Inorganica Chimica Acta, 34 (1979) 107–112
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Synthesis and Characterization of Alkyl- and Aryltin(IV) Monothiocarbamates

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Received September 23, 1978

The preparation of dialkyl- and diaryltin(IV) N,N'-dialkylmonothiocarbamates from the alkylammonium salt of the ligand and the appropriate diorganotin(IV) chlorides is described.

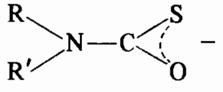
The compounds $R_2Sn(R'_2mtc)_2$ *and* $Ph_3Sn(R'_2mtc)$ *(R = alkyl, aryl;* R'_2 *= Me, Et; mtc = monothiocarbamate anion) are monomeric in dichloromethane or chloroform and are non-electrolytes in nitromethane.* ^1H *nmr spectra of* $CDCl_3$, CD_2Cl_2 *and benzene solutions of* $R_2Sn(R'_2mtc)_2$ *indicate that the dialkyltin(IV) moiety is non-linear (*$J^{119}Sn–^1H_{CH_3}$ ca. *80 Hz) and that the N-alkyl substituents in the monothiocarbamate ligand are magnetically non-equivalent. Stereochemical non-rigidity of* $Me_2Sn(Me_2mtc)_2$ *in* CD_2Cl_2 *is observed in the* ^1H *nmr spectrum. Two isomeric species are observed with coalescence occurring at –30 °C to give a single species that shows restricted rotation of the N-methyl substituents. Further coalescence of these two equal intensity N-methyl signals occurs at 55 °C.*

A value of $J^{119}Sn–CH_3$ *(*^1J *= 552 Hz) for the carbon bonded directly to tin in* $Et_2Sn(Me_2mtc)_2$ *suggests that this type of compound involves six-coordination of the tin atom with Sn–S bonding being stronger than Sn–O bonding.*

The $Ph_3Sn(R'_2mtc)$ *species have distorted trigonal bipyramidal geometry with the oxygen of the bidentate monothiocarbamate in one of the axial positions.*

Introduction

There is continuing interest in the study of metal complexes derived from the monothiocarbamate ligand 1*. A number of transition metals in various oxidation states has been successfully complexed with this ligand including V [1], Mo [2], Mn [3, 4], Fe [2, 5–7], Co [8], Ni [9–13], Rh [14, 15], Pd [2, 12], Pt [2, 12], Cu [16], Ag [17, 18], Au [15], Zn [19, 20], Cd [19], and Hg [19].



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In contrast, there has been little detailed investigation of complexes of the monothiocarbamate ligand with main-group metals apart from Tl [21] and several organotin(IV) species. In the latter investigations some trimethyltin(IV) N,N-dimethylmonothiocarbamates have been isolated and ^1H nmr studies have shown that the compounds in solutions of non-coordinating solvents have restricted rotation of the N-alkyl substituents at ambient temperature. Structures involving four-, five- and polymeric coordination have been postulated [22–24]. The preparation of $(CH_3)_3Sn(Me_2mtc)$ by an insertion reaction of carbonyl sulfide according to equation (1) has been reported [25].

$$Me_3SnNMe_2 + COS = Me_3SnOSCNMe_2 \qquad (1)$$

A similar reaction involving carbon dioxide gave the corresponding carbamate compound. The observation that the reaction of carbon disulfide with this carbamate occurs according to equation (2)

$$Me_3SnOOCNMe_2 + CS_2 = Me_3SnSSCNMe_2 \quad (2)$$

has been used to suggest that the Sn–S bond in these compounds is much stronger than the Sn–O bond [25].

Although the synthesis of some mixed carbamate complexes of dimethyltin(IV), some containing the monothiocarbamate ligand, has been reported [26], no detailed studies on the monothiocarbamato- compounds appear to have been made.

In the present paper we report the preparation and characterization of a series of complexes of the form $R_2Sn(R_2mtc)_2$ and $R_3Sn(R_2mtc)$ and their solution behaviour in non-coordinating solvents.

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*The N,N'-disubstituted monothiocarbamate anion, R_2NCOS^-, is abbreviated to R_2mtc; dithiocarbamate, $R_2NCS_2^-$ = R_2dtc; thioselenocarbamate, R_2NCSSe = R_2tsc; monoselenocarbamate, R_2NCSeO = R_2msc; Me = methyl, Et = ethyl, nBu = n-butyl, Ph = phenyl, Bz = benzyl.

Experimental

Preparation of Ligands

Dialkylammonium salts of the N,N'-dimethyl- or diethylmonothiocarbamates were prepared by reaction of the appropriate secondary amine with carbonyl sulfide gas [21, 27]. The diethylammonium salt of N,N'-diethylmonothiocarbamate was obtained as a white crystalline solid and the corresponding methyl derivative was prepared *in situ* and was not isolated.

Preparation of Organotin(IV) Compounds

$R_2Sn(R'_2mtc)_2$ $(R = Me, Et, Ph;\ R'_2 = Me_2, Et_2)$

The reaction of the appropriate diorganotin(IV) dichloride with the required dialkylammonium-N,N-disubstituted monothiocarbamate in a 1:2 mol ratio in dry acetone as solvent afforded a white precipitate of the dialkylammonium chloride. This precipitate was removed by filtration and the filtrate was evaporated under a gentle stream of dinitrogen to give colourless needle shaped crystals of diorganotin(IV) bis(N,N'-disubstituted monothiocarbamate) in yields in excess of 90 per cent. The products may be recrystallized from chloroform, dry acetone or heptane.

$Ph_3SnR'_2(mtc)$ $(R'_2 = Me_2, Et_2)$

The compounds were prepared by mixing in a 1:1 mol ratio the appropriate alkylammonium ligand and triphenyltin(IV) chloride in acetone. The precipitated alkylammonium chloride was removed by filtration and the filtrate was evaporated in a stream of air to give a white crystalline material in almost quantitative yield. The compounds may be recrystallized from chloroform or dry acetone.

Analyses

Analyses for C, H, N, and S were performed by the Australian Microanalytical Service, C.S.I.R.O., and are reported together with melting points in Table I.

Physical Measurements

Molecular weight determination was carried out at 37 °C in dichloromethane or chloroform solutions using a Perkin Elmer Model 115 vapor phase osmometer calibrated with benzil. Conductances were measured at ambient temperature on a Philips PR9500/02 conductance bridge. Mass spectra were recorded on a JEOL MS-100 spectrometer. The chamber temperature was varied between 100 and 250 °C at 70 e.v. ^1H nmr spectra were measured on approximately 0.1*M* solutions, when solubility permitted, in CD_2Cl_2, $CDCl_3$, CCl_4 and C_6H_6. All chemical shifts are reported relative to tetramethylsilane as an internal reference. Ambient temperature spectra (approx. 37 °C) were measured on a Perkin Elmer R12A spectrometer and variable temperature spectra were recorded on a Varian Associates A60D instrument. Both spectrometers operate at 60 MHz. The solvents for variable temperature studies were CD_2Cl_2 (–80 to +55 °C) and $CDCl_3$ (–44 to + 65 °C).

All spectra were recorded at a sweep rate of 0.5 Hz sec^{-1} at radio-frequency power levels well below saturation of observed resonances. Probe temperatures were calibrated using methanol.

^{13}C nmr spectra of the compounds in $CDCl_3$ with tetramethylsilane as internal reference were measured using a JEOL JNM-PS-100 Fourier Transform spectrometer operating at 25.15 MHz.

Infrared spectra of solids were measured as potassium bromide discs or as mulls in Nujol (no significant differences in band positions or intensities were observed). Solution spectra were measured in solutions of Analytical Reagent grade carbon tetrachloride and chloroform. A Perkin Elmer Model 457 spectrometer calibrated with polystyrene was used.

Results and Discussion

The compounds reported in Table I are white crystalline materials that were obtained in yields in

TABLE I. Analytical Data for Organotin(IV) Monothiocarbamates.

Compound	M.p. °C	Analysis							
		%C		%H		%N		%S	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$Me_2Sn(Me_2mtc)_2$	170–171	26.6	26.9	5.3	5.1	8.0	7.8	17.8	18.0
$Me_2Sn(Et_2mtc)_2$	81–82	34.7	34.9	6.3	6.3	6.4	6.8	15.8	15.5
$Et_2Sn(Me_2mtc)_2$	105–106	31.1	31.2	5.7	5.8	7.1	7.3	16.7	16.7
$Et_2Sn(Et_2mtc)_2$	62–63	36.4	38.1	6.8	6.9	6.0	6.4	14.0	14.5
$Ph_2Sn(Me_2mtc)_2$	108–110	42.0	44.9	5.3	4.6	6.4	5.8	11.8	13.3
$Ph_2Sn(Et_2mtc)_2$	124–126	49.3	49.2	5.4	5.6	4.7	5.2	11.2	11.9
$Ph_3Sn(Me_2mtc)$	84–86	54.3	55.5	4.9	4.7	3.0	3.1	6.9	7.1
$Ph_3Sn(Et_2mtc)$	94–96	57.3	57.3	5.3	5.2	3.3	2.9	6.7	6.7

TABLE II. Molecular Weight Data for Organotin(IV) Monothiocarbamates.

Compound	Solvent	Concentration (mol dm^{-3} × 10^2)	Molecular Weight	
			Found	Calc.
$Me_2Sn(Me_2mtc)_2$	CH_2Cl_2	2.44	369	357
		6.71	380	
$Me_2Sn(Et_2mtc)_2$	CH_2Cl_2	2.64	464	413
		7.57	428	
$Et_2Sn(Me_2mtc)_2$	$CHCl_3$	0.22	441	385
		0.87	486	
		1.28	451	
$Et_2Sn(Et_2mtc)_2$	$CHCl_3$	0.29	420	441
		0.80	462	
		1.29	456	
$Ph_2Sn(Me_2mtc)_2$	$CHCl_3$	0.14	538	481
		0.50	552	
		1.05	579	
$Ph_2Sn(Et_2mtc)_2$	$CHCl_3$	0.58	541	537
		1.18	549	
		1.31	484	
$Ph_3Sn(Me_2mtc)$	$CHCl_3$	0.20	477	454
		0.63	478	
		1.52	477	
$Ph_3Sn(Et_2mtc)$	$CHCl_3$	0.23	478	482
		0.81	497	

excess of 90 per cent. All the compounds were found to be non-electrolytes in nitromethane.

Molecular weight determinations were made using vapor phase osmometry on chloroform or dichloromethane solutions. The results are shown in Table II. Generally the compounds are monomeric under these conditions, although minor association appears to occur for $Et_2Sn(Me_2mtc)_2$ and $Ph_2Sn(Me_2mtc)_2$.

A parent ion peak of very low relative intensity was observed only for $Me_2Sn(Et_2mtc)_2$, $Et_2Sn(Me_2mtc)_2$, $Ph_3Sn(Me_2mtc)$ and $Ph_3Sn(Et_2mtc)$. There was no evidence for associated species containing tin and no metastable peaks were observed for any of the compounds.

The ambient temperature (37 °C) solution ^1H nmr spectra for $R_2Sn(R'_2mtc)_2$ and $Ph_3Sn(Me_2mtc)$ compounds all display magnetic non-equivalence of the N-alkyl groups with a solvent dependent separation of the observed N-CH_3 doublet of 6–14 Hz. The Sn–R resonances are observed as a singlet for R = Me and as multiplets, which are characteristic of equivalent or degenerate groups for R = Et and Ph. The results of these determinations are given in Table III.

Variable temperature ^1H nmr experiments on $Me_2Sn(Me_2mtc)_2$ in CD_2Cl_2 solution in the range −80° to +67 °C gave the following results:

(a) At temperatures below −30°, *two* Sn-CH_3 resonances of unequal intensity (δ 1.10 ppm, $J^{119}Sn–^1H_{CH_3}$ = 72 Hz; δ 1.01 ppm, $J^{119}Sn–^1H_{CH_3}$ = 78 Hz) and *four* major N-CH_3 resonances of comparable intensity were observed. In addition, there was evidence of additional N-CH_3 resonances of very low intensity which may be due to the presence of the free ligand. The latter resonances remain constant in intensity and position over the temperature range.

(b) The compound is stereochemically non-rigid on the ^1H nmr time-scale. Two separate and distinct coalescence phenomena were observed. In a low temperature, *ca.* −30 °C, process in CD_2Cl_2 the collapse of the Sn-CH_3 doublet to a singlet is accompanied by coalescence of the N-CH_3 quartet to an equal intensity doublet in a common process. In addition at 55 °C (CD_2Cl_2 solution) and 58 °C ($CDCl_3$ solution) this N-CH_3 doublet gives a single resonance at 2.97 ppm.

Certain structural inferences may be made from this information. In particular values of $J^{119}Sn–^1H_{CH_3}$ have been used to indicate the extent of linearity in CH_3–Sn–CH_3 arrangements. Honda *et al.* [28] have made extensive use of an observation of Holmes and Kaesz [29] that relates the magnitude of the coupling constant to the extent which the C–Sn–C bond angle approaches 180°. Thus, on the basis of $J^{119}Sn–^1H_{CH_3}$ = 84.0 Hz for $Me_2Sn(Me_2dtc)_2$ in $CDCl_3$, a non-linear arrangement is strongly suggested [28]. A *trans* arrangement of methyl groups is expected to lead to J values in the region of 100 Hz [29].

In the present situation the observed $J^{119}Sn–^1H_{CH_3}$ values are in accord with a significantly distorted *trans* or *cis* arrangement of the two methyl groups. Similar conclusions have been made for

TABLE III. ^{1}H Nmr Spectra of Organotin(IV) Monothiocarbamates[a,b].

Compound	Resonance			
	Assignment	δ (ppm)[c]		
		CCl_4	C_6H_6	
$Me_2Sn(Me_2mtc)_2$	N-CH_3	3.11 2.93	1.98 1.86	
	Sn-CH_3	0.98	0.79	$J^{119}Sn-^1H_{CH_3}$ = 83(CCl_4), 78(C_6H_6) Hz
$Me_2Sn(Et_2mtc)_2$	C-CH_3[d]	1.27 1.17	0.28	
	N-CH_2[e]	3.45 3.31	2.56	
	Sn-CH_3	0.99	0.77	$J^{119}Sn-^1H_{CH_3}$ = 83(CCl_4), 81(C_6H_6) Hz
$Et_2Sn(Me_2mtc)_2$	N-CH_3	3.12 2.93	2.02 1.91	
	Sn-C_2H_5[f]	1.5	1.2	
$Ph_2Sn(Me_2mtc)_2$	N-CH_3	3.12(6.5) 2.87(5)	1.62(5) 1.85(3)	
	Sn-C_6H_5[g]	7.82(3.5) 7.37(10)	h	
$Ph_3Sn(Me_2mtc)$	N-CH_3	3.05 2.82	1.95 1.74	

[a] Probe temperature 37 °C. [b] Values in brackets are integrations if not unity. [c] Internal reference tetramethylsilane. [d] Centres of two overlapping triplets in CCl_4, broadened triplet in C_6H_6. [e] Two overlapping quartets in CCl_4, unsymmetrical sextet in C_6H_6. [f] Centres of complex multiplets. [g] Centres of two complex multiplets. [h] Signal obscured by solvent resonance.

$Me_2Sn(Me_2dsc)$ [30] $Me_2Sn(Et_2dsc)_2$ [30], $Me_2Sn(Me_2msc)_2$ [31] and $Me_2Sn(Et_2msc)_2$ [31].

The ^{1}H nmr spectrum at 37 °C of the ethylammonium salt of N,N-diethylmonothiocarbamate in carbon tetrachloride shows a triplet for each of the methyl groups centred at 1.28 and 1.08 ppm. Such a result indicates that there is no restricted rotation of the N-ethyl substituents in the free ligand. However, when the ligand is coordinated in $Me_2Sn(Et_2mtc)_2$ restricted rotation of the ligand Et-substituents is observed at probe temperature. A similar situation holds for all of the $R_2Sn(R_2mtc)_2$ compounds reported here. The resonance positions of the non-equivalent R-substituents of the monothiocarbamate ligands are shown in Table III. The separations are solvent dependent and a similar effect that has been observed for $Me_2Sn(Me_2msc)_2$ [31], $Me_2Sn(Etmsc)_2$ and $Me_2Sn(Me_2tsc)_2$ [32] has been attributed to specific solvation effects.

The ^{13}C spectrum of $Et_2Sn(Me_2mtc)_2$ in $CDCl_3$ at 35 °C has the following signals relative to internal tetramethylsilane: 176.24 ppm, singlet (COS); 42.23, 37.50 ppm, doublet with peaks of equal intensity (N-CH_3); 19.66, 11.40 ppm, two singlets of equal intensity (Sn-CH_2CH_3). The observance of the two N-CH_3 signals is due to restricted rotation, a feature that was observed also in the ^{1}H nmr spectra of these compounds (Table III).

The values of $^{119}Sn-^{13}C$ coupling constants due to carbon atoms bonded directly to tin (^1J) have been used to propose structures of organotin(IV) compounds. As a first approximation the supposed hybridization of the tin(IV) atom is related to the magnitude of ^1J. Thus, compounds of the type Et_xSnX_{4-x} (where X is a monodentate ligand) of known tetrahedral structure have $^1J^{119}Sn-^{13}C$ values in the range 320–425 Hz in non-coordinating solvents [33]. The present compounds typified by $Et_2Sn(Me_2mtc)_2$ (^1J = 552 Hz) do not involve tetrahedral coordination of Sn(IV). Compounds of 6-coordinate octahedral structure such as $R_2Sn(acac)_2$ (acac = 2,4-pentanedione anion) have ^1J *ca.* 900 Hz [33, 34] while 5-coordinate species have ^1J in a range intermediate between the 4- and 6-coordinate species. It has been pointed out, however, that caution should be taken in making such correlations especially if there are gross differences in substituents in a series of compounds [35, 36].

The single crystal X-ray structure analysis [37] of $Me_2Sn(Me_2dtc)_2$ shows the compound to involve 6-coordinated tin but significant distortions from a regular octahedral arrangement of donor atoms occur.

In particular, the Sn–S bond lengths are 2.515, 2.497, 2.954 and 3.061 Å, with the latter two being significantly longer than the former pair. The C–Sn–C bond angle in the Me_2Sn- moiety is 136° and is thus significantly distorted from linearity. The structure may better be described as containing a distorted tetrahedral $(CH_3)_2SnS_2$-coordination sphere with a very weak attachment of two additional sulphur atoms from the bidentate dithiocarbamate ligands. The ^{13}C nmr spectra [35] of $CDCl_3$ solutions of $Bz_2Sn(Et_2dtc)_2$ (^1J = 537 Hz) and $nBu_2Sn(Bz_2dtc)_2$ (^1J = 604 Hz) which are likely to have solid state structures similar to $Me_2Sn(Me_2dtc)_2$ show ^1J values similar to those observed for $Et_2Sn(Me_2mtc)_2$. Although the magnitude of ^1J does not necessarily preclude a 5-coordinate structure [35] with one ligand acting in a monodentate fashion, it seems reasonable to suggest that the present $R_2Sn(R'_2mtc)_2$ compounds have structures similar to that of the corresponding $R_2Sn(R'_2dtc)_2$ species with the two monothiocarbamate oxygen atoms bonded weakly and the sulphur atoms more strongly bonded to the tin. The preference for Sn–S rather than Sn–O bonding in this class of compound is clearly shown by the fact that carbon disulfide readily replaces the oxygen atoms in trimethyltin(IV) N,N-dimethylcarbamate to form the corresponding dithio-derivative [25]. The gross features of the solid and solution structures of $R_2Sn(R'_2mtc)_2$ are likely to be similar because no significant change is observed in the infrared spectra of the compounds in either phase (*vide infra*).

The low temperature (<–30 °C) ^1H nmr spectra of $Me_2Sn(Me_2mtc)_2$ indicate the presence of two isomeric forms in unequal amounts. Both isomers have a non-linear $H_3C–Sn–CH_3$ arrangement because $J^{119}Sn–^1H_{CH_3}$ = 72 and 78 Hz. The exact nature of the isomeric forms is not known.

The infrared spectrum of monothiocarbamate complexes is dominated by a broad intense band due to coupled $C\overset{\ldots}{-}N$, $C\overset{\ldots}{-}O$ stretching frequencies around 1500–1600 cm^{-1} [2, 10]. All the compounds in the present study have a very intense and broad band in this region (Table IV). The position and intensity of this band and others in the infrared spectra are little affected by the medium studied *i.e.* Nujol mull, potassium bromide disc, or carbon tetrachloride solution. This indicates that the solid structure is essentially retained in solution.

TABLE IV. Infrared Spectra of Organotin(IV) Monothiocarbamates.

Compound	$\nu_{C\overset{\ldots}{-}N,\ C\overset{\ldots}{-}O}$
$Me_2Sn(Me_2mtc)_2$	1585
$Me_2Sn(Et_2mtc)_2$	1578
$Et_2Sn(Me_2mtc)_2$	1580
$Et_2Sn(Et_2mtc)_2$	1570
$Ph_2Sn(Me_2mtc)_2$	1586
$Ph_2Sn(Et_2mtc)_2$	1570
$Ph_3Sn(Me_2mtc)$	1600
$Ph_3Sn(Et_2mtc)$	1590

It has been suggested previously [9, 15] that if $\nu_{C\overset{\ldots}{-}N,\ C\overset{\ldots}{-}O}$ occurs above 1545 cm^{-1} then the monothiocarbamate is present as a monodentate ligand bonded through the sulfur atom. However, caution should be taken in making such assignments because $\nu_{C\overset{\ldots}{-}N,\ C\overset{\ldots}{-}O}$ occurs at 1545 cm^{-1} in bis(cyclotetramethylene thiocarbamato)bis(pyrrolidine)cobalt(II). This complex has chelated thiocarbamate ligands although the Co–O bond length of 2.157 Å is considerably longer than normally found [8].

The infrared spectra of $Ph_3Sn(Me_2mtc)$ and $Ph_3Sn(Et_2mtc)$ have strong absorptions at 1600 and 1590 cm^{-1}, respectively, that are assigned to $\nu_{C\overset{\ldots}{-}N,\ C\overset{\ldots}{-}O}$. The similarity of the band position to that found for the $R_2Sn(R'_2mtc)_2$ species suggests that the monothiocarbamate is bound to the tin in a similar manner. The $J^{119}Sn–^{13}C$ value for $Ph_3Sn(Me_2mtc)$ in $CDCl_3$ solution is 600 Hz [35] a value well outside the range expected for tetrahedral 4-coordination. The most likely structure for $Ph_3Sn(R_2mtc)$ species is that of a distorted trigonal bipyramid. By analogy to the known structures of $Me_3Sn(Me_2dtc)$ [38, 39] and $Ph_3Sn(Et_2dtc)$ [40] which involve asymmetrical bidentate coordination of the dithiocarbamato ligand with the shorter Sn–S bond being in the equatorial plane containing the R_2Sn group, and the longer Sn–S bond in an axial position, it is likely that in the monothiocarbamato complexes considered here that the oxygen is the axial donor atom.

Infrared spectral data on $Me_3Sn(Me_2msc)$ and $Me_2Sn(Me_2msc)_2$ have been used to infer that the former compound involves 4-coordination of the monothiocarbamate ligand and that the oxygen atom is not coordinated [31].

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