Derivatives of Bivalent Germanium, Tin, and Lead. Part X.[1] Tin(II) Bis(phenoxides), Bis(*O*-methyl dithiocarbonate), and Bis(diethyldithiocarbamate)

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Tin(II) bis(phenoxides), $Sn(OR)_2$ (I), have been synthesised in high yield from bis(methylcyclopentadienyl)tin and 2 mol of phenol in benzene or tetrahydrofuran (thf); *o*-aminophenol yields a compound of composition $Sn_2(OR)_3$ due to some Sn–N covalent bond formation. The reaction of $Sn(OMe)_2$ with phenols does not give (I), but $[(p\text{-}MeC_6H_4O)SnOSn(OC_6H_4Me\text{-}p)]$, (IV), has been isolated from the reaction with *p*-cresol. Mössbauer spectra of the compounds (I) and (IV) indicate the presence of polymeric lattices in which adjacent tin atoms are bridged by oxide and phenoxide oxygen atoms in an infinite array. Tin(II) bis(diethyldithiocarbamate), $[Sn(S_2CNEt_2)_2]$, and bis(*O*-methyl dithiocarbonate), $[Sn(S_2COMe)_2]$, have been obtained by metathesis between tin(II) chloride and $K[S_2CNEt_2]$ or $K[S_2COMe]$. The Mössbauer parameters for the dithiocarbonate are substantially different from those for the diethyldithiocarbamate which is known to possess a structure based on a distorted trigonal bipyramid with the tin lone pair occupying a sp^2 hybrid orbital, and suggests a structure in which dithiocarbonate chelates the tin atoms in such a way that the four sulphur atoms are disposed almost tetrahedrally about the metal.

GENERAL high-yield procedures for the synthesis of tin(II) alkoxides and phenoxides are not as yet available. In spite of their obvious high stability, heterocyclic Sn^{II} derivatives of difunctional phenols have been obtained only in very poor yield by a variety of routes.[2] Attempted syntheses of tin(II) bis(phenoxides) by the esterification of anhydrous and hydrated tin(II) oxide with various phenols and alcohols in the presence of copper metal or copper oxides as catalysts yielded mononuclear products only in the case of phenol and 2-ethylhexanol. In all other cases, oligomers of the types $R(OSn)_nOR$ (n = 2 or 3) were obtained. Similar results were obtained when tin(II) sulphide or acetate were used.[3] Simple tin(II) alkoxides, however, may be prepared in almost quantitative yield by the addition of triethylamine to tin(II) chloride in the corresponding alcohol.[4] In this paper we report a high yield route to tin(II) bis(phenoxides).

Physical and analytical data for the complexes

Compound	M.p. (θc/°C)	Mössbauer spectra (mm s⁻¹) δ	Δ	Analyses (%) Found C	H	N	Calc. C	H	N
$Sn(OC_6H_4Me\text{-}p)_2$	161	3.21_5	1.74	50.7	4.40		50.5	4.25	
$Sn(OC_6H_4Cl\text{-}p)_2$	189	3.20	1.67	39.15	2.20		38.55	2.15	
$Sn(OC_6H_4NH_2\text{-}p)_2$	>210 (decomp.)	3.15	1.69	42.65	3.85	8.35	43.05	3.60	8.35
$Sn(OC_6H_4NO_2\text{-}p)_2$	>130 (decomp.)	3.42	1.47	36.5	2.25	6.45	36.5	2.05	7.10
$Sn(OC_6H_4Me\text{-}m)_2$	214	3.10	1.81	49.3	4.60		50.5	4.25	
$Sn(OC_6H_4NH_2\text{-}m)_2$	>230 (decomp.)	3.52	1.85	42.95	3.60	8.00	43.05	3.60	8.35
$Sn(OC_6H_4Me\text{-}o)_2$	*ca.* 60 (decomp.)	3.13	1.97_5	49.95	5.00		50.5	4.25	
$Sn(OC_6H_3Me_2\text{-}2,6)_2$	116	3.13	1.97	52.4	5.25		52.25	5.00	
$Sn(OC_6H_3Me_2\text{-}3,5)_2$	231—234	3.14	1.69	52.45	4.95		52.25	5.00	
$Sn(OC_5H_4N\text{-}3)_2$	63—65	2.96	1.93	41.2	2.95	8.00	39.15	2.60	9.15
$Sn(OMe)_2$ [a]		3.02	1.97						
o-Phenylenedioxytin(II) [b]		2.95	1.76						
2,3-Tolylenedioxytin(II) [b]		3.09	1.89						
2,3-Naphthylenedioxytin(II) [b]		3.08	1.82						
2,2′-Biphenylylenedioxytin(II) [b]		3.13	1.98						

[a] Ref. 5. [b] Ref. 2.

RESULTS AND DISCUSSION

Continuing our study[1] of the protolysis of cyclopentadienyltin compounds, we have found that bis(methylcyclopentadienyl)tin reacts with substituted phenols in a 1 : 2 molar ratio in dry benzene or tetrahydrofuran (thf) to afford tin(II) bis(phenoxides), (I), in

$$[Sn(C_5H_4Me)_2] + 2HOR \longrightarrow \underset{(I)}{Sn(OR)_2} + 2MeC_5H_5 \quad (1)$$

essentially quantitative yield. Compounds (I) are generally white amorphous or microcrystalline solids, except for the amino-substituted derivatives which are coloured, which undergo slow oxidative hydrolysis in air (Mössbauer spectroscopy). The *o*- and *p*-cresol and 2,6-xylenol derivatives show some solubility in benzene and thf, but the remainder are insoluble in organic solvents. Tin-119*m* Mössbauer data are listed in the

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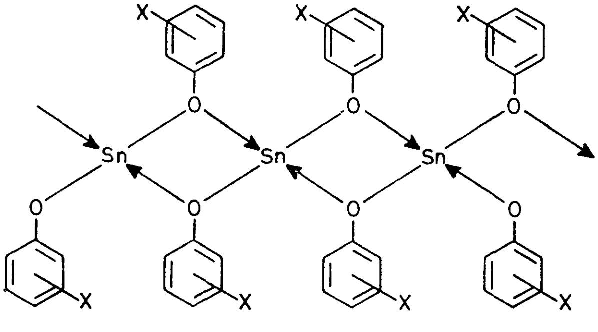
[1] Part IX, A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 1722.

[2] G. T. Cocks and J. J. Zuckerman, *Inorg. Chem.*, 1965, **4**, 592; J. J. Zuckerman, *J. Chem. Soc.*, 1963, 1322; H. J. Emeléus and J. J. Zuckerman, *J. Organometallic Chem.*, 1964, **1**, 328.

[3] D. E. Fenton, R. R. Gould, P. G. Harrison, T. B. Harvey, G. M. Omietanski, K. C. T. Sze, and J. J. Zuckerman, *Inorg. Chim. Acta*, 1970, **4**, 235.

[4] J. S. Morrison and H. M. Haendler, *J. Inorg. Nuclear Chem.*, 1967, **29**, 393.

Table, together with those for related compounds. The isomer shifts fell in the range 3.10—3.52 mm s^{-1}, higher than those of heterocyclic tin(II) phenoxides (2.95—3.13 mm s^{-1}) [2] and tin(II) dimethoxide (2.92 mm s^{-1}),[5] indicating a lower degree of covalency in the tin–oxygen bonds of (I) than in the heterocyclic phenoxides or the dimethoxide. As expected, the isomer shift, and therefore the Sn–O bond polarity, increased with increasing electron-withdrawing nature of the ring substituent. The Mössbauer spectra persisted at ambient temperatures suggesting that compounds (I) possess a solid-state structure involving phenoxide bridges (II) similar to that postulated for $Sn(OMe)_2$.[4] The tin–oxygen stretching frequency occurs as a strong band at 560 cm^{-1} in $Sn(OMe)_2$,[4] but, because of the complex nature of the i.r. spectra, the position of this band could not be located with reasonable certainty for any of compounds (I).



(II)

The reaction of $[Sn(C_5H_4Me)_2]$ with *o*-aminophenol did not give the expected tin(II) bis(*o*-aminophenoxide), but rather crystals of a homogeneous material of composition $Sn_2(OR)_3$, (III). The Mössbauer spectrum for this compound consisted of a quadrupole-split doublet with an isomer shift of 2.85 mm s^{-1}, significantly lower than the compounds (I), and quadrupole splitting of 2.14 mm s^{-1}, demonstrating identical, or very similar, electronic environments for all tin atoms. In the i.r. spectrum, the N–H stretching vibrations occurred at 3 290 and 3 255 cm^{-1}, *ca.* 150—200 cm^{-1} lower than those in the parent phenol indicating N→Sn co-ordination. Valency considerations necessitate participation of the amino-groups in the reaction and the formation of covalent Sn–N bonds.

Tin(II) dimethoxide is generally less reactive than cyclopentadienyltin(II) compounds, and reaction with substituted phenols is not a satisfactory route to (I). However, in the reaction with *p*-cresol, the dimer μ-oxo-bis(*p*-tolyloxytin), (IV), analogous to the oligomers obtained from SnO and phenols,[2] was produced after reflux in benzene. The Mössbauer spectra of (IV) also consisted of a quadrupole-split doublet with isomer shift 2.98 mm s^{-1} and quadrupole splitting 2.225 mm s^{-1}.

$$Sn(OMe)_2 + 2HOC_6H_4Me\text{-}p \longrightarrow [(p\text{-}MeC_6H_4O)SnOSn(OC_6H_4Me\text{-}p)] \quad (2)$$
$$\text{(IV)}$$

Replacement of the phenoxide group by oxide causes a decrease in isomer shift, and hence 5*s*-electron density at tin, illustrating the increased covalent nature of the Sn–O(oxide) bond in contrast to the Sn–OR bond. Observation of a resonance at ambient temperatures again strongly suggests the presence of a polymeric lattice, in which now presumably both oxide and phenoxide oxygen atoms bridge adjacent tin atoms.

Tin(II) bis(diethyldithiocarbamate), (V), and bis-(*O*-methyl dithiocarbonate), (VI), were obtained as white and golden-yellow crystalline solids, respectively, by substitution of $SnCl_2$ by potassium diethyldithiocarbamate or *O*-methyl dithiocarbonate. Both compounds are freely soluble in thf and benzene, being monomeric in the latter solvent (osmometry). The crystal structure of (V) has been determined.[6] Co-ordination at tin is based on a distorted pseudo-trigonal bipyramid with both dithiocarbamate groups chelating the metal, the lone pair being stereochemically active and occupying the third equatorial position in an approximately sp^2 hybrid orbital. The distribution of valence electrons thus deviates significantly from cubic, giving rise to the observed quadrupole splitting of 1.20 mm s^{-1}. Despite the similarity of the $MeOCS_2^-$ and $Et_2NCS_2^-$ groups, the Mössbauer parameters for (V) and (VI) differ considerably. The isomer shift increased from 3.26 in (V) to 3.60 mm s^{-1} in (VI), corresponding to an increase in tin 5*s* electron density. The quadrupole splitting on the other hand decreased to the barely resolvable value of 0.56 mm s^{-1}, indicating a nearly cubic distribution of valence electrons about the metal atom. These data suggest that, on replacement of dithiocarbamate by *O*-alkyl carbonate groups, the tin lone-pair becomes preferentially located in the spherically symmetrical 5*s* orbital hence increasing $[\psi_{5s}(0)]^2$ and the isomer shift, and the two *O*-alkyl carbonate ligands chelate the tin in such a way as to achieve a nearly tetrahedral disposition of sulphur atoms about tin. The small observed quadrupole splitting probably arises from distortion from ' local ' T_d symmetry to D_{2d}.

$$[Sn(S_2CNEt_2)_2] \xleftarrow[-2KCl]{2K[S_2CNEt_2]} SnCl_2 \xrightarrow[-2KCl]{2K[S_2COMe]} [Sn(S_2COMe)_2]$$
$$\text{(VI)}$$

EXPERIMENTAL

All manipulations involving bivalent tin compounds were made under an atmosphere of dry, oxygen-free, argon or nitrogen. Bis(methylcyclopentadienyl)tin was prepared from lithium methylcyclopentadienide and tin(II) chloride in tetrahydrofuran (thf). Tin(II) dimethoxide was obtained on addition of triethylamine to $SnCl_2$ in methanol as solvent according to the method of Morrison and Haendler.[4]

I.r. spectra were recorded using Perkin-Elmer 457 or 521 spectrometers. Tin-119*m* Mössbauer spectra were obtained against a $Ba[^{119m}SnO_3]$ source (The Radiochemical Centre, Amersham) using a Harwell spectrometer calibrated using iron foil and β-tin. Data reduction to Lorentzian line

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[5] P. G. Harrison and S. R. Stobart, *J.C.S. Dalton*, 1973, 940.

[6] J. Potenza and D. Mastropaolo, *Acta Cryst.*, 1973, **B29**, 1830.

shapes was effected by usual least-squares methods. Isomer shifts are quoted relative to SnO_2. Molecular weights were determined in benzene using a Mechrolab osmometer.

The syntheses of the tin(II) bis(phenoxides), (I), were essentially very similar, and physical and analytical data are in the Table. Full experimental details are therefore only given for one example.

Tin(II) *Bis*(m-*aminophenoxide*).—A solution of *m*-aminophenol (0.61 g, 5.58 mmol) in thf (25 cm^3) was added slowly with stirring to a solution of [$Sn(C_5H_4Me)_2$] (0.77 g, 2.78 mmol) in dry benzene (20 cm^3) under an atmosphere of argon. Immediately, the reaction mixture became turbid and on gently warming, until the mixture began to reflux, a finely divided, very pale pink, solid was progressively precipitated. The product was filtered off under argon, washed, and dried *in vacuo* to yield a very pale pink amorphous *solid* (0.82 g, 88%).

Reaction of [$Sn(C_5H_4Me)$] *with* o-*Aminophenol*.—No immediate reaction was apparent when a solution of *o*-$H_2NC_6H_4OH$ (0.73 g, 6.69 mmol) in thf (25 cm^3) was added slowly to a solution of [$Sn(C_5H_4Me)$] (0.93 g, 3.34 mmol) in benzene (10 cm^3). On warming to reflux temperature, the dark-green colour of the phenol gradually faded. After refluxing the mixture for 9 h a grey precipitate appeared which was filtered off under argon and dried *in vacuo* to yield a pale grey *solid* (0.72 g, 77%), m.p. (sealed tube) 213 °C (Found: C, 38.0; H, 3.35; N, 7.00. $C_{18}H_{19}N_3O_3Sn_2$ requires C, 38.55; H, 3.05; N, 7.50%).

Reaction of $Sn(OMe)_2$ *with* p-*Cresol*.—A solution of the phenol (0.74 g, 6.8 mmol) in benzene (10 cm^3) was added to a suspension of $Sn(OMe)_2$ (0.62 g, 3.4 mmol) also in benzene (25 cm^3). The $Sn(OMe)_2$ began to dissolve during the addition giving finally a slightly turbid solution. After stirring for 12 h the mixture was filtered and reduced in volume. Addition of diethyl ether produced μ-*oxo-bis-*(p-*tolyloxytin*) (0.71 g, 89%) as a white solid, m.p. (sealed tube) 217 °C (Found: C, 35.75; H, 3.10. $C_7H_7O_{1.5}Sn$ requires C, 35.95; H, 3.45%).

Tin(II) *Bis*(O-*methyl dithiocarbonate*).—To $SnCl_2$ (9.60 g, 50.6 mmol) in thf was added a solution of potassium *O*-methyl dithiocarbonate (14.6 g, 109 mmol) in ethanol, and the mixture stirred for 4 h. A dark brown precipitate appeared which was filtered off and the yellow filtrate concentrated. Small yellow needles of the *product* were obtained which were filtered off, washed, and dried *in vacuo*, m.p. (sealed tube) 113—115 °C, ν(C=S) at 570 cm^{-1}, τ 5.82 (O*Me*) (Found: C, 14.55; H, 1.80. $C_4H_6O_2S_4Sn$ requires C, 14.45; H, 1.80%).

Tin(II) *Bis*(*diethyldithiocarbamate*).—This compound was obtained as above from $SnCl_2$ and potassium diethyldithiocarbamate in thf as a white *solid*, m.p. (sealed tube) 112 °C (Found: C, 29.35; H, 4.80; N, 6.00. $C_{10}H_{20}N_2S_4Sn$ requires C, 28.9; H, 4.85; N, 6.75%).

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