Synthesis, spectroscopic characterization and structural studies of organotin monothiocarbonates. Crystal structures of Ph₃Sn[SCO₂Me] and Ph₃Sn[SCO₂(i-Pr)]

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Abstract: *O*-alkyl monothiocarbonate (monoxanthate) derivatives of tin were obtained by the reaction of a sodium salt of the monothiocarbonic acid with an organotin chloride to give Ph₃Sn[SCO₂R], Ph₂Sn[SCO₂R]₂, and Me₃Sn[SCO₂R], where R = Me and i-Pr. The compounds have been characterized by infrared, Raman, ¹H NMR, and ¹³C NMR spectroscopy, as well as mass spectrometry, and in two cases by X-ray crystallography. Ph₃Sn[SCO₂Me] (1) and Ph₃Sn[SCO₂(i-Pr)] (2), crystallize in the triclinic space group $P\overline{1}$ (no. 2) with cell parameters a = 10.218(4), b = 10.568(6), c = 9.366(7) Å, $\alpha = 106.73(5)$, $\beta = 96.99(5)$, $\gamma = 85.55(4)^{\circ}$, V = 960(1) Å³, and Z = 2 for 1; and a = 14.793(2), b = 17.856(3), c = 9.813(3) Å, $\alpha = 103.86(5)$, $\beta = 98.36(5)$, $\gamma = 106.85(4)^{\circ}$, V = 2343(1) Å³, and Z = 2 for 2. The latter has two molecules in the asymmetric unit. The immediate environment about tin in both 1 and 2 is that of the expected distorted tetrahedron. However, the orientation of the monothiocarbonate group is such that there is an Sn-O intramolecular interaction of 3.040(8) for 1 and 3.05(2) Å on average for 2. Thus, the considerable distortion is consistent with a tendency to form a five-coordinate, trigonal bipyramidal species with one of the O-Sn-C angles approaching 180° (153.4(4) for 1 and an average of 157.1(6) for 2). Estimations of the Pauling partial bond orders suggest this weak Sn-O interaction is slightly stronger than the corresponding Ge-O interaction in the analogous germanium derivative, Ph₃Ge[SCO₂Me].

Key words: structure, tin, methyl, phenyl, isopropyl, monothiocarbonates.

Résumé : On a préparé des dérivés de l'étain avec du monothicarbonate (monoxanthate) de *O*-alkyle (Ph₃Sn[SCO₂R], Ph₂Sn[SCO₂R] et Me₃Sn[SCO₂R] dans lesquels R = Me ou i-Pr) en faisant réagit du sel de sodium de l'acide monothiocarbonique avec un chlorure d'organoétain. On a caractérisé ces composés par spectroscopies infrarouge, Raman et RMN du ¹H et du ¹³C ainsi que par spectroscopie de masse et, dans deux cas, par diffraction des rayons X. Le Ph₃Sn[SCO₂Me], **1**, et Ph₃Sn[SCO₂i-Pr], **2**, cristallisent dans le groupe d'espace $P\overline{1}$ (no. 2) avec a = 10,218(4), b = 10,568(6) et c = 9,366(7) Å, $\alpha = 106,73(5)$, $\beta = 96,99(5)$ et $\gamma = 85,55(4)^{\circ}$, V = 960(1) Å³ et Z = 2 pour le composé **1** et a = 14,793(2), b = 17,856(3) et c = 9,813(3) Å, $\alpha = 103,86(5)$, $\beta = 98,36(5)$ et $\gamma = 106,85(4)^{\circ}$, V = 2343(1) Å³ et Z = 2 pour le composé **2**. Ce dernier composé comporte deux molécules dans la maille asymétrique. L'environnement immédiat autour de l'étain de ces deux composés correspond à celui attendu pour un tétraèdre déformé. Toutefois, l'orientation du groupe monothiocarbonate est tel que l'on observe une interaction Sn-O intramoléculaire de 3,040(8) Å pour **1** et de 3,05(2) Å pour **2**. La déformation importante est donc en accord avec une tendance à former une espèce pentacoordinée trigonale bipyramidale dans laquelle les angles O-Sn-C se rapprochent de 180° (153,4(4) pour **1** et une moyenne de 157,1(6) pour **2**). Des évaluations à partir des ordres partiels de liaison de Paulin suggèrent que cette interaction Sn-O faible est un peu plus forte que l'interaction correspondante Ge-O du composé germaniun analogue, Ph₃Ge[SCO₂Me].

Mots clés : structure, étain, méthyle, phényle, isopropyle, monothiocarbonates.

[Traduit par la Rédaction]

Introduction

O-alkyl dithiocarbonate (xanthate) derivatives have been extensively studied but the chemistry of monothiocarbonates (monoxanthates) has received considerably less attention and most of the relatively few reports have involved transition metal complexes (1). In addition to reports on alkali salts (2), two reports by us have appeared on main group element monothiocarbonates describing some organotellurium (3) and organogermanium (4) derivatives. Considerably more

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work has appeared on dithio derivatives of tin than of germanium, but we were unable to find any reports on monothiocarbonate organotin derivatives. Surprisingly, we found these even more difficult to isolate pure than their germanium analogues but we were able to confirm the formation of five *O*-alkyl monothiocarbonate derivatives $Ph_3Sn[SCO_2R]$ (R = Me and i-Pr), $Ph_2Sn[SCO_2(i-Pr)]_2$, $Ph_2SnCl[SCO_2(i-Pr)]$, and MeSn[SCO_2Me] by NMR, infrared, and Raman spectroscopy, as well as mass spectrometry. We also have obtained the X-ray crystal structures of $Ph_3Sn[SCO_2Me](1)$ and $Ph_3Sn[SCO_2(i-Pr)](2)$.

Among the many reports on dithio derivatives of tin, those of relevance to this work include discussions of ligand coordination modes and coordination number in a variety of dithiocarbamates (5), a series of publications on dithiocarbonates (6), and a structural study of $Ph_3Sn[S_2CO(i-Pr)]$ (7). An examination of tin(IV) 1-pyrrolecarbothioates (8), including $Ph_3Sn[SOCNC_4H_4]$, and a comparison of the structures of the monothiocarbamate, $Ph_3Sn[SCON(CH_2)_4O]$, with the analogous dithiocarbamate are also of interest (9). Bidentate linkages appear to be favored in organotin derivatives with dithio-ligands as exemplified in dithiophosphates such as $Ph_2Sn[S_2P(Oi-Pr)_2]_2$ (10) and dithiocarbamates such as $BuSn[S_2CN(Et)_2]_3$ (11) in both of which tin atoms are in octahedral sites. However, monodentate linkages appear to be often found with triphenyltin derivatives such as in $Ph_3Sn[S_2P(OEt)_2]$ (12). The range of mono-, aniso-, and bidentate ligands will be discussed in some detail.

Experimental

Materials

The starting materials (Ph₃SnCl, Ph₂SnCl₂, and Me₃SnCl) were obtained from Aldrich; 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 salts, NaSCO₂R, where R = Me and i-Pr, were prepared as described in the literature (4) and their purity checked by ¹H and ¹³C NMR spectroscopy. No further purification was necessary.

Preparation of $Ph_3Sn[SCO_2Me]$ (1) and $Ph_3Sn[SCO_2(i-Pr)]$ (2)

Typically, Ph₃SnCl (0.25 g, 0.65 mmol) and an excess of dried NaSCO₂Me (0.10 g, 0.88 mmol) were placed in a previously evacuated flask and solvent (CH₂Cl₂, ca. 15 mL) was added under N₂. The mixture was stirred for 2 h at room temperature, followed by filtration to remove NaCl and excess of starting salt, and then evaporation under vacuum gave Ph₃Sn[SCO₂Me] (1) as a colorless solid. Recrystallization from a $CH_2Cl_2 - n$ -hexane mixture gave colorless crystals (0.20 g, 0.45 mmol), yield 70%, mp 86°C. Peaks in the mass spectrum corresponding to ¹²⁰Sn in a typical tin cluster were seen at m/z (relative intensity): 442 ((Ph₃SnSCO₂Me)⁺, 3%), 365 ((Ph₂SnSCO₂Me)⁺, 10%), 351 $((Ph_3Sn)^+, 100\%), 305 ((Ph_2SnOMe)^+, 45\%), 274 ((Ph_2Sn)^+, 45\%))$ 30%), 197 ((PhSn)⁺, 9%). IR (Raman) (cm⁻¹) main features: v(O=CSOC) 1669 vs, v(OSC-OMe) 1148 vs br, v(OSO-CH₃) 1090 sh, p-phenyl [1002 (100)], $\pi(SCO_2)$ 817 ms, f-phenyl 731 vs, v-phenyl 698 vs, v(SnS-C) 658 m [658 (55)], vphenyl 447 s, $\delta(SCO_2)$ 426 m, v(Sn-S) [333 (10)]. ¹H NMR:

 $(CDCl_3)$ δ 3.63 [3H, OCH₃, s]; 7.41–7.44 [9H, Sn-C₆H₅ – meta + para]; 7.63–7.68 [6H Sn-C₆ H_5 – ortho]. ¹³C NMR: (CDCl₃) δ 54.82 [OCH₃]; 129.03, 130.04, 136.57, 136.74 $[Sn-C_6H_5]$. In the same fashion $Ph_3Sn[SCO_2(i-Pr)]$ (2) was prepared as a colorless solid. Recrystallization from a $CH_2Cl_2 - n$ -hexane mixture gave colorless crystals (0.30 g, 0.71 mmol, yield 86%), mp 92-93°C. Peaks in the mass spectrum corresponding to ¹²⁰Sn were seen at m/z (relative intensity): 469 ((Ph₃SnSCO₂(i-Pr) – H)⁺, 2%), 393 $((Ph_2SnSCO_2(i-Pr))^+, 8\%), 351 ((Ph_3Sn)^+, 100\%), 333$ main features: v(O=CSOC) 1663 vs, v((OSC-O(i-Pr)) 1169 vs, v(OSO-CH(CH₃)₂) 1093 vs, p-phenyl [1001 (100)], $\pi(SCO_2)$ 848 m, f-phenyl 731 s, v-phenyl 698 s, v(SnS-C) 655 w [657 (45)], y-phenyl 446 ms, δ(SCO₂) 433 sh, v(Sn-S) [335 (15)]. ¹H NMR: (CDCl₃) δ 1.04 [6H, OCH(CH₃)₂, d, J(HH) 6.2 Hz]; 4.88 [1H, OCH, sept, J(HH) 6.2 Hz]; 7.40– 7.42 [9H, Sn-C₆ H_5 – meta + para]; 7.64–7.67 [6H Sn-C₆ H_5 - ortho]. ¹³C NMR: (CDCl₃) δ 21.61 [OCCH₃]; 72.65 [OCH]; 129.98, 129.96, 136.47, 136.71 [Sn-C₆H₅].

Preparation of $Ph_2Sn[SCO_2(i-Pr)]_2$ (3)

Typically, Ph₂SnCl₂ (0.25 g, 0.72 mmol) and NaSCO₂(i-Pr) (0.25 g, 1.76 mmol) were placed in a flask and solvent (CH₂Cl₂, ca. 15 mL) was added under N₂. The mixture was stirred for 2 h at room temperature, followed by filtration and evaporation under vacuum to give Ph₂Sn[SCO₂(i-Pr)]₂, **3**, (0.3 g, 0.59 mmol) as a colorless solid, (0.30 g, 0.59 mmol), yield 81.5%, mp 83-84°C. Peaks in the mass spectrum corresponding to ¹²⁰Sn in a typical tin cluster were seen at m/z(relative intensity): 512 (($Ph_2Sn[SCO_2(i-Pr)]_2$)⁺, 1%), 393 ((PhSn)⁺, 35%). Attempts at recrystallization failed to yield any X-ray quality crystals. IR (Raman) (cm⁻¹) main features: v(O=CSOC) 1642 vs, v((OSC-O(i-Pr)) 1176 vs, v(OSO-CH(CH₃)₂) 1091 vs, p-phenyl [999 (100)], π (SCO₂) 847 ms, f-phenyl 732 ms, v-phenyl 695 ms, v(SnS-C) 655 vw [658 (45)], y-phenyl 445 m, $\delta(SCO_2)$ 428 m, v(Sn-S) [344 (15)]. ¹H NMR: (CDCl₃) δ 1.06 [12H, OCH(CH₃)₂, d, J(HH) 6.2 Hz]; 4.86 [2H, OCH, sept, J(HH) 6.2 Hz]; 7.43-7.45 $[6H, Sn-C_6H_5 - meta + para]; 7.82-7.85 [4H Sn-C_6H_5 - meta + para]; 7.82-7.85 [4H$ *ortho*]. ¹³C NMR: (CDCl₃) δ 21.58 [OCCH₃]; 73.48 [OCH₃]; 129.07, 130.46, 135.35, 135.73 [Sn-C₆H₅].

Formation and identification of Ph₂SnCl[SCO₂(i-Pr)] (4) and Me₃Sn[SCO₂Me] (5)

Typically, Ph₂SnCl₂ (0.30 g, 0.87 mmol) and dried NaSCO₂(i-Pr) (0.12 g, 0.87 mmol) were introduced into a round-bottomed flask, followed by the addition of dried CH₂Cl₂ (ca. 15 mL). The mixture was stirred for ca. 2 h at which time the NaCl that had formed was filtered off and the solvent allowed to evaporate under vacuum to produce Ph₂SnCl[SCO₂(i-Pr)] (4) as a white solid (0.31 g, 0.73 mmol, yield 83%). IR (Raman) (cm⁻¹) main features: v(O=CSOC) 1629 ms, br, v((OSC-O(i-Pr)) 1261 s, v(OSO-CH(CH₃)₂) 1095 vs, *p*-phenyl [1000 (100)], π (SCO₂) 803 ms br, *f*-phenyl 728 vs, *v*-phenyl 692 vs, v(SnS-C) 656 mw [658 (45)], *y*-phenyl 448 m br, δ (SCO₂) 430 sh, v(Sn-S) [340 (5)], v(Sn-Cl) [276 (9)]. ¹H NMR: (CDCl₃) δ 1.26 [6H,

Parameter	1	2
a (Å)	10.218(4)	14.793(2)
b (Å)	10.568(6)	17.856(3)
c (Å)	9.366(7)	9.813(3)
α (°)	106.73(5)	103.86(2)
β (°)	96.99(5)	98.36(2)
γ (°)	85.55(4)	106.85(1)
V (Å ³)	960(1)	2343(1)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> 1 (no. 2)	$P\overline{1}$ (no. 2)
Mol. wt. (g mol^{-1})	444.11	983.33
Z	2	2
Crystal dimensions (mm)	$0.41 \times 0.36 \times 0.21$	$0.45 \times 0.40 \times 0.21$
ρ (calcd.) (g cm ⁻³)	1.52	1.33
μ , cm ⁻¹	14.46	11.9
Transmission factors	0.58-1.00	0.73-1.00
Temperature (°C)	23	23
Radiation (Å)	Μο Κα 0.71096	Μο Κα 0.71096
Monochromator	Highly oriented graphite	Highly oriented graphite
Scan method	$\omega - 2\theta$	$\omega - 2\theta$
Scan speed (°/min)	32	16
Max. (20)	50	45
Total reflections measured	3591	5218
No. of unique data	3382	4929
No. of obsd. data $(I \ge 3\sigma(I))$]	1619	1511
No. of parameters (NP)	127	169
$R = \sum \ F_{\rm o} - F_{\rm c} /\sum F_{\rm o} /$	0.0543	0.0544
$R_{\rm w} = \left[\sum w(F_{\rm o} - F_{\rm c})^2 / \sum wF_{\rm o}^2\right]^{1/2}$	0.0452	0.0583
Goodness of fit	1.72	1.85
Largest shift/e.s.d, final cycle	0.001	0.001
Largest residual electron density (e Å ⁻³)	0.09	0.76

Table 1. Summary of crystal data, intensity collection, and structural refinement for Ph₃[SnSCO₂Me] (1) and 2Ph₃Sn[SCO₂(i-Pr)] (2).

OCH(CH₃)₂, d, J(HH) 6.2 Hz]; 5.00 [1H, OCH, sept, J(HH) 6.2 Hz]; 7.47–7.50 [6H, Sn-C₆ H_5 – meta + para]; 7.84–7.87 [4H Sn-C₆ H_5 – ortho]. ¹³C NMR: (CDCl₃) δ 21.74 [OCCH₃]; 75.38 [OCH₃]; 129.26, 130.98, 135.19, 136.61 $[Sn-C_6H_5]$. Attempts at recrystallization did not yield any crystals, but rather resulted in decomposition. In a similar manner as described for the preparation of 1 and 2, Me₃Sn[SCO₂Me] (5), was formed as a colorless viscous liquid by starting with Me₃SnCl and an excess of NaSCO₂Me. IR (Raman) (cm⁻¹) main features: v(O=CSOC) 1630 m, v(OSC-OMe) 1260 vs, v(OSO-CH₃) 1034 vs br, π (SCO₂) 865 s, ρ(SnCH₃) 799 vs, ν(SnS-C) 662 m, ν(Sn-C_{asvmm}) 532 m, v(Sn-C_{symm}) 506 mw. ¹H NMR: (CDCl₃) δ 0.53 [9H, Sn(CH₃)₃, J(SnH) 64.2 Hz], 3.68 [3H, OCH₃]. ¹³C NMR: $(CDCl_3) \delta -2.50 [SnCH_3], 53.51 [OCH_3].$ For both 4 and 5, the ¹H and ¹³C NMR spectra taken immediately after separation indicated the presence of only one product.

Attempted formation and identification of Ph₂Sn[SCO₂Me]₂ and Ph₂SnCl[SCO₂Me]

In a manner similar to the successful preparation of **3** and **4**, substituting NaSCO₂Me for NaSCO₂(i-Pr) did not result in the formation of pure Ph₂Sn[SCO₂Me]₂ or Ph₂SnCl[SCO₂Me] but rather in mixtures. The NMR spectra in each case were consistent with the presence of differing amounts of both of the desired compounds.

Physical measurements

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 ¹H and ¹³C {H} NMR spectra were recorded on a Bruker 300 FT/NMR spectrometer at 300.133 and 75.471 MHz, respectively, in CDCl₃ using Me₄Si 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. The mass spectra were recorded on a Kratos Profile GC-MS Spectrometer.

X-ray crystallographic analysis

Colorless block crystals of $Ph_3Sn[SCO_2Me]$ (1) and $Ph_3Sn[SCO_2(i-Pr)]$ (2) were sealed in thin-walled glass capillaries and mounted on a Rigaku AFC6S diffractometer, with graphite-monochromated MoK α radiation. Operating at 50 kV and 35 mA.

Cell constants corresponded to triclinic cells whose dimensions are given in Table 1, along with other experimental details. Based on statistical analysis of intensity distribution

Table 2. Selected interatomic distances (Å) and angles (°) for $Ph_3Sn[SCO_2Me]$ (1)

Bond	Distance (Å)	Bond	Angle (°)
Sn(1)—S(1)	2.444(4)	S(1)-Sn(1)-C(3)	97.5(3)
Sn(1)—C(3)	2.10(1)	S(1)-Sn(1)-C(9)	112.3(3)
Sn(1)—C(9)	2.12(1)	S(1)-Sn(1)-C(15)	112.2(3)
Sn(1)—C(15)	2.12(1)	C(3)-Sn(1)-C(9)	112.6(4)
S(1)—C(1)	1.76(1)	C(3)-Sn(1)-C(15)	111.4(4)
C(1)—O(1)	1.20(1)	C(9)-Sn(1)-C(15)	109.9(4)
C(1)—O(2)	1.34(1)	Sn(1)-S(1)-C(1)	95.4(5)
O(2)—C(2)	1.43(1)	S(1)-C(1)-O(1)	125(1)
Sn(1)O(1)	3.040(8)	S(1)-C(1)-O(2)	109.2(9)
S(1)O(1)	2.636(9)	O(1)-C(1)-O(2)	126(1)
		C(1)-O(2)-C(2)	115(1)
		S(1)-Sn(1)-O(1)	56.2(2)
		O(1)Sn(1)-C(15)	153.4(4)

and the successful solution and refinement of the structures, the space group was determined to be $P\overline{1}$ (no. 2) for both 1 and 2. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. In the case of 2, data collection stopped automatically at 45.0° because the crystal had decayed, therefore a decay correction was applied.

The structure was solved by direct methods (13) and all calculations were performed using the TEXSAN (14) crystallographic software package of Molecular Structure Corp.² All of the non-hydrogen atoms were refined anisotropically for 1, but for 2 only the thio carbon atom was treated anisotropically along with the other non-hydrogen atoms. The phenyl groups were treated as fixed rings with C-C distances set at 1.39 Å in 2 and an attempt was made to model the i-Pr group of one of the molecules in the asymmetric unit which was badly disordered. Hydrogen atoms, other than those of the disordered group, were included in their idealized position with C—H set at 0.95 Å and isotropic thermal parameters set at 1.2 times that of the carbon to which they were attached.

The unweighted and weighted agreement factors and standard deviation of an observation of unit weight³ are given in Table 1. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ , and various classes of indices showed no unusual trends. Important distances and bond angles are given in Tables 2 and 3 and the molecular structures of the two compounds are displayed as ORTEP diagrams in Figs. 1-3. The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, final fractional coordinates and thermal parameters for hydro-

Table 3. Selected interatomic distances (Å) and angles (°) for $2Ph_3Sn[SCO_2(i-Pr)]$ (2)

Bond	Distance (Å)	Bond	Angle (°)
Sn(1)—S(1)	2.42(1)	S(1)-Sn(1)-C(5)	113.1(7)
Sn(1) - C(5)	2.12(2)	S(1)-Sn(1)-C(11)	100.7(8)
Sn(1) - C(1)	2.11(2)	S(1)-Sn(1)-C(17)	110.3(8)
Sn(1) - C(1)	2.16(3)	C(5)-Sn(1)-C(11)	106.7(9)
S(1) - C(1)	1.80(4)	C(5)-Sn(1)-C(17)	114.2(8)
C(1)—O(1)	1.16(5)	C(11)-Sn(1)-C(15)	111(1)
C(1)—O(2)	1.35(6)	Sn(1)-S(1)-C(1)	94(2)
O(2)—C(2)	1.52(5)	S(1)-C(1)-O(1)	127(4)
Sn(1)O(1)	3.04(3)	S(1)-C(1)-O(2)	106(3)
S(1)O(1)	2.66(3)	O(1)-C(1)-O(2)	127(4)
		C(1)-O(2)-C(2)	118(2)
		S(1)-Sn(1)-O(1)	56.8(6)
		O(1)Sn(1)-C(11)	157.5(9)
Sn(2)—S(2)	2.46(1)	S(2)-Sn(2)-C(27)	111.2(7)
Sn(2)—C(27)	2.16(2)	S(2)-Sn(2)-C(33)	100.3(8)
Sn(2)—C(33)	2.13(2)	S(2)-Sn(2)-C(39)	100.6(7)
Sn(2)—C(39)	2.08(2)	C(27)-Sn(2)-C(33)	109.5(8)
S(2)—C(23)	1.78(5)	C(27)-Sn(2)-C(39)	114.3(7)
C(23)—O(31)	1.25(5)	C(33)-Sn(2)-C(39)	112(1)
C(23)—O(4)	1.31(6)	Sn(2)-S(2)-C(23)	97(2)
O(4)—C(24a)	1.6(1)	S(2)-C(23)-O(3)	122(4)
O(4)—C(24b)	1.4(1)	S(2)-C(23)-O(4)	113(3)
Sn(2)O(3)	3.06(3)	O(3)-C(23)-O(4)	125(4)
S(2)O(3)	2.66(3)	C(23)-O(4)-C(24a)	111(4)
		C(23)-O(4)-C(24b)	108(4)
		S(2)-Sn(2)O(3)	56.4(6)
		O(3)Sn(2)-C(33)	156.7(9)

gen atoms, and all bond distances and angles have been deposited.4

Calculation of Pauling partial bond orders

The formula proposed by Pauling (15) for calculating the bond orders of partial bonds is given by $d_n - d = -0.60 \log d_n$ *n*, where d_n is the bond length for bond number, *n*, and *d* is the length of the single bond of the same type. Based on the C—C single bond of 1.54 Å, Pauling's formula gives a bond length of 1.36 Å for n = 2; 1.72 Å for n = 0.5; and 1.90 Å for n = 0.25. These give percentage increases in bond length for the partial bonds of approximately 12 and 23% respectively for n = 0.5 and 0.25. It is reasonable to assume that similar relationships relating bond order to interatomic distances for the much longer secondary interactions or partial bonds involving Sn and S should utilize percentage differences "normalized" to 1.54 as follows rather than absolute differences. Pauling's relationship, which can be written as $n = 10^X$, where $X = (d - d_n)/0.6$, can be modified to allow

²Least-squares function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2C + R^2B) + (pF_o^2)^2]/(Lp)^2$, S = scan rate, C = totalintegrated peak count, R = ratio of scan time to background counting time, Lp = Lorentz-polarization factor, and p = p factor.³Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/N_o - N_v)^{1/2}$, where $N_o = \text{number of observations and } N_v = \text{number of } N_v$

variables.

⁴Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON, Canada K1A 0S2 (http://www.nrc.ca/cisti/irm/unpub_e.shtml). Tables of atomic coordinates for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Structure factor amplitudes are no longer being deposited and may be obtained directly from the author.

Fig. 1. ORTEP plot of the molecule $Ph_3Sn[SCO_2Me]$ (1). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

for percentage differences "normalized" to 1.54 to give X = $[1.54(d - d_n)/d]/0.6$ or $X = 2.57(d - d_n)/d$. Assuming the Sn—S single bond length approximates to the sum of the respective covalent radii (16), the corresponding values for Sn—S single and partial bonds for various values of n are 2.40 Å (n = 1.0), 2.50 (0.75), 2.68 (0.50), 2.95 (0.25), and 3.33 Å (n = 0.10). Similarly, relative to a Sn—O single bond length of 2.14 Å, the corresponding values for Sn—O partial bonds are 2.24 (0.75), 2.40 (0.50) 2.65 (0.25), and 2.97 Å (n = 0.10); relative to a Ge—O single bond length of 1.96 Å, the Ge-O partial bonds are 2.05 (0.75), 2.19 (0.50), 2.43 (0.25), and 2.72 Å (n = 0.10); and relative to a Ge—S single bond length of 2.26 Å, the corresponding values for Ge-S partial bonds are 2.37 (0.75), 2.53 (0.50), 2.79 (0.25), and 3.13 Å (n = 0.10). These calculated values appear to be compatible with the sum of the van der Waals radii of Sn, Ge, S, and O (17) and by way of comparison, the "valencies" for partial Sn-O bonds have been calculated as 2.43 (0.30) and 2.66 (0.20) (18).

Results and discussion

The preparation of O-alkyl monothiocarbonate derivatives of triphenyl-, diphenyl-, and trimethyl-tin(IV) compounds was attempted by the reaction of the sodium salt of the monothiocarbonic acid in dried CH_2Cl_2 as solvent with the appropriate organotin chloride using a standard Schlenk line in accord with the reactions

[1] $R_3SnCl + NaSCO_2R' \Rightarrow R_3Sn[SCO_2R'] + NaCl$

 $[2] \qquad R_2SnCl_2 + 2NaSCO_2R' \Rightarrow R_2Sn[SCO_2R']_2 + 2NaCl$

[3] $R_2SnCl_2 + NaSCO_2R' \Rightarrow R_2SnCl[SCO_2R'] + NaCl where R = Me, Ph, R' = Me, i-Pr.$

Fig. 2. ORTEP plot of the two molecules of $Ph_3Sn[SCO_2(i-Pr)]$ (2) in the asymmetric unit. The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted and only one set of the carbon atoms in partially occupied positions are shown for the disordered i-Pr group for clarity.



Fig. 3. ORTEP plots illustrating the core around tin including the Sn-O interaction for (*a*) the molecule $Ph_3Sn[SCO_2Me]$ (1) and (*b*) the molecule of $Ph_3Sn[SCO_2(i-Pr)]$ (2) that does not contain a disordered i-Pr group. The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms and the carbon atoms of the phenyl rings other than those attached to tin omitted for clarity.





The compounds $Ph_3Sn[SCO_2Me]$ (1), $Ph_3Sn[SCO_2(i-Pr)]$ (2), $Ph_2Sn[SCO_2(i-Pr)]_2$ (3), $Ph_2SnCl[SCO_2(i-Pr)]$ (4), and $Me_3Sn[SCO_2Me]$ (5) were isolated but only 1 and 2 gave X-ray quality crystals. In reactions [1] and [2], the salts were used in considerable excess relative to the stoichiometric requirements to ensure complete reaction. By contrast, exact stoichiometric amounts were used in reaction [3] to favor the formation of the mixed chloro derivatives. When reactions [2] and [3] were attempted using NaSCO_2Me, only mixtures containing $Ph_2Sn[SCO_2Me]_2$ and $Ph_2SnCl[SCO_2Me]$ resulted in both cases. In general, all of the compounds are susceptible to moisture and air on exposure to the atmosphere, and all were readily dissolved in chloroform — which was therefore used as the preferred solvent for recording NMR spectra.

The ¹H NMR spectra of compounds 1-5 confirm that the products are over 98% pure relative to any hydrogencontaining impurities and integration ratios are as expected. The signals due to the phenyl groups in compounds 1 and 2 (two sets of peaks between 7.40 and 7.68 ppm) are very similar in appearance and position to those of the analogous germanium derivatives (two sets of peaks between 7.36 and 7.64 ppm) (4). The monothiocarbonate ligands give the expected first order spectra with chemical shifts comparable to those of the corresponding salts. As observed for the corresponding OCH_n -groups in the germanium analogues, the chemical shifts of hydrogen atoms on the carbon atom attached to oxygen are similar for a given monothiocarbonate regardless of the number of phenyl groups attached to tin (4.88 ppm for $Ph_3Sn[SCO_2CH(CH_3)_2]$ (2) and 4.86 ppm for $Ph_2Sn[SCO_2CH(CH_3)_2]_2$ (3). In $Ph_2SnCl[SCO_2CH(CH_3)_2]$ (4), the chemical shifts for the protons in both phenyl and ligand groups are slightly downfield compared to the bis compound, 3, which is consistent with the electronegativity of Cl being slightly larger than that of the monothiocarbonate group. In Me₃Sn[SCO₂Me] (5) the CH_3 chemical shift of the methyl group attached to tin is also very close to the value in Me₃Ge[SCO₂Me] (0.57 ppm). The similarity of all of the spectra is indicative that the environments of the monothiocarbonate groups in solution are identical in all compounds. In the ¹³C NMR spectra, the chemical shifts of monothiocarbonate groups are similar regardless of whether methyl or phenyl groups are attached to tin or the number of such groups, again as was observed in the analogous germanium derivatives. For the carbon atom in the SCO₂ groups, the chemical shifts range from 170.28 to 172.67 ppm for all compounds except for 4; again reflecting the presence of the more electronegative Cl atom. The similar values of the ¹³C NMR chemical shifts in the monothiocarbonate ligands is again consistent with the presence of similar monothiocarbonate linkages in solution.

The crystal structures of $Ph_3Sn[SCO_2Me]$ (1) and $Ph_3Sn[SCO_2(i-Pr)]$ (2)

Both $Ph_3Sn[SCO_2Me]$ (1) and $Ph_3Sn[SCO_2(i-Pr)]$ (2) crystallize in the space group $P\overline{1}$ (No. 2), but with two independent molecules in the asymmetric unit for 2. The ORTEP diagrams in Figs. 1 and 2 illustrate that the immediate environments about tin in both $Ph_3Sn[SCO_2Me]$ (1) and $Ph_3Sn[SCO_2(i-Pr)]$ (2) are that of a distorted tetrahedron. As was found for the analogous germanium derivatives,

 $Ph_3Ge[SCO_2Me]$ and $Ph_3Ge[SCO_2(i-Pr)]$ (4), the three C-Sn-C angles range from 109.9(4) to $112.6(4)^{\circ}$ in 1 and 106.7(9) to $114.3(7)^{\circ}$ in 2 with averages of 111.3(14) and 111.3(29)°, respectively; while those of the S-Sn-C angles range from 97.5(3) to $112.3(3)^{\circ}$ in 1 and 100.7(8) to $113.1(7)^{\circ}$ in 2 with averages of 107(8) and 107(6)^{\circ}, respectively. Alternatively, it is notable that one of the S-Sn-C angles is considerably smaller $(97.5(3) \text{ in } 1 \text{ and } 100.5(3)^{\circ}$ average in 2) than the rest of the five angles around Sn (average 111.7(11) in **1** and $111.1(24)^{\circ}$ in **2**); all five being close to or slightly larger than the all-tetrahedral angle. A similar phenomenon was noted for $Ph_3Sn[SCO_2N(CH_2)_4O]$, Ph₃Sn[SOCNC₄H₄], Ph₃Sn[S₂CO(i-Pr)], and Ph₃Sn[S₂P(OEt)₂] where the smaller S-Sn-C angles were 95.7(1), 98.2(1), 100.0(1), and 100.09(1)°, respectively, (9, 8, 7, 12). The three Sn—C distances, ranging from 2.10(1) to 2.12(1) in 1 and 2.13(3) Å (average) in 2, are among the shorter reported for the four triphenyltin derivatives mentioned above which range from 2.123(3) to 2.149(5) Å, and similar to that in the cyclic dithiophosphate derivative, Ph₃Sn[S₂POCMe₂CMe₂O] (19) (2.106(8) to 2.134(9) Å).

The Sn—S bond lengths of 2.444(4) in 1 and 2.44(3) Å (average) in 2 are similar to those in $Ph_3Sn[SCO_2N(CH_2)_4O]$ (2.446(2) Å), Ph₃Sn[S₂CO(i-Pr)] (2.445(1) Å), Ph₃Sn[SOCNC₄H₄] (2.453(1) Å), $Ph_3Sn[S_2P(OEt)_2]$ (2.4582(9) Å), and $Ph_3Sn[S_2POCMe_2CMe_2O]$ (2.436(3) Å); all of which have been described as containing monodentate ligands. Bidentate ligands with essentially identical Sn—S bonds, for example $Ph_2Sn[S_2P(O(i-Pr)_2]_2$ (10) (2.689 (1) and 2.678 (1) Å), are appreciably longer than the 2.444 (4) Å found in 1. These bidentate ligands have a partial Pauling bond order of ca. 0.50 compared to the Sn—S bonds in 1 and 2 with bond orders of ca. 0.91. However, examples of bidentate ligands with more variance in Sn-S bond lengths, also referred to as unsymmetrical or anisobidentate, are exemplified by $BuSn[S_2CN(Et)_2]_3$ (11), where Sn—S bonds range from 2.619(7) to 2.860(6) Å, and Ph₂SnCl[S₂CO(i-Pr)]₂ (20), where a range of 2.5 to 2.8 Å is quoted. These have bond orders ranging from ca. 0.78 to 0.32. In $Sn[S_2COEt]_4$ (21), two types of Sn—S distances are reported: those in bidentate ligands ranging from 2.562(2) to 2.627(2) Å) and those in monodentate ligands being 2.494 (2) Å. However, the second sulfur atoms in the latter cases are 2.916(10) Å from tin, giving an Sn—S distance that is only marginally longer than in species where the ligands are described as unsymmetrical bidentate ligands. Given that wave functions are continuous, it is reasonable to assume ever weakening partial bonds as the Sn-S distances increase. Our simplistic calculations based on Pauling's method (15) gave partial bond orders of 0.80 to 0.28 for Sn—S distances of 2.49–2.92 Å.

In the absence of a second sulfur atom, the terminal O atom in both **1** and **2** is oriented towards tin; the Sn—O distances of 3.040(8) and 3.05(1) Å (average) in **1** and **2**, respectively being significantly less than the sum of the van der Waals radii of 3.57 Å. In Fig. 3 and Table 4, the core about tin is shown with the inclusion of the Sn—O bond in the coordination sphere. Similarly, in Ph₃Sn[S₂CO(i-Pr)] the O atom of the propoxy group, rather than the terminal S atom as is normally the case, is oriented toward tin, and it was proposed that the Sn—O distance of 2.950(3) Å was sufficiently shorter than the sum of the Van der Waals radii

	$Ph_3Sn[SCO_2Me]$ (1)	$2Ph_3Sn[SCO_2(i-Pr)]$ (2)	Ph ₃ Sn[SCON(CH ₂) ₄ O]	Ph ₃ Ge[SCO ₂ Me]
$\overline{\text{Sn}(1)}$ -S(1)	2.444(4)	2.44(3)	2.446(2)	2.253(3)
Sn(1)—O(1)	3.040(8)	3.05(2)	2.809(2)	3.112(7)
Sn(1)—C(3)	2.10(1)	2.12(1)	2.127(5)	1.931(9)
Sn(1)—C(9)	2.12(1)	2.14(3)	2.127(5)	1.946(9)
Sn(1)—C(15)	2.12(1)	2.12(6)	2.149(5)	1.950(9)
O(1)-Sn(1)-C(15)	153.4(4)	157.1(6)	153.8(1)	155.5(3)
O(1)-Sn(1)-C(9)	86.0(3)	83.7(8)	86.6(1)	89.0(3)
O(1)-Sn(1)-C(3)	79.6(3)	79.5(21)	80.7(1)	75.4(3)
O(1)-Sn(1)-S(1)	56.2(2)	56.2(3)	59.8(9)	56.4(1)

Table 4. Interatomic distances (Å) and angles (°) around M involving the M–O interaction in $Ph_3Sn[SCO_2Me]$ (1)^{*a*} 2Ph₃Sn[SCO₂(i-Pr)] (2)^{*b*} Ph₃Sn[SCON(CH₂)₄O],^{*c*} and Ph₃Ge[SCO₂Me]^{*b*,*d*}.

^aThe atom numbering is that used for Ph₃Sn[SCO₂Me].

^bThe average of the corresponding bonds and angles for the two molecules in the asymmetric unit.

^cRef. (9).

^{*d*}Ref. (4).

to indicate a significant degree of interaction between the Sn and O atoms (7). Hence the environment around tin can be described as a distorted trigonal bipyramid. By contrast, in a study of organotin(IV)1-pyrrolecarbothioates (8) Sn-O distances ranging from 2.424(3) to 2.523(2) Å were considered bonding, while those from 2.65 to 3.242 Å were described as non-bonding (8), as was the distance of 2.809(4) Å in Ph₃Sn[SCOCN(CH₂)₄O] (9). As discussed above for Sn—S partial bonds, it is reasonable to simply assume that the partial bonds get weaker as the Sn-O distance gets longer. Thus, Sn—O distances of 2.424(3) to 2.523(2) can be assigned partial bond orders of 0.46 to 0.35 and those from 2.65 to 3.242 bond orders from 0.24 to 0.05. This is essentially a spherical model therefore the bond orders are probably underestimated. The Sn—O distance in Ph₃Sn[SCO₂Me] (1) of 3.040(8) Å corresponds to a bond order of 0.08 to complement the Sn—S bond length of 2.444(4) Å with a bond order of 0.91. The corresponding Ge—O distance in Ph₃Ge[SCO₂Me] (3.112(7) Å) can be assigned a bond order of only 0.03, compared with a bond order for the Ge-S bond (2.253(3) Å) of 1.02, so on a relative scale the interaction with the terminal C=O bond is less significant for germanium. The comparative features presented in Table 4 for $Ph_{3}Sn[SCO_{2}Me]$ (1), $Ph_{3}Sn[SCO_{2}(i-Pr)]$ (2), $Ph_{3}Sn[SCON(CH_{2})_{4}O]$, and Ph₃Ge[SCO₂Me] show striking similarities. Quite clearly, each molecule has one O-Sn-C angle much closer to 180° (153.4(4) to 157.1(6)°) and the other two much closer to 90° (75.4 to 89.0°) as expected for distortion based on the trigonal bipyramid.

The terminal C=O bond length of 1.20(1) Å in **1** is similar to that in Ph₂Te[SCO₂(i-Pr)]₂ (1.203(9) Å), where the ligand was considered to be anisobidentate (4). The SC—O bond of 1.34(1) is significantly shorter than the SCO—C bond of 1.43(1) Å. The shortening of the SC—O bond relative to the SCO—C bond is also clear in **2**, despite the poorer refinement, and is consistent with the π -bond character being only of significance within the planar SCO₂ core. The angles in the planar core (e.g., O=C-O (126(1)°), O=C-O (125(1)° and O-C-S 109.2° for **1**) indicate that the C=O bond is clearly most strongly involved in the delocalized π -bonding, as was found for the organogermanium- and organotelluriummonothiocarbonates (3,4). The SnS—C distance of 1.76(1) Å for **1**, which is marginally shorter than the sum of the covalent radii of S and C is also essentially the same as in the Ge and Te analogues, close to the value found in $Ph_3Sn[S_2CO(i-Pr)]$ (1.748(5) Å), and longer than the typical value (ca. 1.70 Å) for a symmetrical bidentate dithiocarbonate.

Infrared and Raman spectra

In general, monothiocarbonates appear to be relatively poor scatterers and the quality of the Raman spectra is such that no attempt is made at extensive assignments. However, the assignment of distinctive characteristic features is possible by using the same factors described for the analogous germanium (4) and tellurium (3) derivatives, along with comparisons with other related dithioacid tin species (6, 21), and these are provided in linear form for each compound in the experimental section. There is a marked similarity between the spectra of $Ph_2Sn[SCO_2(i-Pr)]_2$ (**3**) and $Ph_2Te[SCO_2(i-Pr)]_2$ (3) which is consistent with the similar atomic masses of tin and tellurium and with the similar orientations of the monothiocarbonate groups despite the differences in overall structure. While it is reasonable to assume that there will be significant coupling between the four stretching vibrations of the SCO₂C unit, the positions of the three peaks that dominate the infrared spectra in the 1700-1000 cm⁻¹ region suggest these arise primarily from the stretching of the three C-O bonds. Thus, for example, in $Ph_2Sn[SCO_2(i-Pr)]_2$ (3) the three very strong broad peaks are seen at 1642 (mainly C=O stretching), 1176 (mainly C-O stretching), and 1091 cm⁻¹ (mainly O—CH(CH₃)₂ stretching); compared with 1653, 1149, and 1088 cm⁻¹ in Ph₂Te[SCO₂(i-Pr)]₂ and 1698, 1159, and 1087 cm⁻¹ in Ph₂Ge[SCO₂(i-Pr)]₂. The strong band corresponding to that at 1640 cm⁻¹ is observed at lower wave-number, between 1550 and 1614 cm⁻¹, in NaSCO₂R salts (4), which is consistent with the presence of a strong terminal C=O bond in the monothiocarbonate derivatives. Any association with the metal is apparently similar for tin and titanium and least significant for germanium, as shown by the bond orders calculated for the structures of $Ph_3Sn[SCO_2Me]$ (1) in which the band is seen at 1669 cm⁻¹ and that of $Ph_3Ge[SCO_2Me]$ in which it is at 1695 cm⁻¹. The fourth stretching vibration associated with the SCO₂C core, which is presumably primarily v(SnS-C), is seen between 655 and 662 cm⁻¹ as a weaker feature in the infrared and

fairly strong feature in the Raman effect. This is within the expected region for a C—S single bond stretch and is at lower wave number than in the salts where the C—S bond would have more partial π -bond character. Two distinctive peaks seen in **1–4** within the ranges 813–848 and 412–418 cm⁻¹ can be assigned to the out-of-plane mode, $\pi(SCO_2)$, and to one of the in-plane bends, $\delta(SCO_2)$, which were similarly assigned in the tellurium derivatives to ca. 848 and 416 cm⁻¹. The assignment of $\pi(CO_3)$ in a variety of carbonate salts is in the region of 830–873 cm⁻¹ suggesting that the π -electron delocalization is similar in all of these planar groups. In **5**, the feature attributable to $\pi(SCO_2)$ is obscured by the very intense and typical peaks assignable to the CH₃ rocking modes of the methyl groups attached to tin.

In the phenyltin derivatives (1-4) the characteristic and very distinctive *f*-phenyl and *v*-phenyl modes, which are both of similar intensity, are observed at ca. 736 and 695 cm^{-1} , along with y-phenyl at ca. 447 cm⁻¹; all three features being essentially the same in the tellurium and germanium analogues (3, 4). In Me₃Sn[SCO₂Me] (5) two peaks are seen at 532 and 506 cm^{-1} , which are not seen in the spectra of the phenyltin derivatives. These clearly correspond to the asymmetric and symmetric Sn-C stretching vibrations at almost identical positions to those in Me₃SnSMe (531 and 509 cm^{-1}) (22) suggesting very similar environments about Sn in 5 and the simple sulfide. In the latter, v(Sn-S) is seen at 341 cm⁻¹ but generally for dithioacid derivatives it is assigned at higher wave-number as exemplified by the range 356-394 cm⁻¹ for a variety of tin dithiocarbamate derivatives (23). In organotin chlorides, the Sn—Cl stretching vibrations have been typically assigned to the 344–360 cm⁻¹ region as they were in a detailed examination of low frequency vibrational spectra of group 14 phenyl compounds including Ph₃SnCl and Ph₂SnCl₂ (24). By contrast, in mixed halide ligand derivatives such as Me₂SnCl[S₂CNMe₂], v(SnCl) is assigned at a much lower wave-number, 268 cm⁻¹. This was the basis of our assignment of the low frequency modes in **4**.

Concluding comments

The isolation of organotin monothiocarbonates proved to be more difficult than for the corresponding organogermanium derivatives. The X-ray structures of Ph₃Sn[SCO₂Me] (1) and Ph₃Sn[SCO₂(i-Pr)] (2) demonstrate a preference for the orientation of the terminal C=O oxygen atom towards tin, at least in the solid state. The resulting weak intermolecular interaction indicates an anisobidentate link that is relatively more significant than in the corresponding germanium derivative. Thus the distortions from "all-tetrahedral" angles around tin are consistent with the formation of a weak Sn-O link that gives a distorted trigonal bipyramidal arrangement around tin. In dithio derivatives, there is often a tendency for Ph₃SnL species with symmetrical bidentate ligands to disproportionate to the bis species, Ph₂SnL₂ on recrystallization giving rise to a trans octahedral structure. This clearly is not the case for Ph₃Sn[SCO₂Me] and Ph₃Sn[SCO₂(i-Pr)] and indeed we were not able to isolate X-ray quality crystals for Ph₂Sn[SCO₂Me]₂ or Ph₂Sn[SCO₂(i-Pr)]₂; consistent with the ligands being essentially monodentate in solution as is indicated by the NMR spectra.

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