

ORGANOTIN(IV) N,N-DISUBSTITUTED DITHIOCARBAMATES

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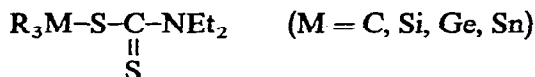
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(Received November 16th, 1966; in revised form March 24th, 1967)

The purpose of this work was to prepare organometallic dithiocarbamates of a typical element, such as tin, and to study their properties in order to try and understand their structures.

At the beginning of the present work passing mention was found in the patent literature of compounds somewhat related to ours and claimed to have fungicidal action¹ or to stabilize polychloroethylene², but they were not characterized. Recently, however, similar compounds were reported³ but no suggestion was made about the structure. $\text{Me}_3\text{Sn}(\text{SSCNMe}_2)$ was also reported⁴ recently, being prepared from $\text{Me}_3\text{SnNMe}_2$ and CS_2 ; its structure was discussed on the basis of an assignment of the IR spectrum, but no definite conclusion was drawn.

It is widely held that dithiocarbamates are bidentate and contain chelated rings; the alternate structure with unchelated rings and monodentate dithiocarbamates is not considered generally. Chelated dithiocarbamate rings are surely present in some transition⁵⁻⁸ and typical⁹ element derivatives; but in the case of Group IV elements, evidence for chelation is necessary, because an ester-type structure, like



cannot be excluded and is the obvious one for carbon. Indeed, S-alkyl esters of dithiocarbamic acid are well known, being prepared also by a route formally analogous to one of our synthetic procedures. Besides, examples of a derivative of this ester-type structure were reported for arsenic¹⁰ and recently for $\text{Ru}(\text{NO})(\text{SSCNET}_2)_3$ ⁸.

RESULTS

Preparation

It was carried out according to at least one of the following procedures, the resulting compounds being described in Table 1:

- (A) and (B) $\text{R}_3\text{SnCl} + \text{NaSSCNR}'_2 \rightarrow \text{NaCl} + \text{R}_3\text{Sn}(\text{SSCNR}'_2)$
(C) $\text{R}_3\text{SnOH} + \text{CS}_2 + \text{NHR}'_2 \rightarrow \text{R}_3\text{Sn}(\text{SSCNR}'_2) + \text{H}_2\text{O}$
(D) $\text{SnX}_4 + 2 \text{NaSSCNR}'_2 \rightarrow 2 \text{NaX} + \text{X}_2\text{Sn}(\text{SSCNR}'_2)_2$
(E) $\text{X}_2\text{Sn}(\text{SSCNR}'_2)_2 + 2 \text{NaY} \rightarrow 2 \text{NaX} + \text{Y}_2\text{Sn}(\text{SSCNR}'_2)_2$

Y, X = halide ion; R = alkyl or aryl group

The first reaction was carried out in homogeneous phase (procedure *B*) when acetone was used as a solvent; but it goes also in benzene (procedure *A*), though a longer reaction time was required: in all cases the same compound was obtained, also when steric isomerism was possible, as in the $R_2Sn(SSCNR'_2)_2$ compounds. It was found

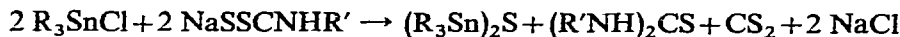
TABLE 1

COMPOUNDS OBTAINED AND ANALYTICAL DATA

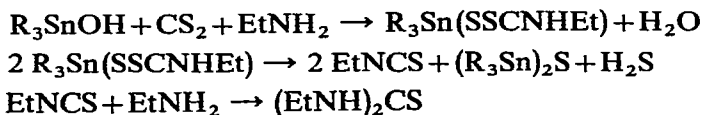
No.	Compound and synthesis	M.p. (°C) and colour	C ^a	H ^a	N ^a	Mol.wt. ^{a,b}	Crystallised from
(I)	Et ₃ Sn(SSCNEt ₂) A, B, C	liquid white	37.8	7.2	4.2	323	(b.p. 165°/2)
			37.3	7.1	4.0	354.1	
(II)	Et ₂ Sn(SSCNEt ₂) ₂ A, B	84 white	36.1	6.7	6.4	446	EtOH (subl. 180°/0.1)
			35.5	6.4	5.9	473.3	
(III)	Ph ₃ Sn(SSCNEt ₂) A, B	132-3 white	55.7	5.0	2.7	532	Benzene/P. ether
			55.4	5.1	2.8	498.3	
(IV)	Ph ₂ Sn(SSCNEt ₂) ₂ A, B	145-6 yellow	46.1	5.2	5.4	606	Benzene/P. ether
			46.4	5.3	4.9	569.4	
(V)	Ph ₃ Sn(SSCNPh ₂) A, B	194-5 white	62.8	4.4	2.5	557	Benzene/P. ether
			62.0	5.2	2.3	600.4	
(VI)	Ph ₂ Sn(SSCNPh ₂) ₂ B	117-8 ^d pale yellow	59.6	4.3	3.5	680	Benzene/ligroin
			59.9	4.0	3.7	701.6	
(VII)	Cl ₂ Sn(SSCNEt ₂) ₂ ^c D	220-1 pale yellow	24.8	4.0	6.3	ins.	Acetone
			24.7	4.1	5.8		
(VIII)	Br ₂ Sn(SSCNEt ₂) ₂ ^c E	220 yellow	21.2	3.4	5.0	ins.	Acetone
			20.9	3.5	4.9		
(IX)	I ₂ Sn(SSCNEt ₂) ₂ ^c E	202 yellow	18.2	3.0	4.4	ins.	Acetone
			18.0	3.0	4.2		

^a Found/calculated. ^b Osmomeric, in CHCl₃ or C₆H₆. ^c Not conducting in C₆H₅NO₂. ^d Lit.³ m.p. 216-8°.

impossible to obtain the latter compounds by alkylation of $X_2Sn(SSCNR_2)_2$ compounds by means of ethereal ethylmagnesium bromide: extensive decomposition took place. The attempted preparation of many organotin N-monosubstituted-dithiocarbamates ($R' = C_2H_5, C_6H_5, C_6H_{11}$) was unsuccessful, when procedures *A*, *B* and *C* were used. Bis(trisorganotin) sulphide was isolated, together with an N,N'-disubstituted thiourea, instead of the expected compounds:



The probable formation of an unstable (trisorganotin)N-alkyldithiocarbamate is supported by the known¹¹ facile decomposition of Cu(II), Pb(II), Fe(II), or Zn(II) N-monosubstituted dithiocarbamate to metal sulphide, H₂S and organic isothiocyanate. Our hypothetical intermediate compound might decompose in the same way, and the organic isothiocyanate formed would then react with excess of amine to afford the isolated thiourea derivatives plus bis(trisorganotin)sulphide:



The isolation of only one compound of formula $R_2Sn(SSCNR'_2)_2$, also when different syntheses were used, and the impossibility of obtaining this type of compound by alkylation of $Cl_2Sn(SSCNR_2)_2$ with $RMgX$ gave some hint that the unchelated structure was not to be excluded a priori. A four-coordinate, tetrahedral tin(IV) derivative would not give rise to geometrical isomerism, and a free C=S bond might explain the reaction with the Grignard reagent together with the absence of alkylated tin compound in the reaction mixture. Alkylation of the related $Cl_2AuSSCNR_2$ was successful¹².

Infrared spectra

The infrared spectra (Table 2) of the compounds described here are quite similar in the NaCl region, either in solution (CCl_4 and CS_2) or in the solid state (Nujol and hexachlorobutadiene mull), so that it can be assumed that no remarkable change takes place on passing from the solid state to the solution.

In all the compounds there is a strong band at *ca.* 1500 cm^{-1} , the so called "thioureide band", found also in many other chelated dithiocarbamates^{13,14}. This band is due to the vibration of C-N bond with partial double bond and polar character. This absorption was found also in the spectra of $Me_2NCSSMe$ and $Et_2NCSSEt$; we believe that no evidence can be surely found here either for or against a chelated structure, although the slight shift from the value observed in NaS_2CNEt_2 was taken⁸ as evidence for one monodentate group in $Ru(NO)(SSCNEt_2)_3$. When the IR spectra (NaCl region) of $(Et_2NCSS)_2Zn$ and of $Et_2NCSSEt$ were compared, either in solution or in the solid state, only the region around 1000 cm^{-1} was found to be different in a meaningful way. The chelated compound showed only one strong band here (995 cm^{-1} in CS_2 , CCl_4 and nujol) while the ester shows a doublet (1005 and 983 cm^{-1}). Since it is known¹⁵ that the C=S stretching frequency is to be found in a wide range, and that the value is around 1000 cm^{-1} in thiobenzanilide and related compounds, it can be assumed that one of the two strong bands in the doublet, present in the ester and not in the zinc derivative, should be assigned to uncomplexed C=S stretching. Similar conclusions, are reached when the sodium derivative is considered instead of the zinc compound. In accurate work on the infrared spectra of thioamides and selenoamides¹⁶ similar absorption bands were found to be due to a fairly pure C-S vibration. In the infrared spectrum of the N,N-dimethylthioformamide the C-S band was found at 975 cm^{-1} . However, this band is at an unusually high frequency because the CS band of thioamides and thioureas were normally found below 850 cm^{-1} ¹⁶.

In the unchelated dithiocarbamate moiety the double bond character of the C-S bond should be more than that in thioamides, so that the absorption band due to the C-S vibration should be found at higher frequencies. In fact a fairly pure C=S bond was recently found in $RhCl(CS)(PPh_3)_2$ ¹⁷, which shows a C-S stretching frequency at 1299 cm^{-1} . When the IR spectra of $X_2Sn(SSCNEt_2)_2$ were examined ($X = Cl, Br, I$), only one strong band at *ca.* 985 cm^{-1} and not a doublet was found in the region $1000 \pm 70\text{ cm}^{-1}$; this supports chelation.

TABLE 2

RELEVANT INFRARED SPECTRA

(I) film	(II) CCl ₄ /CS ₂	(VII) mull	Zn(SSCNEt ₂) ₂ mull	EtSSCNEt ₂ film
1492 sh	1494 sh	1528 s, br	1510 sh	
1486 s	1484 s		1501 s	
1463 m, br	1460 s	1462 s	1460 m	1485 s
	1439 m	1438 s	1437 s	1454 m
1423 s	1427 s		1430 s	1438 m
1415 s	1423 s		1378 m	1416 s
1376 m	1367 s	1377 m	1361 m	1376 w
			1357 m	1353 m
1300 w	1302 m	1290 w	1300 m	1300 w
1266 s	1257 s	1273 s	1273 s	1267 s
1206 s	1207 s	1198 s	1210 s	
	1169 w		1205 s	1207 s
1138 m	1138 s	1144 m	1146 m	1140 m
1092 w	1090 m	1091 m	1096 w	1091 w
1072 w	1072 m	1072 m	1080 m	
1066 w	1066 m	1068 m	1071 m	1073 w
		1059 m	1059 w	1067 w
1006 m	1010 sh			1005 m
988 m	990 m	985 m	995 s	983 m
955 w	947 m		917 m	916 m
911 w	912 m	907 m	909 m	
			852 w	
832 w	833 m	834 m	838 w	830 w
		787 sh	786 sh	
772 w	770 w	780 w	775 w	775 w
674 m	680 m			738 w
599 vw	600 vw	607 vw	608 vw	591 vw
566 w	592 vw	564 m	563 m	561 w
	564 m			
	522 vw			
502 m	502 vw		503 vw	493 w
480 m	482 w	488 w		^a
427 vw	424 w		421 w	
394 w	^{a,b}	391 sh	395 w	
379 w		378 m	374 w	
		309 sh	330 vw	
		304 m		
276 w		288 m		

^a Recorded down to 400 cm⁻¹ only. ^b As Nujol mull from 700 cm⁻¹

The frequency shift of the C-N vibration to higher wave number when a halide replaces an alkyl group is in agreement rather with a *cis*- than with a *trans*-configuration, which should scarcely be affected by such a change. Indeed, the related and the probably tetrahedral gold(III)¹² derivatives show a frequency shift similar to that observed here. No shift could be observed in our compounds when a phenyl replaced an alkyl group, because the 1500 cm⁻¹ region is obscured by the phenyl absorption. However, the shift cannot be more than *ca.* 20 cm⁻¹, otherwise it could

have been observed; such a small value may be due to a mesomeric effect. Unfortunately, the position of the absorption bands in the region $1000 \pm 70 \text{ cm}^{-1}$ cannot be obtained in the related ethyl- and phenyltin(IV) derivatives, since the region is masked by a strong absorption due to the organic radical bonded to the tin atom: SnEt_4 has a very strong band at 1012 cm^{-1} , due to CH_2 twisting¹⁸; absorption in the same region was found¹⁹ also for a long series of aryltin(IV) derivatives. So, while IR evidence strongly supports chelation when X is halogen, no decisive evidence is available here for the related alkyl and aryl derivatives. This applies also to the reported $\text{Me}_3\text{Sn}(\text{SSCNMe}_2)$ ⁴. It is known that overtone and combination bands are present in Me_4Sn , at 1050 and 1029 cm^{-1} .

In $\text{Me}_3\text{Sn}(\text{SSCNMe}_2)$ two bands were found at 1047 and 1027 cm^{-1} ; since they are not strong, there is no decisive evidence in favour of a structure with a monodentate dithiocarbamate group. Besides, the very weak band found at 1538 cm^{-1} cannot be assigned to the stretching vibration of a polar and asymmetric bond like $\text{C}=\text{N}^+$: it is better regarded as an overtone of the very strong band found at 772 .

For sake of comparison, we recorded the IR spectrum of the compound $\text{As}(\text{SSCNET}_2)_3$, for which a partially unchelated structure had been proposed by Malatesta in 1940¹⁰, on the evidence given by the high dipole moment (5.0 Debye), while Fe(III), Co(III) and Cr(III) derivatives have a lower dipole moment (1.2–1.6 D). The compound does show two bands in the region around 1000 cm^{-1} , a strong and a medium one in agreement with the original proposal and with the recent²⁰ X-ray structure determination of $[\text{As}(\text{C}_6\text{H}_4\text{O}_2)_2]^-$, where the arsenic atom has a stereochemically-active inert pair.

Moreover, comparison of the infrared spectra of $\text{Ru}(\text{NO})(\text{SSCNET}_2)_3$ which has one unchelated dithiocarbamate moiety, and of $\text{Ru}(\text{SSCNET}_2)_3$, shows that in the nitrosyl compound⁹ there is an additional band at $970\text{--}980 \text{ cm}^{-1}$.

All this evidence seems to support quite well our assignment of one of the two intense bands found at around 1000 cm^{-1} in the spectrum of EtSSCNET_2 to the uncomplexed $\text{C}=\text{S}$ stretching. To obtain more decisive evidence about the steric configuration of the $\text{Cl}_2\text{Sn}(\text{SSCNR}_2)_2$ compounds ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$), their IR spectra were recorded down to 200 cm^{-1} . Comparison with the spectrum of $\text{Zn}(\text{SSCNET}_2)_2$ and with that of the bromo compound allows the assignment of the bands at *ca.* 300 cm^{-1} to $\text{Sn}\text{--}\text{Cl}$ stretching; since a stronger and a weaker band are observed octahedral *cis* configuration is favoured. The different intensity of the two $\text{Sn}\text{--}\text{Cl}$ stretching bands rule out a tetrahedral unchelated coordination of the tin atom, since in this case the two absorption bands should be of comparable intensity like in R_2SnCl_2 ²¹.

A similar argument cannot be used for the $\text{Sn}\text{--}\text{C}$ stretching frequency in $\text{R}_2\text{Sn}(\text{SSCNET}_2)_2$ compounds, because in the 500 cm^{-1} region there is a ligand band.

Electric dipole moments

Dielectric constants and density measurements were carried out on the solution of those compounds of ours which were soluble enough for the purpose (Table 3). The resulting electric dipole moments are given in Table 4. We assumed ${}_A P = 0.20 \text{ }_E P$ and ${}_A P = 0$, but the results are not very much influenced by the value assumed for ${}_A P$.

In any case an anomalous and high value of ${}_A P$, can be excluded. Indeed it was found by Malatesta¹⁰ that atomic polarisation is rather small in metal dithio-

TABLE 3

DIELECTRIC CONSTANT AND DENSITY MEASUREMENTS

1000 w_2	100 $\Delta\epsilon_{12}$	100 w_2	1000 ΔV_{12}
Et₂Sn(SSCNEt₂)₂			
6.571	2.1	1.057	5.15
6.948	2.3	1.672	7.42
10.72	3.0	1.871	8.35
12.88	3.9		
Ph₂Sn(SSCNEt₂)₂			
5.757	2.17	0.642	3.41
6.941	2.42	1.023	4.72
1.043	4.02	1.466	6.81
1.305	4.81		
Ph₂Sn(SSCNPh₂)₂			
6.393	2.88	1.097	5.91
13.00	6.21	1.612	8.50
13.66	6.52	1.773	8.02
Ph₃Sn(SSCNPh₂)			
3.825	0.55	0.951	4.22
5.911	0.75	1.836	8.31
7.720	1.12	2.053	9.04
9.933	1.90		
10.74	1.71		
13.26	2.31		
Et₃Sn(SSCNEt₂)			
11.06	3.07	1.377	4.57
12.07	3.45	3.516	12.81
28.29	7.47	3.816	13.94
Ph₃Sn(SSCNEt₂)			
5.757	1.22	1.137	6.25
6.801	1.58	1.635	7.79
15.60	3.95	1.951	8.58

TABLE 4

DIPOLE MOMENTS

Compounds	α_0	$-\beta$	${}_{\infty}P_2$ (cm^3)	${}_E P^a$ (cm^3)	${}_{\infty}P + {}_{\lambda}P$ (cm^3)	μ^b (D)	$\mu_{20\%}^c$ (D)
Et ₂ Sn(SSCNEt ₂) ₂	3.00	0.45	363.8	118.9	244.9	3.46	3.29
Ph ₂ Sn(SSCNEt ₂) ₂	3.78	0.47	519.2	149.0	370.2	4.26	4.08
Ph ₂ Sn(SSCNPh ₂) ₂	4.75	0.49	828.4	209.2	619.2	5.50	5.31
Ph ₃ Sn(SSCNEt ₂)	2.49	0.47	332.9	130.2	202.6	3.15	2.94
Ph ₃ Sn(SSCNPh ₂)	1.57	0.44	299.2	160.3	138.9	2.61	2.28
Et ₃ Sn(SSCNEt ₂)	2.66	0.37	259.0	85.0	174.0	2.92	2.77

^a Calculated using the atomic, structural and group refractivities from the ref. 37. ^b Dipole moment obtained when no atomic polarization was assumed. ^c Dipole moment obtained assuming that the atomic polarization was 20% of the electronic polarization.

carbamates, which differ in this regard from other chelates such as acetylacetonates²² or dithiophosphinates²³. If monodentate dithiocarbamate groups are assumed, $\text{Et}_2\text{Sn}(\text{SSCNET}_2)_2$ and $\text{Ph}_2\text{Sn}(\text{SSCNET}_2)_2$ should have a comparable dipole moment, being the tin atom tetrahedral, while the difference is not negligible (0.9 Debye).

If bidentate dithiocarbamate groups are therefore assumed, a symmetric and *trans*-structure would require a zero or a rather low dipole moment; its numerical value should be comparable for $\text{Et}_2\text{Sn}(\text{SSCNET}_2)_2$, $\text{Ph}_2\text{Sn}(\text{SSCNET}_2)_2$, for a series of square planar bis(dialkyldithiocarbamates) of divalent metals studied by Malatesta (1.2–1.5 Debye)¹⁰ and for N,N,N',N'-tetramethyl-*p*-phenyldiamine (1.23 Debye). The values found here are not in agreement with an octahedral *trans*-structure. If the hypothesis of an equilibrium between *cis*- and *trans*-structure and labile chelation is taken into account, the dipole moment data indicate a rather high proportion of octahedral *cis*-form in the equilibrium mixture. A higher value of the dipole moment of $\text{Ph}_2\text{Sn}(\text{SSCNET}_2)_2$ than that of $\text{Ph}_2\text{Sn}(\text{SSCNET}_2)_2$ was expected since the ethyl group is known to be less electronegative than the phenyl group; while the lower value for $\text{Et}_2\text{Sn}(\text{SSCNET}_2)_2$ than for $\text{Ph}_2\text{Sn}(\text{SSCNET}_2)_2$ might be due to the mesomeric effect, as pointed out by Malatesta²⁴ in a study of electric dipole moment of a series of organotin compounds.

If the dipole moments of $\text{Et}_3\text{Sn}(\text{SSCNET}_2)$ and $\text{Ph}_3\text{Sn}(\text{SSCNET}_2)$ are compared with that of EtSSCNET_2 ¹⁰, it can be seen that the difference is rather small. This could be in agreement with some percentage of monodentate dithiocarbamate group in the solution.

Nuclear magnetic resonance and electronic spectra

The NMR data are given in Table 5. The S-ethyl N,N-diethyldithiocarbamate showed two different kinds of methylene protons; the bigger of the two methylene signals, 41 cps broad and without detectable fine structure, was assigned to the N-bonded alkyl; its shape is probably related to the coupling with ¹⁴N²⁵. No such influence of ¹⁴N nucleus was found in the tin-containing compounds, so that a presence of a chelate dithiocarbamate moiety might be possible though not required on this basis. *Cis* and *trans* isomers are possible for $\text{R}_2\text{Sn}(\text{SSCNR}'_2)_2$ compounds and their NMR spectra might be different²⁶. Owing to the rather complicated pattern due to phenyl or ethyl groups bonded to tin only the signals due to the protons of the

TABLE 5
RELEVANT NMR DATA

Compound ^a	¹ H NMR data	
	$\tau(\text{CH}_3)^b$ triplet	$\tau(\text{CH}_2)$ quartet
$\text{Zn}(\text{Et}_2\text{NCSS})_2$	6.66 ^b	6.12
$\text{Ph}_2\text{Sn}(\text{Et}_2\text{NCSS})_2$	8.72	6.23
$\text{Ph}_3\text{Sn}(\text{Et}_2\text{NCSS})$	8.73	6.13
$\text{Et}_2\text{Sn}(\text{Et}_2\text{NCSS})_2$	8.70 ^c	6.15 ^c
EtSSCNET_2^d	8.72, 8.78	6.19 ^e , 6.78 ^f

^a CDCl_3 solution. ^b *J* was always 7–8 cps. ^c N-bonded ethyl group. ^d Neat; the same pattern was observed in CDCl_3 and CCl_4 solution. ^e Relative area 2; 41 cps broad. ^f Relative area 1; sharp peak.

chelated ring could be used. Only one type of such signals was observed, but we did not feel entitled to assign a *trans* configuration^{26,27} to $\text{Ph}_2\text{Sn}(\text{SSCNEt}_2)_2$ or $\text{Et}_2\text{Sn}(\text{SSCNEt}_2)_2$ on this ground. Indeed, there is a reasonable doubt that the local symmetry of the NR_2 moiety and not the total symmetry of the molecule has to be considered since the observed protons are rather far away from the tin atom. Besides, an equilibrium between *cis* and *trans* form²⁸, due to labile chelation²⁹, might be present so that only an average signal is seen.

A labile chelation, through the sulphur atoms, seems to be confirmed by electronic spectra.

All the tin compounds show three absorption bands (Table 6), two of them can be assigned to the $\pi \rightarrow \pi^*$ transitions of the dithiocarbamate moiety³¹ (ca. 260 and 280 $m\mu$). The third band is weak (ca. 330–340 $m\mu$), it can be assigned to the $n \rightarrow \pi^*$ transition³¹.

This transition shifts of ca. 15–30 $m\mu$ from the tin-containing compounds to

TABLE 6
ELECTRONIC SPECTRA

Compound	λ_{max} ($m\mu$)	$\log \epsilon$	Solvent
$\text{Et}_2\text{Sn}(\text{SSCNEt}_2)_2$	256	4.30	EtOH
	272	4.22	
	328 (sh)	2.40	
	258	4.42	CHCl_3
	278	4.26	
	330 (sh)	2.41	
$\text{Et}_3\text{Sn}(\text{SSCNEt}_2)$	255	4.10	EtOH
	282	3.98	
	340	1.90	
$\text{Ph}_2\text{Sn}(\text{SSCNEt}_2)_2$	254	4.25	CHCl_3
	280 (sh)	3.91	
	308 (sh)	2.71	
$\text{Ph}_3\text{Sn}(\text{SSCNEt}_2)$	255	4.25	CHCl_3
	295	3.71	
	335 (sh)	2.25	
$\text{Et}_2\text{NCS}_2\text{Na}$	260	4.16	CH_3CN
	287	4.10	
	355	1.78	
$\text{Ph}_2\text{NCS}_2\text{Na}$	267	4.90	CH_3CN
	298	4.90	
	420	2.45	
$\text{Zn}(\text{SSCNEt}_2)_2$	263	4.57	CHCl_3
	281	4.35	
	312	3.05	
$\text{Me}_2\text{NCS}_2\text{Na}$	253	4.13	H_2O
	279	4.14	
	344	1.74	
Me_2NCSSMe	248	3.95	EtOH
	275	4.06	
	330	1.08	

the corresponding sodium salt. This is in agreement with the change of the charge on the sulphur atom which must be bonded to the tin atom. Besides, the spectra in acetonitrile of some compounds, *e.g.* $\text{Ph}_2\text{Sn}(\text{SSCNet}_2)_2$, $\text{Et}_2\text{Sn}(\text{SSCNet}_2)_2$, do not obey the Lambert–Beer law. The formation of a variable percentage of an adduct with acetonitrile may be responsible for the observed deviation from the Lambert–Beer law. The formation of this adduct with CH_3CN requires a labile chelation of the dithiocarbamate moiety in the $\text{R}_2\text{Sn}(\text{SSNet}_2)_2$ compounds, unless a seven-coordinated tin is assumed.

DISCUSSION

Very little is known up to now on the question of which physical measurements may serve as criteria for structure and chelation in dithiocarbamates and related compounds. With the present work we suggest an infrared method: the absence of the free C=S stretching is evidence for a bidentate and chelating dithiocarbamate group.

We believe that this criterion is more reliable than that based⁸ on the shift brought upon by coordination of the IR “thioureide” band of the dithiocarbamate group. Other physical data such as dipole moments in solution, NMR and electronic spectra seem not to provide conclusive evidence on the question of the chelation of the dithiocarbamate moiety.

However, these physical data can give a general picture of these compounds and they will assume a wider significance if some structural analyses by X-ray diffraction could support in the crystalline state the conclusions reached by these methods. We believe that dipole moment measurements in solution which have been used from 1940 in the field of the dithiocarbamates¹⁰, could be very helpful if supported by some X-ray diffraction result.

In this work we have found that, on the base of the IR evidence, the compounds of general formula $\text{X}_2\text{Sn}(\text{SSCNR}_2)$ ($\text{X} = \text{halogen}$) seem to have in the solid state a *cis* octahedral coordination. Similarly, *cis*-configuration was found³⁰ for $\text{Cl}_2\text{Sn}(\text{acetylacetonato})_2$, while *trans*-configuration was assigned to other complexes of the type R_2SnL_2 ($\text{R} = \text{Me, Ph}$; $\text{L} = \text{various bidentate ligands, including acetylacetonato}$)³⁰.

We believe that the compounds of formula $\text{R}_2\text{Sn}(\text{SSCNR}'_2)_2$ are also hexacoordinated, but in this case the direct IR evidence is lacking owing to the presence of other infrared absorption bands in the region $1000 \pm 70 \text{ cm}^{-1}$. However, dipole moments in solution support quite well a *cis*-octahedral coordination of the tin atom in these compounds. On the contrary, no evidence at all could be obtained for the chelation in compounds of formula $\text{R}_3\text{Sn}(\text{SSCNR}'_2)$.

Since the acceptor properties of the tin atom were found³² to decrease on replacing the halogen atoms by less electronegative organic groups, the chelated structures, must be more stable in $\text{X}_2\text{Sn}(\text{SSCNR}_2)_2$ compounds than in $\text{R}_2\text{Sn}(\text{SSCNR}'_2)_2$ compounds. This is also proved both by the electronic spectra, which show that the chelation in $\text{R}_2\text{Sn}(\text{SSCNR}'_2)_2$ is labile in solution.

Owing to the great tendency of R_3SnX compounds to give pentacoordination³³ a similar labile chelation could be present in $\text{R}_3\text{Sn}(\text{SSCNR}'_2)$ derivatives, but we have no evidence at all for this; only a X-ray investigation or Mössbauer spectra could demonstrate the structure of these species.

EXPERIMENTAL

Melting points were determined on a Leitz Heitzschmikroskop and were not corrected. Infrared spectra in the NaCl region were recorded on Perkin-Elmer instruments mod. 137 and 237; the other IR spectra on 21 (KBr optics) or 621 (grating) instrument. Dielectric constants were measured on a WTW dipolmeter DMOI. Electronic spectra were recorded on Beckmann DK2 instrument; ^1H NMR spectra on Perkin-Elmer R-10 instrument operating at 60 Mc, using tetramethylsilane as internal standard. Molecular weight determinations were carried out on a Mechrolab Osmometer.

Organotin(IV) compounds³⁴, sodium N,N-dithiocarbamates³⁵, and substituted thioureas were prepared according to literature methods.

$\text{Zn}(\text{SSCNET}_2)_2$ was a commercial sample, crystallized from benzene and toluene/alcohol, m.p. 177° ; EtSSCNET_2 was prepared according to ref. 10, and twice distilled (b.p. $148^\circ/25$ mm). The organotin(IV) compounds obtained are either white or pale yellow, stable to air and to heat; they are all monomeric in benzene or chloroform solution and nonconducting in nitrobenzene; sometimes they can be sublimed or distilled under reduced pressure. The compounds with alkyl or aryl groups bonded directly to tin are soluble in common organic solvents, less soluble in aliphatic hydrocarbons, practically insoluble in water; the compounds containing halogen-tin bonds are rather insoluble in common organic solvents.

The compounds obtained are described in Table 1, where analytical data are also given; physico-chemical data are given in the tables.

Organo- or halogeno-tin(IV) N,N-dialkyldithiocarbamates

They were prepared according to one or more of the procedures described here.

(A). A solution of triethyltin chloride (7.0 ml) in benzene (50 ml) was refluxed until no chloride ion was detectable in the solution (approx. 10 h) in the presence of $\text{NaSSCNET}_2 \cdot 3\text{H}_2\text{O}$ (10.1 g). The filtered solution was evaporated to dryness under vacuum and the residue purified by distillation (twice) at $165^\circ/2$ mm: a 60% yield of triethyltin N,N-diethyldithiocarbamate was obtained.

(B). A solution of triethyltin chloride (1.05 g) in acetone (5 ml) was added to a saturated solution of $\text{NaSSCNET}_2 \cdot 3\text{H}_2\text{O}$ (0.32 g) in the same solvent. The filtered solution was evaporated to dryness, the residue was extracted with benzene (3×10 ml). The solution was again evaporated to dryness under reduced pressure, yielding triethyltin N,N-diethyldithiocarbamate (1.4 g or 91%), which was then purified as above.

(C). Excess carbon disulphide and excess diethylamine were added to an alcoholic solution of triethyltin hydroxide. The solution was evaporated to dryness; the residue was washed with water and then extracted with ether. After drying over CaCl_2 , the solvent was evaporated and the product isolated as above.

(D). A solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (13.7 g) and of $\text{NaSSCNET}_2 \cdot 3\text{H}_2\text{O}$ (15.9 g) in water (100 ml in all) was heated on a water bath for ca. 0.5 h. The filtered precipitate was air-dried and extracted with methylene chloride (9×20 ml); the extract was concentrated under reduced pressure to yield a pale yellow solid (3.8 g), which was crystallized from acetone (120 ml): sparingly soluble in acetone, methylene chloride, chloroform, acetonitrile, tetrachloroethylene; insoluble in benzene, ethanol and dioxane; not conducting in nitrobenzene solution even after addition of pyridine

(1 : 2 molar). The residue left after extraction with CH_2Cl_2 showed no infrared band due to organic function beside OH and did not take fire.

(E). An acetone solution of $\text{Cl}_2\text{Sn}(\text{SSCNET}_2)_2$ (0.5 g) was shaken with the same weight of NaI for 1 h; the filtered solution was evaporated to dryness and then crystallized from acetone, yielding the corresponding iodide (0.16 g).

Attempts to prepare organotin(IV) N-monosubstituted-dithiocarbamate

(A). From organotin halide and sodium N-alkyldithiocarbamate. A solution of triphenyltin chloride (3.4 g) in benzene (60 ml) was refluxed in the presence of $\text{NaSSCNHEt} \cdot 3\text{H}_2\text{O}$ (2.5 g) for 23 h. The filtered solution was concentrated to a small volume and a white solid (3.1 g) was precipitated on adding light petroleum. This solid, m.p. $133\text{--}140^\circ$, was crystallized twice from ethanol, yielding snow-like crystals, m.p. $145\text{--}146^\circ$; lit.²⁰ for bis(triphenyltin)sulphide $145\text{--}146^\circ$ (Found: C, 59.32; H, 4.29. $\text{C}_{36}\text{H}_{30}\text{SSn}_2$ calcd.: C, 59.1; H, 4.1%); its infrared spectrum was the same as that reported in the literature¹⁹. The mother liquors were collected and evaporated to dryness; the residue was crystallized twice from benzene/light petroleum to yield a white, crystalline, tin-free compound, m.p. 73° , identified as N,N-diethylthiourea from the underpressed melting point with an authentic sample, m.p. 76° . From similar reactions with triethyltin chloride and sodium dithiocarbamate, sodium N-cyclohexyldithiocarbamate and sodium N-ethylthiocarbamate low yields of N,N'-diphenylthiourea were isolated and identified by means of C,H,N analyses, m.p. and IR spectrum.

(B). From organotin hydroxide, amine and carbon disulphide. Aniline (0.446 ml) and CS_2 (0.31 ml) were added to a solution of triethyltin hydroxide (1.038 g) in nitrogen-saturated water (50 ml). After shaking overnight, an oily, white precipitate was formed; after drying on a porous tile, it had m.p. 157° ; it was identified as N,N'-diphenylthiourea by mixed m.p. From a similar reaction where cyclohexylamine was employed instead of aniline, an oil was obtained; this, after treatment with petroleum ether and sublimation ($120^\circ/0.5$ mm) yielded a few white crystals identified as N,N'-dicyclohexylthiourea from the mixed m.p.

Electric dipole moments

Dipole moments (Table 5) were calculated by the Halverstadt-Kumler³⁶ formula:

$${}_{\infty}P_2 = \frac{3V_1\alpha_0}{(\epsilon_1 + 2)^2} + (V_1 + \beta) \frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

The dielectric constant variation $\Delta\epsilon_{12}$ and the specific volume variation ΔV_{12} were found linear functions of the weight fraction w_2 (Table 4) over the concentration range investigated.

ACKNOWLEDGEMENT

We thank the Consiglio Nazionale delle Ricerche for financial support.

SUMMARY

Compounds with general formulas $\text{R}_3\text{Sn}(\text{SSCNR}'_2)$ (R = Et, Ph, R') or $\text{R}_2\text{Sn}(\text{SSCNR}'_2)_2$ (R = halogen, Et, Ph; R' = Et, Ph) were prepared and their physical

data are reported and discussed. In $X_2Sn(SSCNEt_2)_2$ an octahedral *cis* coordination of the tin atom is shown to be present with a chelated dithiocarbamate moiety. A similar labile type of coordination seems to exist in solution for the corresponding organotin derivatives. In the case $R_3Sn(SSCNR'_2)$, no sure evidence was found for or against the chelation of the dithiocarbamate moiety. A discussion as to what physical measurements actually serve as convincing criteria of structure and chelation in dithiocarbamates is presented.

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