y	z	U_{eq},[a] Å^2 × 10^3
Ge	0.0000	0.1947 (2)	0.2500	43.3 (2)
S1	−0.0433 (2)	−0.0302 (5)	0.1620 (2)	62.3 (4)
S2	−0.1272 (3)	0.0106 (6)	0.0087 (2)	87.8 (5)
O	−0.0778 (6)	0.301 (1)	0.1001 (4)	72 (1)
C1	−0.0864 (8)	0.112 (2)	0.0857 (6)	58 (1)
C2	−0.111 (1)	0.431 (3)	0.0420 (8)	116 (2)
C3	0.0892 (5)	0.340 (1)	0.2161 (4)	57 (1)
C4	0.1055 (5)	0.526 (1)	0.2441 (4)	84 (2)
C5	0.1670 (5)	0.639 (1)	0.2171 (4)	67 (2)
C6	0.2122 (5)	0.565 (1)	0.1620 (4)	70 (2)
C7	0.1958 (5)	0.378 (1)	0.1340 (4)	57 (1)
C8	0.1344 (5)	0.266 (1)	0.1610 (4)	47 (1)

[a] U_{eq} is defined as one-third of the trace of the orthogonal U_{ij} tensor.

Physical Measurements. The elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. The density measurement was performed by the flotation method (C_6H_6/CCl_4). The ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 FT NMR spectrometer in $CDCl_3$ solutions. The infrared spectra were recorded on a Nicolet 5DX FT spectrometer as CsI pellets or Nujol mulls or as neat liquids between CsI plates. The Raman spectra were recorded on a Spectra-Physics 164 instrument using the 5145-Å exciting line of an argon ion laser with samples sealed in capillary tubes. The melting points were determined on a Fisher-Johns apparatus.

X-ray Crystallographic Analysis. A prismatic crystal of $Ph_2Ge[S_2COMe]_2$ was sealed in a thin-walled glass capillary and mounted on a Syntex $P2_1$ diffractometer. The X-ray diffraction data were collected by the procedures described elsewhere.[6] The systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) indicated the space group $C2/c$ (C_{2h}^6, No. 15). The least-squares refinement of the setting angles of 15 reflections $15 < 2\theta < 30°$ led to the cell dimensions given

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Table III. Interatomic Distances (Å) and Angles (deg) for $Ph_2Ge[S_2COMe]_2$[a]

Ge–S1	2.262 (3)	C1–O	1.33 (2)
Ge–C3	1.918 (8)	C2–O	1.43 (2)
S1–C1	1.76 (1)	Ge···O	2.920 (8)
S2–C1	1.62 (1)	ring C_3–C_8 fixed C–C	1.395
S1–Ge–S1′	93.4 (2)	S2–C1–O	127.7 (9)
C3–Ge–C3′	117.1 (3)	C1–O–C2	116.7 (1)
S1–Ge–C3	108.6 (2)	S1–Ge···O	57.8 (2)
S1–Ge–C3′	113.3 (2)	S1–Ge···O′	151.2 (2)
Ge–S1–C1	102.7 (5)	C3–Ge···O	80.6 (3)
S1–C1–S2	120.4 (9)	C3–Ge···O′	84.3 (3)
S1–C1–O	111.9 (8)	O···Ge···O′	150.9 (2)
ring C_3–C_8 fixed C–C–C	120.0		

[a] Standard deviations in parentheses. A primed atom indicates the symmetry-equivalent position: $-x, y, {}^1/_2 - z$.

Table IV. ^{1}H NMR Chemical Shifts for the Organogermanium Dithiocarbonates[a,b]

	Ge–CH_3/ Ge–C_6H_5	OCH_3/OCH_2	CCH_3
$Me_2Ge[S_2COMe]_2$	1.31 (6 H, s)	4.10 (6 H, s)[c]	
$Me_2Ge[S_2COEt]_2$	1.36 (6 H, s)	4.53 (4 H, q)[d]	1.42 (6 H, t)[d]
$Ph_2Ge[S_2COMe]_2$	7.46–7.75 (10 H, m)	3.79 (6 H, s)[c]	
$Ph_2Ge[S_2COEt]_2$	7.43–7.75 (10 H, m)	4.28 (4 H, q)[d]	0.97 (3 H, t)[d]

[a] The spectra were recorded in $CDCl_3$ and reported in ppm from Me_4Si. [b] Number of protons and multiplicities are in parentheses (s = singlet; q = quartet; t = triplet; m = multiplet). [c] In the sodium salt this peak is seen at 4.01 ppm. [d] In the sodium salt these peaks are seen at 4.49 and 1.37 ppm.

Table V. ^{13}C NMR Chemical Shifts for the Organogermanium Dithiocarbonates[a–c]

	Ge–CH_3/Ge–C_6H_5	OCH_3/ OCH_2	CS	C–CH_3
$Me_2Ge[S_2COMe]_2$	7.28	60.81	213.80	
$Me_2Ge[S_2COEt]_2$	7.44	71.10	212.73	13.74
$Ph_2Ge[S_2COMe]_2$	128.78, 130.59, 133.65, 133.82	60.34	211.05	
$Ph_2Ge[S_2COEt]_2$	128.78, 130.75, 133.64, 134.15	69.94	210.11	13.07

[a] The spectra were recorded in $CDCl_3$ and reported in ppm from Me_4Si. [b] In the D_2O solution of NaS_2COMe, peaks are seen at 60.75 and 233.12 ppm. [c] In the D_2O solution of NaS_2COEt, peaks are seen at 14.67, 71.28, and 233.71 ppm.

in Table I. During data collection, the intensities of three monitor reflections measured after every 100 reflections decreased by approximately 9%, and the appropriate scaling factors were applied. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. A summary of crystal and refinement data is given in Table I.

The position of the germanium atom was obtained from a sharpened Patterson synthesis, and those of the remaining non-hydrogen atoms were determined from subsequent difference Fourier maps. The phenyl rings were constrained to a regular hexagon with C–C bond distances of 1.395 Å and C–C–C angles of 120.0°. Phenyl and methyl hydrogen atoms were also included in their idealized positions with C–H set at 0.95 Å and with isotropic thermal parameters set at 0.01 Å^2 greater than that of the carbon atom to which they were bonded. During the final stages of the anisotropic full-matrix least-squares refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized by using a weighting scheme of the form $w = 1/[\sigma^2(F) + \rho F^2]$ to a final ρ value of 0.000001 with convergence at $R = 0.0654$ and $R_w = 0.0674$ based on 93 variables and 725 unique reflections.

Sources of scattering factors and computer programs used have been given elsewhere.[6] The final atomic coordinates and equivalent isotropic thermal parameters are given in Table II for the non-hydrogen atoms, and important distances and bond angles are given in Table III. Additional crystallographic data are available as supplementary material.

Results and Discussion

The synthesis of *O*-methyl and *O*-ethyl dithiocarbonate derivatives of dimethyl- and diphenylgermane is readily achieved in 60–86% yield by the action of the appropriate sodium salt with dichlorodimethyl- or dichlorodiphenylgermane in CS_2 as solvent in accord with the general equation

$$R_2GeCl_2 + 2NaS_2COR' \rightarrow R_2Ge[S_2COR']_2 + 2NaCl$$

$$R = Me, Ph;\ R' = Me, Et$$

The compounds are susceptible to moisture and air, at least on long exposure. The diphenyl derivatives are both colorless solids as is $Me_2Ge[S_2COMe]_2$. However, $Me_2Ge[S_2COEt]_2$ is a viscous liquid. The compounds readily dissolve in chloroform, which was used as the solvent for the NMR spectroscopic studies.

NMR Spectra. The ^{1}H and ^{13}C{H} NMR spectra data are presented in Tables IV and V. In the ^{1}H NMR spectra, the ligand chemical shifts are close to and bracket those of the corresponding sodium salt. The signals due to the R groups attached to Ge are similar for both the *O*-methyl and the *O*-ethyl xanthate analogues and are comparable to those of other bissubstituted dimethyl- or diphenylgermanium compounds. Thus, Me_2GeL_2 species give Ge–CH_3 signals at 1.21 ppm for L = $S_2P(OEt)_2$,[2] 1.29 ppm for L = $S_2P(OMe)_2$,[2] and 1.37 ppm for L = S_2CNMe_2,[6] and Ph_2GeL_2 derivatives give phenyl resonances between 7.2 and 7.7 ppm for L = $S_2P(OMe)_2$,[1] 7.1–7.7 ppm for L = $S_2P(OEt)_2$,[2] and 7.1–7.9 ppm for L = S_2CNEt_2.[5]

In the ^{13}C NMR spectra, four sets of peaks are observed that are assignable to *C*S, Ge–*C*H_3/Ge–*C*$_6H_5$, O*C*H_3/O*C*H_2, and C–*C*H_3. The chemical shifts of the ligand methyl and ethyl carbon resonances in the germanium compounds are similar to those of the corresponding sodium salts even though the latter are dissolved in D_2O. However, the chemical shifts of the dithio carbon resonances of the germanium compounds are considerably shifted relative to those of the sodium salts, which occur at approximately 234 ppm. In other dithio germanium complexes, the *C*–S resonance was reported at 196.9 ppm for $Me_2Ge[S_2CNMe_2]_2$[6] and 193.0 ppm for $Ph_2Ge[S_2CNEt_2]_2$.[5] For a mixed ligand Te(IV) complex[16] containing the *O*-ethyl dithiocarbonate ligand, the ^{13}C NMR spectrum showed the ligand resonances at 14.4, 71.0 and 219.9 ppm, compared with 12.6, 50.6, and 200.9 ppm for the diethyldithiocarbamato ligand. Thus when attached to tellurium(IV), the *C*–S resonance is at ca. 220 and 201 ppm for *O*-ethyl dithiocarbonate and *N*,*N*-diethyldithiocarbamate respectively compared to ca. 212 and 193 ppm for the germanium derivatives. The larger shift from the salt for the germanium derivatives could reflect greater covalent character.

Infrared and Raman Spectra. Attempts at detailed analysis have led to a variety of conflicting assignments of CS and CO group frequencies including ν(CS) to 1143–1262 cm^{-1} and ν(CO) to 1020–1077 cm^{-1},[17] but ν(CS) to 1020–1070 cm^{-1} and ν(CO) to 1110–1140 and 1200 cm^{-1},[18] for metal xanthates containing different hydrocarbon groups. Also structural implications were made on the basis of assignments of ν(CO) to 1114–1188 and 1250–1325 cm^{-1} for several methyl and ethyl xanthates of transition metals.[19] It has been suggested that the presence of two CO and two CS bands in the 1205–1240- and 1030–1055-cm^{-1} regions, respectively, is indicative of tin(IV) xanthates while only one band in each region is observed for tin(II) xanthates.[9] As part of preparative studies of organotin and organolead xanthates,[15,20] a detailed assignment of the spectrum of Ph_3GeS_2COEt placed ν(CO) at 1214 cm^{-1} and the two ν(CS) bands at 1042 and 861 cm^{-1}.[15]

Attempts to extrapolate from assignments of these bands to structural implications based on the relative importance of different degrees of delocalization of the S_2COC group largely ignore the fact that the two CO and two CS stretches are all highly coupled[21]

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Table VI. Selected Features and Their Assignments (in cm^{-1}) in the Vibrational Spectra of Dimethyl- and Diphenylgermanium Xanthates[a,b]

$Me_2Ge[S_2COMe]_2$		$Me_2Ge[S_2COEt]_2$		$Ph_2Ge[S_2COMe]_2$		$Ph_2Ge[S_2COEt]_2$		
IR[c]	Raman[d]	IR[c]	Raman[e]	IR[e]	Raman[d]	IR[c]	Raman[d]	assignt
1225 s, br	1222 (3)	1212 vs		1223 vs		1212 s		$\nu(S_2COC)_a$
1144 m	1169 (9)	1112 s		1150 m	1154 (14)	1110 m	1111 (6)	$\nu(S_2COC)_b$
1062 vs, br	1071 (65)	1046 vs	1052 (54)	1058 vs	1060 (48)	1039 vs, br	1048 (55)	$\nu(S_2COC)_c$
850 m		850 s, br	850 (18)					$\rho(CH_3(Ge))$
	643 (79)	660 w	653 (82)	645 w	646 (63)	643 w	643 (21)	$\nu(S_2COC)_d$
632 w	630 (3)	633 mw	630 (20)					$\nu(Ge-CH_3)_{asym}$
581 w	579 (15)	588 w	585 (100)					$\nu(Ge-CH_3)_{sym}$
463 w	469 (10)	470 w	470 (42)	464 m	468 (17)	463 m	483 (6)	$\delta(C-O-C)$
	418 (43)	440 sh	438 (42)	410 sh	419 (37)	423 w	420 (20)	$\nu(Ge-S)_{asym}$
391 w	390 (13)	377 m, br	364 (57)	398 m, br			380 (20)	$\nu(Ge-S)_{sym}$

[a] Parentheses denote relative intensities in the Raman effect. [b] s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very. [c] Run as CsI pellets. [d] Run as a solid in a glass capillary. [e] Run as a neat liquid in a glass capillary.

and as a result are likely to give four bands in the regions ca. 1200, 1100, 1020, and 600 cm^{-1} regardless of changes in bonding. Thus predictions of ionic versus covalent bonding or monodentate versus bidentate linkages would appear to be largely fortuitous if proven correct. With this in mind we have chosen to make group assignments in Table VI using a notation arbitarily chosen as $\nu(S_2COC)$ with subscripts a, b, c, and d. There are distinct features corresponding to these four fundamentals in the sodium salts of methyl and ethyl xanthate. Three appear as the prominent features in the IR spectra at 1187 (Me) and 1142 (Et), 1111 (Me) and 1109 (Et), and 1047 (Me) and 1051 cm^{-1} (Et), with extremely weak corresponding peaks in the Raman effect. The fourth is the prominent feature in the Raman effect at 620 (Me) and 666 cm^{-1} (Et). The four features are seen in approximately the same positions in all of these germanium derivatives, with $\nu(S_2CO_2)_a$ being shifted the most and to a considerably higher wavenumber. The features assignable to the Ge–C stretching vibrations in the dimethylgermanium derivatives have wavenumbers essentially identical with those in Me_2GeBr_2.[22] Thus C–Ge bonds of similar lengths with similar C–Ge–C bond angles might well be expected for the xanthate derivatives as was found for the dibromide, suggesting that the coordination about germanium is probably similar to the distorted tetrahedron found for Me_2GeBr_2.[23]

Molecular Structure of $Ph_2Ge[S_2COMe]_2$. The crystal structure of diphenylbis(*O*-methyl dithiocarbonato)germanium (Figure 1 and Table III) confirms that the immediate environment about germanium is a distorted tetrahedron. The C–Ge–C′ angle of 117.1 (3)° is slightly less opened up than those in Me_2GeBr_2,[23] Me_2GeCl_2,[24] and $Ph_2Ge[S_2CNMe_2]_2$[5] of 124 (7), 121 (4) and 121.8 (1)°, respectively. The Ge–C bond distance of 1.918 (8) Å is also comparable to those reported for the corresponding dithiocarbamate [1.928 (3) Å][5] and dithiophosphate [1.931 (7)] Å.[1] From vapor-phase electron diffraction, bond distances of 1.928 (6) and 1.91 (1) Å were obtained from Me_2GeCl_2[24] and Me_2GeBr_2,[23] respectively.

The Ge–S bond length of 2.262 (3) Å is essentially the sum of the covalent radii [2.26 Å],[25] slightly longer than that observed in $Ph_2Ge[S_2P(OMe)_2]_2$ [2.257 (2) and 2.253 (2) Å][1] but shorter than that found in $Ph_2Ge[S_2CNEt_2]_2$ [2.271 (1) Å][5] and in $Me_2Ge[S_2CNMe_2]_2$ [2.275 (2) and 2.281 (2) Å].[6] The S–Ge–S′ angle of 93.4 (2)° is closed down much more than the X–Ge–X angles of 105 (2)° for Me_2GeCl_2 and 104 (2)° for Me_2GeBr_2 but much less than the S–Ge–S angle of 84.4° in $Ph_2Ge[S_2CNMe_2]_2$.[5] The closing down allows the oxygen atoms to take up specific positions 2.920 (8) Å from germanium. Although this distance is less than the sum of the van der Waals radii, 3.47 Å,[25] it is considerably more than the sum of the covalent radii, 1.96 Å.[26] Even though this secondary interaction must be very weak, it nevertheless appears to be important enough to enforce the absence of a secondary interaction with the nonbonding sulfur atoms in contrast to the dithiocarbamates where the Ge⋯S nonbonding distances range from 3.183 (1) Å in $Ph_2Ge[S_2CNEt_2]_2$[5] to as short as 2.685 (2) Å in $Me_2Ge[S_2CNMe_2]I$,[27] compared to the sum of the van der Waals radii, 3.75 Å.[25] The accommodation of this secondary S interaction in dithiocarbamates presumably accounts for the even smaller S–Ge–S angle in $Ph_2Ge[S_2CNMe_2]_2$.[5] On a relative scale, the Ge⋯S secondary interactions for the dithiocarbamates are 20-40% longer than the sum of the covalent radii, whereas the Ge⋯O distance in this xanthate is approximately 50% longer. The large difference in the C=S [1.62 (1) Å] and C—SGe [1.76 (1) Å] bond lengths also suggests that the xanthate is essentially monodentate. The former is similiar to the 1.61 Å value found for the double bond in $H_2C{=}S$,[28] and the latter is only slightly shorter than the 1.81 Å length found for the single bond in $H_3C{-}SH$.[29] The bidentate ligands in $Sn[S_2COEt]_4$ have carbon–sulfur distances that are almost equivalent as well as equivalent metal–sulfur distances, while the two monodentate ligands have C–S bonds that are far from equivalent.[9] The difference is less marked in the case of $Sn[S_2COMe]_2$ where the "C=S" distance in one of the ligands is 1.662 (9) Å and the "C—SM" distance is 1.707 (10) Å.[11] However, in this case, the xanthate ligand is more bidentate than anisobidentate with M–S distances of 2.603 (3) and 2.813 (3) Å, respectively. In general, the difference in the two C–S bond lengths is significant but less marked for monodentate ligands that have the second S atom

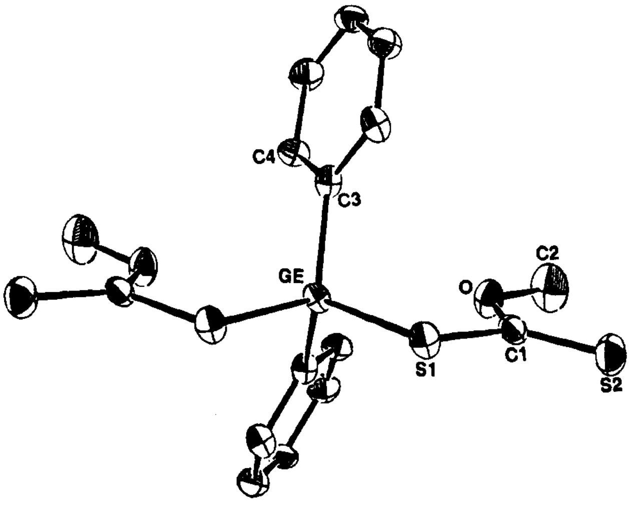

Figure 1. ORTEP drawing of $Ph_2Ge[S_2COMe]_2$ with thermal ellipsoids drawn at the 20% probability level.

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oriented toward the metal center as is exemplified by the structure of $[Et_4N][Te(S_2COEt)_3]$.[30] The xanthate ligands in bis(*O*-ethyl xanthato)bis(quinolin-8-olato)tin(IV), like those in $Ph_2Ge[S_2COMe]_2$, are oriented with the oxygen, not the second sulfur atom in the nonbonding position nearest the metal, and they too show similar large differences in the C=S and C—S bond lengths.[10]

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Supplementary Material Available: Tables SI–SIII, listing full experimental details, anisotropic thermal parameters for non-hydrogen atoms, and final fractional coordinates and thermal parameters for hydrogen atoms (3 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Studies of Sodium Complexes of *sym*-Dibenzo-14-crown-4 Ionizable Lariat Ethers

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Two lariat ethers of *sym*-dibenzo-14-crown-4 with acetate and propanoate pendant arms were synthesized and used to complex the Na^+ ion. The crystal structures of these two complexes and that of the Na^+ complex with (*sym*-dibenzo-14-crown-4-oxy)acetate were determined by X-ray diffraction. Molecular mechanics calculations indicated that intramolecular cation–anion bonding is possible for these complexes, but it was not found in any of these crystals. In the crystals of the acetate and propanoate derivatives there is intermolecular cation–anion bonding, and in the oxyacetate the cation is bonded to the O atom within the arm. Crystal data for $Na(C_{20}H_{21}O_6)\cdot H_2O\cdot CH_3OH$: monoclinic, $P2_1/c$, $a = 11.50$ (2) Å, $b = 17.40$ (3) Å, $c = 10.89$ (2) Å, $\beta = 101.72$ (1)°, $V = 2133.7$ Å^3, $Z = 4$. Refinement based on 3088 reflections with $I_o > \sigma(I_o)$ gave $R(F) = 0.052$. Crystal data for $Na(C_{21}H_{23}O_6)\cdot 2H_2O$: monoclinic, $P2_1/c$, $a = 12.95$ (1) Å, $b = 16.78$ (2) Å, $c = 9.58$ (1) Å, $\beta = 95.8$ (2)°, $V = 2071.0$ Å^3, $Z = 4$. Refinement based on 1273 reflections with $I_0 > 2\sigma(I_0)$ gave $R(F) = 0.065$. Crystal data for $Na(C_{20}H_{21}O_7)\cdot 3C_2H_5OH\cdot 0.5H_2O$: orthorhombic, $Pca2_1$, $a = 27.53$ (1) Å, $b = 12.008$ (5) Å, $c = 9.043$ (4) Å, $V = 2989.4$ Å^3, $Z = 4$. Refinement based on 1565 reflections with $I_o > 2\sigma(I_o)$ gave $R(F) = 0.060$.

Introduction

Lariat ethers were synthesized originally to increase the complexing ability of macrocyclic ethers through participation in the bonding by properly oriented side-arm donor atoms.[1-3] Later it was shown that the presence of ionizable functionalities on the side arms facilitated the phase transfer of cations by solvent extraction.[4] Crystal structure analyses have provided many examples of N-pivot lariat ethers in which an ether-coordinated cation is also bonded to one or more atoms of the sidearm.[5-11] As yet, there has appeared only one C-pivot lariat ether complex showing intramolecular bonding by the side-arm anion.[12]

Data on the kinetics and equilibria involved in the complexation of alkali-metal and alkaline-earth-metal ions in solution have been interpreted as indicating participation of the side-arm anions in intramolecular bonding for the cases of 18-crown-6 polycarboxylates[13] and (*sym*-dibenzo-16-crown-5-oxy)acetate.[14] The existence of such bonding is supported in the first case by the crystal structures of the Ca^{2+} and Sr^{2+} complexes of a similar 18-crown-6 ring substituted with two acetate ions that bond directly to these cations.[12] Relevant to the second case are the known crystal structures of complexes of closely related ligands, Li(**3**)$\cdot 7.5H_2O$[15] and Na(**4**)$\cdot H_2O\cdot 2$EtOH;[16] in neither of these is the anion bonded to the cation. There is, however, a bond between the O atom of the side arm and the Na^+ ion in Na(**4**)$\cdot 2H_2O\cdot$EtOH and a indirect linkage through a water molecule between the Li^+ ion and the O atom of the side arm in Li(**3**)$\cdot 7.5H_2O$.

The present study of lariat ethers was done to examine the structural constraints on the interactions between side-arm carboxylate ions and cations that are coordinated by the attached macrocycle. Of special interest was whether replacing the O atom in the side arm with a C atom in a ligand such as **3** facilitates intramolecular cation–anion bonding. To this end we have synthesized the lariat ethers having acetate and propanoate groups replacing the oxy acetate as the side arm of **3** and complexed these new ligands with the Na^+ ion to produce Na(**1**)$\cdot H_2O\cdot$MeOH and Na(**2**)$\cdot 2H_2O$. We also made Na(**3**)$\cdot 3$EtOH$\cdot 0.5H_2O$ for com-

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