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THE STRUCTURE OF ORGANOTIN MERCAPTOESTERS

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Summary

This paper describes the structural differences existing among various organotin mercaptoesters of the general formula $R_nSn[S(CH_2)_{1-2}COOR']_{4-n}$. Infrared and Mössbauer spectroscopies were the methods of choice to investigate such differences and they have revealed that thioglycolate and 3-mercaptopropionate esters adopt cyclic *cis-* or *trans*-trigonal bipyramidal as well as *trans*-octahedral configurations, according to the composition of the organotin compounds and their mode of preparation. Structural relationship among organotin mercaptides and thioacetates are also discussed.

Introduction

Organotin mercaptides and mercaptoesters of the general formula $R_nSn(SR')_{4-n}$ are generally obtained by the reaction of the corresponding organotin halides or oxides with mercaptans [1 - 3] or mercaptoesters [4 - 6]. Due to their extensive industrial application as polymer additives, a large number of such compounds have been prepared and described, mainly in the patent literature. However, because of their relative instability at elevated temperature, the physical properties of organotin mercaptoesters have not been well described and no mention is made in the literature of the possible structural differences existing among mono-, di-, and trihydrocarbyltin mercaptoester derivatives. Nor have possible structural changes resulting from different preparative methods ever been considered. Because these compounds are, in general, liquids at room temperature the present investigation was undertaken to explore the possibility of differentiating the various structural features of organotin mercaptides and mercaptoesters by means of indirect experimental methods, such as infrared spectroscopy and resonance absorption of low energy γ radiation (Mössbauer effect) [7].

Experimental

Infrared spectra of the liquid samples were taken on thin neat liquid films using cesium iodide plates at ambient temperature on a Perkin—Elmer model 225 spectrometer. Full spectra were recorded at scan speeds of ≈ 30 to 100 $cm^{-1} \cdot min^{-1}$ while the C—O stretching region (1900 to 1500 cm^{-1}) was scanned at 10 to 20 $cm^{-1} \cdot min^{-1}$ using the expanded scale option. Solid compounds were run as ≈ 1% samples in KBr under the same conditions as the liquids. The Mössbauer methodology used in the present study has been described in detail in an earlier communication from this laboratory [8].

Tri-n-butyltin-S-isooctyl-3-mercaptopropionate

A solution of 59.6 g (0.1 mol) of bis(tri-n-butyltin) oxide in 100 ml of n-hexane was added slowly to a refluxing solution of 43.6 g of isooctyl-3-mercaptopropionate in 100 ml of n-hexane. The reaction mixture was kept at reflux until 1.8 ml of water had been collected, then stripped of its solvent on a flash evaporator. The resulting 50 g of colorless liquid represented a quantitative yield of tri-n-butyltin-*S*-isooctyl-3-mercaptopropionate, decomposing when heated above 160° under vacuum. n_D^{25} 1.5482. (Found: C, 54.86; H, 9.39; O, 6.19; S, 6.30; Sn, 23.75; $(C_4H_9)_3SnSCH_2COOC_8H_{17}$ calcd.: C, 54.33; H, 9.71; O, 6.29; S, 6.26; Sn, 23.35%). Infrared, cm^{-1}: 2957 (vs), 2920 (vs), 2860 (s), 1730 (vs), 1460 (s), 1415 (w), 1375 (m), 1273 (vs), 1120 (s), 1070 (w), 870 (m), 690 (m), 595 (m), 325 (s).

cis-Di-n-butyltin-S,S'-bis(methylthioglycolate)

A solution of 16.8 g (0.2 mol) of sodium bicarbonate in 100 ml of water was added dropwise to a refluxing solution of 30.4 g (0.1 mol) of di-n-butyltin dichloride and 21.2 g (0.2 mol) of methylthioglycolate in 250 ml of n-hexane. The foaming was controlled by the rate of addition of the aqueous sodium bicarbonate and, upon subsiding of the carbon dioxide evolution, refluxing was continued for one additional hour. The organic phase of the reaction mixture was decanted, filtered over anhydrous magnesium sulfate and the solvent was distilled on a flash evaporator. The resulting 44 g of colorless liquid represented a quantitative yield of *cis*-di-n-butyltin-*S,S'*-bis(methylthioglycolate). This compound could not be distilled as it tends to darken rapidly on heating above 150°. n_D^{25} 1.5374. (Found: C, 38.02; H, 6.30; O, 14.98; S, 14.51; Sn, 26.23. $(C_4H_9)Sn(SCH_2COOCH_3)_2$ calcd.: C, 37.94; H, 6.36; O, 14.44; S, 14.47; Sn, 26.78%). Infrared, cm^{-1}: 2960 (vs), 2920 (vs), 2870 (s), 2860 (s), 1738 (vs), 1710 (s, sh), 1460 (s, sh), 1433 (vs), 1375 (w), 1300 (vs), 1200 (vs), 1180 (s), 1150 (vs), 1125 (s), 1075 (m), 1000 (s), 960 (w), 875 (s), 770 (w), 700 (s), 675 (m), 590 (m), 500 (w), 400 (s), 300 (vs).

trans-Di-n-butyltin-S,S'-bis(benzylthioglycolate)

A mixture of 30.4 g (0.1 mol) of di-n-butyltin dichloride and 33.6 g (0.2 mol) of benzylthioglycolate was kept under agitation and a nitrogen blanket at 90° for 24 h or until complete exhaustion of the HCl evolution. Pale yellow liquid (55 g) *trans*-di-n-butyltin-*S,S'*-bis(benzylthioglycolate) was recovered. The compound was chlorine free and decomposed when heated to ≈ 170°

under vacuum (2 mmHg). Any residual free thioester was eliminated by emulsification in a water wash, followed by filtration over anhydrous magnesium sulfate. n_D^{25} 1.5433. (Found: C, 51.00; H, 5.62; O, 11.39; S, 11.21; Sn, 20.98. $(C_4H_9)_2Sn(SCH_2COOC_6H_5)_2$ calcd.: C, 50.81; H, 5.68; O, 11.28; S, 11.30; Sn, 21.09%). Infrared, cm^{-1}: 3050 (m), 3030 (m), 2959 (vs), 2921 (vs), 2870 (s), 2855 (s), 1738 (vs), 1675 (vs), 1485 (s), 1460 (vs), 1425 (s), 1375 (s), 1290 (vs), 1270 (vs), 1186 (vs), 1147 (vs), 1076 (m), 998 (s), 960 (s), 900 (w), 872 (m), 820 (w), 740 (vs), 693 (vs), 596 (m), 490 (m), 325 (s).

cis-Diphenyltin-S,S'-bis(isooctylthioglycolate)

A reaction mixture consisting of 36.8 g (0.1 mol) of diphenyltin dichloride, 40.6 g (0.2 mol) of isooctylthioglycolate and 20.2 g (0.2 mol) of triethylamine, in 350 ml of n-hexane, was kept at reflux under agitation for three hours. A quantitative amount of triethylamine hydrochloride was separated by filtration and the solvent was distilled on a flash evaporator. Pale yellow *cis*-diphenyltin-*S*,*S'*-bis(isooctylthioglycolate) was obtained (69 g). This compound is sensitive to hydrolysis and decomposes upon attempt to distill it under vacuum. n_D^{25} 1.5448. (Found: C, 57.01; H, 7.09; O, 9.32; S, 9.69; Sn, 17.10. $(C_6H_5)_2Sn(SCH_2COOC_8H_{17})_2$ calcd.: C, 56.56; H, 7.12; O. 9.42; S, 9.44; Sn, 17.47%). Infrared, cm^{-1}: 3045 (m), 2980 (vs), 2885 (vs), 1735 (vs), 1705 (s, sh), 1460 (s), 1430 (vs), 1380 (m), 1292 (vs), 1185 (vs), 1148 (vs), 1125 (s, sh), 1070 (s), 1020 (m), 995 (s), 883 (w), 725 (vs), 691 (vs), 570 (w), 438 (s), 350 (s).

trans-Methyltin-S,S',S''-tris(isooctylthioglycolate)

A solution of 24 g (0.1 mol) of methyltin trichloride and 61.2 g (0.3 mol) of isooctylthioglycolate was kept under agitation and a nitrogen blanket at 90° for 24 h or until complete exhaustion of HCl evolution. Colorless *trans*-methyltin-*S*,*S'*,*S''*-tris(isooctylthioglycolate) was obtained (74 g). The compound was chlorine free and decomposed upon attempt to distill it under vacuum. n_D^{25} 1.5108. (Found: C, 49.98; H, 8.22; O, 13.00; S, 12.86; Sn, 15.60. $CH_3Sn(SCH_2COOC_8H_{17})_3$ calcd.: C, 50.06; H, 8.13; O, 12.91; S, 12.93; Sn, 15.96%). Infrared, cm^{-1}: 2945 (vs), 2920 (s, sh), 2865 (s), 1733 (vs), 1458 (s), 1400 (m), 1373 (m), 1360 (w), 1318 (s), 1287 (vs), 1192 (vs), 1143 (vs), 973 (m), 882 (w), 772 (m), 570 (w), 315 (s).

Methyltin-S,S'-bis(isooctylthioglycolate) chloride

A mixture of 24.1 g (0.1 mol) of methyltin trichloride and 40.6 g (0.2 mol) of isooctylthioglycolate in solution in 150 ml of n-heptane was kept at reflux under anhydrous conditions until all evolution of HCl had subsided. Evaporation of the solvent afforded 57 g, or a quantitative yield, of methyltin-*S*,*S'*-bis(isooctylthioglycolate) chloride, a colorless liquid boiling with decomposition at 175°. n_D^{25} 1.4978. (Found: C, 43.43; H, 7.25; O, 11.00; S, 11.23; Cl, 6.36; Sn, 20.92; mol. weight (by osmometry), 583. $CH_3Sn(SCH_2COOC_8H_{17})_2Cl$ calcd.: C, 43.80; H, 7.18; O, 11.11; S, 11.14; Cl, 6.16; Sn, 20.61%; mol. weight, 576). Infrared, cm^{-1}: 2950 (vs), 2900 (s), 2852 (m), 1732 (vs), 1660 (vs), 1465 (m), 1400 (m), 1345 (s), 1200 (vs), 880 (w), 780 (w), 733 (w), 685 (w), 540 (w), 456 (w), 400 (m), 323 (s).

Results and discussion

Two distinct methods of preparation were used in this work to obtain the organotin mercaptides whose spectral properties are summarized in Tables 1 - 3. One method involves the condensation of the organotin halide and the thiocompound in the presence of an HCl acceptor such as aqueous sodium bicarbonate or triethylamine, the other consists in letting HCl evolve freely in an anhydrous, inert atmosphere. It should be noted that the reaction carried out under anhydrous conditions is always considerably slower than the one carried out in the presence of water, indicating in the latter cases a rapid hydrolysis of the organotin halide into the corresponding oxide which then, apparently, reacts much more easily with a thiol function than anhydrous organotin halide. This is undoubtedly the case where trialkyltin mercaptides are prepared quite rapidly from bis(trialkyltin) oxides and mercaptans.

The isomer shifts observed (+1.37 to +1.64 mm/sec with respect to $BaSnO_3$) indicate that all of the compounds here reported can be considered as derivatives of Sn^{IV} and that no reduced species are present.

The trihydrocarbyltin derivatives

The narrow range of δ and ΔE_Q values for tri-n-butyltin methylthioglycolate, sodium thioglycolate, and dodecyl mercaptide respectively [cpds. (I) to (IV)], suggests that these compounds are all isostructural, with Mössbauer parameters similar to those of the trialkyltin mercaptides which have been reported [9]. The carbonyl stretching region in the IR spectra of the Sn^{IV} mercaptoesters shows a single peak at 1738 cm^{-1}, unshifted from the absorption observed for the free ligands. Concurrently, the sodium carboxylate absorption at 1600 cm^{-1} remains unchanged upon formation of the organotin mercaptide. Thus, no bonding interaction other than that between the tin and sulfur atoms appears to affect the tin atom, for trialkyltin mercaptides and mercaptoesters do not seem to differ in structure, regardless of the size and composition of the ligand beyond the sulfur atom or the mode of preparation of the compounds.

The dihydrocarbyltin derivatives

In contrast to the trialkyl substituted tin compounds discussed above, the dialkyltin homologs present striking structural differences depending upon the nature and size of the ligands as well as the synthetic methods employed to prepare the organotin compounds.

The isomer shift and quadrupole splitting values of the dialkyltinbis(dodecylmercaptide) confirm its tetrahedral structure but the situation changes significantly when thioglycolic or mercaptopropionic esters are used as ligands.

The infrared spectrum of di-n-butyltin bis(isooctylthioglycolate) prepared in presence of aqueous sodium bicarbonate shows (Fig. 1) a considerable broadening and splitting of the carbonyl stretching absorption, one band remaining at 1738 cm^{-1}, the other moved to 1708 cm^{-1}, a shift of 30 cm^{-1}. Although the a priori expectation is that increasing the number of methylene groups between the sulfur atom and the carboxylate function of the ligand should have but little effect on the bonding interaction between the metal and the

(continued on p. 432)

TABLE 1

INFRARED AND MÖSSBAUER DATA FOR TRIALKYLTIN(IV) MERCAPTIDES AND MERCAPTOESTERS

Compounds		Prep.[a]	C=O (cm^{-1})		Δ	Sn—S(cm^{-1})	T(K)[b]	δ (mm/sec)[c]	ΔE_Q(mm/sec)[d]
(I)	$(C_4H_9)_3SnSCH_2COOCH_3$	W	1736		2	325	83	1.51	1.80
(II)	$(C_4H_9)_3SnSCH_2COOC_8H_{17}$	W	1735		3	829	80	1.44	1.66
(III)	$(C_4H_9)_3SnSCH_2COONa$	W		1600		337	84	1.45	1.59
(IV)	$(C_4H_9)_3SnSC_{12}H_{25}$	W				335	84	1.50	1.44

[a] W = wet, D = dry preparative method. [b] Temperatures refer to Mössbauer measurements. [c] Isomer shift, ± 0.02 mm/sec with respect to the centre of a room temperature $BaSnO_3$—$BaSnO_3$ spectrum. [d] Quadrupole splitting, ± 0.02 mm/sec. Δ $=\nu_1/\nu_2$ where ν_1 is the shift (in cm^{-1}) of the carbonyl frequency of the ligand bonded only through the sulphur atom, compared to the *free-ligand* carbonyl frequency, and ν_2 is the shift of the carbonyl frequency of the ligand (if any) *also bonding* through the carbonyl oxygen.

TABLE 2

INFRARED AND MÖSSBAUER DATA FOR DIALKYLTIN(IV) MERCAPTIDES AND MERCAPTOESTERS[a]

Compounds		Prep.	C=O (cm^{-1})		Δ	Sn—S(cm^{-1})	T(K)	δ (mm/sec)	ΔE_Q(mm/sec)
(V)	$(C_4H_9)_2Sn(SC_{12}H_{25})_2$	W				340	82	1.44	1.58
(VI)	$(CH_3)_2Sn(SC_{12}H_{25})_2$	W				343	83.5	1.44	1.59
(VII)	$(CH_3)_2Sn(SCH_2C_6H_5)_2$	W				345	82	1.44	1.65
(VIII)	$(CH_3)_2Sn(SCH_2COOC_8H_{17})_2$	W	1738	1705	0/33	330	82	1.37	2.20
(IX)	$(CH_3)_2Sn(SCH_2COOC_8H_{17})_2$	D	1738	1675	0/63	335	83	1.45	3.22
(X)	$(C_4H_9)_2Sn(SCH_2COOCH_3)_2$	W	1738	1710	0/28	330	84	1.52	2.28
(XI)	$(C_4H_9)_2Sn(SCH_2COOCH_3)_2$	D	1738	1685	0/53	335	82	1.57	3.33
(XII)	$(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$	W	1734	1708	4/28	330	82	1.53	2.28
(XIII)	$(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$	D	1738	1680	0/58	340	84	1.53	3.25
(XIV)	$(C_4H_9)_2Sn(SCH_2COOCH_2C_6H_5)_2$	W	1735	1705	3/33	335	83	1.57	2.26
(XV)	$(C_4H_9)_2Sn(SCH_2COOCH_2C_6H_5)_2$	D	1738	1675	0/63	340	82	1.64	3.35
(XVI)	$(C_6H_5)_2Sn(SCH_2COOC_8H_{17})_2$	D(Et_3N)	1735	1700	3/38	350	83	1.37	1.79
(XVII)	$(C_6H_5)_2Sn(SCH_2COOC_8H_{17})_2$	D	1738	1665	0/73	350	84	1.44	2.21
(XVIII)	$(CH_3)_2Sn(SCH_2CH_2COOC_8H_{17})_2$	W	1735		3	345	83	1.43	1.86
(XIX)	$(C_4H_9)_2Sn(SCH_2CH_2COOCH_3)_2$	W	1738		0	342	84	1.47	1.97
(XX)	$(C_4H_9)_2Sn(SCH_2CH_2COOC_8H_{17})_2$	W	1838		0	342	83	1.50	1.89
(XXI)	$(C_4H_9)_2Sn(SCH_2CH_2COOC_8H_{17})_2$	D	1734	1715	4/23	345	83	1.66	3.45
(XXII)	$(C_6H_5)_2Sn(SCH_2CH_2COOC_8H_{17})_2$	W	1737		1	350	83	1.40	1.52
(XXIII)	$(C_4H_9)_2Sn(SCOCH_3)_2$	W		1670		380	83	1.53	2.75

[a] For symbols see Table 1.

TABLE 3

INFRARED AND MÖSSBAUER DATA FOR MONOALKYLTIN(IV) MERCAPTIDES AND MERCAPTOESTERS[a]

Compounds	Prep.	C=O (cm^{-1})		Δ	Sn–S(cm^{-1})	$T(K)$	δ(mm/sec)	ΔE_Q(mm/sec)
(XXIV) $CH_3Sn(SC_{12}H_{25})_3$	W				352	82	1.47	1.16
(XXV) $CH_3Sn(SCH_2COOC_8H_{17})_3$	W	1738	1700	0/38	345	83	1.45	1.74
(XXVI) $CH_3Sn(SCH_2COOC_8H_{17})_3$	D	1730	1663	8/57	350	84	1.33	2.35
(XXVII) $C_4H_9Sn(SCH_2COOCH_3)_3$	W	1738	1670	0/68	343	83	1.40	2.34
(XXVIII) $C_4H_9Sn(SCH_2COOC_8H_{17})_3$	W	1737	1700	1/38	340	82	1.61	1.70
(XXIX) $C_4H_9Sn(SCH_2COOC_8H_{17})_3$	D	1737	1670	1/68	343	82	1.42	2.35
(XXX) $C_4H_9Sn(SCH_2COOCH_2C_6H_5)_3$	W	1738	1695	0/43	343	84	1.56	1.72
(XXXI) $C_4H_9Sn(SCH_2CH_2COOC_8H_{17})_3$	W	1738		0	350	84	1.43	1.45
(XXXII) $CH_3Sn(SCH_2COOC_8H_{17})Cl_2$	D		1650	78	362	83	1.23	2.31
(XXXIII) $CH_3Sn(SCH_2COOC_8H_{17})_2Cl$	D	1738	1650	0/78	323	80	1.28	2.32

[a] For symbols see Table 1.

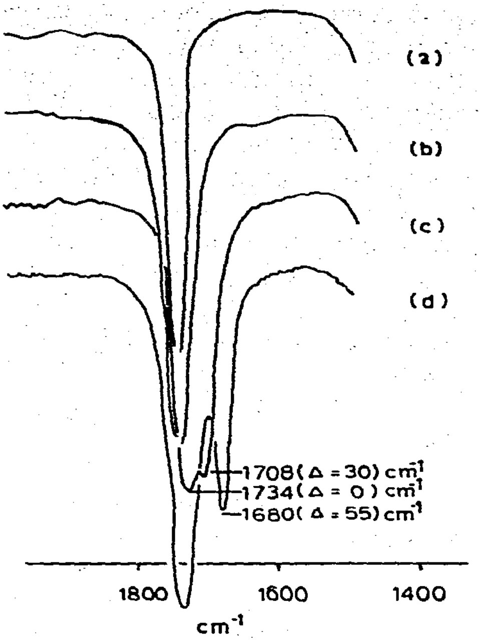

Fig. 1. Infrared spectra of the carbonyl region of dialkyltin mercaptoesters showing as reference the narrow C=O absorption of the free isooctylthioglycolate ligand (a). The carbonyl region of $(C_4H_9)_2Sn(SCH_2CH_2COOC_8H_{17})_2$ reveals a significant band broadening (b), while the *cis*-$(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$, prepared in presence of water, shows a splitting of the carbonyl absorption resulting in two vibrations at 1734 and 1708 cm^{-1} respectively (c). The *trans*-homolog, prepared anhydrously, shows a further shift of the bonded carbonyl to 1680 cm^{-1} (d).

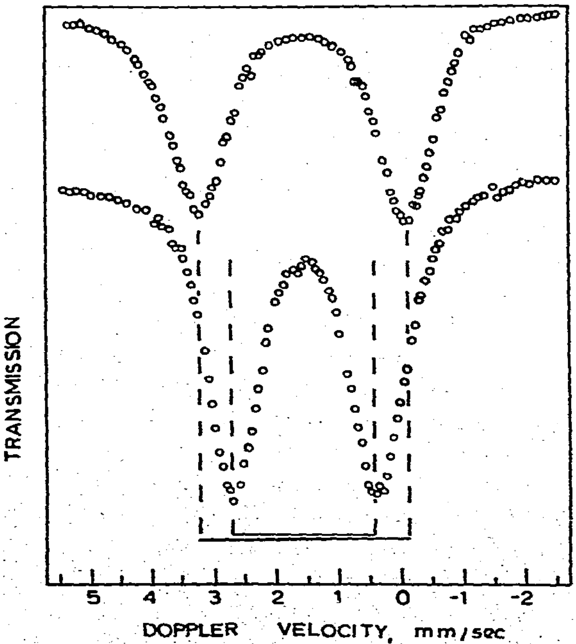

Fig. 2. ^{119}Sn Mössbauer spectra of $(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$ prepared under anhydrous conditions (top curve) and in the presence of water (bottom curve) as discussed in the text. Although the isomer shifts which are observed in the two cases are essentially identical (1.528 and 1.529 mm/sec, respectively) the difference in structure is clearly reflected in the difference in the quadrupole splitting parameter (3.251 and 2.275 mm/sec, respectively). The spectra were obtained at 83 ± 1 K, using a room temperature $BaSnO_3$ source as discussed in the text.

ligand (CH_2 groups acting as blocking groups with respect to charge delocalization through the ligand), just the contrary is observed. The quadrupole splitting (Fig. 2) observed in di-n-butyltin bis(isooctylthioglycolate) (XII) is some 0.39 ± 0.04 mm/sec larger than it is in the mercaptopropionate homolog (XX). This observation is readily understood in the light of the accompanying infrared data which suggest that one of the two ester ligands is unidentate through the sulfur atom only, while the other is bidentate, forming a cyclic entity with the metal atom bonded to both the sulfur atom and the carbonyl oxygen of the ester. For the thioglycolate compound, the resultant heterocyclic ring is five membered, while for the mercaptopropionate this ring is six membered. The difference in the quadrupole splitting parameter which is observed is a direct consequence of the difference in the steric requirements of the two cyclic structures and is directly ascribable to the bond angles imposed on the metal—ligand interaction.

One of two possible structures which are consistent with this interpretation is that in which the two alkyl groups assume *cis*-positions around the five coordinate tin atom, and the lone pair of electrons on the ester carbonyl are involved in the bonding interaction to the metal atom. The other possible structure is one in which the two alkyl groups occupy equatorial positions around the 5-coordinate metal atom. The presently available data are insufficient to distinguish between these two possibilities.

When the same compound is prepared under anhydrous conditions (XIII), its infrared spectrum (Fig. 1) reveals further changes. While one carbonyl stretching vibration still remains unchanged at 1738 cm^{-1}, a second sharp band of about the same intensity as the unshifted one appears at 1680 cm^{-1}, or a shift of 55 cm^{-1}! The quadrupole splitting value (Fig. 2) has now increased to 3.25 mm/sec, pointing to a further increase of the imbalance in the *p*-electron population. The greater infrared shift as well as the increase of the ΔE_Q value lead to the plausible formation of a complex having one unidentate and one bidentate ligand assuming a *trans*-bipyramidal structure.

The structural implications of Mössbauer* and infrared spectroscopic data can only give indirect evidence concerning the stereochemistry of the two alkyl groups relative to each other. Hence a structure for the dialkyltin bis(thioglycolate) ester compounds in which the unidentate ligand occupies a coordination site *trans*- to the sulfur atom of the bidentate ligand cannot be ruled out. However, the large change in the quadrupole splitting parameter in going from the compound obtained by the "wet" synthesis to the product obtained under anhydrous conditions strongly suggest that in the latter, the two alkyl groups occupy a *trans*- or nearly *trans*- position relative to each other.

The data summarized in Table 2 show that all of the dialkyltin bis(thioglycolic esters) prepared in this study adopt the *cis*-configuration when the reaction is carried out in presence of an HCl acceptor and the *trans*-configuration when prepared under anhydrous conditions without an HCl acceptor. This striking result can be accounted for by the following mechanism:

In the presence of water and a base, the dialkyltin dihalide is rapidly hydrolized to the corresponding oxide. On reaction with the ligand, the attack

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*A number of recent reviews of the structural information on organotin compounds which can be extracted from ^{119}Sn Mössbauer data have been published; see for example refs. 7 and 10.

of the entering group occurs at the pentacoordination site adjacent to the oxygen of the organotin oxide by one of the lone electron pairs of the carbonyl group. The SH group reacts by abstraction of the oxide oxygen to form water with the help of the second free thioglycolate, the latter occupying the last available coordination site on the trigonal bipyramid as a unidentate ligand. The *cis*-configuration of the two alkyl groups is readily preserved during the conversion of the dialkyltin oxide to the corresponding mercaptoester.

Under anhydrous conditions, on the other hand, the attack by the carbonyl oxygen of the thioglycolate ester ligand on the dialkyltin dihalide presumably occurs at the pentacoordination site adjacent to the two alkyl group substituents and transforms the distorted tetrahedral structure of the reactant into a *trans*-trigonal bipyramidal configuration. Elimination of HCl between the mercaptide group of the oxygen bonded ligand results in cyclization of this group, while the elimination of a second molecule of HCl leads to the formation of a tin—sulfur bond to the unidentate thioglycolate ester. Since essentially similar observations are made in the case of reactions of dialkyltin dihalides with 3-mercaptopropionate esters, it appears that ligand cyclization can be effected when both five and six member heteroatomic rings involving the metal atom are formed.

Similar ligand displacements are presumed to occur when organotin thioglycolates are prepared in the presence of anhydrous triethylamine as an HCl acceptor. As in the case of reactions carried out in presence of water, diphenyltin bis(isooctylthioglycolate), for example, retains a *cis*-trigonal bipyramidal configuration when Et_3N is used as an anhydrous scavenger. Organotin halides are known to form unstable complexes with various amino compounds [11], and it is thus reasonable to expect that the formation of such an intermediate will be followed by a ligand exchange between triethylamine and the carbonyl oxygen of the thioglycolate, in which the *cis*-configuration of the two phenyl groups is preserved.

In order to examine further the influence of variation of the tin—carbonyl group distance on the structure of organotin mercaptoesters, the spectroscopic properties of di-n-butyltin bis(thioacetate)(XXIII) have been examined in detail. The infrared spectrum of this compound shows no absorption in the 1670 cm^{-1} region which is characteristic of free thioacetic acid, while there is an intense band at 1630 cm^{-1}. The quadrupole splitting observed for this compound is 2.75 mm/sec at 83°K. These results suggest a pseudo octahedral structure in which both thioacetate ligands are acting as bidentate moieties, with the two alkyl groups occupying essentially *trans*-positions with respect to each other.

The magnitude of the ΔE_Q parameter and the 40 cm^{-1} shift observed in the infrared spectrum suggest that there is considerable departure from a regular octahedral configuration. Since the present data are insufficient to differentiate between a *cis*- and *trans*-configuration of the two oxygen (or sulfur) atoms of the ligands, it is not possible to speculate meaningfully on the departure from linearity of the C—Sn—C bond axis. That such non linearity (lack of cylindrical symmetry) may be appreciable, arises from the observation that the quadrupole splitting normally associated with *trans*-octahedral structure in compounds of the type R_2SnL_2 (where L is a bidentate ligand) having axial symmetry ($\eta = 0$) fall in the range of 3.3 to 4.5 mm/sec.

The monohydrocarbyltin derivatives

The structural differences between the mercaptide complexes and the corresponding thioglycolates are appreciable and are reflected in significant changes both in the infrared and Mössbauer spectra of these compounds. The sizeable increase of the ΔE_Q value from 1.16 mm/sec for methyltin tris (dodecyl mercaptide) (XXIV) to 1.7 mm/sec for the tris(thioglycolate) implies, along with the shift and intensity ratio of the infrared absorptions, that the complex is trigonal bipyramidal with one bidentate and two unidentate thioglycolate ligands on the tin atom.

Analogously the infrared spectrum of n-butyltin tris(isooctylthioglycolate) prepared in aqueous medium (XXVIII), Fig. 3 shows a broad, strong absorption at 1738 cm^{-1} accompanied by a shoulder at 1700 cm^{-1}. The quadrupole splitting observed for this compound is 1.70 mm/sec, similar to that noted for (XXV). Here again, one may reasonably suspect that the reaction mechanism is similar to the one described above for the formation of the dialkyltin analog.

The infrared spectrum of the corresponding compound prepared under anhydrous conditions (XXIX) shows two strong absorptions, one at 1738 cm^{-1} characteristic of the non-bonded carbonyl in the thioglycolate ligand, the second, at 1670 cm^{-1}. The quadrupole splitting value has further increased to 2.35 mm/sec while the isomer shift has decreased from 1.61 to 1.42 mm/sec. These observations can be accounted for by postulating a change from pentacoördination in (XXVIII) to hexacoordination in (XXIX) by HCl elimination and ring closure involving one of the thioglycolate ester ligands. The 0.19

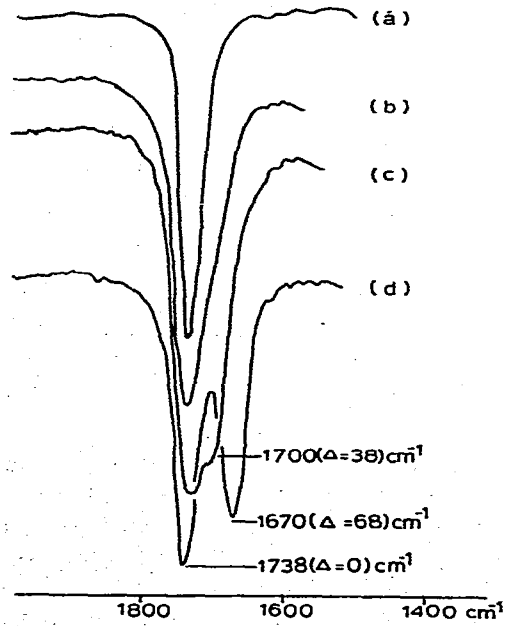

Fig. 3. Infrared spectra of the carbonyl region of monoalkyltin mercaptoesters. The unshifted C=O absorption of free isooctylthioglycolate (a) is compared with the broadened absorption of $(C_4H_9)Sn(SCH_2CH_2COOC_8H_{17})_3$ (b) and the splitting of the *cis*- (c) and *trans*-$(C_4H_9)Sn(SCH_2COOC_8H_{17})_3$ (d), respectively, revealing the different character of the thioglycolate ligands on the tin atom.

mm/sec decrease in the isomer shift can be ascribed to the increase in shielding of the *s*-electron charge density at the metal atom nucleus due to an increase in the *d*-electron population in going from sp^3d to sp^3d^2 hybridization.

The formation of the octahedral complex containing one unidentate and two bidentate thioglycolate ester ligands can be envisioned as occurring by the sequential elimination of two molecules of HCl following the coordination of the first two ester ligands, after which the third ligand occupies the remaining octahedral coordination site through sulfur atom bonding. Depending upon which five coordination site of the tetrahedral alkyltin trihalide is originally attacked by the first thioglycolate, the relative position of the alkyl substituent and the unidentate thioglycolate ligand in the product may be either *cis* or *trans* to each other. Although the present data available does not furnish conclusive evidence for either configuration, the facts that, (*a*) the carbonyl attack in dialkyltin analogs occur at the five coordination site adjacent to the alkyl groups and, (*b*) that the line widths of the two carbonyl stretching absorptions of the monobutyltin derivatives are equivalent, inclines us to prefer the *trans*-configuration. It should also be noted that monoalkyltin derivatives of methylthioglycolate (XXVII) form directly the *trans*-octahedral complexes even when prepared in presence of water and that this structure is no longer affected by the method of preparation. It is suspected that the short methyl groups either increase the basicity of the carbonyl oxygen attacking the monohydrocarbyltin trihalides or reduce the steric hindrance of the five membered ring complex as to render the *d* orbitals of the tin atom more readily available for bonding.

Finally, we have observed that one or two of the three chlorine atoms of alkyltin trichlorides may be displaced selectively by mercaptoesters to form the corresponding monomeric organotin mercaptoester dihalides and dimercaptoester monohalides. While the infrared spectrum of the methyltin bis(thioglycolate) chloride (XXXIII) reveals the two carbonyl stretching vibrations at 1735 cm^{-1} and 1660 cm^{-1}, characteristic of the unidentate thioglycolate ligand and the bonded carbonyl oxygen of the bidentate thioglycolate ligand, respectively, the spectrum of the methyltin thioglycolate dichloride (XXXII) shows only one strong absorption at 1650 cm^{-1} supporting a structure in which the ligand is both sulfur and oxygen bonded to the metal, the other three coordination sites being filled by two halogens and an alkyl ligand.

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