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Synthesis and characterization of dithiocarbonate (xanthate) derivatives of various methyl-, t-butyl- and n-butylgermanes. Crystal structures of $MeGe[S_2COEt]_3 \cdot 0.37CS_2$ and $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$

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Abstract

The *O*-alkyl dithiocarbonate (xanthate) derivatives $MeGe[S_2COMe]_3$, $MeGe[S_2COEt]_3$, $MeGe[S_2CO(i\text{-}Pr)]_3$, $t\text{-}BuGe[S_2COEt]_3$, $t\text{-}BuGe[S_2CO(i\text{-}Pr)]_3$, $n\text{-}Bu_3Ge[S_2COEt]$ and $n\text{-}Bu_3Ge[S_2CO(i\text{-}Pr)]$ have been prepared in 64–70% yields by reaction of the sodium or potassium salt of the dithiocarbonic (xanthic) acid with trichloromethyl-, t-butyltrichloro- or tri-n-butylchlorogermane. The compounds were characterized by elemental analysis and infrared, Raman and ^1H and ^{13}C NMR spectroscopy. The molecular structures of $MeGe[S_2COEt]_3$ and $MeGe[S_2CO(i\text{-}Pr)]_3$ were determined and CS_2 was found in the crystal lattices. $MeGe[S_2COEt]_3 \cdot 0.37CS_2$ (**2**), which crystallizes as monoclinic in space group $P2_1/c$ (No. 14), has the cell parameters $a = 12.253(8)$, $b = 7.520(4)$, $c = 24.32(1)$ Å, $\beta = 103.74(4)°$, $V = 2177(2)$ Å^3, $Z = 4$, $R = 0.0667$, $R_w = 0.0632$. $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$ (**3**), which crystallizes as triclinic in space group $P\bar{1}$ (No. 2), has the cell parameters $a = 14.81(1)$, $b = 14.82(1)$, $c = 14.04(1)$ Å, $\alpha = 93.01(7)$, $\beta = 114.19(5)$, $\gamma = 60.09(4)°$, $V = 2392(7)$ Å^3, $Z = 4$, $R = 0.0662$, $R_w = 0.0672$. In both compounds, the immediate environment about germanium is very similar corresponding to a distorted tetrahedron in which the three monodentate dithiocarbonates subtend very similar angles so that the average of the three S–Ge–C angles is 115.9(2)° in **2** and 115.9(3)° in **3** and the average of the S–Ge–S angles is 102.3(2)° in both **2** and **3**. The Ge–C bond is 1.92(2) Å in **2** and 1.91(1) and 1.92(1) Å in the two independent molecules in **3**, and the Ge–S bonds average to 2.249(1) Å in **2** and 2.249(3) Å in **3**. All of the dithiocarbonate groups are oriented in an identical fashion so that the average Ge---O distance is 2.93(1) in **2** and 2.916(6) Å in **3**, with the non-bonded sulfur atoms turned away from the germanium center.

Introduction

As part of a general study of the structure–reactivity relationships in compounds containing a germanium–sulfur bond, we reported on various phenylgermanium xanthate derivatives [1, 2]. Phenyl derivatives were chosen because it was assumed they would be more likely to yield X-ray quality crystals and thus provide definitive solid state structures. On the other hand, there was an interest in the possible development of germanium–sulfur derivatives as fuel additives and to this end it was assumed that alkyl-substituted germanes should provide a more appropriate medium in terms of dissolution in base oil. Thus we undertook a study of a cross section of O-alkyldithiocarbonate derivatives with methyl-, t-butyl- and n-butylgermanes; the selection also being dictated to some extent by the ready availability of organogermanium starting compounds.

Experimental

Materials

Trichloromethylgermane (Alfa) was purified by trapping it out at −23 °C. The other chlorogermanes were used as supplied. Sodium *O*-methyl dithiocarbonate and potassium *O*-ethyl and *O*-isopropyl dithiocarbonate were prepared by adding a slight excess of CS_2 into a mixture of equimolar amounts of NaOH or KOH and ROH, where R = Me, Et and i-Pr, in the manner described previously [3], and their purity checked by ^1H and ^{13}C NMR spectroscopy. Distilled carbon disulfide (dried over P_4O_{10}) was used as the solvent in all reactions involving an alkylchlorogermane and a xanthate salt. The reactions were carried out on a vacuum line to

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exclude air and moisture essentially by using the method outlined earlier [4].

Preparation of tris(O-alkyl dithiocarbonato)-methylgermanes

Typically, the salt NaS_2COMe (0.926 g, 0.712 mmol) was placed in a round bottom flask and was held at −196 °C. The flask was then degassed followed by distillation of CS_2 (10 ml) onto the salt. Trichloromethylgermane (0.2 ml, 1.78 mmol) was then distilled into the flask. The Dewar flask containing the liquid nitrogen was removed from around the reaction vessel and the temperature of the mixture was allowed to reach ambient. The mixture was stirred for 5 h and then the solid NaCl was removed by filtration. The volume of the solvent was reduced *in vacuo* and the yellow solution was kept in the refrigerator. $MeGe[S_2COMe]_3$ (**1**) was obtained as a yellow oil (65% yield) on slow evaporation of the solvent. Similarly, using KS_2COEt and $KS_2CO(i\text{-}Pr)$ as the xanthate salts, $MeGe[S_2COEt]_3$ (**2**): fine needle-shaped pale yellow crystals, yield 64%, m.p. 62–64 °C, and $MeGe[S_2CO(i\text{-}Pr)]_3$ (**3**): yellow block-shaped crystals, yield 70%, m.p. 72–75 °C, were prepared.

Preparation of tris(O-alkyl dithiocarbonato)-t-butylgermanes

Typically, the salt KS_2COEt (0.561 g, 3.50 mmol) and $t\text{-}BuGeCl_3$ (0.257 g, 1.0 mmol) were placed in a round-bottom flask and degassed. The solvent, CS_2 (9 ml), was then distilled into the vessel held at −196 °C. The mixture was allowed to warm to ambient temperature and stirred for 4 h. The solid KCl was then removed by filtration and the solvent was pumped off *in vacuo* to yield $t\text{-}BuGe[S_2COEt]_3$ (**4**) as a yellow oil; yield 70%. *Anal.* Calc. for $C_{13}H_{24}O_3S_6Ge$: C, 31.57; H, 4.90. Found: C, 31.74; H, 4.60%. Similarly, using $KS_2CO(i\text{-}Pr)$, $t\text{-}BuGe[S_2CO(i\text{-}Pr)]_3$ (**5**): yellow amorphous solid, yield 55%, m.p. 52–55 °C, was prepared. *Anal.* Calc. for $C_{16}H_{30}O_3S_6Ge$: C, 35.89; H, 5.64. Found: C, 34.58; H, 5.79%.

Preparation of (O-alkyl dithiocarbonato)-tri-n-butylgermanes

Typically, carbon disulfide (7 ml) was distilled into the reaction vessel containing previously degassed KS_2COEt (0.21 g, 1.31 mmol) and $n\text{-}Bu_3GeCl$ (0.256 g, 0.92 mmol) which was held at −196 °C. The mixture was allowed to warm up gradually to ambient temperature and stirred for *c.* 5 h before the KCl formed was filtered off. The solvent was then pumped off to eventually leave $n\text{-}Bu_3Ge[S_2COEt]$ (**6**) as a yellow oil; yield 65%. *Anal.* Calc. for $C_{15}H_{32}OS_2Ge$: C, 49.34; H, 8.83. Found: C, 49.33; H, 8.78%. Similarly, using $KS_2CO(i\text{-}Pr)$, $n\text{-}Bu_3Ge[S_2CO(i\text{-}Pr)]$ (**7**): yellow oil, yield 64%, was prepared. *Anal.* Calc. for $C_{16}H_{34}OS_2Ge$: C, 50.68; H, 9.03. Found: C, 48.65; H, 8.73%.

Physical measurements

Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ont., Canada. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 FT NMR spectrometer in $CDCl_3$ solutions. IR spectra were recorded on a Nicolet 5DX FT spectrometer as CsI pellets or Nujol mulls or as neat liquids between CsI plates. Raman spectra were recorded on a Spectra-Physics 164 spectrometer 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

Crystals of $MeGe[S_2COEt]_3 \cdot 0.37CS_2$ (**2**) and $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$ (**3**) were sealed in thin-walled glass capillaries 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 15 carefully centered reflections in the range $12.7 < 2\theta < 15.3°$ for **2** and $28.9 < 2\theta < 34.8°$ for **3**, corresponded to a monoclinic cell for **2** and a triclinic cell for **3**, dimensions being given in Table 1. On the basis of the systematic absences of $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) in the case of **2**, packing considerations, statistical analysis and successful solution and refinement of the structures, the space groups were determined to be $P2_1/c$ (C^5, No. 14) for **2** and $P\bar{1}$ (Ci^1, No. 2) for **3**.

The pertinent details of data collection are presented in Table 1 in abbreviated form. In the case of **2**, the intensities of three representative reflections which were measured after every 150 reflections declined by 21% and consequently a linear correction factor was applied. In the case of **3**, the crystal decayed so much at 23 °C that collection was stopped. However, data collected at −28 °C showed no significant signs of decay. The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on azimuthal scans of several reflections was applied in each case.

The structures were solved by direct methods [5]. Only germanium and sulfur atoms were refined anisotropically for **2** because the data were limited as a result of decay and the thermal parameters are relatively large. All of the non-hydrogen atoms were treated anisotropically for **3**. Hydrogen atoms were included in their idealized positions with C–H set at 0.95 Å and with thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final

TABLE 1. Crystallographic data for $MeGe[S_2COEt]_3 \cdot 0.37CS_2$ (**2**) and $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$ (**3**)

Chemical formula	$C_{10.37}H_{18}S_{6.74}O_3Ge$	$C_{13.5}H_{24}S_7O_3Ge$
Formula weight	479.37	531.35
a (Å)	12.253(8)	14.81(1)
b (Å)	7.520(4)	14.82(1)
c (Å)	24.32(1)	14.04(1)
α (°)	90.00	93.01(7)
β (°)	103.74(4)	114.19(5)
γ (°)	90.00	60.09(4)
V (Å^3)	2177(2)	2393(7)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	4
T (°C)	23	−28
λ (Å)	0.71069	0.71069
Absorption coefficient, μ (cm^{-1})	20.68	19.60
Transmission factors	0.73–1.00	0.77–1.00
2θ Angle, max. (°)	45	50
Scan type	ω–2θ	ω–2θ
Scan width (°)	$(0.80+0.3 \tan \theta)$	$(1.57+0.3 \tan \theta)$
Scan speed (° min^{-1})	32.0 (in ω)	32.0 (in ω)
Background time/scan time	0.5	0.5
Total reflections measured	3294	8856
Unique data used	873 ($I<10.0\sigma(I)$)	3454 ($I<10.0\sigma(I)$)
No. parameters (NP)	126	442
R	0.0667	0.0662
R_w	0.0632	0.0672
GOF	1.73	1.85

cycles of full-matrix least-squares refinement* converged (largest parameter shift was 0.0002 (for **2**) and 0.0001 (for **3**) times its e.s.d.) with unweighted and weighted agreement factors of:

$$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.0667 \text{ (for } \mathbf{2}\text{)}$$

$$\text{and } 0.0662 \text{ (for } \mathbf{3}\text{)}$$

$$R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}=0.0632 \text{ (for } \mathbf{2}\text{)}$$

$$\text{and } 0.0672 \text{ (for } \mathbf{3}\text{)}$$

The standard deviation of an observation of unit weight** was 1.73 for **2** and 1.85 for **3**. The weighting scheme was based on counting statistics and included a factor ($p=0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_o|-|F_c|)^2$ 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 0.56 and −0.51 e$^-$/Å^3, respectively, for **2** and 0.35 and −1.46 e$^-$/Å^3 for **3**.

Neutral atom scattering factors were taken from Cromer and Waber [6]. Anomalous dispersion effects were included in F_c [7]; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer [8]. All calculations were performed using the TEXSAN [9] crystallographic software package of the Molecular Structure Corporation.

The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables 2 and 3, important distances and bond angles in Tables 4 and 5, and ORTEP diagrams in Figs. 1 and 2. See also 'Supplementary material'.

Results and discussion

The synthesis of a variety of dithiocarbonate derivatives of alkylgermanes is readily achieved in 55–74% yield by the action of the appropriate sodium or potassium salt of an *O*-alkyl dithiocarbonic acid with trichloromethyl-, t-butyltrichloro- or tri-n-butylchlorogermane in CS_2 as solvent in accord with the equations

$$MeGeCl_3+3MS_2COR \longrightarrow MeGe[S_2COR]_3+3MCl$$

(where M=Na, K; R=Me, Et, i-Pr)

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

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

TABLE 2. Final fractional coordinates and B_{eq} for non-hydrogen atoms of $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.37CS_2$ with standard deviations in parentheses

Atom	x	y	z	B_{eq}
Ge	0.2051(2)	0.1485(3)	0.6417(1)	4.5(1)
S(1)	0.1777(5)	−0.1091(8)	0.6836(2)	5.4(3)
S(2)	−0.0237(5)	−0.2726(8)	0.7051(3)	6.1(4)
S(3)	0.1158(5)	0.0997(8)	0.5510(2)	5.9(4)
S(4)	0.0857(7)	0.327(1)	0.4509(3)	9.0(5)
S(5)	0.3864(5)	0.130(1)	0.6382(2)	6.0(4)
S(6)	0.5954(6)	0.132(1)	0.7272(3)	9.5(5)
S(7)	0.397(1)	0.100(2)	0.4755(5)	15(1)
O(1)	−0.013(1)	0.037(2)	0.6590(5)	5.0(4)
O(2)	0.204(1)	0.407(2)	0.5525(5)	5.5(4)
O(3)	0.390(1)	0.146(2)	0.7447(6)	5.4(3)
C(1)	0.164(2)	0.361(3)	0.6757(9)	6.4(6)
C(2)	0.035(2)	−0.116(3)	0.6820(8)	4.6(5)
C(3)	−0.137(2)	0.057(3)	0.6545(1)	6.6(7)
C(4)	−0.167(2)	0.236(4)	0.625(1)	8.9(8)
C(5)	0.135(2)	0.296(3)	0.516(1)	6.0(6)
C(6)	0.234(2)	0.577(4)	0.530(1)	9.4(8)
C(7)	0.325(3)	0.644(4)	0.571(1)	13(1)
C(8)	0.458(2)	0.136(3)	0.709(1)	5.3(5)
C(9)	0.440(2)	0.137(3)	0.807(1)	6.1(6)
C(10)	0.352(2)	0.126(4)	0.833(1)	9.3(8)
C(11)	1/2	0	1/2	9(2)

$$t\text{-}BuGeCl_3 + 3KS_2COR' \longrightarrow t\text{-}BuGe[S_2COR']_3 + 3KCl$$

$$n\text{-}Bu_3GeCl + KS_2COR' \longrightarrow n\text{-}Bu_3Ge[S_2COR'] + KCl$$

(where $R' = Et$, i-Pr)

The success of these preparations was gratifying because it had not been possible to obtain pure samples of the phenyl analogues of the tris-substituted species, $PhGe[S_2COMe]_3$ and $PhGe[S_2COEt]_3$ [2], and it had been noted earlier that while attempts to prepare $Cl_2Sn[S_2COR]_2$ species were successful, attempts to prepare the corresponding mono and tris compounds were not [10].

Although all of the compounds are stable in chloroform (see below), they are sensitive to air and moisture when the isolated compounds are exposed for any length of time to air at room temperature. Also, although we were able to solve the crystal structure of two compounds, the methyl derivatives are stable for only a matter of hours when held at room temperature and were therefore not sent away for elemental analyses. However, all of the compounds are well characterized by NMR, IR and Raman spectroscopy. They are readily soluble in chloroform, which was used as the preferred solvent for recording NMR spectra, and the spectra recorded over time remain unchanged suggesting that the xanthates are stable in solution. They were also found to be soluble and stable in base-oil.

TABLE 3. Final fractional coordinate and B_{eq} for non-hydrogen atoms of $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50Cs_2$ with standard deviations in parentheses

Atom	x	y	z	B_{eq}
Ge(1)	0.7200(1)	0.4570(1)	0.3127(1)	2.5(1)
Ge(2)	0.3243(1)	0.1503(1)	0.1871(1)	2.4(1)
S(1)	0.9082(3)	0.3264(3)	0.3925(3)	3.2(3)
S(2)	1.1178(3)	0.3079(3)	0.4014(3)	3.7(3)
S(3)	0.7225(3)	0.5932(3)	0.3875(3)	3.1(3)
S(4)	0.5358(4)	0.7967(3)	0.3928(3)	3.7(3)
S(5)	0.6408(4)	0.4104(3)	0.3928(3)	3.3(3)
S(6)	0.6304(4)	0.2204(3)	0.4083(3)	3.9(3)
S(7)	0.1360(3)	0.2831(3)	0.1093(3)	3.3(3)
S(8)	−0.0731(3)	0.2995(3)	0.0987(3)	3.9(3)
S(9)	0.4051(3)	0.1972(3)	0.1102(3)	3.2(3)
S(10)	0.4214(3)	0.3854(3)	0.1040(3)	3.5(3)
S(11)	0.3192(3)	0.0166(3)	0.1074(3)	3.2(3)
S(12)	0.5037(3)	−0.1855(3)	0.0965(3)	3.5(3)
S(13)	0.9111(5)	0.2184(4)	0.6284(4)	6.0(5)
S(14)	1.0347(5)	0.1740(5)	0.8712(5)	6.4(5)
O(1)	0.9006(7)	0.4689(7)	0.2884(7)	2.7(7)
O(2)	0.5082(7)	0.6551(7)	0.2797(7)	2.9(7)
O(3)	0.7181(8)	0.2601(7)	0.2956(7)	3.1(7)
O(4)	0.1443(8)	0.1365(6)	0.2099(7)	3.0(7)
O(5)	0.3338(8)	0.3431(7)	0.2161(7)	3.1(7)
O(6)	0.5325(8)	−0.0452(7)	0.2110(7)	3.1(7)
C(1)	0.647(1)	0.482(1)	0.161(1)	4(1)
C(2)	0.976(1)	0.376(1)	0.356(1)	3(1)
C(3)	0.945(1)	0.523(1)	0.254(1)	4(1)
C(4)	0.848(1)	0.592(1)	0.150(1)	5(1)
C(5)	0.975(2)	0.584(1)	0.335(2)	6(2)
C(6)	0.575(1)	0.688(1)	0.346(1)	2(1)
C(7)	0.381(1)	0.721(1)	0.237(1)	4(1)
C(8)	0.347(1)	0.696(1)	0.315(2)	6(2)
C(9)	0.333(1)	0.694(1)	0.129(1)	6(2)
C(10)	0.667(1)	0.288(1)	0.363(1)	4(1)
C(11)	0.751(1)	0.160(1)	0.263(1)	4(1)
C(12)	0.751(2)	0.174(1)	0.159(1)	6(2)
C(13)	0.864(2)	0.079(2)	0.345(2)	7(2)
C(14)	0.398(1)	0.117(1)	0.340(1)	3(1)
C(15)	0.069(1)	0.231(1)	0.144(1)	3(1)
C(16)	0.102(1)	0.084(1)	0.247(1)	4(1)
C(17)	0.201(1)	0.012(1)	0.354(1)	6(2)
C(18)	0.072(2)	0.022(2)	0.166(2)	6(2)
C(19)	0.382(1)	0.318(1)	0.146(1)	3(1)
C(20)	0.301(1)	0.444(1)	0.250(1)	4(1)
C(21)	0.311(1)	0.425(1)	0.361(1)	5(1)
C(22)	0.183(1)	0.525(1)	0.169(1)	5(1)
C(23)	0.464(1)	−0.077(1)	0.142(1)	2(1)
C(24)	0.663(1)	−0.114(1)	0.251(1)	5(1)
C(25)	0.692(1)	−0.090(1)	0.167(1)	6(2)
C(26)	0.711(1)	−0.085(1)	0.354(1)	5(1)
C(27)	0.970(1)	0.194(1)	0.747(2)	4(1)

NMR spectra

The ^1H and $^{13}C\{H\}$ NMR spectra data are presented in Tables 6 and 7. The ^1H NMR spectra confirm that the products are over 98% pure relative to any hydrogen-containing impurities, and integrations are as expected for all species. The ^1H NMR spectra of all of the methylgermanium derivatives (**1**–**3**) show the expected

TABLE 4. Interatomic distances (Å) for $MeGe[S_2COEt]_3 \cdot 0.37CS_2$ (**2**) and $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$ (**3**) with standard deviations in parentheses

$MeGe[S_2COEt]_3 \cdot 0.37CS_2$ (**2**)		$MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$ (**3**)			
Ge-S(1)	2.251(6)	Ge(1)-S(1)	2.249(5)	Ge(2)-S(7)	2.259(5)
Ge-S(3)	2.247(6)	Ge(1)-S(3)	2.236(5)	Ge(2)-S(9)	2.248(4)
Ge-S(5)	2.248(6)	Ge(1)-S(5)	2.256(4)	Ge(2)-S(11)	2.244(5)
Ge-C(1)	1.92(2)	Ge(1)-C(1)	1.91(1)	Ge(2)-C(14)	1.92(1)
S(1)-C(2)	1.74(2)	S(1)-C(2)	1.73(1)	S(7)-C(15)	1.75(1)
S(2)-C(2)	1.56(2)	S(2)-C(2)	1.64(1)	S(8)-C(15)	1.64(1)
S(3)-C(5)	1.75(2)	S(3)-C(6)	1.75(1)	S(9)-C(19)	1.74(1)
S(4)-C(5)	1.57(2)	S(4)-C(6)	1.62(1)	S(10)-C(19)	1.62(1)
S(5)-C(8)	1.75(2)	S(5)-C(10)	1.72(2)	S(11)-C(23)	1.74(1)
S(6)-C(8)	1.64(2)	S(6)-C(10)	1.62(1)	S(12)-C(23)	1.61(1)
O(1)-C(2)	1.35(2)	O(1)-C(2)	1.34(1)	O(4)-C(15)	1.34(1)
O(1)-C(3)	1.51(2)	O(1)-C(3)	1.45(2)	O(4)-C(16)	1.45(1)
O(2)-C(5)	1.36(2)	O(2)-C(6)	1.33(1)	O(5)-C(19)	1.37(1)
O(2)-C(6)	1.47(3)	O(2)-C(7)	1.47(1)	O(5)-C(20)	1.45(2)
O(3)-C(8)	1.33(2)	O(3)-C(10)	1.36(2)	O(6)-C(23)	1.35(1)
O(3)-C(9)	1.49(2)	O(3)-C(11)	1.43(2)	O(6)-C(24)	1.51(2)
C(3)-C(4)	1.52(3)	C(3)-C(4)	1.49(2)	C(16)-C(17)	1.53(2)
C(6)-C(7)	1.40(3)	C(3)-C(5)	1.49(2)	C(16)-C(18)	1.49(2)
C(9)-C(10)	1.39(3)	C(7)-C(8)	1.51(2)	C(20)-C(21)	1.53(2)
		C(7)-C(9)	1.52(2)	C(20)-C(22)	1.49(2)
		C(11)-C(12)	1.49(2)	C(24)-C(25)	1.52(2)
		C(11)-C(13)	1.46(2)	C(24)-C(26)	1.48(2)
Ge---O(1)	2.93(2)	Ge(1)---O(1)	2.922(8)	Ge(2)---O(4)	2.916(9)
Ge---O(2)	2.91(2)	Ge(1)---O(2)	2.905(9)	Ge(2)---O(5)	2.93(1)
Ge---O(3)	2.95(2)	Ge(1)---O(3)	2.93(1)	Ge(2)---O(6)	2.892(9)
Ge---S(2)	4.724(7)	Ge(1)---S(2)	4.738(6)	Ge(2)---S(8)	4.733(6)
Ge---S(4)	4.718(7)	Ge(1)---S(4)	4.721(6)	Ge(2)---S(10)	4.731(5)
Ge---S(6)	4.743(8)	Ge(1)---S(6)	4.739(6)	Ge(2)---S(12)	4.730(6)
S(7)-C(11)	1.47(1)	S(13)-C(27)	1.50(2)	S(14)-C(27)	1.56(2)

singlets due to the methyl groups on germanium at 1.78, 1.75 and 1.69 ppm, respectively. Chemical shifts have been correlated to the effective electronegativity of the group attached to germanium so that, for example, within the series $MeGeCl_3$, $MeGeBr_3$ and $MeGeI_3$, the chemical shifts of the methyl protons are 1.58, 1.98 and 2.61, respectively [11], with the various mixed species falling systematically between these values [12]. It was noted, for the corresponding $MeGe[S_2CNEt_2]_3$ species [13], that the chemical shift of its methyl proton of 1.93 ppm was close to the value of that in $MeGeBr_3$, whereas the value of 1.75 ppm for $MeGe[S_2COEt]_3$ is closer to that reported for $MeGeCl_2Br$ of 1.74 ppm [12]. Thus the effective electronegativity of the xanthate appears to be greater than that of the corresponding dithiocarbamate. The chemical shifts of the CH_3 and CH_2 protons of the ethyl groups in the two tris compounds $MeGe[S_2COEt]_3$ (**2**) and $t\text{-}BuGe[S_2COEt]_3$ (**4**) are essentially identical 1.44 and 4.57, and 1.45 and 4.58 ppm, respectively, but differ somewhat from the values reported in the aromatic substituted analogue, $PhGe[S_2COEt]_3$, where the values were 1.23 and 4.45 ppm [2]. Similarly, while the CH_3 and CH protons of the iso-propyl groups in $MeGe[S_2CO(i\text{-}Pr)]_3$ (**3**) and $t\text{-}BuGe[S_2CO(i\text{-}Pr)]_3$ (**5**) are essentially identical, see Table 6, those of $PhGe[S_2CO(i\text{-}Pr)]_3$ do differ with values of 1.22 and 5.53 ppm [2]. The peaks attributable to the CH_3 protons of the t-butyl group are seen as the expected intense singlets in compounds **4** and **5** at 1.42 and 1.39 ppm, respectively. The chemical shifts of the ethyl and isopropyl protons of the ligands in the mono-substituted tri-n-butyl germanium xanthates have similar shifts to those of the tris compounds. The four groups of peaks arising from the n-butyl groups cover the same range for both compounds **6** and **7**, namely 1.43–0.85 ppm, which is very similar to that observed in the starting material, $n\text{-}Bu_3GeCl$, where triplets and multiplets are centered at 0.88, 1.12, 1.33 and 1.43 ppm.

The ^{13}C NMR spectra of all three methyl germanium derivatives, **1**, **2** and **3**, show peaks due to the methyl group attached to germanium at 12.56, 12.99 and 13.14 ppm, respectively. In $MeGeCl_3$ and $MeGeBr_3$, the methyl peak appears at 15.92 and 20.37 ppm, respectively [14]. A peak at 60.86 ppm in compound **1** is assignable to the CH_3 of the methoxy group in the ligand. This is essentially in the same position as the 60.75 ppm observed in the starting salt, NaS_2COMe. Similarly,

TABLE 5. Angles (°) for $MeGe[S_2COEt]_3 \cdot 0.37CS_2$ (**2**) and $MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$ (**3**) with standard deviations in parentheses

$MeGe[S_2COEt]_3 \cdot 0.37CS_2$ (**2**)		$MeGe[S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$ (**3**)			
S(1)–Ge–S(3)	102.3(2)	S(1)–Ge(1)–S(3)	102.5(2)	S(7)–Ge(2)–S(9)	102.9(2)
S(1)–Ge–S(5)	102.7(3)	S(1)–Ge(1)–S(5)	102.4(2)	S(7)–Ge(2)–S(11)	102.5(2)
S(1)–Ge–S(7)	102.0(3)	S(3)–Ge(1)–S(5)	102.0(2)	S(9)–Ge(2)–S(11)	101.7(2)
S(1)–Ge–C(1)	116.0(7)	S(1)–Ge(1)–C(1)	115.7(5)	S(7)–Ge(2)–C(14)	116.1(4)
S(3)–Ge–C(1)	116.2(6)	S(3)–Ge(1)–C(1)	116.4(4)	S(9)–Ge(2)–C(14)	116.6(4)
S(5)–Ge–C(1)	115.5(7)	S(5)–Ge(1)–C(1)	115.7(4)	S(11)–Ge(2)–C(14)	114.9(5)
Ge–S(1)–C(2)	105.8(9)	Ge(1)–S(1)–C(2)	103.1(5)	Ge(2)–S(7)–C(15)	102.3(5)
Ge–S(3)–C(5)	104.6(8)	Ge(1)–S(3)–C(6)	103.4(5)	Ge(2)–S(9)–C(19)	103.6(5)
Ge–S(5)–C(8)	103.1(8)	Ge(1)–S(5)–C(10)	104.0(5)	Ge(2)–S(11)–C(23)	104.1(5)
S(1)–C(2)–S(2)	124(1)	S(1)–C(2)–S(2)	120.3(8)	S(7)–C(15)–S(8)	119.5(8)
S(3)–C(5)–S(4)	124(2)	S(3)–C(6)–S(4)	120.5(8)	S(9)–C(19)–S(10)	121.3(8)
S(5)–C(8)–S(6)	120(1)	S(5)–C(10)–S(6)	121.7(9)	S(11)–C(23)–S(12)	122.3(8)
S(1)–C(2)–O(1)	109(2)	S(1)–C(2)–O(1)	112.6(9)	S(7)–C(15)–O(4)	112.8(9)
S(3)–C(5)–O(2)	109(2)	S(3)–C(6)–O(2)	111.3(9)	S(9)–C(19)–O(5)	112(1)
S(5)–C(8)–O(3)	114(2)	S(5)–C(10)–O(3)	112(1)	S(11)–C(23)–O(6)	110(1)
S(2)–C(2)–O(1)	127(2)	S(2)–C(2)–O(1)	127(1)	S(8)–C(15)–O(4)	128(1)
S(4)–C(5)–O(2)	127(2)	S(4)–C(6)–O(2)	128(1)	S(10)–C(19)–O(5)	127(1)
S(6)–C(8)–O(3)	126(2)	S(6)–C(10)–O(3)	126(1)	S(12)–C(23)–O(6)	128(1)
C(2)–O(1)–C(3)	117(2)	C(2)–O(1)–C(3)	119(1)	C(15)–O(4)–C(16)	119(1)
C(5)–O(2)–C(6)	118(2)	C(6)–O(2)–C(7)	121(1)	C(19)–O(5)–C(20)	120(1)
C(8)–O(3)–C(9)	118(2)	C(10)–O(3)–C(11)	121(1)	C(23)–O(6)–C(24)	119(1)
O(1)–C(3)–C(4)	104(2)	O(1)–C(3)–C(4)	105(1)	O(4)–C(16)–C(17)	106(1)
O(2)–C(6)–C(7)	107(2)	O(1)–C(3)–C(5)	109(1)	O(4)–C(16)–C(18)	107(1)
O(3)–C(9)–C(10)	107(2)	O(2)–C(7)–C(8)	108(1)	O(5)–C(20)–C(21)	105(1)
		O(2)–C(7)–C(9)	106(1)	O(5)–C(20)–C(22)	108(1)
		O(3)–C(11)–C(12)	106(1)	O(6)–C(24)–C(25)	108(1)
		O(3)–C(11)–C(13)	109(1)	O(6)–C(24)–C(26)	104(1)
		C(4)–C(3)–C(5)	112(2)	C(17)–C(16)–C(18)	112(1)
		C(8)–C(7)–C(9)	114(1)	C(21)–C(20)–C(22)	115(1)
		C(12)–C(11)–C(13)	113(1)	C(25)–C(24)–C(26)	115(1)
S(7)–C(11)–S′(7)	180.00	S(13)–C(27)–S(14)	176(1)		

Symmetry equivalent position: prime indicates $1-x$, $-y$, $1-z$.

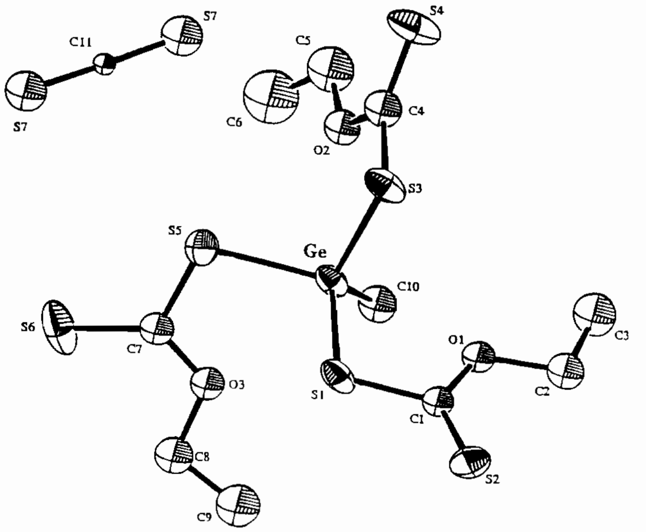

Fig. 1. ORTEP plot of the molecule $MeGe[S_2COEt]_3 \cdot 0.37CS_2$. The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

chemical shifts of the CH_2 and CH_3 carbon atoms of the ethoxy groups in compounds **2**, **4** and **6**, see Table 7, are not very different from those of the salt, KS_2COEt, at 71.28 and 14.67 ppm, respectively. The same can be said for the chemical shifts of the CH and CH_3 carbon atoms of the isopropoxy groups in compounds **3**, **5** and **7** when compared to the values of 78.80 and 21.59 ppm in $KS_2CO(i\text{-}Pr)$. However, in all of the compounds, the chemical shift of the CS_2 carbon is clearly different from that of the corresponding salt. In the salts, MS_2COR, the peaks are at 233.12, 233.71 and 232.82 ppm for R = Me, Et and i-Pr, respectively. By contrast the CS_2 peak is seen in all of the tris-substituted compounds, **1**–**5**, in the range 208.37–210.27 ppm. The considerable upfield shift presumably reflects the fact that the environment about the thiocarbon atom is most altered by the formation of a bond to germanium by one of the sulfur atoms. The shift is less marked in the mono-substituted derivatives, **7** and **8**. A similar trend was noted for the $Ph_3Ge[S_2COR]$ and $PhGe[S_2COR]_3$ analogues [2]. In view of the trends noted for the ^1H NMR spectra, it is not surprising that the two peaks assigned to $C(CH_3)_3$ and $C(CH_3)_3$ in

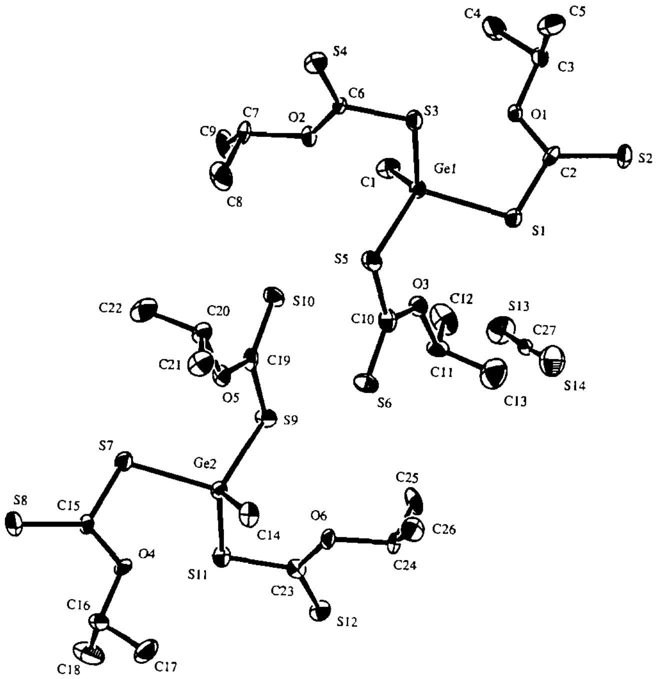

Fig. 2. ORTEP plot of the molecule MeGe[$S_2CO(i\text{-}Pr)]_3 \cdot 0.50CS_2$. The atoms are drawn with 25% probability ellipsoids. Hydrogen atom are omitted for clarity.

the t-butylgermanium derivatives, **4** and **5**, give similar values to those observed in the starting material t-$BuGeCl_3$ of 43.27 and 24.82 ppm; the larger differences being for the carbon attached to germanium. For the tri-n-butylgermanium derivatives, **6** and **7**, the four peaks of the n-C_4H_9 group are seen at positions very comparable, but by no means identical, to those in n-Bu_3GeCl in which they are seen at 13.60 , 18.73, 25.79 and 26.21 ppm.

Infrared and Raman spectra

Distinctive features in the vibrational spectra of the three methylgermanium xanthates, **1**–**3**, are listed in Table 8. As expected, the spectra are dominated by features attributable to the S_2COC skeleton of the three xanthate ligands in contrast to that of $MeGeCl_3$ where the most dominant features are attributable to the CH_3 rock at 825 cm^{-1} (IR), the Ge–C stretch at 629 cm^{-1} (IR and Raman), the Ge–Cl asymmetric stretch at 424 cm^{-1} (IR) and the Ge–Cl symmetric stretch at 396 cm^{-1} (Raman) [15]. The methylgermanium Ge–CH_3 rocking mode is evident in the spectra of **1**–**3** but it is now relatively weak. Similarly, the peak attributable to ν(Ge–C) is only a weak band or shoulder in the IR spectrum of all three compounds, but is clearly identified in the Raman spectra at 615, 609 and 602 cm^{-1} for **1**, **2** and **3**, respectively. The shift in wave number suggests that the Ge–C bond in the xanthates is slightly weaker and longer than in $MeGeCl_3$ where it is unusually short [16]. The Ge–S stretching modes are evident as Raman bands in the range 410–423 cm^{-1} for the asymmetric and 360–392 cm^{-1} for the symmetric mode, the latter being the strongest feature for all three compounds. The splitting between the bands is much smaller for the methylxanthate suggesting that the S–Ge–S angle may be closer to 90° than is the case for the ethyl and isopropyl analogues. This is consistent with **2** and **3** having larger S–Ge–S angles to accommodate the greater steric requirements of ethyl and isopropyl groups as was found for $Ph_2Ge[S_2CO(i\text{-}Pr)]_2$ compared with $Ph_2Ge[S_2COMe]_2$ [1, 2]. The three characteristic strong bands in the IR spectra of **1**–**3** assignable to $\nu(S_2COC)_a$, $\nu(S_2COC)_b$ and $\nu(S_2COC)_c$ are seen in **3** at 1245, 1088 and 1029 cm^{-1}, respectively. These positions are very close to those found for $PhGe[S_2CO(i\text{-}Pr)]_3$ and thus confirm the correctness of the assignment of the band at 1086 cm^{-1} in the phenyl analogues where there was overlap with the q-phenyl vibration [2]. The fourth $(S_2COC)_d$ band is readily assigned in all three compounds to the most intense band in the 650–700 cm^{-1} region in the Raman effect in agreement with the $PhGe[S_2COR]_3$ analogues [2].

TABLE 6. ^1H NMR chemical shifts for compounds 1–7[a, b]

	$GeCH_3/GeC(CH_3)_3/GeC_4H_9$	$OCH_3/OCH_2/OCH$	$OCCH_3$	J(HH')
$MeGe[S_2COMe]_3$ (**1**)	1.78 (3H, s)	4.10 (9H, s)		
$MeGe[S_2COEt]_3$ (**2**)	1.75 (3H, s)	4.57 (6H, q)	1.44 (9H, t)	7.2
$MeGe[S_2CO(i\text{-}Pr)]_3$ (**3**)	1.69 (3H, s)	5.60 (3H, sept)	1.42 (18H, d)	6.2
t-$BuGe[S_2COEt]_3$ (**4**)	1.42 (9H, s)	4.58 (6H, q)	1.45 (9H, t)	7.2
t-$BuGe[S_2CO(i\text{-}Pr)]_3$ (**5**)	1.39 (9H, s)	5.63 (3H, sept)	1.42 (18H, d)	6.2
n-$Bu_3Ge[S_2COEt]$ (**6**)	1.44–0.85 (27H, m)[c]	4.50 (2H, q)	1.36 (3H, t)	7.2
n-$Bu_3Ge[S_2CO(i\text{-}Pr)]$ (**7**)	1.43–0.84 (27H, m)[d]	5.65 (1H, sept)	1.35 (6H, d)	7.2

[a] The spectra were recorded in $CDCl_3$ and reported in ppm from Me_4Si using $CHCl_3$ as a second standard. [b] Number of protons and multiplicities are in parentheses (s = singlet, t = doublet, q = quartet, t = triplet, sept = septet, m = multiplet). [c] Triplets centered at 0.88 and 1.17 ppm; multiplets centered at 1.29 and 1.42 ppm. [d] Triplets centered at 0.87 and 1.16 ppm; multiplets centered at 1.29 and 1.41 ppm.

TABLE 7. ^{13}C NMR chemical shifts for compounds 1–7[a]

	$GeCH_3/GeC(CH_3)_3/GeC_4H_9$	$OCH_3/OCH_2/OCH$	$OCCH_3$	CS_2
MeGe[S_2COMe]$_3$ (**1**)	12.56	60.86		210.27
MeGe[S_2COEt]$_3$ (**2**)	12.99	71.37	13.72	209.22
MeGe[S_2CO(i-Pr)]$_3$ (**3**)	13.14	80.01	21.23	208.37
t-BuGe[S_2COEt]$_3$ (**4**)	42.84, 28.55	71.71	13.82	209.50
t-BuGe[S_2CO(i-Pr)]$_3$ (**5**)	41.71, 28.44	80.59	21.23	208.66
n-Bu$_3$Ge[S_2COEt] (**6**)	26.92, 26.03, 16.41, 13.51	69.97	13.74	214.94
n-Bu$_3$Ge[S_2CO(i-Pr)] (**7**)	26.98, 26.01 16.53, 13.59	79.01	21.26	214.30

[a] The spectra were recorded in $CDCl_3$ and reported in ppm from Me_4Si.

TABLE 8. Selected features and their assignments in the vibrational spectra of compounds 1–3[a, b]

MeGe[S_2COMe]$_2$ (**1**)		MeGe[S_2COEt]$_3$ (**2**)		MeGe[S_2CO(i-Pr)]$_3$ (**3**)		Assignments
IR[c]	Raman[d]	IR[c]	Raman[d]	IR	Raman[d]	
1225s br	[e]	1222s br	[e]	1245s	[e]	$\nu(S_2COC)_a$
1154s	[e]	1111s	[e]	1088s	[e]	$\nu(S_2COC)_b$
1057s br	[e]	1033vs	[e]	1029vs	[e]	$\nu(S_2COC)_c$
818mw	[e]	811mw	[e]	828sh	[e]	ρCH_3
642m	645 (80)	690w	690 (53)	689vw	691 (89)	$\nu(S_2COC)_d$
618sh	615 (30)	608w	609 (50)	600w	602 (17)	ν(Ge–C)
462s	461 (23)	445sh	438 (30)	471sh	471 (22)	δCOC
418s	410 (73)	423w	422 (58)	423w	419 (26)	$\nu(Ge–S)_{asym}$
394s	392 (100)	368w	360 (100)	376vw	369 (100)	$\nu(Ge–S)_{sym}$

[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 neat samples solid or liquid, in a glass capillary. [e] Not observed.

TABLE 9. Selected features and their assignments in the vibrational spectra of compounds 4–7[a, b]

t-BuGe[S_2COEt]$_3$ (**4**)[c]	t-BuGe[S_2CO(i-Pr)]$_3$ (**5**)[c]		n-Bu$_3$Ge[S_2COEt] (**6**)[d]		n-Bu$_3$Ge[S_2CO(i-Pr)] (**7**)[d]		Assignments
IR[e]	IR[e]	Raman[f]	IR[e]	Raman[f]	IR[e]	Raman[f]	
1211vs br	1253s	[g]	1203vs br	[g]	1216vs	[g]	$\nu(S_2COC)_a$
1110m	1087s	[g]	1109m	[g]	1085vs	[g]	$\nu(S_2COC)_b$
1037vs br	1022vs	1032 (100)	1050vs br	1050 (69)	1033vs	1041 (100)	$\nu(S_2COC)_c$
692m	689w	691 (50)	696m	691 (10)	689m	691 (40)	$\nu(S_2COC)_d$
530m	530vw	534 (27)	557w	554 (5)	557w	550 (20)	$\nu(Ge–C)_{asym}$
[h]	[h]	[h]	455	[g]	455m	464 (21)	$\nu(Ge–C)_{sym}$
421m	425w	417 (19)	359w	359 (15)	352w	355 (17)	$\nu(Ge–S)_{asym}$
365	362vw	369 (53)	[h]	[h]	[h]	[h]	$\nu(Ge–S)_{sym}$

[a] Parentheses denote relative intensities in the Raman effect. [b] s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very. [c] Strong features in the IR spectrum seen at 1464 and 1366 cm^{-1} for **4** and 1465 and 1378 cm^{-1} for **5** attributable to $\delta(CH_3)_3C$. [d] Strong features in both the IR and Raman spectra seen at 2958 (IR) and 2961 (R) cm^{-1} in **6** and 2960 (IR) and 2951 (R) in **7** attributable to $\nu(CH_2)_n$ modes. [e] Run as CsI pellets. [f] Run as neat samples in a glass capillary. [g] Not observed. [h] In compounds **4** and **5** there is only one ν(Ge–C) and in compounds **6** and **7** only one ν(Ge–S).

The four (S_2COC) stretching modes in the spectra of t-BuGe[S_2COEt]$_3$ (**4**) and t-BuGe[S_2CO(i-Pr)]$_3$ (**5**) are observed in similar positions as found for **2** and **3** (Table 9). The same is true for the Ge–S asymmetric and symmetric stretching modes which suggests that the structures are more dependent on the requirements imposed by the xanthate than by the organic group attached to germanium. The band assigned to ν(Ge–C), at 534 and 530 cm^{-1} in **4** and **5**, respectively, is at much lower wave number than in related compounds but close to that found for t-BuGeCl$_3$ at 549 cm^{-1}. This suggests a weak Ge–C bond which is not surprising for a t-butyl group. There are many peaks associated with the t-butyl group in the IR spectrum of t-BuGeCl$_3$ but two at 1463 and 1366 cm^{-1}, which arise from $(CH_3)_3C$ deformations, are particularly distinctive and are also evident in the spectra of **4** and **5**.

The vibrational data for n-Bu$_3$Ge[S$_2$COEt] (**6**) and n-Bu$_3$Ge[S$_2$CO(i-Pr)] (**7**) are also presented in Table 9. The spectra are unusual relative to those of other xanthates so far reported [1, 2] because of the dominance of peaks due to CH$_n$ modes. Thus, although the Raman spectra are not of good quality, even peaks arising from CH$_n$ stretching vibrations are distinctive and peaks in the 750 to 300 cm^{-1} region are so numerous that it is difficult to assign the Ge–C and Ge–S vibrations based on Raman spectra. However, the three (S$_2$COC) vibrations, which are normally so dominant in the IR spectra, are still strong, readily assignable features that show close similarities to the corresponding modes in Ph$_3$Ge[S$_2$COEt] and Ph$_3$Ge[S$_2$CO(i-Pr)] [2]. Although there is a strong, broad peak at 694 cm^{-1} in the IR spectrum of n-Bu$_3$GeCl, it has no counterpart in the Raman spectrum. Thus the band in the Raman effect at 691 cm^{-1} in both **6** and **7** can be assigned with confidence to ν(S$_2$COC)$_a$. The assignment of ν(Ge–S) is to slightly lower wave number than is observed for ν(Ge–Cl) in n-Bu$_3$GeCl as is to be expected.

Molecular structures of MeGe[S$_2$COEt]$_3$·0.37CS$_2$ (2) and MeGe[S$_2$CO(i-Pr)]$_3$·0.50CS$_2$ (3)

The crystal structures of tris(*O*-ethyl dithiocarbonato)methylgermane (**2**) and tris(*O*-isopropyl dithiocarbonato)methylgermane (**3**) (Figs. 1 and 2 and Tables 3 and 4) confirm that in both compounds the immediate environment about germanium is that of the expected distorted tetrahedron. This is gratifying because the similarity of the vibrational spectra of the ethyl- and isopropylxanthate derivatives suggested that these structures should be similar. The average of the S–Ge–C angles are identical in both species, 115.9(2)° in **2** and 115.9(3)° in **3** as, of course, are the S–Ge–S angles, 102.3(2)° in both **2** and **3**. The latter angle is close to the value of 103.2(1)° in Ph$_2$Ge[S$_2$CO(i-Pr)]$_2$ [2] and is in marked contrast to the corresponding angle in Me$_2$Ge[S$_2$CNMe$_2$]$_2$ and Ph$_2$Ge[S$_2$CNEt$_2$]$_2$ where the anisobidentate dithiocarbamates subtend S–Ge–S angles of 87.0(1) or 84.4(1)°, respectively [13, 17]. In Ph$_2$Ge[S$_2$P(OMe)$_2$]$_2$, where the dithiophosphate groups are monodentate, the S–Ge–S angle is again 103.4(1)° [18]. The monodentate nature of the dithiocarbonate groups in **2** and **3** is emphasized by the fact that the Ge---S non-bonding distances average out to 4.728(8) Å ion **2** and 4.732(3) Å in **3** compared to aniso-bonded Ge---S distances in dithiocarbamates that are typically 3.078(2) Å, as in Me$_2$Ge[S$_2$CNMe$_2$]$_2$ [17]. Thus, it is the oxygen atom, rather than the second sulfur atom of the xanthate group, that is oriented towards germanium. However, the average Ge---O distances of 2.93(1) Å in **2** and 2.916(6) Å in **3**, which are typical of those in related molecules [1, 2], suggest that any favorable interaction is minimal compared to the secondary bonded sulfur atom in a dithiocarbamate at a similar distance. The Sn---O distance of 2.950(3) Å in Ph$_3$Sn[S$_2$CO(i-Pr)] [19] is also similar, and it was pointed out that the distance was *c.* 0.7 Å less than the sum of the van der Waals radii of tin and oxygen and so only a weak interaction could be postulated. If such an interaction exists in the analogous germanium compounds then it is presumably weaker still.

The Ge–C bond lengths of 1.92(2) Å in **2** and 1.91(1) and 1.92(1) Å in the two independent molecules of **3** are close to but slightly shorter than the average Ge–C distances found in a number of phenylgermanium xanthates such as Ph$_3$Ge[S$_2$COMe], 1.93(1); Ph$_3$Ge[S$_2$CO(i-Pr)], 1.937(5); and Ph$_2$Ge[S$_2$CO(i-Pr)]$_2$, 1.933(8) [2]. They are also similar to the Ge–C bond length in Me$_2$GeCl$_2$ of 1.928(6) Å [20], but longer than the Ge–C bond in MeGeCl$_3$ of 1.90(1) Å [17]. In discussing the vibrational spectrum of the MeGe[S$_2$COR]$_3$ species, it was noted that ν(Ge–C) was shifted to lower wave number relative to its position in MeGeCl$_3$ by some 20 cm^{-1}, presumably reflecting the presence of a slightly weaker, longer bond.

The average Ge–S distances of 2.249(1) Å for **2** and 2.249(3) Å for **3** are essentially identical to those reported for Ph$_3$Ge[S$_2$COMe], 2.249(4) Å, and Ph$_2$Ge[S$_2$CO(i-Pr)]$_2$, 2.251(3) and 2.252(3) Å [2]. In general the Ge–S bonds are shorter in xanthates than in dithiocarbamates, where the linkages are best described as anisobidentate. Thus the average Ge–S bond length is 2.278(4) Å in Me$_2$Ge[S$_2$CNMe$_2$]$_2$ [17] and 2.271(1) Å in Ph$_2$Ge[S$_2$CNEt$_2$]$_2$ [13].

The three xanthate groups all show marked differences in the bond lengths of the short C=S terminal bond (av. 1.59(3) Å in **2** and 1.625(5) Å in **3**) compared to the long C–SGe single bond (av. 1.747(3) Å in **2** and 1.743(5) Å in **3**). The S$_2$C–O bond is shorter (av. 1.347(9) Å in **2** and 1.348(6) Å in **3**) than the O–CR bond (av. 1.49(1) Å in **2** and 1.46(2) Å in **3**) indicating that there is considerably more π-bond character in the OCS$_2$ bonds than in the OCR bonds. Finally, there are no close contacts between neighboring atoms.

Conclusions

A variety of alkylgermanium dithiocarbonates (xanthates) have been prepared. Although the neat compounds tend to dissociate over a short time they are stable in solution. Assignments for the S$_2$CO vibrational modes are confirmed that had been only tentatively proposed for the phenyl analogues. The similarity of all of the appropriate features in the NMR and IR spectra, suggests that all of the xanthate groups are similarly bonded in all these alkylgermanium derivatives. In the two cases where X-ray quality crystals were obtained, the xanthate groups are shown to be monodentate with the non-bonding sulfur atom oriented away from the germanium center.

Supplementary material

Tables of anisotropic thermal parameters for non-hydrogen atoms, final fractional coordinates and thermal parameters for hydrogen atoms and calculated and observed structure factors may be obtained directly from the authors on request.

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