Journal of Organometallic Chemistry, 56 (1973) 175–183

THE STRUCTURE OF ORGANOTIN MERCAPTOCARBOXYLATES

C. H. STAPFER
Cincinnati Milacron Chemicals, Inc., New Brunswick, N.J. 08903 (*U.S.A.*) (*U.S.A.*)
and R. H. HERBER
School of Chemistry, Rutgers University, New Brunswick, N.J. 08903 (*U.S.A.*)

(Received October 30th, 1972)

SUMMARY

The preparation of a number of new organotin(IV) mercaptocarboxylates is reported. The structures of these compounds, a number of which are liquids at room temperature, has been elucidated by means of infrared and ^{119}Sn Mössbauer spectroscopy and by appropriate molecular weight determination, ω-mercaptocarboxylic acids form 2/1 adducts with monoalkyltin(IV) oxides in which one of the ligands retains a free SH group. With dialkyltin(IV) oxides the resultant 1/1 adducts are linear polymers. With bis(trialkyltin(IV)) oxides, two different organotin(IV) mercaptocarboxylates are formed: a binuclear monomer in which one metal atom is chelated by both oxygen atoms of the carboxyl group while the other trialkyltin moiety is bonded through the sulfur atom of the thiol group, and a polymeric compound containing both bridging carboxylate ligands and free mercaptan groups.

INTRODUCTION

Mercaptocarboxylic acids such as thioglycolic and β-mercaptopropionic acids are known to react with dialkyltin oxides and halides to form the corresponding dialkyltin mercaptocarboxylates[1]. Although these compounds have long been recognized for their practical usefulness as polymer additives[2], only recently has an attempt been made to investigate their structures[3]. Structural features of mono- and trihydrocarbyltin mercaptocarboxylates, on the other hand, have never been reported in the literature. It is the purpose of the present investigation to clarify the structural differences existing between mono- di-, and trihydrocarbyltin mercaptocarboxylates prepared from the condensation of the corresponding organotin oxides and ω-mercaptocarboxylic acids. Infrared spectroscopy and resonance absorption of low energy γ radiation (Mössbauer effect)* were the experimental methods of choice to establish structural relationship among these compounds and to correlate the observed spectroscopic properties with other chemical and physical parameters.

---

* For a general review of this field, see ref. 4.

EXPERIMENTAL

Molecular weights of all products examined were determined by osmometry in methyl ethyl ketone solution.

Infrared spectra of solid compounds were obtained on ~1% weight samples in KBr, using a Perkin–Elmer Model 225 grating spectrometer. Liquid samples were examined as thin films on CsI plates in the range 4000–200 cm^{-1}. Full spectra were recorded at scan speeds of ~30 to 100 cm^{-1} · min^{-1} while the C=O stretching region (1900 to 1500 cm^{-1}) was scanned at 10 to 20 cm^{-1} · min^{-1} using the expanded scale option.

The Mössbauer spectrometer used in this work was of the constant acceleration type described earlier[5], using a barium stannate ^{119}Sn source at room temperature. Spectrometer calibration was effected using 0.8 mil NBS standard reference material natural iron foil (SRM-1541) and the usual magnetic hyperfine spectrum fitting procedure[6]. All isomer shifts reported in the present paper are with respect to the center of a room temperature $BaSnO_3$ absorber spectrum run with the same source, and are identical within the quoted experimental error to spectra based on a stannic oxide standard. The solid samples were mounted as thin layers of microcrystalline powder between 1 mil aluminum foil in a copper sample holder attached to the copper cold finger of a standard transmission geometry liquid nitrogen Dewar flask. Sample temperatures were monitored using a calibrated thermocouple and remained constant (±1 K) during the time necessary to accumulate the spectra. At least 10^6 counts were scaled at each velocity point. Since the resonance effect magnitude in these samples is typically ~5% at liquid nitrogen temperature, the signal to (statistical) noise ratio is >50. Data reduction was effected either manually using the statistical procedure described earlier[7] or by means of a least squares fitting procedure using the Rutgers CCIS IBM 360/67 Computer. The program used in these calculations fits n Lorentzians in which line position, line width and effect magnitudes are unrestrained variables. Replicate spectra gave values of the Mössbauer parameters which agreed with each other to better than ±0.02 mm · s^{-1}.

Poly(n-butyltin dithioglycolate)

A suspension of 19.3 g (0.1 mol) of n-butylstannoic acid in 250 ml of toluene was kept under agitation at reflux while 18.4 g (0.2 mol) of freshly distilled thioglycolic acid was added dropwise. Upon recovery of 3.6 ml of condensation water, the precipitated reaction product was filtered, washed with acetone and dried. The resulting 35 g of a fine, white and insoluble amorphous solid represented a quantitative yield of poly(n-butyltindithioglycolate) melting with decomposition at 270°. Found: C, 26.88; H, 4.01; O, 17.65; S, 18.11; Sn, 33.18. $[C_8H_{14}O_4S_2Sn]_n$ calcd.: C, 26.91; H, 3.95; O, 17.93; S, 17.97; Sn, 33.25%. Infrared (cm^{-1}): 2960 vs, 2910 s, 2860 m, 1600 vs, 1455 m, 1387 s, 1355 vs, 1290 w, 1248 w, 1222 m, 1173 s, 1140 m, 980 m, 890 vs, 777 vs, 700 s, 675 s, 570 m, 510 m, 387 vs, 300 s.

Di-n-butyltin γ-mercaptobutyrate

A solution of 12.1 g (0.1 mol) of γ-mercapto butyric acid in 50 ml of n-hexane was added dropwise to a refluxing suspension of 24.9 g (0.1 mol) of di-n-butyltin oxide in 100 ml of n-hexane. After one hour at reflux, 1.8 ml of water had been eliminated and the solvent was distilled off on a flash evaporator. The resulting clear syrupy liquid crystallized into 35 g of white needles melting at 98° and representing a quantitative yield of di-n-butyltin γ-mercaptobutyrate. Found: C, 40.92; H, 7.01; O, 9.27; S, 9.02; Sn, 34.01; Mol. weight: 1400. $C_{12}H_{24}O_2SSn$ calcd.: C, 41.05; H, 6.89; O, 9.11; S, 9.13; Sn, 33.81%; Mol. weight: 351. Infrared (cm^{-1}): 2900 vs, 2840 vs, 1545 vs, 1430 vs, 1370 s, 1327 s, 1210 m, 1263 vs, 1175 w, 1148 m, 1072 m, 1012 m, 873 m, 864 m, 793 w, 673 s, 635 s, 350 w.

Bis(tri-n-butyltin) thioglycolate

A solution of 9.3 g (0.1 mol) of thioglycolic acid in 50 ml of toluene was added to a refluxing solution of 59.6 g (0.1 mol) of bis(tri-n-butyltin) oxide in 100 ml of toluene. The reaction mixture was kept at reflux for one hour or until 1.8 ml of water was recovered. The toluene was removed by flash evaporation and the 67 g of residual colorless liquid represented a quantitative yield of bis(tri-n-butyltin) thioglycolate, decomposing rapidly when heated above 150° under vacuum. n_D^{20} 1.5097. Found: C, 46.60; H, 8.40; O, 4.73; S, 4.59; Sn, 34.88; Mol. weight: 654. $C_{26}H_{56}O_2SSn_2$ calcd.: C, 46.80; H, 8.46; O, 4.75; S, 4.80; Sn, 35.13%; Mol. weight: 670. Infrared (cm^{-1}): 2950 vs, 2860 vs, 1644 vs, 1460 vs, 1417 s, 1375 s, 1335 vs, 1200 vs, 1160 m, 1072 vs, 1020 m, 960 m, 878 s, 690 vs, 670 vs, 598 s, 509 m, 385 w, 335 s.

Poly(tri-n-propyltin) thioglycolate

A mixture of 51.2 g (0.1 mol) of bis(n-propyltin) oxide and 18.6 g (0.2 mol) of thioglycolic acid was kept under agitation at 115° for two hours. During the reaction, the mixture was thoroughly sparged with nitrogen in order to eliminate any residual condensation water. Upon collection of 1.8 ml of water in a trap, the residual 34 g of clear liquid slowly solidified when cooled and represented a quantitative yield of poly(tri-n-propyltin thioglycolate), melting at 105–110°. Found: C, 38.35; H, 6.71; O, 9.25; S, 11.29; Sn, 35.70; Mol. weight 1348. $C_{11}H_{24}O_2SSn$ calcd.: C, 38.97; H, 7.13; O, 9.43; S, 9.45; Sn, 35.01%; Mol. weight: 339. Infrared (cm^{-1}): 2935 vs, 2655 vs, 1550 vs, 1455 s, 1450 vs, 1390 vs, 1215 vs, 1154 m, 1062 s, 1020 w, 990 s, 935 m, 890 m.

DISCUSSION OF RESULTS

The Mössbauer parameters for the organotin mercaptocarboxylates which have been extracted from the spectroscopic data, have been summarized in Table 1, together with related data for a number of model compounds which have been examined under essentially identical conditions.

Monoalkyltin mercaptocarboxylates. The reaction between n-butylstannoic acid and thioglycolic acid (TGA) proceeds rapidly to yield a product having a metal to mercapto acid ligand ratio of 1/2, and can be represented by the following reaction

$$\text{n-}C_4H_9Sn(O)OH + 2\,HSCH_2COOH \rightarrow [(\text{n-}C_4N_9)Sn(O_2CCH_2SH)(O_2CCH_2S)]_n + H_2O$$

The Mössbauer parameters of this product (I) indicate the presence of a single tin site (line width $\sim 1.2\ mm \cdot s^{-1}$ uncorrected), but are insufficient by themselves to indicate conclusively the coordination of the metal atom. The infrared spectrum shows a single absorption band at $\sim 1600\ cm^{-1}$, indicating that all four carboxylate oxygens

TABLE 1

MOLECULAR WEIGHT AND ^{119}Sn MÖSSBAUER PARAMETERS FOR THE COMPOUNDS DISCUSSED IN THE TEXT

Compound	*mol. wt.*	*Temp.*[a] (*K*)	*I.S.*[b,c] *mm·s*$^{-1}$	*Q.S.*[c] *mm·s*$^{-1}$
(*a*) *Monoalkyltin compounds*				
(I) $[(C_4H_9)Sn(O_2CCH_2SH)(O_2CCH_2S)]_n$		84	1.31	2.67
(*b*) *Dialkyltin compounds*				
(II) $[(CH_3)_2SnSCH_2CH_2COO]_n$	1525	84	1.33	3.20
(III) $[(C_4H_9)_2SnSCH_2COO]_n$	1250	82	1.42	3.23
(IV) $[(C_4H_9)_2SnSCH_2CH_2COO]_n$	1382	82	1.42	3.21
(V) $[(C_4H_9)_2SnSCH_2CH_2COO]_n$	1400	83	1.48	3.23
(VI) $[(C_6H_5)_2SnSCH_2COO]_n$	1322	80.5	1.26	3.22
(*c*) *Trialkyltin compounds*				
(VII) $(C_3H_7)_3SnSCH_2COOSn(C_3H_7)_3$	589	81	1.48 1.46	1.86[a] 3.51[b]
(VIII) $(C_4H_9)_3SnSCH_2COOSn(C_4H_9)_3$	677	82	1.40 1.40	1.75[a] 3.77[b]
(IX) $[(CH_3)_3SnO_2CCH_2SH]_n$	1298	83	1.35	3.21
(X) $[(C_3H_7)_3SnO_2CCH_2SH]_n$	1702	83	1.37	3.35
(XI) $[(C_6H_5)_3SnO_2CCH_2SH]_n$	1785	83	1.36	2.46
(XII) $(C_4H_9)_3SnSC_{12}H_{25}$	—	84	1.50	1.44
(XIII) $(C_4H_9)_3SnSCH_2COONa$	—	84	1.45	1.59
(XIV) $(C_4H_9)_3SnO_2CCH_2CH_3$	372	82	1.59	3.90

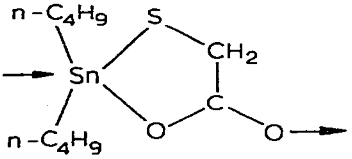
[a] Absorber temperature ±1 K

[b] Isomer shift with respect to the center of a room temperature $BaSnO_3$–$BaSnO_3$ reference spectrum.

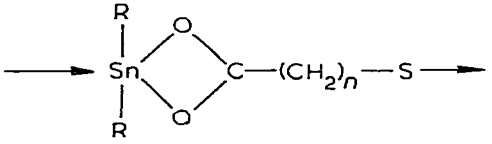
[c] ±0.03 mm·s^{-1}.

are metal bonded, and that this group adopts a cyclic bidentate structure (*vide infra*) in both ligands. In view of the polymeric nature of this material, the metal atom presumably adopts a hexacoordinate configuration in which the sulfur atom of one of the ligands occupies the sixth coordination site. The corresponding 3/2 adduct could not be obtained under similar reaction conditions as those which sufficed to yield the 1/2 product.

Dialkyltin mercaptocarboxylates. A series of compounds of the general stoichiometry $[R_2SnS(CH_2)_mCOO]_n$ has been prepared in which $R=CH_3$, n-C_4H_9, C_6H_5 and $m=1,2$ or 3 to ascertain the consequence of increasing progressively the number of methylene groups between the sulfur atom and the carboxylate function. Okawara *et al.*[3] have suggested a ring structure for dibutyltin thioglycolate of the form

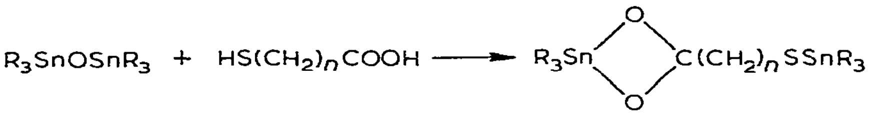


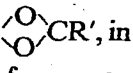
in which the ligand is assumed to form a five membered cyclic moiety involving the metal atom. Under this model it is reasonable to assume that the quadrupole splitting parameter—which is sensitive to the bond angles involved in the metal ligand interaction would reflect a change in the ring size brought about by increasing the number of methylene groups in the ligand. An inspection of the data summarized in Table 1(b) (compounds II to VI) shows that this, in fact, is not observed and that the Q.S. parameter is essentially identical for all five compounds. This result, in conjunction with the molecular weight data in methyl ethyl ketone solution suggests that these compounds are, in fact, linear polymers in which both oxygen atoms of a given mercaptocarboxylate are bonded to the same metal atom, with the fifth coordination site (in addition to the two alkyl groups) being occupied by the sulfur atom of the bridging ligand:

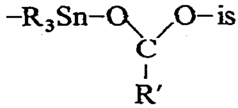


Turning now to the interpretation of the infrared spectra, we shall concern ourselves in the following discussion primarily with the carbonyl region (1300–1650 cm^{-1}) as being most informative concerning the ligand–metal interactions. It is worth noting, however that the infrared spectrum of (II) shows three bands [510 s, 534 m and 556 s], two of which can reasonably be assigned to the Sn–C symmetric and asymmetric stretch in a dimethyltin(IV) compound. Since both a tetracoordinate or pentacoordinate R_2Sn compound lack a center of symmetry, both tin carbon vibrations are expected to be both infrared and Raman active, so that the mutual exclusion principle cannot be used to distinguish between these two bonding situations. However, considerable structural information can be inferred from the C=O region of these spectra, since all of the dialkyltin (IV) compounds show a broad absorption band at ~1545 cm^{-1}. The position of this band is essentially independent of the size of the alkyl (or aryl) group, suggesting no appreciable steric hindrance between the organic ligands and the four membered SnOCO cyclic portion of the molecule.

Trialkyltin mercaptocarboxylates. Bis(trialkyltin) oxides react with mercaptocarboxylic acids in two distinct ways depending on the relative ratio of starting reagents. If this ratio is 1/1, a monomeric binuclear organotin mercaptocarboxylate is obtained:



The infrared spectrum of the thioglycolate compounds ($n=1$) shows a strong absorption at 1644 cm^{-1}. Janssen *et al.*[8], in a detailed study of trialkyltin acylates, have shown that a carbonyl stretching frequency in this region is appropriately assigned to a four-membered ring configuration of the type  $R_3Sn\overset{O}{\underset{O}{\diamond}}CR'$, in which the organotin species is monomeric. In triethyltin(IV) acetate this frequency is at 1655 cm^{-1} in solution, but shifts to 1572 cm^{-1} in the solid where a polymer structure of the type



$-R_3Sn-O-\overset{}{\underset{R'}{C}}-O-$ is assumed[9]. Thus, according to these authors, the carbonyl stretching frequency is very sensitive to the mode of interaction of the carboxylate group with the organotin moiety. Similar conclusions have been reported by Stapfer *et al.*[10]. In a recent study[11] of organotin carboxylates in which both OCO stretching frequencies and Mössbauer effect data were reported, it was pointed out that a comparison between mull and solution spectra permitted a clear distinction to be made between pentacoordinate tin atoms (in the solid) and tetracoordinate metal atoms (in CCl_4 solution). However, the assignment of the solution infrared data (carboxyl group frequencies at ~1610 to 1643 and 1335 to 1391 cm^{-1}) to a four-coordinate monomer, rather than to a cyclic, five-coordinate monomer, is at variance with the present interpretation.

The infrared band at ~350 cm^{-1} is assigned to the Sn–S stretching mode.

The Mössbauer spectrum of the butyl homologue (VIII) shows unambiguously the presence of two distinct tin sites, the total spectrum consisting of four resonance maxima as summarized in Fig. 1. Using the data for tributyltin dodecyl mercaptide (XII) and tributyltin propionate as models, it is reasonable to assign the inner doublet (I.S. 1.49 $mm \cdot s^{-1}$, Q.S. 1.81 mm/sec) to the four-coordinate tin atom having three Sn–C and one Sn–S bond (site a) and the outer doublet (I.S. 1.50 $mm \cdot s^{-1}$, Q.S. 3.65 $mm \cdot s^{-1}$) to the five-coordinate tin atom which interacts with both carboxyl oxygens and the three alkyl groups (site b). This assignment leads to an entirely self-consistent picture with respect to the other model compounds which have been

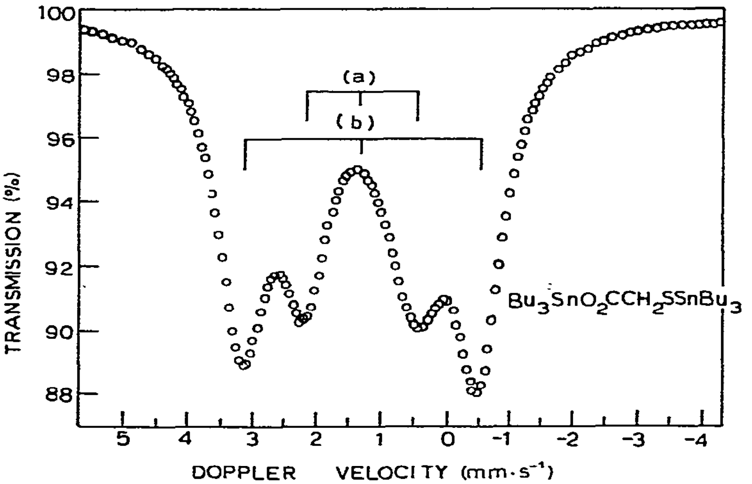


Fig. 1. ^{119}Sn Mössbauer spectrum of $(C_4H_9)_3SnSCH_2COOSn(C_4H_9)_3$ at 82 K. The inner pair of resonance maxima (a) have been assigned to the four-coordinate metal atom while the outer pair of resonance maxima (b) are assigned to the five-coordinate metal atom. Although the two Sn sites reflect essentially the same electron density at the nucleus, the difference in the stereochemistry of the two sites is clearly reflected in the difference in the quadrupole splitting parameter. The ratio of the area under the site b resonance maxima to that under the site a resonance maxima is 1.157, reflecting a larger recoil-free fraction for the five-coordinate metal atom than for the four-coordinate metal atom, as discussed in the text.

examined in this study and clearly show the large difference in the Mössbauer parameters assigned to a four-coordinate and five-coordinate metal atom, each bonded to three alkyl residues, as well as one sulfur or two oxygen atoms, respectively, (XII, XIII, XIV). Comparable four line spectra have been observed in the case of the corresponding propyl compound (VII) in which a similar assignment of the resonance doublet corresponding to the four coordinate tin atom (site a, I.S. 1.48 $\mathrm{mm \cdot s^{-1}}$, Q.S. 1.86 $\mathrm{mm \cdot s^{-1}}$) and the five-coordinate tin atom (site b, I.S. 1.46 $\mathrm{mm \cdot s^{-1}}$, Q.S. 3.51 $\mathrm{mm \cdot s^{-1}}$) can be made. (*See Note added in proof*, p. 183)

In this context it is appropriate to point out one additional interesting feature of these spectra obtained near liquid nitrogen temperature. The ratio of the resonance effect magnitude for the two components of the inner doublet is 0.684 and for the outer doublet is 1.061 at 82 K. In the spectra so far recorded, the intensity of the inner doublet is always less than that of the outer doublet, the area ratio being approximately 1/1.157. Since these compounds are liquids at room temperature and are very rapidly frozen to liquid nitrogen temperature prior to the Mössbauer measurements it is unlikely that the difference in the line intensity for site a and site b could be ascribed to a crystal orientation effect. It is much more likely that the present observation derives from an appreciable difference in the recoil-free fraction of the two metal atoms in the two sites. As has been pointed out earlier[12], in the high temperature limit, the ratio of the recoil-free fractions of two atoms in the same molecule is given by

$$\frac{\ln f}{\ln f_\mathrm{B}} \cong \frac{3E_{\mathrm{R_A}}/2k\theta_\mathrm{A} + 6E_{\mathrm{R_A}}T/k\theta_\mathrm{A}^2}{3E_{\mathrm{R_B}}/2k\theta_\mathrm{B} + 6E_{\mathrm{R_B}}T/k\theta_\mathrm{B}^2}$$

where E_R is the recoil energy of the Mössbauer atom, θ is the corresponding lattice temperature and T is the temperature of the observation. If $T/\theta \geqslant 1$ this equation reduces to

$$\frac{\ln f_\mathrm{A}}{\ln f_\mathrm{B}} = \frac{E_{\mathrm{R_A}}/\theta_\mathrm{A}^2}{E_{\mathrm{R_B}}/\theta_\mathrm{B}^2}$$

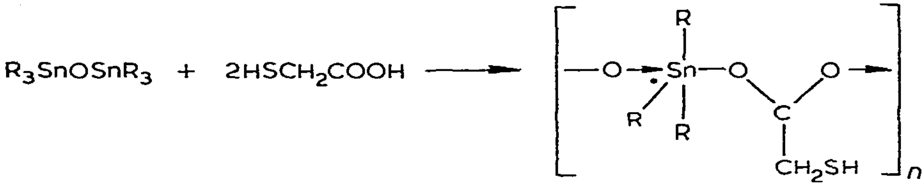
The fact that for the binuclear compounds under discussion this ratio differs significantly from unity (*i.e.* 1.15) implies that the recoil energy (which involves the reciprocal of the effective mass) or the lattice temperature (which involves the vibrational spectrum of the Mössbauer atom) or both differ significantly for the two sites*. In view of the fact that the five-coordinate tin atom (site b) shows a larger recoil-free fraction than the four-coordinate tin atom (site a) it is tempting to associate the higher f value with the larger coordination number, especially via the "effective recoiling mass" influence. However, the present data are insufficient to elucidate this point further, and at present the observed effect can only be discussed on a qualitative phenomenological basis.

Returning now to the reaction between bis(trialkyltin) oxides and mercaptocarboxylic acids, it is observed that when the ratio of reactants is 1/2, the structure of

---

* One of the referees has pointed out that this assumption could be subjected to experimental verification by temperature dependent recoil-free fraction experiments. While this is certainly true in principle, such studies on samples which are liquids at room temperature, are open to considerable uncertainty since only a very small temperature range is accessible for such measurements. However, such measurements on solid samples are certainly feasible and their implications in terms of lattice dynamics have been discussed (See for example ref. 13).

the resulting product is considerably modified:



The Mössbauer spectra of the $R=CH_3$ (IX) and $R=C_3H_7$ (X) members of this series show the presence of only a single tin site. The Q.S. parameter for these compounds is ~0.4 mm · s^{-1} smaller than that assigned to the four-membered cyclic $Sn\genfrac{}{}{0pt}{}{O}{O}C$ moiety in compounds VII, VIII and XIX, and is taken to be characteristic of the $Sn{-}O{-}\underset{\underset{R}{|}}{C}{-}O{-}Sn$ bonding which has been observed[8,14] in trialkyltin acetates. In this context it is appropriate to note that the Q.S. in compounds of the type $[R_3SnOCOCH_3]_n$ where $R=CH_3, C_2H_5, C_4H_9$ are 3.56, 3.35, 3.49 mm · s^{-1} respectively[4,15] in good agreement with the present interpretation. Moreover, this assignment is also confirmed by the infrared data on the carboxyl symmetric and asymmetric absorption band positions. In the trialkyltin acetates studied earlier[4,15], these two bands occur at ~1365 and 1590 cm^{-1} respectively, and are associated with the bridging bidentate behavior of the acetate group, as already noted. In $[(CH_3)_3SnO_2CCH_2SH]_n$ (IX) and $[(C_3H_7)_3SnO_2CH_2SH]_n$ (X), these bands are observed at 1408, 1570 and 1388, 1405, 1560 cm^{-1}, respectively. In the trialkyltin thioglycolates and in tributyltin propionate in which a four-membered cyclic structure occurs involving both oxygen atoms bonded to the same metal atom (VII, VIII, XIV) this characteristic infrared pattern is absent, with the carbonyl band observed at ~1640 cm^{-1} as mentioned above. This assignment is also consistent with the absence of a tin sulfur band in the infrared and the presence of a weak S–H vibrational band of a free mercapto group. The carboxylate absorption has shifted from 1644 to 1550 cm^{-1}, indicating a reduced steric constraint on the bidentate carboxylate function compared to that in the cyclic structure.

CONCLUSION

The present study has shown that the reaction between alkyltin oxides and mercaptocarboxylic acids affords a variety of products whose structure is dependent both on the nature of the reactants and the reaction conditions under which the product is obtained. The structures of these products have been elucidated by means of detailed infrared and Mössbauer spectroscopic methods, and have shown that these methods are sensitive to subtle structural differences in the local environment around the metal atom as well as the steric requirements imposed on the bidentate carboxylate function.

ACKNOWLEDGEMENTS

This work has been supported in part by the U.S. Atomic Energy Commission under Contract At(30-1)-3513 and the present communication constitutes document CH-3513-85. This support is herewith gratefully acknowledged. The authors are indebted to Mr. R. D. Dworkin for the detailed infrared data and Mr. V. N. Prezioso for assistance with the synthetic aspects of this work.

REFERENCES

1 W. A. Gregory, U.S. Pat. 2, 636, 891, 1953.
2 G. P. Mack, U.S. Pat. 2, 914, 506, 1959.
3 M. Wada, M. Harakawa and R. Okawara, *Intern. Conf. Organometal Chem., Moscow, U.S.S.R.*, 1971, Paper 124, V.
4 V. I. Gol'danskii and R. H. Herber, *Chemical Applications of Mössbauer Spectroscopy*, Academic Press, New York, N.Y., 1968.
5 See *e.g.* R. H. Herber and Y. Hazony in A. Weissberger and B. W. Rossiter (Eds.), Physical Methods of Chemistry, Vol. I, Ch. 4, Wiley-Interscience, New York, 1972.
6 J. J. Spijkerman, J. R. DeVoe and J. C. Travis, *Nat. Bur. Stand. Spec. Publ.*, 1970, 260–220; R. H. Herber in I. Gruverman (Ed.), *Mössbauer Effect Methodology, Vol* 6, Plenum Press, New York, N.Y., 1971.
7 R. H. Herber, *The Mössbauer Effect and its Application in Chemistry, Advan. Chem. Ser. No.* 68, American Chemical Society, Washington, D.C., 1967.
8 M. J. Janssen, J. G. A. Luijten and G. J. M. van der Kerk, *Rec. Trav. Chim. Pays Bas*, 82 (1963) 90.
9 I. R. Beattie and T. Gilson, *J. Chem. Soc.*, (1961) 2585; J. G. A. Luijten, M. J. Janssen and G. J. M. van der Kerk, *Rec. Trav. Chim. Pays Bas*, 81 (1962) 202.
10 C. H. Stapfer, R. D. Dworkin and L. B. Weisfeld, *J. Organometal. Chem.*, 24 (1970) 355.
11 B. F. E. Ford and J. R. Sams, *J. Organometal. Chem.* 21 (1970) 345; see also C. Poder and J. R. Sams, *ibid*, 19 (1969) 67.
12 R. H. Herber in *Symposia of the Faraday Society No.* 1: *The Mössbauer Effect*, The Faraday Society, London, 1967, p. 93, and ref. therein.
13 R. H. Herber and Y. Hazony, in I Gruverman (Ed.), *Mössbauer Effect Methodology, Vol.* 8, Phenum Press, New York, 1973.
14 R. Okawara and M. Ohara, *J. Organometal Chem.*, 1 (1964) 360.
15 R. H. Herber, *J. Chem. Phys.*, 54 (1971) 3755.

Note added in proof.

The compound $Bu_3SnSCH_2CO_2SnBu_3$ (VIII) undergoes an unexpected and interesting decomposition: a sample which had been stored for ≈15 months at ≈5° was found to have formed a white solid and a clear liquid supernate. The Mössbauer parameters of the solid (*I.S.* = 1.453 mm/sec at 82K) correspond almost exactly with those of $(Bu_2SnSCH_2CO_2)_n$(III), and the m.p. of the neat solid, a neat sample of (III) and a mixed melting point are identical within about a 4° range. The infrared spectrum of the solid in the range 650 to 3000 cm^{-1} is identical to that of (III). The Mössbauer spectrum of the supernate liquid consists of a broad absorption background plus a sharp singlet resonance (*I.S.* = 1.348 mm/sec at 82K). These data are completely consistent with a decomposition described by the reaction

$$n Bu_3SnSCH_2CO_2SnBu_3 \rightarrow n Bu_4Sn + [Bu_2SnSCH_2COO]_n$$

which can be envisioned as occurring via a butyl group migration between the two metal sites in the original binuclear molecule. A similar reaction—which does not, however, yield a solid product—appears to occur in the analogous tripropyltin(IV) compound (VII).