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Derivatives of Divalent Germanium, Tin and Lead. III. Tin(II) Dithiolates[1,2]

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Tin(II) dithiolates, $Sn[SR]_2$ (R = Me, C_6H_{13}, C_7H_{15}, CH_2Ph, Ph, p-tolyl), and the tin(II)-sulphur heterocycles, $\overline{Sn.S.CH_2.CH_2S}$ and $\overline{Sn.S.C_6H_4Me.S}$, have been synthesised by the protolysis of the tin(II)-carbon bond by thiols. Tin-119m Mössbauer and infra-red spectra are reported, and the structures of the compounds discussed. 2-Thioethanol reacts similarly to give tin(II)di(2-thioethoxide) and not the expected heterocycle $\overline{Sn.S.CH_2.CH_2.O}$.

Introduction

Recent years have witnessed great interest in the preparation and properties of metal thiolates.[3-5] In the chemistry of Group IVB, whilst thiolates of the types $R_nM^{IV}[SR']_{4-n}$, n = 0-3, are well characterised for silicon, germanium, tin and lead,[6] known thiolates of the divalent metals are as yet restricted to the lower two members of the group. Lead(II) dithiolates have been known for a long time,[7,8] and have often found use as synthetic intermediates.[9-11] Recently, a systematic investigation of a large number of lead(II) dithiolates has been reported.[5] In sharp contrast however, as yet only a single tin(II) dithiolate has been characterised.

The problem frequently encountered in attempted syntheses of tin(II) thiolates from stannous chloride dihydrate[12] or hydrated stannous oxide[13] is the facile oxidation of the transient tin(II) dithiolate to the tetrakistin(IV) compound.

Experimental Section

All manipulations were performed under an atmosphere of dry nitrogen or argon. Infra-red spectra were recorded using a Perkin-Elmer 521 spectrometer. Tin-119*m* Mössbauer spectra were recorded at 77°K *vs.* a $BaSn^{119m}O_3$ source. Dimethylcyclopentadienyl)tin was prepared from stannous chloride and the organolithium reagent in anhydrous tetrahydrofuran.[1] Molecular weight determinations were performed using a Mechrolab instrument.

1. *Bis(methanetholato)tin(II).* An exothermic reaction took place when methanethiol was passed through a solution of di(methylcyclopentadienyl) tin(II) (1.02 g, 3.7 mmoles) in benzene (15 ml). *Bis(methanetholato)tin(II)* crystallised out of solution as orange-yellow plates. M.p. (sealed tube) 154-5° (with decomposition). Found: C, 10.8; H, 2.7; Sn, 55.6%. Calc. for $C_2H_6S_2Sn$: C, 11.2; H, 2.8; Sn, 55.8%.

2. *Bis(hexanethiolato)tin(II).* Hexanethiol (0.87 g, 7.38 mmoles) in benzene (2 ml) was added to di-(methylcyclopentadienyl)tin(II) (1.02 g, 3.68 mmoles) also in benzene (5 ml), and an exothermic reaction ensued giving a golden yellow solution. Removal of the solvent, and washing with the minimum amount of pentane gave *bis(hexanethiolato)tin(II)* as a pale yellow solid. M.p. (sealed tube) 66-8°. Found: C, 40.7; H, 7.2; Sn, 33.3%; M, 422 (0.64% in $CHCl_3$). Calc. for $C_{12}H_{26}S_2Sn$: C, 40.8; H, 7.4; Sn, 33,6%; M, 353.

3. *Bis(heptanethiolato)tin(II)* was prepared in a similar way as (2). Heptanethiol (0.93 g, 7.05 mmoles) and di(methylcyclopentadienyl)tin(II) (0.98 g, 3.53 mmoles) gave *bis(heptanethiolato)tin(II)* as a pale yellow solid. M.p. (sealed tube) 63-6°. Found: C, 43.9; H, 7.2; Sn, 29.8%. Calc. for $C_{14}H_{30}S_2Sn$: C, 44.3; H, 7.4; Sn, 31.2%.

4. *Bis(benzylthiolato)tin(II).* The immediate removal of the solvent following the exothermic reaction between benzylthiol (0.91 g, 7.40 mmoles) and di(methylcyclopentadienyl)tin(II) (1.02 g, 3.68 mmoles) each in benzene (10 ml) gave *bis(benzylthiolato)-tin(II)* as a viscous, golden yellow oil. Found: C,

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46.7; H, 3.9; Sn, 32.1%. Calc. for $C_{14}H_{14}S_2Sn$: C, 46.0; H, 3.9; Sn, 32.6%. After ca. 6 hrs. the oil was orange, and 24 hrs, later had become deep red, depositing a dark red solid of unknown composition.

5. *Bis(phenylthiolato)tin(II)*. No apparent reaction took place when thiophenol (0.60 g, 5.55 mmoles) in tetrahydrofuran (5 ml) was added to di(methylcyclopentadienyl)tin(II) (0.75 g, 2.71 mmoles) also in tetrahydrofuran (10 ml). After 10 mins. golden yellow needles of *bis(phenylthiolato)tin(II)* began to be deposited. M.p. (sealed tube) 170° (with decomposition). (Lit. 160-2° (decomp.),[13] 158-160° (decomp.)[14]). Found: C, 43.1; H, 3,3; Sn, 35.0%. Calcd. for $C_{12}H_{10}S_2Sn$: C, 42.8; H, 3.3; Sn 35.3%.

6. *Bis(p-tolylthiolato)tin(II)* was immediately formed as a mass of white needle crystals when *p*-tolylthiol (0.85 g, 6.85 mmoles) in tetrahydrofuran (5 ml) reacted exothermically with di(methylcyclopentadienyl)tin(II) (0.95 g, 3.43 mmoles) in the same solvent (10 ml). M.p. (sealed tube) 165°. Found: C, 45.3; H, 4.0; Sn 32.2%. Calc. for $C_{14}H_{14}S_2Sn$: C, 46.0; H, 3.9; Sn, 32.6%.

7. *1,2-Ethanedithiolatotin(II)* was precipitated immediately when 1,2-ethanethiol (0.36 g, 3.95 mmoles) was added to the organotin(II) reagent (1.0 g, 3.95 mmoles) in benzene (20 ml). M.p. (sealed tube) >230°. Found: C, 11.8; H, 2.2; Sn, 56.3%. Calc. for $C_2H_4S_2Sn$: C, 11.4; H, 1.9; Sn, 56.3%. The compound was recovered unchanged after 6 hr. reflux with excess ethanethiol (6 moles) in benzene.

8. *Toluene-3,4-dithiolatotin(II)* crystallised from solution within a few minutes from the exothermic reaction between toluene-3,4-dithiol (0.66 g, 4.58 mmoles) and di(methylcyclopentadienyl)tin(II) (1.17 g, 4.26 mmoles) both in tetrahydrofuran (10 ml). M.p. (sealed tube) decomp. ca. 170°. Found: C, 31.2; H, 2.5; Sn, 43.0%. Calc. for $C_7H_6S_2Sn$: C, 30.8; H, 2.2; Sn, 43.5%. Addition of excess of the thiol caused the immediate oxidation of the tin(II) compound to *spiro*-bis(toluene-3,4-dithiolato)tin(IV) m.p. 310°.

9. *Tin(II) Di(2-thioethoxide)*. In the exothermic reaction between 2-thioethanol (0.32 g, 4.11 mmoles) and di(methylcyclopentadienyl)tin(II) (1.14 g, 4.12 mmoles) both in benzene (10 ml), a very pale yellow solid was immediately precipitated. M.p. (sealed tube) >230°. Found: C, 17.5; H, 3.6%. Calc. for C_2H_4OSSn: C, 12.3; H, 2.1; Sn, 43.1%. Calc. for $C_4H_{10}O_2S_2Sn$: C, 17.6; H, 3.7; Sn, 43.5%. The compound was identified as *tin(II) di(2-thioethoxide)* rather than bis (2-hydroxyethanethiolato)tin(II) on the basis of its infra-red spectrum (see text).

Discussion

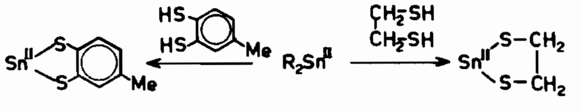
We have previously prepared bis(phenylthiolato)tin(II) by two routes: (i) by the reaction of thiophenol and freshly preparesd tin(II) dimethoxide,[14] and (ii) by the esterification of thiophenol and anhydrous blue-black stannous oxide.[13] Neither method offers the desired synthetic versatility.

The protolysis of the tin-carbon bonds of organotin(II) species has proved a fruitful method for the synthesis of tin(II) derivatives of alcohols, oximes, hydroxylamines, carboxylic acids and phenols.[1] In addition, the method has been used to synthesise tin(II) cyanide[1] and tin(II) nitrate[15] for the first time. The same technique is useful in the present case.

Tin(II) dithiolates (I, R^1 = Me, C_6H_{13}, C_7H_{15}, CH_2Ph, Ph, *p*-tolyl) are formed in high yield when alkane- or arenethiols react with dicyclopentadienyltin(II) or its methylcyclopentadienyl analogue in a 2:1 molar ratio in anhydrous benzene or tetrahydrofuran (equation 1).

$$R_2Sn^{II} + 2R^1SH \rightarrow \underset{\text{I}}{Sn^{II}[SR^1]_2} \qquad (1)$$

1,2-Ethanedithiol and toluene-3,4-dithiol react similarly in a 1:1 ratio to give the tin(II)-sulphur heterocycles, II and III, (equation 2).

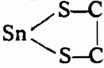


(2)

II III

Confirmation of the preservation of the lower oxidation state is given by the tin-119*m* Mössbauer isomer shifts (Table I), which fall in excess of the value of β-tin (2.65 mm/s), the normally accepted dividing line between the two valence states.[16]

Table I. Tin-119m Mössbauer Parameters.

	δmm/s [a]	Δmm/s [b]	Ref.
$Sn[SPh]_2$	3.51	1.60	*c*
$Sn[SC_7H_{15}]_2$	3.06	1.69	*c*
	3.10	1.84	*c*
$Sn[OCH_2CH_2SH]_2$	3.04	1.95	*c*
SnS	3.24-3.6	0.8-1.13	19

[a] Considered accurate to at least ±0.05 mm/s. [b] Considered accurate to at least ±0.10 mm/s. [c] This work.

The tin(II) dithiolates are yellow solids, some crystalline with sharp melting points, or in one case, the benzylthiolato derivative, a viscous, golden yellow oil. The two tin(II)-sulphur heterocycles, II and III, are infusible, and decompose at high temperatures, and are presumably strongly intermolecularly associated, like the corresponding spiro tin(IV) compound, bis-toluene-3,4-dithiolato)tin(IV).[18] The hexanethiolato-, heptanethiolato- and benzylthiolato-derivatives exhibit excellent solubility in all common organic solvents,

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and colligative measurements (osmometry) show that the former compound is essentially monomeric in dilute chloroform solution.

When exposed to the atmosphere, the tin(II) dithiolates undergo facile oxidation, evidenced by the appearance of a resonance at ca. 0.5 mm/s in the tin(IV) region of the Mössbauer spectra, and, in the infra-red spectra, broad bands at ca. 550 cm^{-1} which may be ascribed to tin-oxygen stretching vibrations.[17] We have noted previously that bis(phenylthiolato)tin(II) is oxidised by excess thiophenol in air to the tetrakistin(IV) derivative, slowly at room temperature but rapidly in refluxing benzene.[14] The toluene-3,4-dithiolato derivative II, behaves similarly. The slightest excess of the reagent causing the immediate formation of the dark-red polymeric bis(toluene-3,4-dithiolato)-tin(IV).[18] Ethane-1,2-dithiolatotin(II), on the other hand, shows no tendency to form the tin(IV) derivative even in the presence of a 6 molar excess of the thiol during 6 hr. in boiling benzene. This is surprising, since attempts to prepare the tin(II) thiolate from the chloride, thiol and triethylamine causes the rapid formation of the tin(IV) derivative.[12]

Bis(methanethiolato)tin(II) when freshly prepared is highly crystalline. On storage under nitrogen at room temperature, the compound slowly becomes amorphous, with the concomitant loss of carbon and hydrogen content. At its melting point this process is accelerated, and the compound rapidly evolves a malodorous gas, presumably dimethyl sulphide, and deposits stannous sulphide (equation 3). Similar pyrolyses are well known for the analogous lead(II) dithiolates.[5]

$$Sn[SMe]_2 \xrightarrow{\Delta H} SnS + Me_2S \tag{3}$$

The tin-119*m* Mössbauer parameters for representative compounds are listed in Table I. The alkanethiolates have isomer shifts lower than that of the previously measured stannous sulphide,[19] whilst the higher value for the phenylthiolato compound is probably due to the increased electron-withdrawing power of the aromatic ring. All the compounds exhibit quadrupole splittings substantially higher than that of stannous sulphide. The origin of this parameters in tin(II) derivatives is as yet somewhat of an enigma, and a knowledge of structural data is really needed for a meaningful discussion. Covalent and point charge models have been used, but neither profers an adequate rationalisation.[20] Three general types of structure are known for covalent tin(II) compounds. (a) Compounds in which the lone pair of electrons is localised in the 5s orbital. The tin then uses the three available 5p orbitals in bonding, resulting in bond angles close to 90°, with either three-coordination, e.g. $SnCl_3^-$ [21] and SnS,[22] or six-coordination, e.g. SnTe and cubic SnSe.[23] (b) The stannous oxide structure in which the tin lies at the apex of a square pyramid whose base is formed by its four nearest neighbour oxygen atoms, which are each in turn tetrahedrally coordinated to four tin atoms.[24] This structure has also been postulated for a number of tin(II)-oxygen heterocycles.[25] (c) Monomeric compounds in which the tin is sp^2 hybridised, resulting in a bond angle at tin of ca. 120° and with the lone pair occupying an orbital with directional character. Dicyclopentadienyltin is the only structurally confirmed example of this type.[26] It seems likely that the freely soluble hexane-, heptane-and benzylthiolato derivatives will have the latter structure, whilst the remainder posses a structure involving strong intermolecular coordination with bridging sulphur atoms.

Table II. Infra-red Spectrum of $Sn[SMe]_2$.[a] (cm^{-1})

	Assignment
1425 m	$\delta_{asym}Me$
1366 vw	2 x ν(S-C)?
1314 m	$\delta_{sym}Me$
1298 w	
951 s	ρMe
945 s	
693 m	ν(S-C)
687 m	
361 m	ν_{aysm}(Sn-S)

Table III. Infra-red Spectrum of Sn . S . CH_2 . CH_2 . S.[a] (cm^{-1})

	Assignment
2930 w	ν(C-H) 2 x 1409?
2895 m	
2810 vw	
1421 m	$\delta(CH_2)$
1409 s	
1292 vw	CH_2 wag
1278 w	
1268 vw sh	
1242 s	ν(C-C)
1111 m	CH_2 twist
920 w	CH_2 rock
821 vs	ν_{asym} (C-S)
722 vw br	
675 vw	
658 w	
639 m	ν_{sym} (C-S)
429 w	Ring angle def.
299 m	ν_{asym}(Sn-S)

[a] Nujol/halocarbon oil mull.

The infra-red spectra of organotin(IV)-sulphur compounds has aroused much interest.[27] The spectrum of bis(methanethiolato)tin(II) is assigned in Table II. Bands at 1425 cm^{-1}, 1314 cm^{-1} and a doublet at 951, 945 cm^{-1} are readily assigned to the antisymmetric and symmetric deformation and rocking modes of

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(27) P.G. Harrison and S.R. Stobart, *J. Organometal. Chem.*, *47*, 89 (1973); and references contained therein.

Table IV. Infra-red Spectra of Sn[SPh]$_2$ and Sn[SCH$_2$Ph]$_2$. (cm^{-1})

Sn[SPh]$_2$ [a]	Sn[SCH$_2$Ph]$_2$ [b]	Assignment
	3110 w	
3080 vvw	3090 m	ν(C-H);
3060 vvw	3070 s	ν(C-C) combinations
	3035 s	
	3010 w	
	2965 w	2m
	2925 m	2n
	2840 w	k+q
	1950 vw br	h+j
	1880 vw br	h+i
	1808 vw br	h+g
	1755 vw br	g+i
	1680 vw br	
1589 w	1602 m	k, ν(C-C)
1573 vw	1586 w	l, ν(C-C)
1563 vw	1565 vw br	
	1545 vw br	2f
1478 w	1494 vs 1478 m sh	m, ν(C-C)
1438 w	1453 vs 1428 m	n, ν(C-C)
1373 w		r+v?
	1335 vw	2v?
1327 vw	1322 w	o, ν(C-C)
1306 vw		
1300 vw		
1272 vw	1291 vw	
	1233 vs	q, x-sens.
	1203 m	ν(C-CH$_2$)
1186 vw	1183 w	a, β(C-H)
1165 vw	1157 w	c, β(C-H)
	1139 w	
1087 w 1084 w		q, x-sens.
1073 w	1071 s	d, β(C-H)
1026 m	1031 s	b, β(C-H)
1002 vw	1004 w	p, ring
985 vw	984 vw	j, γ(C-H)
970 vw	965 vw	h, γ(C-H)
900 vw	915 m	i, γ(C-H)
	864 w	
838 vw	844 w	g, γ(C-H)
	805 m	
737vs	771 vs	f, γ(C-H)
	702 vs	ν(C-S)
697 s sh 692 vs	677 vs	v, φ(C-C)
669 w		r, x-sens.
619 vw	623 w	s, α(CCC)
480 m	569 s	y, x-sens.
430 vw 421 w	479 m	t, x-sens.
361 m 351 m	364 m sh	ν_{asym}(SSnS)
326 w	312 s	ν_{asym}(SSnS)
252 m	285 s sh	U, x-sens.

[a] Nujol/halocarbon oil mull; [b] Liquid film.

the methyl group respectively. The carbon-sulphur stretching frequency occurs as a doublet 693, 687 cm^{-1}. Only a single tin-sulphur stretching frequency could be detected (at 361 cm^{-1}), which is assigned as the antisymmetric mode. The hexanethiolato and heptanethiolato derivatives were qualitatively similar with carbon-sulphur stretching vibrations occurring as strong bands at 724 cm^{-1} and 722 cm^{-1} respectively, and the antisymmetric tin-sulphur stretching vibration at 362 w cm^{-1} and 350 m cm^{-1} respectively. Again the corresponding symmetric modes could not be detected.

The spectrum of the tin(II)-sulphur heterocycle, $\overline{\text{Sn.S.CH}_2\text{.CH}_2\text{.S}}$, is listed in Table III. Fundamentals due to the ethylene residue are readily assigned and require no further comment. Bands at 821 vs cm^{-1} and 639 m cm^{-1} may be assigned to the antisymmetric and symmetric carbon-sulphur stretching modes. Only a single tin-sulphur stretching fundamental at 299 cm^{-1} was observed.

The spectra of Sn[SPh]$_2$ and Sn[SCH$_2$Ph]$_2$ are given in Table IV. The bands due to the presence of monosubstituted benzene rings are assigned using Whiffen's notation.[28] The carbon-sulphur stretching vibration of the latter compound occurs at 702 cm^{-1}, whilst bands at ca. 360 cm^{-1} and ca. 320 cm^{-1} may be assigned to the antisymmetric and symmetric stretching vibrations of the three atom SSnS system.

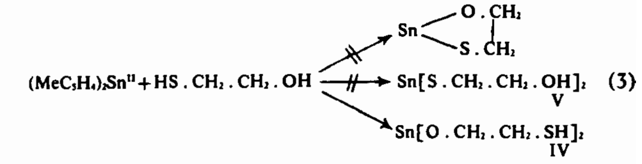
The vibrations due to tin-sulphur stretching fundamentals for the tin(II) dithiolates and structurally similar organotin(IV) compounds are listed in Table V. In general the antisymmetric vibration occurs in excess of 350 cm^{-1} whilst the symmetric mode occurs at lower frequency.

Table V. Tin-Sulphur Stretching Frequencies (cm^{-1}).

Compound	ν_{sym}(SSnS) cm^{-1}	ν_{asym}(SSnS) cm^{-1}	Ref.
Sn[SMe]$_2$	*a*	361	*b*
Sn[SC$_6$H$_{13}$]$_2$	*a*	362	*b*
Sn[SC$_7$H$_{15}$]$_2$	*a*	350	*b*
Sn[SCH$_2$Ph]$_2$	312	364	*b*
Sn[SPh]$_2$	326	361,354	*b*
Sn[SC$_6$H$_4$Me-*p*]$_2$	335	375	*b*
$\overline{\text{Sn . S . CH}_2\text{ . CH}_2\text{ . S}}$	*a*	299	*b*
$\overline{\text{Sn . S . C}_6\text{H}_4\text{Me . S}}$	322,309,295	369	*b*
Me$_2$Sn[SMe]$_2$	340	*a*	27
Ph$_2$Sn[SPh]$_2$	345	355	29
[R$_2$SnS]$_3$	322,343	364	30

R = Me, Et, ^{n}Br. [a] Not observed. [b] This work.

The reaction between 2-thioethanol and di(methylcyclopentadienyl)tin(II) is of interest. In spite of the use of equimolecular ratio of reactants in an attempt to synthesise the analogue of the heterocycle III, microanalysis showed the reaction to have proceeded in a 1:2 ratio (equation 3), yielding a product which



was insoluble in common organic solvents. Choice between the two possible formulations is aided by the infra-red spectrum. For the other alkanethio derivatives the region 400-600 cm^{-1} was clear; the Sn-S stretching vibration occurring at lower energy and

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the C-S stretching vibration at higher energy. In the spectrum of the 2-thioethanol derivative, however, there occurs a very strong, very broad band at 550 cm^{-1}, whilst no Sn-S stretching vibration could be discerned. Tin(II) alkoxides exhibit characteristically a similar intense, broad band wich has been assigned to the Sn-O stretching vibration.[17] Thus the compound is assigned the tin-oxygen bonded structure, IV, rather than the tin-sulphur bonded structure, V. Carbon-oxygen and carbon-sulphur stretching vibrations occur at 1048vs cm^{-1}, 1007vs cm^{-1} and 676 m cm^{-1} respectively. The S-H stretching vibration, expected as a weak band at *ca.* 2550-2600 cm^{-1}, could not be detected.

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