© *Proc. Indian natn. Sci. Acad.*, **47**, A, No. 5, 1981, pp. 511–554

Printed in India.

Review Article (Organometallic Chemistry)

SOME ORGANOMETALLIC CARBOXYLATES OF MAIN GROUP ELEMENTS—A REVIEW

E. N. VASANTA, R. BOHRA *and* R. C. MEHROTRA

Chemical Laboratories, University of Rajasthan, Jaipur-302 004, India

In view of the growing interest in the industrial applications as well as structural features arising from varying modes of bonding, the existing knowledge about organometallic carboxylates has been reviewed.

Beginning with a detailed summary of the methods employed in their synthesis from different starting materials, brief up-to-date accounts are presented of their general reactions and structural features as revealed by different physico-chemical techniques.

The evidence about the different modes of bonding of carboxylate groups in these derivatives as obtained essentially from their infrared spectra (and supported by NMR, Mössbauer and mass spectral data) has been examined critically and has been correlated (wherever possible) with the actual structural information available from X-ray crystallographic studies.

Keywords : Organometal (B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi and Te) Carboxylates; Modes of Bonding and Structures; Applications

INTRODUCTION

ORGANOMETALLIC carboxylates have been known for over a century, but interest in these has increased considerably during the last few decades due to their wide industrial applications as well as the varying modes of bonding and structures exhibited by them. The first synthesis of dialkyltin diacetate appears to have been published by Cahours (1860) and the next publication in the general field of organometallic carboxylates describes synthesis of *n*-propyl-acetoxy silane by Pope (1881). During the next three quarters of a century, the growing interest in the field of metal carboxylates is reflected in a number of review articles (Rosenberg *et al.*, 1960; Okawara & Wada, 1967; Okawara & Hara, 1971; Zubieta & Zuckerman, 1978; Oldham, 1968; Garner & Hughes, 1975; Doedens, 1976; Catterick & Thornton, 1977; and Cassellato *et al.*, 1978) and rather detailed accounts of these derivatives in monographs (Willemsens, 1964; Shapiro & Frey, 1968; Glockling, 1969; Poller, 1970; and Lesbre *et al.*, 1971) dealing with specific metals. The purpose of the present review is to provide up-to-date (1980) information on the advancements made in the rapidly developing field of organometallic carboxylates, particularly during the last decade. Of the wide variety of compounds studied, this review would focus attention mainly on the chemistry of simple carboxylic acid derivatives of the main group (III, IV, V and VI) elements.

PREPARATIVE METHODS

A. Metal Alkyls and Aryls

The use of metal alkyls and aryls as materials for the preparation of a wide variety of organometallic complexes is very well established (Singh *et al.*, 1974; and Mehrotra *et al.*, 1975, 1978). This type of preparative method is comparatively simple, providing an edge over other methods.

Simple metal alkyls or aryls of boron (Topchiev *et al.*, 1959, 1960; Toporcer, 1965; and Kudo & Nose, 1975), aluminium (Weidlein, 1969, 1970; and Zemina *et al.*, 1970), gallium (Weidlein, 1970; Coates & Hayter, 1953; and Hausen *et al.*, 1978), indium (Clark & Pickard, 1967, 1968; Hausen, 1972; and Hausen & Schwering, 1973), thallium (Glushkova & Kocheshkov, 1957*a*, *b*; Deacon *et al.*, 1965; Kurosawa & Okawara, 1967; Deacon, 1967; and Razuvaev *et al.*, 1970), silicon (Andrianov & Astakhin, 1963; Bell *et al.*, 1974*a*, *b*; Luneva *et al.*, 1975; Lisovin & Komarov, 1978; Drake *et al.*, 1976, 1977); and Andrianov *et al.*, 1976, 1977), tin (Syutkina *et al.*, 1973; Anderson, 1962; Henderson & Holliday, 1965; Ford *et al.*, 1969*a*, *b*; Vyazankin & Bychkov, 1965; Peruzzo *et al.*, 1969*a*, *b*, 1970, 1972, 1974*a*, *b*, 1975; Kolosova *et al.*, 1974; Kozuka & Nakagami, 1977; Abraham *et al.*, 1973, 1975, 1977; Garner & Hughes, 1974; Hester, 1970; and Hester & Mascord, 1973), lead (Wirth *et al.*, 1969; Mayerle & Craig, 1969; Leebrick *et al.*, 1969; and Buschhoff, 1971*a*, *b*); arsenic (Cadogan & Gosney, 1974); antimony (Schmidbauer *et al.*, 1971) and tellurium (Pant, 1972, 1974; and Pant *et al.*, 1973) undergo metal-carbon (polar) bond cleavage with carboxylic acids or metal carboxylates [e.g., $Tl(OOCCF_3)_3$ (Bell *et al.*, 1974), $Hg(OOCCH_3)_2$ (Abraham *et al.*, 1973, 1975, 1977), CH_3COONa (Hester, 1970; Hester & Mascord, 1973), CH_3COOAg (Anderson, 1962; and Pant, 1974), $Sn(OOCCH_3)_4$ (Mel'nichenko *et al.*, 1971) and $Pb(OOCCH_3)_4$ (Buschhoff, 1971*a*, *b*; Cadogan & Gosney, 1974; Pant, 1972, 1974; and Pant *et al.*, 1973)].

It has been suggested by Henderson and Holliday (1965) that in compounds of the type, $R_2Sn(CH=CH_2)_2$, (R = alkyl, vinyl or phenyl), vinyl groups are cleaved more readily from tin atoms than any alkyl groups, but less readily than phenyl moieties. However, only 70 per cent cleavage of phenyltin bond takes place, in the reaction of tetraphenyltin with the carboxylic acids, even after prolonged heating at higher temperatures. It has also been observed that different types of acids behave differently in these reactions; trifluoroacetic acid removed three vinyl groups from $Sn(CH=CH_2)_4$, whereas formic acid caused a complete cleavage at 110 °C. Generally, at ambient temperatures only two vinyl groups are removed by carboxylic acids.

An interesting synthesis of trivinyltin carboxylates (Peruzzo *et al.*, 1970) has been described employing tetravinyltin in the presence of Hg(I) ions, generated electrolytically in methanol containing sodium carboxylates, which also functions as a supporting electrolyte. A series of vinyltin carboxylates have also been obtained by the following reactions (Kaez & Stone, 1960; Garner & Hughes, 1975; and Garner *et al.*, 1975, 1976) :

$$(CH_2{=}CH)_4Sn + nR'COOH \rightarrow (CH_2=CH)_{4-n}Sn(OOCR')_n + (4-n)CH_2=CH_2$$

(n = 1 to 4; R′ = CH_3, CF_3)

Trimethyltin chloride also undergoes Sn — C bond cleavage by acetic acid and halogenated carboxylic acids at 100 °C to afford dimethyltin chloride carboxylates (Wang & Shreeve, 1970, 1972) :

$$(CH_3)_3SnCl + RCOOH \rightarrow (CH_3)_2SnCl(OOCR) + CH_4$$

(R = CH_3, CF_3, CCl_3, $CClF_2$, CHF_2, CH_2Cl, CH_2F, CH_2I, CH_2Br, C_2F_5)

Several workers (Mel'nichenko *et al.*, 1971; Cohen & Dillard, 1970; Honnick & Zuckerman, 1978, 1979; and Okawara *et al.*, 1960) have synthesised diorganotin chloride carboxylates, $R_2SnClOOCR'$ (R = Me, Et, Bu; R′ = Me, Ph, CH_2Cl, $CHCl_2$, CCl_3) by reacting tetraalkyltin with dichlorotin diacetate, diorganotin dichlorides with triorganotin carboxylates and the transacyloxylation reactions between $R_2SnClOOCCH_3$ and R′COOH :

$$R_4Sn + Cl_2Sn(OOCCH_3)_2 \rightarrow 2R_2SnCl(OOCCH_3)$$

(Mel'nichenko *et al.*, 1971)

(R = Et, Bu)

$$R_2SnCl(OOCCH_3) + R'COOH \rightarrow R_2SnCl(OOCR') + CH_3COOH$$

(Honnick & Zuckerman, 1978, 1979)

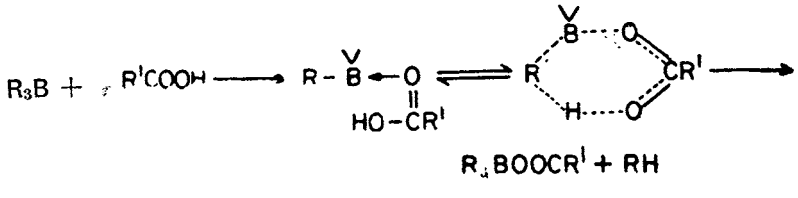
$$R_2SnCl_2 + R'_3Sn(OOCR'') \rightarrow R_2SnCl(OOCR'') + R'_3SnCl$$

(Cohen & Dillard, 1970)

(R = Me, Ph; R′ = Me, Ph, Bu; R″ = Me, CH_2Cl, Ph)

Bismuth-carbon bond is cleaved by a wide variety of carboxylic acids, yielding the corresponding hydrocarbon and bismuth tricarboxylates (Harrison, 1970). It is not possible to isolate the monocarboxylate derivatives by this reaction, but the reaction can be controlled for the isolation of the bis-carboxylate products (*Neth. Appl.*, 1964).

Very few studies are available on the kinetics and mechanism of the reactions involved in the above synthetic procedures. The mechanism for the reaction between R_3B and R′COOH to yield $R_2B(OOCR')$ was studied by Toporcer *et al.*, in 1965, indicating the following sequence for the cleavage of carbon-boron bond by carboxylic acids :



(Toporcer *et al.*, 1965)

Abraham *et al.* (1973) have reported that in the reactions of mercuric carboxylates with tetraalkyltins in methanol, rate constants for the attack of the species $(RCOO)_2Hg$, increase along the series: t-Bu $<$ Et $<$ Me $<$ Ph $<$ $ClCH_2CH_2$ $<$ $MeOCH_2$ $<$ $ClCH_2$, suggesting an open transition state for the S_E2 substitutions. However, Abraham *et al.* (1975) also reported the rate of constants for the removal of the alkyl group (R) from the compounds, $RSnPr^i_3$ with R = Me, Et, *n*-Pr, *i*-Bu, *neo*-Pen and *i*-Pr by mercuric acetate in methanol at 30 °C and showed that the reactivity is markedly affected by the size of the group, R.

B. Organometallic Hydrides

Although much less exploited due to their reducing properties, an equally good method for obtaining organometallic carboxylates is by the reaction of carboxylic acids with organometallic hydrides. Comparatively much less work has been carried out (Anderson, 1957; Sawyer & Kuivila, 1960, 1962; Khudobin & Kharitonov, 1975; Willemsens, 1964; Shapiro & Frey, 1968; Glockling, 1969; Poller, 1970; and Lesbre *et al.*, 1971) in these directions. Reactions of triorganosilicon hydride, R_3SiH (R = Et, Ph) with carboxylic acids, R'COOH with R' = $PhCH_2$, $PhCH=CH_2$ $HOOC-CH_2-CH_2-COOH$, yielded quantitative amounts of (97–99 per cent) triorganosilicon carboxylates in the presence of Ni catalyst at 100–228 °C (Khudobin & Kharitonov, 1975).

Triethylgermanium hydride (Anderson, 1957) yields the corresponding new esters when heated with strong acids like CF_3COOH, C_2F_5COOH and n-C_3F_7COOH. The weak acid, acetic acid reacts with the hydride in the form of silver salt:

$$(C_2H_5)_3GeH + CF_3COOH \rightarrow (C_2H_5)_3GeOOCCF_3 + H_2$$

(Anderson, 1957)

$$(C_2H_7^i)_2GeH_2 + 2AgOOCCH_3 \rightarrow (C_3H_7^i)_2Ge(OOCCH_3)_2 + H_2 + 2Ag$$

(Anderson, 1957)

Organotin hydrides (Sawyer & Kuivila, 1960, 1962; Weber & Becker, 1962; and Kuivila, 1964) give different products depending on the acid used and the organic group present:

$$3Bu^n_2SnH_2 + 6R'COOH \rightarrow 3Bu^n_2Sn(OOCR')_2 + 6H_2$$

(Sawyer & Kuivila, 1960)

(R' = H, CH_3, $ClCH_2$, Cl_2CH, CCl_3, CF_3, C_6H_5, ClC_6H_4, $CH_3C_6H_4$)

$$2R_2SnH_2 + 2R'COOH \rightarrow \underset{\displaystyle R'COO}{\overset{\displaystyle R_2Sn}{\diagdown}} - \underset{\displaystyle OOCR'}{\overset{\displaystyle SnR_2}{\diagdown}} + 3H_2$$

(Sawyer & Kuivila, 1960, 1962)

(R = C_4H_9, C_6H_5; R' = CH_3, C_6H_5)

$$Bu_2SnH_2 + Bu_2Sn(OOCCH_3)_2 \rightarrow \begin{matrix} Bu_2Sn & - & SnBu_2 \\ | & & | \\ H_3CCOO & & OOCCH_3 \end{matrix} + H_2$$ (Sawyer & Kuivila, 1960)

It has been observed that (Kuivila, 1964) low yields of the dicarboxylates were obtained with haloacetic acid. A direct reaction between triethyltin hydride and lead tetraacetate at 50 °C in benzene medium has been reported (Christen & Neuman, 1972) to yield 99 per cent triethyltin acetate:

$$2Et_3SnH + Pb(OOCCH_3)_4 \xrightarrow[C_6H_6]{50\ ^\circ C} 2Et_3Sn(OOCCH_3) + H_2 + Pb(OOCCH_3)_2$$

C. Organometallic Oxides and Hydroxides

The treatment of organometallic oxides or hydroxides with the appropriate acids (acid anhydrides) in suitable organic solvents also yields carboxylates of a number of metals. Organometallic oxides or hydroxides like R_2SnO or R_3SnOH (Okawara *et al.*, 1960; Luijten *et al.*, 1963; Yasuda *et al.*, 1964; Okawara & Hara, 1964; Maeda *et al.*, 1966; Maeda & Okawara, 1967; Babak & Siskova, 1969; Biserni & Peruzzo, 1974; Robert & Adam, 1976, 1977; Deacon & Farquharson, 1977; Boboli *et al.*, 1978) Ph_3AsO (Cadogan & Gosney, 1974), $Ph_3Sb(OH)_2$ (Doak *et al.*, 1965) and Me_3SbO (Shindo & Okawara, 1966) react with carboxylic acids, acid anhydrides and acid halides to give the respective organometallic carboxylates :

$$Ph_3SnOH + R'COOH \rightarrow Ph_3SnOOCR' + H_2O$$ (Biserni & Peruzzo, 1974)

$$R_2SnO + (R'CO)_2O \rightarrow R_2Sn(OOCR')_2$$ (Maeda *et al.*, 1966; Maeda & Okawara, 1967)

($R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5$; $R' = CH_3, CF_3, CCl_3$)

$$Ph_3AsO + (CH_3CO)_2O \rightarrow Ph_3As(OOCCH_3)_2$$ (Cadogan & Gosney, 1974)

$$Ph_3Sb(OH)_2 + 2HCOOH \rightarrow Ph_3Sb(OOCH)_2 + 2H_2O$$ (Doak *et al.*, 1965)

Triorgano- and diorgano-tin derivatives of amino carboxylic acids (Frankel *et al.*, 1965; Ho & Zuckerman, 1973*a*, *b*, *c*; Ho *et al.*, 1975; and Hall & Zuckerman, 1977) (alanine, leucine, iso-leucine, valine, glycine, glycylglycine and β-alanine) have been synthesised from stannol or bis (triorganotin) oxides with the appropriate amino-acids :

$$R_3SnOH + HAA \rightarrow R_3SnAA + H_2O$$

(R = methyl, cyclohexyl and HAA = amino acids)

D. Organometallic Alkoxides and Acetates

Metal alkoxides (Bradely *et al.*, 1978) react readily with carboxylic acids to form metal acylates with the liberation of alcohol, which may be removed azeotropically

with a solvent like benzene. The method was developed by Mehrotra (1953, 1965) for the synthesis of aluminium tri-, di- and mono-soaps, the existence of which had been doubted for a long time by earlier workers (Eigenberger, 1940; McGee, 1949; and Gray & Alexander, 1949). The technique has been extended to the preparation of many organometal carboxylates.

Alkoxy moieties are replaced by carboxylate groups during the reaction of organometallic alkoxides of Si (Armitage & Tarassoli, 1973; Yarosh & Voronkov, 1974*a*, *b*; Andrianov *et al.*, 1974, 1975; Armitage & Sinden, 1975; Voronkov *et al.*, 1976; and Narain & Kaur, 1978), Ge (Magnuson & Knaub, 1965; and Mathur & Mehrotra, 1967), Sn (Voronkov *et al.*, 1972,), and Sb (Meinema & Noltes, 1972; and Matsumura *et al.*, 1971) with carboxylic acids:

$$Me_3SiOMe + n\text{-}Bu_3SnOOCH_3 \rightarrow Me_3SiOOCCH_3 + n\text{-}Bu_3SnOMe$$

(Armitage & Tarassoli, 1973)

$$HC \equiv CSiR_{3-n}(OMe)_n + \xrightarrow{Ac_2O} HC \equiv CSiR_{3-n}(OOCCH_3)_n + nMeOH$$

(Yarosh & Voronkov, 1974)

$$R_2Sb(OMe)_3 + CH_3COOH \rightarrow R_2Sb(OOCCH_3)_3 + 3MeOH$$

(Meinema & Noltes, 1972)

(R = Me, Et, Pr, Bu, Ph)

$$R_3Sb(OC_2H_5)_2 + 2HXCH_2COOH \rightarrow R_3Sb(XCH_2COO)_2 + 2C_2H_5OH$$

(Matsumura *et al.*, 1971)

(R = Me, cyclohexyl or Ph; X = S or O)

For the preparation of diarylthallium trifluoroacetates, the following methods have been employed (Taylor *et al.*, 1975):

(*a*) Disproportionation of arylthallium bis (trifluoroacetates)

$$ArTl(OOCCF_3)_2 \xrightarrow{\text{acetone}} Ar_2TlOOCCF_3$$

(*b*)
$$ArBr \xrightarrow[Et_2O]{Mg} ArMgBr$$

$$ArMgBr \xrightarrow[Et_2O]{TTFA} Ar_2TlBr \xrightarrow[EtOH\text{-}H_2O]{KOH} Ar_2TlOH$$

$$Ar_2TlOH \xrightarrow[H_2O]{TFA} Ar_2TlOOCCF_3$$

(TTFA = Thallium(III) trifluoroacetate; TFA = Trifluoroacetic acid)

$M^+[XCH_2Si(OOCCF_3)_4]$(X = H, Cl; M = Na, Et_3NH) were prepared by treating $XCH_2Si(OOCCF_3)_3$ with $CF_3COO^-M^+$ in MeCN. $[Et_3NH]^+XCH_2Si(OOCCH_3)_4$ (X = Cl, Br, I) were prepared from $XCH_2Si(OOCCH_3)_3$ and $Et_3NH^+OOCCH_3^-$ (Pestunovich *et al.*, 1978, 1979).

Reactions of a number of aryllead triacetates with trifluoroacetic acid lead to the formation of aryllead *tris* trifluoroacetates (Bell *et al.*, 1974*a*, *b*).

E. Organometallic Halides

A large number of organometallic carboxylates have been synthesised by using organometallic halides (Gilman & Yablunky, 1941; Gilman & Yale, 1951; Gerrard *et al.*, 1958; Mehrotra & Pant, 1963; Alleston *et al.*, 1963; Anderson, 1964; Frankel *et al.*, 1967; Srivastava & Tandon, 1967; Hota & Willis, 1968; Srivastava & Bhattacharya, 1968; Goel, 1969; Goel & Prasad, 1970; Goel *et al.*, 1970, 1971, 1975; Lee, 1970; Goel & Ridley, 1972; McWhinnie & Dance, 1973; Gol'din *et al.*, 1973; Voronkov *et al.*, 1974; Belyakova *et al.*, 1974; Kohama & Matsumoto, 1974; Voronkov *et al.*, 1979; Reinheckel *et al.*, 1975; Vos *et al.*, 1975; Knips & Huber, 1976; Novikova *et al.*, 1976; Meinema & Marten, 1977; Ol'dekop *et al.*, 1979; Bajpai *et al.*, 1979; Drake & Hemmings, 1973; and Barker *et al.*, 1974) as starting materials. For example, organometallic carboxylates of B (Gerrard *et al.*, 1958); Tl (Lee, 1970) Si (Mehrotra & Pant, 1963; Goldin *et al.*, 1973; Voronkov *et al.*, 1974; Belyakova *et al.*, 1974; and Kohama & Matsumoto, 1974), Ge (Srivastava & Tandon, 1967; and Hota & Willis, 1968), Sn (Alleston *et al.*, 1963; Anderson, 1964; Frankel *et al.*, 1967; Srivastava & Bhattacharya, 1968; Voronkov *et al.*, 1974; and Meinema & Marten, 1977), Pb (Vos *et al.*, 1975), Sb (Goel, 1969; Goel *et al.*, 1971; Goel & Ridley, 1972; and Bajpai *et al.*, 1979), Bi (Goel & Prasad, 1970) and Te (Pant, 1974) have been prepared by the reaction of corresponding organometallic halides with carboxylic acids or with their alkali metal salts (silver, sodium, or thallium):

$$R_{n-m}MX_m + mR'COOM' \rightarrow R_{n-m}M(OOCR')_m + mM'X$$

[X = Cl, Br; M′ = Ag, Na, Tl]

These reactions have generally been carried out in non-aqueous solvents like benzene, methanol, tetrahydrofuran, carbon tetrachloride, chloroform and methylene dichloride. After the removal of the metal halide and excess solvent, the products can be in general purified by recrystallization or vacuum distillation.

F. Miscellaneous Methods

A wide variety of organometallic carboxylates were isolated by the so called "metallation" or "oxymetallation" reactions. The chemistry of "thallation" or "oxythallium" has been studied by several workers (Pande & Winstein, 1964; McKillop *et al.*, 1969, 1971, 1974; Lee, 1970, 1975; Kurosawa & Okawara, 1970; Taylor *et al.*, 1971; Uemura *et al.*, 1976, 1979, 1980; and Deacon & Smith, 1980).

In these reactions, thallium group replaces a hydrogen atom attached to carbon to form a thallium-carbon bond :

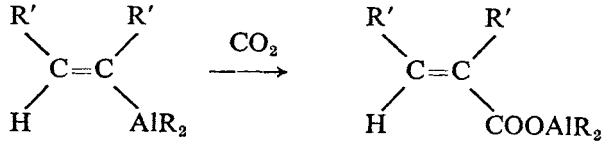
$$ArH + Tl(OOC'R)_3 \xrightarrow{R'COOH} ArTl(OOCR')_2 + R'COOH$$

(R′ = alkyl or aryl)

Monoalkylthallium(III) dicarboxylates, $RTl(OOCR')_2$, have been synthesized from dialkylthallium carboxylates, RR′Tl(OOCR″) (R = Me, Et; R′ = allyl, Pr, Ph, 4-MeC_6H_4; R″ = Me, Ph) and mercuric carboxylates (Abe *et al.*, 1970; Kurosawa & Okawara, 1967, 1970; Kurosawa *et al.*, 1968; and Tanaka *et al.*, 1969). Alkyl (cyano) thallium acetates (Kurosawa *et al.*, 1968, 1969; Tanaka *et al.*, 1969, 1970; and Fukumoto *et al.*, 1970) have been prepared by the reaction between alkyltin compound, thallic acetate and sodium cyanide.

Aryllead carboxylates are synthesized by direct plumbylation methods (Willemsens *et al.*, 1972; Vos & Wolters, 1972; Vos *et al.*, 1973; and Bell *et al.*, 1979*a*, *b*).

Another novel method for the preparation of metal carboxylates is the insertion reactions of carbon dioxide. The reactions of carbon dioxide with organometallic compounds occur *via* carbon dioxide insertion into the metal-carbon bond, e.g., if triethylaluminium is added dropwise with stirring to the solvent saturated with CO_2, organoaluminium carboxylates are produced (Ziegler, 1956). Carbon dioxide insertion into the vinylaluminium bond proceeds with the formation of the carboxylate derivatives of aluminium (Eisch & Foxton, 1968).



It has been found (Inoue & Yokov, 1971) that in the reaction between $Et_2Zn.L$ (where L = N,N,N′,N′—tetramethylene diamine, dipyridyl and N-methylimidazole) and CO_2, organic nitrogen bases catalyze CO_2 insertion at Zn-carbon bond.

$$Et_2Zn.L + CO_2 \rightarrow EtCOOZnEt.L$$

A number of metal derivatives of different carboxylic acids have been synthesized by this technique. For example, salts of magnesium (Nesmeyanov & Kocheshkov, 1960), silicon and tin (Semenova & Kamarov, 1972) are synthesized, by employing CO_2 insertion process. The preparations of dimethyl ethyl silyl carboxylates and tin carboxylates (Semenova & Komarov, 1972) have taken place by inserting CO_2 at the silicon (tin)—oxygen and silicon (tin)—nitrogen bonds under very mild conditions. (Davies & Harrison, 1967; Bloodworth *et al.*, 1967; and Cragg & Lappert, 1966).

$$R_2R'SnOR'' + CO_2 \rightarrow R_2R'SnOOC(OR'')$$

$$R_2R'SiNR''_2 + CO_2 \rightarrow R_2R'SiOOCNR''_2$$

A series of salts of bivalent metals like Zn(II) with acetic and formic acids have also been reported (Seifullina *et al.*, 1978).

Reactions of aminoacids, $NH(CH_2COOH)_2$ and p-$HOC_6H_4NHCH_2COOH$ with $(Me_3Si)_2NH$ (Vostokov, 1978; and Yurtanov *et al.*, 1978) gave compounds of the type, $NH(CH_2COOSiMe_3)_2$ and $Me_3SiOC_6H_4NH - CH_2COOSiMe_3$ respectively.

General Properties

A. Hydrolysis

In general, organometallic carboxylates are hydrolytically unstable. For example, carboxylates of boron are hydrolysed by cold water to the carboxylic acid and boric, boronic and boronous acids (Gerrard *et al.*, 1958); $(CH_3)Tl(OOCCH_3)_2$ (Kurosawa & Okawara, 1967) is stable in the solid state, but in aqueous solution, it decomposes slowly at room temperature and rapidly when heated.

From the hydrolysis reactions (Alleston *et al.*, 1963) of dialkyltin dicarboxylates, $R_2Sn(OOCCH_3)_2$, (R = Me, Bu), stable products of the type, $[R_4Sn_2(OOCCH_3)_2O]$ have been isolated, which are dimeric in non-polar solvents:

$$2R_2Sn(OOCCH_3)_2 \xrightarrow[CH_2N_2]{H_2O} R_4Sn_2(OOCCH_3)_2O + 2CH_3COOH.$$

(R = Me, Et, Bu)

Alleston *et al.* (1963), on the basis of ^1H and ^{119}Sn magnetic resonance spectroscopy suggested that compounds of the type, $R_4Sn_2(OOCR')_2O$ contain four and five co-ordinate tin, probably in the cyclic structure. Phenyltin tricarboxylates (Henderson & Holliday, 1965) may be hydrolysed to yield the following products:

$$C_6H_5Sn(OOCR)_3 + H_2O \rightarrow C_6H_5Sn(OOCR)O + 2RCOOH.$$

Phenyltellurium triacetate can be readily hydrolysed to give the oxide of phenyltellurium acetate and acetic acid (Pant, 1972):

$$PhTe(OOCCH_3)_3 \xrightarrow{HOH} PhTe\begin{matrix}\nearrow O \\ \searrow OOCCH_3\end{matrix} + 2CH_3COOH.$$

B. Decarboxylation and Disproportionation

Acyloxyboron derivatives (Gerrard *et al.*, 1958) undergo disproportionation, when subjected to distillation under vacuum:

$$2B(OOCR)_3 \rightarrow [B(OOCR)_2]_2O + (RCO)_2O \qquad \text{(Gerrard } et\ al.\text{, 1958)}$$

$$3R'B(OOCR)_2 \rightarrow (R'BO)_3 + 3(RCO)_2O \qquad ,, \qquad ,,$$

$$2R'_2BOOCR \rightarrow (R'_2B)_2O + (RCO)_2O \qquad ,, \qquad ,,$$

During the thermal rearrangements of organosilicon or organogermanium compounds, in which silicon or germanium is directly attached to a carboxylic acid, migration of —OH or —OR′ from carbon to silicon or germanium takes place by the elimination of the carboxyl group as carbon monoxide (Brook, 1955):

$$R_3MC(=O)—OR' \rightarrow R_3M—OR' + CO \qquad \text{(Brook, 1955)}$$

(M = Si, Ge; R′ = H, CH_3, C_6H_5)

Trialkyltin hydrides may be obtained by the thermal decomposition of the corresponding formates (Hara & Okawara, 1965) under reduced pressure:

$$R_3SnOOCH \rightarrow R_3SnH + CO_2 \qquad \text{(Hara \& Okawara, 1965)}$$

On heating dibutyltin diacetate (Zhivukhim *et al.*, 1962) with dibutyltin dibutoxide, a polystannoxane derivative with butoxy and acetoxy groups at the terminal positions were obtained. Decarboxylation (Deacon & Farquharson, 1977) of some polyfluorophenyltin,-germanium,-silicon and-lead carboxylates yields polyfluorophenyltin,-germanium,-silicon and-lead compounds. The thermal decomposition of organometallic heavy metal trihaloacetates, $Me_3Sn(OOCCX_3)$, $Ph_3SnOOCCX_3$ (X = Cl, Br), $Ph_3PbOOCCCl_3$ and $Ph_2SbOOCCCl_3$ in cyclooctene solution has been studied in detail (Seyferth *et al.*, 1966, 1968, 1969). Only the tin derivatives were found to undergo transfer of dihalocarbene to olefins to produce gem-dihalocyclopropanes. The mechanism of these CX_2 transfer reactions has not been postulated, but a process involving decarboxylation and CX_2 transfer from the R_3SnCX_3 intermediate was suggested:

$$R_3SnOOCCX_3 \rightarrow R_3SnCX_3 + CO_2$$

$$R_3SnCX_2 + \text{>C=C<} \longrightarrow RS_3nX + \text{>C(C)C<}(CX_2) \qquad \text{(Seyefrth } \textit{et al.}\text{, 1966, 1968, 1969)}$$

(X = Cl, Br; CH_3, C_6H_5)

Thermal decomposition and decarboxylation reactions of Tl(Deacon, 1970; Cummins, *et al.*, 1971; Sartori & Adelt, 1973/1974; Sartori & Frohn, 1974; Deacon *et al.*, 1976; and Deacon & Phillips, 1978), Sn (Reichle, 1969; Matsuda *et al.*, 1970*a*, *b*; and Kozuka & Nakagami, 1977), and Pb (Deacon & Felder, 1970; and Cookson *et al.*, 1974) have been reported. The pyrolysis of $Me_3SnOOCCBrPh_2$, $Me_3SnOOCCHBrPh$, $Me_3SnOOCCBrMe_2$ and $Me_3Sb(OOCCHBrPh)_2$ gave trimethyl metal bromide and the corresponding polyester (Okada & Okawara, 1973).

C. Addition Reactions

The Lewis acid behaviour of organosilicon and organotin carboxylates has been studied by Graddon and Rana (1977*a*, *b*). A thermodynamic study of the adduct formation of 1 : 1 products of $R_2Si(OOCCH_3)_2$, $R_3Si(OOCCH_3)$ and $R_2Sn(OOCR')_2$, (R = Me, Bu, Ph; R′ = Me, Et, Pr) in benzene with oxygen, nitrogen and phosphorus containing ligands (such as Et_3N, Py, PyNO, $BuNH_2$, $PhCH_2NH_2$,

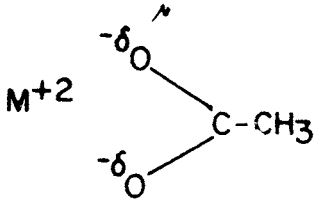
DMSO, $NPBu_3$, 4-methyl pyridine and 1–10, phenanthroline) has shown that adduct stabilities are not much different from those of the corresponding organotin compounds, but the enthalpies of formation of the adducts with silicon compounds are considerably greater.

The stability constants of (Aritomi *et al.*, 1975) some benzoate complexes, $(CH_3)_2Pb(OOCC_6H_4Y)_2$ (Y = H, *p*-OCH_3, *o*-CH_3, *m*-CH_3, *p*-CH_3) with donor ligands like (tert-phosphine oxide) R_3PO, (hexamethylphosphotriamide) HMPA, DMSO, DMF, Py were carried out in methylene chloride. The stability constants for the benzoate complexes exhibit larger values.

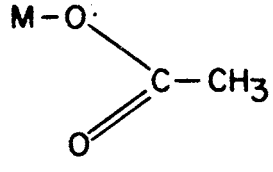
Some organometallic haloacetates of the type, $Br_2CHCOOSiMe_3$, $Cl_2CCOOSiMe_3$, $Cl_3CCOOSnBu_3$ or $(Cl_3CCOO)_2SbMe_3$ react with Ph_3P to yield corresponding organometallic halides and $Ph_3P(O)$ (Okada & Okawara, 1972).

Spectroscopic Studies and Structures

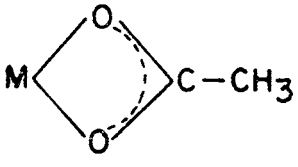
A number of physico-chemical techniques including actual determination of crystal structures by X-rays have been employed during the last 2–3 decades to elucidate the structural aspects of a number of organometallic carboxylates. On the basis of these studies, it is well established, especially on the basis of IR spectral interpretations that the carboxylate groups are capable of binding metals in different ways:



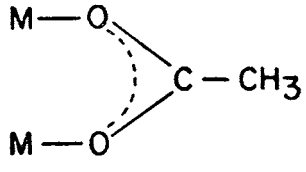
I
Ionic



II
Unidentate



III
Bidentate
(Chelating)



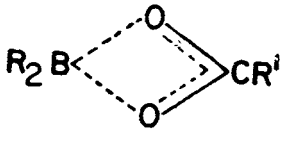
IV
Bidentate
(Bridging)

In view of the above, this section begins with an account of the information gained by vibration spectral and X-ray crystallographic studies followed by supporting evidence provided by NMR, Mössbauer and Mass spectra.

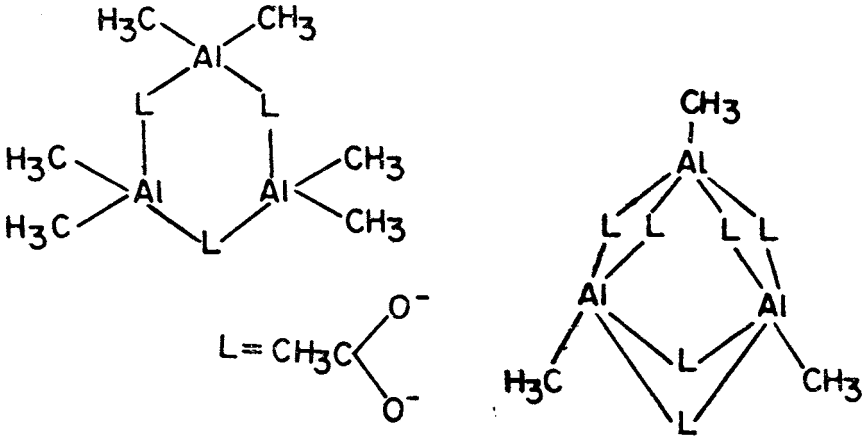
A. Vibration Spectra and X-ray Crystallography

Several workers (Zachariasen, 1940; Jones & McLaren, 1954; Wilmshurst, 1955; Morris & Bush, 1956; Itoh & Bernstein, 1956; Nakamura, 1958, 1963; Lappert, 1962; Grigore'v, 1963; Shevchenko, 1963; Spinner, 1964; Caligne *et al.*, 1970; and Alcock *et al.*, 1976) have reported the infrared spectra of a variety of carboxylic acids and their metal derivatives. The IR spectral data of carboxylic acids indicated an unsymmetrical structure for the free acids (Grigore'v, 1963; and Shevchenko, 1963). The IR spectrum of sodium acetate (Zachariasen, 1940; Jones & McLaren, 1954; Wilmshurst, 1955; Morris & Bush, 1956; Itoh & Bernstein, 1956; Nakamura, 1958, 1963; Lappert, 1962; Nakamura, 1963; Grigore'v, 1963; Shevchenko, 1963; and Spinner, 1964) has been discussed showing C–O antisymmetric (1575 cm^{-1}) and C–O symmetric stretching (1415 cm^{-1}) frequencies. Hence, the band at $\sim$ 1740 cm^{-1} due to the carbonyl group (C=O), indicating the presence of free carboxylic acids, disappears on the formation of salts, which depict characteristic bands in the ranges 1540–1650 and 1280–1440 cm^{-1}, alongwith a series of other bands due to the COO– moiety. The separations between the intense antisymmetric carboxylate stretch and the symmetric stretch and the trends in the position of these bands have been very widely used in assigning structures from infrared spectra. In comparison with $NaOOCCH_3$, one may find the spectra of unidentate acetate groups showing a large increase in the antisymmetric stretching COO and a similar decrease in the symmetric stretching COO. As the size of the elements in a group (e.g., C, Si, Ge, Sn and Pb) increases, a weak interaction with the second oxygen of the COO might take place and the compound may tend to change from structure II to III. The differences between these 2 types have been shown in the higher intensity of antisymmetric COO moiety, in the unidentate coordination than in the bidentate bridging coordination. The use of $\Delta\nu(\nu_8 - \nu_3)$ [difference between antisymmetric and symmetric stretchings], has also been proposed for distinguishing between chelation and a bridging coordination (structures III and IV). Alcock *et al.* (1976) has demonstrated with suitable examples, the applications and limitations of IR spectral studies in assigning different types of bondings present in metal carboxylates.

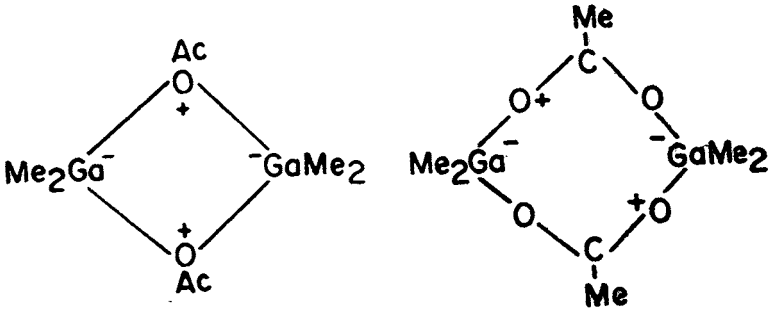
The IR spectra of the carboxylate derivatives of boron were studied by Lappert *et al.* (1958). A chelated structure has been assigned for the dialkylboron monocarboxylate derivatives.



On the basis of IR and Raman spectroscopy, a trimeric structure has been suggested for alkylaluminium acetates (Weidlein, 1969, 1970) [$R_2AlOOCMe$ and $RAl(OOCMe)_2$ (R = Me, Et)] as follows:



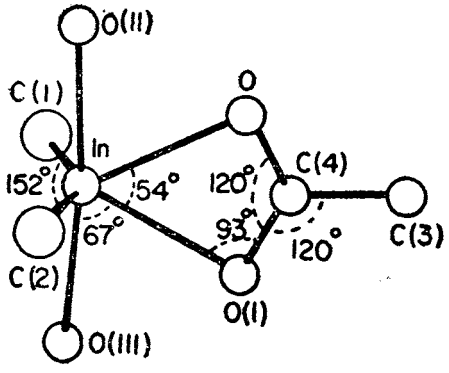
Dimethylgallium acetate (Coates & Hayter, 1953) is dimeric in solution. An ionic as well as a dimeric (in acetone) structure with resonance in the carbonyl groups have been proposed (given below):



Hausen *et al.* (1978) have observed from X-ray crystal analysis that in the methylgallium compound, $MeGa(OOCMe)_2$, the monomers are bonded together by acetate groups forming polymers.

Dimethylindium acetate and trifluoroacetate are non-conducting in nitromethane and depict monomeric behaviour in the same solvent. An ionic formulae of the type, $(CH_3)_2In^+(OOCCH_3^-$ or $OOCCF_3^-)$ is, therefore, ruled out (Clark & Pickard, 1968). The carbonyl absorption in the IR spectrum of the trifluoroacetate appears at 1620 cm^{-1}, as compared with 1780 cm^{-1} in the spectrum of trifluoroacetic acid, suggesting strong interaction of the carbonyl group.

Besides the IR and Raman spectra, crystal structures of $R_2In(OOCCH_3)$, (R = Me, Et) have been determined by X-ray analysis (Habeeb & Tuck, 1973; and Einstein *et al.*, 1973). Coordination number six is assigned for indium in these derivatives. The molecules are linked into chains giving rise to a polymeric structure. $Et_2InOOCCH_3$ (Hausen & Schwering, 1973) crystallizes in the orthorhombic space group Pnma with a, 8.140 ± 0.02, b, 7.41 ± 0.02 and c, 15.13 ± 0.03Å, d(calcd.) 1.64, d(exptl.) 1.61, and Z = 4. The crystal structure of polymeric solid $(CH_3)_2InOOCCH_3$ reported by Einstein *et al.* (1973) consists of six coordinate indium atoms, with each indium surrounded by two methyl groups (approximately *trans*) and a bidentate acetate moiety as well as being coordinated to the acetate group of the two neighbouring molecules. The molecules are bonded into chains giving rise to a polymeric type of lattice:

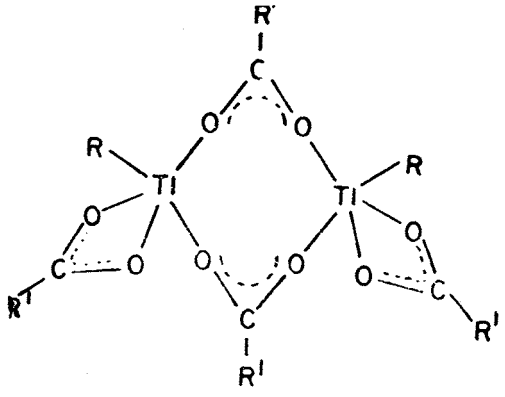


A dimeric intermediate, $[CH_3In(OOCCH_3)HTDT]_2$ (Habeeb & Tuck, 1974) is obtained by the reaction between toluene 3,4-dithiol (H_2TDT) and dimethylindium (III)acetate. The variational and ^1H NMR spectra of this intermediate show the presence of CH_3 group bonded to In and an acidic hydrogen atom of the HTDT.

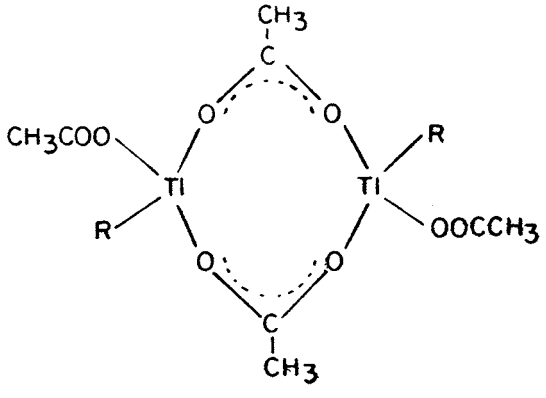
$$(CH_3)_2InOOCCH_3 + H_2TDT \xrightarrow[-CH_4]{C_2H_5OH} [CH_3In(OOCCH_3)HTDT]_2$$

$$-2CH_4 \mid \text{DMSO} \longrightarrow In(OOCCH_3)TDT \longleftarrow \text{DMSO} \mid -2CH_4$$

In monoalkyl thallium derivatives, RTl $(OOCR')_2$(R = CH_3, C_2H_5; R′ = CH_3, $C_3H_7^i$ and $C_4H_9^i$) (Kurosawa & Okawara, 1967, 1969; and Tanaka *et al.*, 1969) thallium is in a penta coordinate environment. Because of the dimeric nature and the presence of bridging carboxylate moieties, a penta coordinate structure (A) is assigned for thallium carboxylates in the solid state and a four coordinate environment (B) for Tl in the solution state (Kurosawa & Okawara, 1967; Lee, 1975; and Kurosawa & Okawara, 1970).



(A)

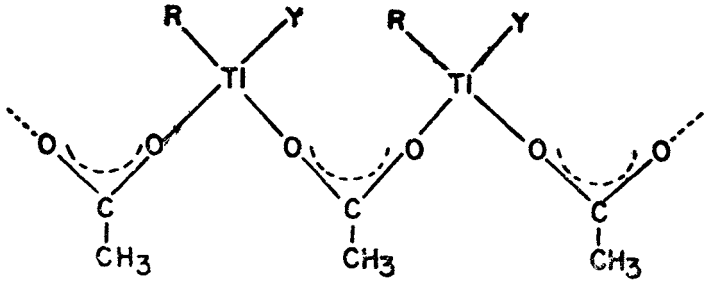


(B)

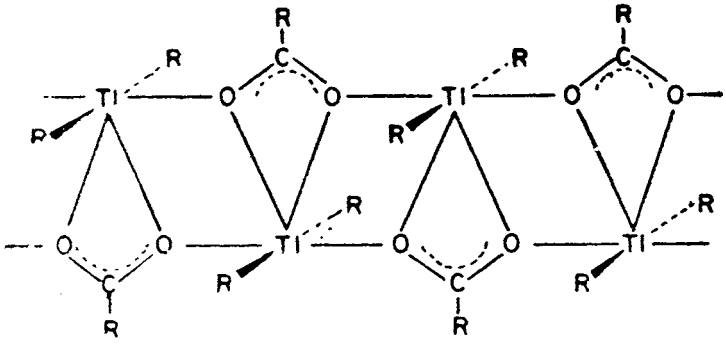
Some mono-alkyl(aryl)thallium carboxylates of the type, R(X)Tl($OOCCH_3$) (R = Me, Et, Pr, Ph; X = $OOCCH_3$, CN) have been assigned the polymeric structure (A-1) in the solid state (Kurosawa *et al.*, 1968; Fukomoto *et al.*, 1970; and Lee, 1970).

Different types of structures of organothallium trifluoroacetates have been suggested using vibrational spectral analysis (Deacon *et al.*, 1965; Reichle, 1969; Deacon 1970; Deacon & Felder, 1970; Cummins *et al.*, 1971; Sartori & Adelt, 1973, and Deacon & Phillips, 1974; Deacon *et al.*, 1976; Deacon & Farquharson, 1977; 1974; Cookson *et al.*, 1978). Compounds of the type, $(C_6F_5)_2Tl(OOCR)$ (R = CH_3, CF_3, C_6F_5) have been shown to possess a four coordinate thallium with bridging carboxylate moieties. The presence of both bidentate chelating and bridging ligands has been suggested, indicating the polymeric structure (B-1) for $R_2Tl(OOCR')$,

with six coordinate thallium rather than a structure based on four coordinate thallium (Chow & Britton, 1975).



(A-1)



(B-1)

Dimethylthallium trifluoroacetate is highly ionised in methanol, showing an ionic or weakly bridging CF_3COO ions (Deacon *et al.*, 1965). Conductivity measurements (Lee, 1970) of phenylthallium(III) acetate was studied in acetone and methanol. In methanol, the acetate and fluoroacetate have very low conductance. In acetone, conductance of trifluoroacetate increases slowly, suggesting slow solvolysis of the Tl—X bond (X=$OOCCH_3$, $OOCCF_3$).

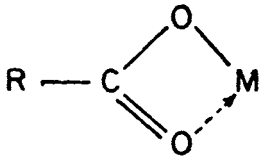
In organotin carboxylates, the carboxylate moiety has been shown to function in different ways, i.e., as unidentate, bidentate bridging or bidentate chelating ligands. Generally, the spectra of unidentate acetate groups show a large increase in C—O antisymmetric stretching and a similar decrease in C—O symmetric stretching vibrations, which are corresponding approximately to C=O and C—O. In Table I, C—O antisymmetric (ν_8) and C—O symmetric stretching frequencies (ν_3) of some Group IV organometallic carboxylates are summarized. The position of these bands suggests unidentate nature of the carboxylate moiety (Alcock *et al.*, 1976).

A perusal of the data in Table I indicates that there is a decrease in C—O antisymmetric and C—O symmetric stretching vibrations as the group is descended. This might be due to the increased polarity of the M—O bonds. The decrease in the C—O stretchings may also be due to a weak interaction with the second oxygen

TABLE I

Compound	(ν_8)	(ν_3)	($\nu_8 - \nu_3$)	*Ref.*
MeCOOMe	1771	1248	523	(Wilmshurst, 1957)
$Me_3SiOOCMe$	1725	1267	458	(Okawara *et al.*, 1960)
$Me_2Ge(OOCMe)_2$	1698	1267	431	(Luijten *et al.*, 1963)
$Et_3Sn(OOCMe)$ (soln)	1655	1302	353	,, ,,
$Ph_3Pb(OOCMe)$ (soln)	1623	1311	312	,, ,,

atom as the size of M increases and the compounds may adopt a bidentate chelating unsymmetrical structure:



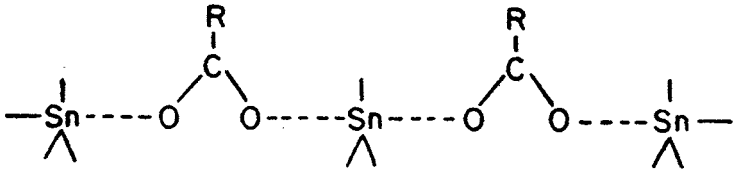
Several workers have reported the IR and Raman spectroscopic measurements for silyl and germyl derivatives of CH_3COOH, CCl_3COOH and CF_3COOH acids (Srivastava *et al.*, 1962, 1963; Augus & Stobart, 1975; and Drake *et al.*, 1977). A four coordinate environment has been assigned for silicon and germanium in these derivatives. The structure of potassium triformatostannate(II) consists of the close packing of discrete pyramidal $Sn(OOCH)_3^-$ ions and potassium ions (Jelen & Lindqvist, 1969).

Okawara *et al.* (1960) interpreted the IR spectra of some triorganotin carboxylates as superposition of the absorptions of the carboxylic acid anion and organotin cation. Freeman (1958) also postulated the ionic nature of the bonding in these derivatives.

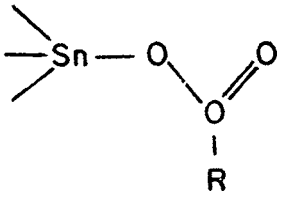
However, Beattie and Gilson (1961) suggested that the IR spectra of $R_3SnOOCCH_3$—could be better explained by a structure with bridging acetate groups and five coordination number for tin, which was later confirmed by Luijten *et al.* (1963).

From the IR spectra of various triorganotin carboxylates, $R_3Sn(O_2CR')$ it has generally been concluded that in the crystalline state these carboxylates are linear polymers with bridging carboxylate and planar triorganotin groups (when R = alkyl) (Peruzzo *et al.*, 1969*a*, *b*, 1970, 1972, 1974*a*, *b*, 1975; Ford *et al.*, 1969*a*, *b*; Hester, 1970; Hester & Mascord, 1973; Okawara *et al.*, 1960; Luijten *et al.*, 1963; Okawara & Hara, 1963, 1964; Bisarni & Peruzzo, 1974; Lohmann, 1965; Reichle, 1966; Vilarem & Maire, 1966; Simons & Graham, 1967*a*, *b*; Van den Berghe *et al.*, 1968; Plazzogna *et al.*, 1970; Tanaka, 1970; Morikawa, 1975, 1976; and Stapfer *et al.*, 1970). The carboxylate groups with C_2 symmetry are alternatively arranged in one direction by the

coordination of each oxygen atom of CO_2 moiety to tin atom (C). These compounds are monomeric in dilute solutions, having tin in the four coordinate environment (D).

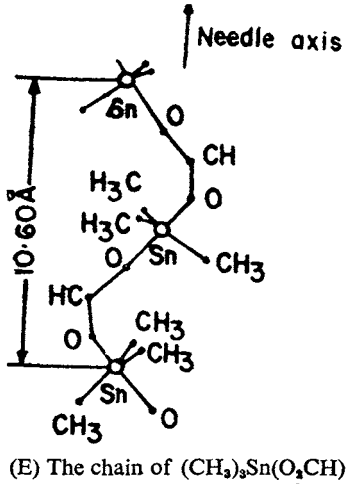


(C) In solid state



(D) In solution state

For example, on the basis of infrared and far-infrared spectra of trialkyltin formate and acetate, it has been proposed by several workers (Okawara *et al.*, 1960; Luijten *et al.*, 1963; Okawara & Hara; 1963; 1964; Cummins & Dunn, 1964; Donaldson *et al.*, 1964; Poller, 1965; Reichle, 1966; Vilarem & Maire, 1966; Simons & Graham, 1967*a*, *b*; Van den Berghe *et al.*, 1968; and Tanaka, 1970) that these are polymeric with bridging formoxy or acetoxy groups. A strong absorption band at 1590–1615 cm^{-1} and a band at 1360–1380 cm^{-1} show the bridging nature of formoxy and acetoxy moiety leading to a linear polymeric chain with five coordination number for tin atom. In solution, these bridges are broken down, showing IR absorption frequencies at



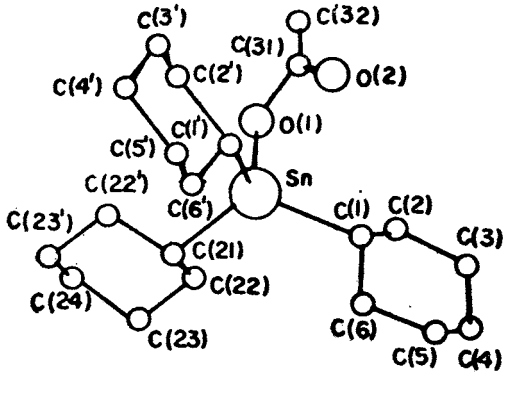
(E) The chain of $(CH_3)_3Sn(O_2CH)$

1655–1665 cm^{-1} and 1242–1302cm^{-1} arising from a free carboxylate moiety. The bridging, polymeric structure of the carboxylate derivatives account for the insolubility of these compounds.

Although the complete structural analysis of the simplest compound $(CH_3)_3Sn(O_2CH)$ has never appeared, the polymeric structure (E) (*on page* 528) containing formoxy and planer $(CH_3)_3Sn$ groups arrange alternatively along a helical chain has been indicated by Okawara (1965).

IR spectra of trivinyltin carboxylates, (Henderson & Holliday, 1965; Peruzzo *et al.*, 1969, 1970, 1972; Garner & Hughes, 1974, 1975; Peruzzo *et al.*, 1974*a*, *b*, 1975; Kaez & Stone, 1960; Biserni & Peruzzo, 1974; and Plazzogna *et al.*, 1970), $(CH_2 = CH)_3SnOOCX$, (X = CH_3, C_2H_5, CH_2Cl, $CHCl_2$, CF_3) have been examined. Carboxylate group frequencies change significantly through this series of compounds from values characteristic of ionic to the ester type. Characterization of compounds of the type, $R_3SnOOCR'$ (R = alkyl or aryl, R' = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CHF_2, CFH_2 and CF_3) have also been made by several workers (Luijten, 1963; Cummins & Dunn, 1964; Simons & Graham, 1967*a*, *b*; Van den Berghe *et al.*, 1968), on the basis of a variety of physico-chemical studies.

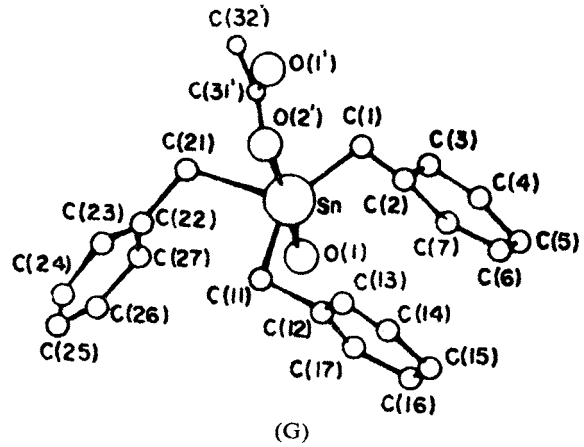
In general compounds of the type $R_3Sn(O_2CR')$ in solid state have a bridging polymeric structure, if the group R is not very bulky. For example, tribenzyltin acetate is a polymer. The structure (F) of the compound has been confirmed by X-ray analysis (Alcock & Timms, 1968*b*; and Ho & Zuckerman, 1973). In this and similar compounds, tin is in a five coordinate environment. Triorganolead acetates exhibit similar behaviour while silicon and germanium acetates are always monomeric (Luijten *et al.*, 1963). If the group R in compounds of the type $R_3Sn(O_2CR')$ is bulky, steric hindrance plays a major role in preventing polymerisation. For example, trineophyltin-formate, -acetate, -perfluoroacetate, (Reichle, 1966) and



(F)

(F) The molecular structure of tribenzyltin acetate, showing the atomic numbering. The primed atoms of the acetate group are related to the unprimed ones (omitted) by a screw axis.

tricyclohexyltin acetate (Alcock & Timms, 1968*a*) are monomers in both solid and solution state. X-ray crystal structure of tricyclohexyltin acetate shows that tin is in four coordinate environment (G).

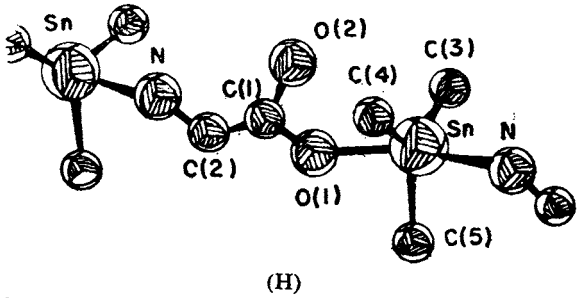


(G)

(G) The molecular structure of tricyclohexyltin acetate, showing atomic numbering. Primed atoms are related to the unprimed ones by a mirror plane.

It has been reported (Ho & Zuckerman, 1973*a*, *b*; Ho *et al.*, 1975; Hall & Zuckerman, 1977; and Frankel *et al.*, 1965) that in compounds of the type, R_3SnAA (R = methyl, butyl and cyclohexyl, AA is the anion of glycine (gly), DL-α-alanine (ala), DL-α-amino-n-butyric acid (but), DL-α-valine (val), DL-α-leucine (leu), L-α-isoleucine (isoleu), β-alanine (β-ala) and glycylglycine (glygly), the methyl and the butyl derivatives are aminocoordinated. The cyclohexyl derivatives, except Cyh_3Sn (gly), Cyh_3Sn (β-ala) and Cyh_3Sn(glygly), are non-amino coordinated.

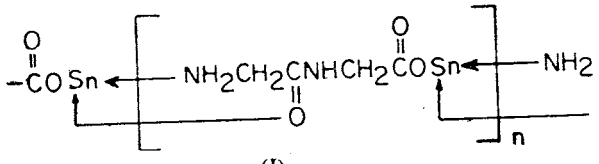
Crystal structure of trimethyltin glycinate, $Me_3Sn(OOCCH_2NH_2)$ reported by Ho and Zuckerman (1975) consists of tetragonal crystals with $a = b = 7.839$; $c = 14.659$Å, space group P4, or $P4_3$, $Z = 4$. The structural analysis (H) confirms the presence of amino-nitrogen coordination and the distorted trigonal bipyramidal geometry about the tin atom. The Me_3Sn skeleton is non-planar in this derivative.



(H)

(H) Portion of the one dimensional chain stereochemistry of $Me_3Sn(OOCCH_2NH_2)$.

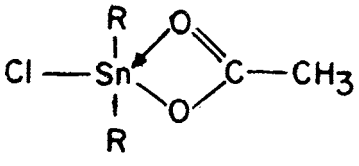
Tricyclohexyltin glycylglycinate $Cyh_3Sn(glygly)$ has been assigned a polymeric structure or a structure (I) in which each tin atom is linked to the terminal nitrogen and amide carboxyl oxygen atom of the dipeptide of the second molecule:



(I)

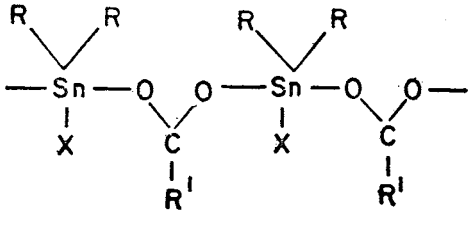
A series of triorganotin (Bu, Ph, Cy, Np) and diorganochlorotin (Me, Bu) derivatives of L-cysteine, DL-homocysteine and DL-pencillamine have been reported by several workers (Grenie & Garrigon-Lagrange, 1972; Domazetis *et al.*, 1978; and Smith *et al.*, 1979).

The IR spectra of dialkyltin chloride carboxylates (Wang & Shreeve, 1970, 1972; Cohen & Dillard, 1970; Wade *et al.*, 1963; and Okawara & Hara, 1964) show the usual asym (COO) stretching vibrations at 1550(S) cm^{-1} and $\nu_{sym}(COO)$ at 1210cm^{-1}. Solution (in $CHCl_3$ or CH_2Cl_2) IR spectra show a shift to higher frequencies of $\nu_{asym}(COO)$, indicating a change of structure (J). It has been suggested that these derivatives are chelated monomers in solution and COO bridged polymers in the solid state with penta coordinate tin atom (Okawara & Hara, 1964);



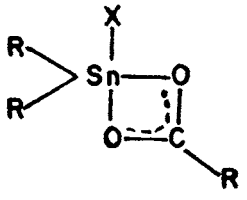
(J)

The structure proposed (Honnick & Zuckerman, 1978, 1979) for diorganotin chloride haloacetates consists of bridging acetoxy groups in the axial positions, with the two organic groups and the halogen atom in the equatorial positions (K):



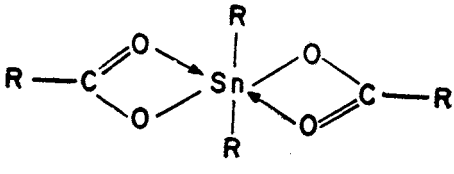
(K) Solid-state structure

The other possible structure assigned by the same authors involves a penta coordinate tin atom with the acetoxy groups bridging from the axial to equatorial positions with halogen in the axial position [see (L)]. The authors could not distinguish between these two structures on the basis of IR or Mössbauer spectra.



(L) Solution-state structure

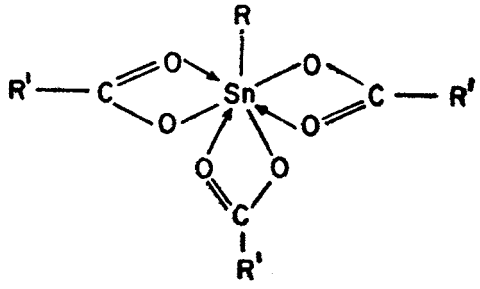
Dialkyltin dicarboxylates (Maeda *et al.*, 1966; and Maeda & Okawara, 1967) have been suggested to be monomeric with hexa-coordinated tin atom, with C_{2v} symmetry of – OOC unit in the carbonyl group, both in the liquid state and in solution; the diacetate has a chelated type structure. A strong band appeared at 1607 cm^{-1} is assignd to $\nu COO_{asym.}$ and a band at 1380 cm^{-1} is due to $\nu_{sym}COO$ stretching vibration. Dialkyltin diacetate in solution shows an additional band at 1560–1570 cm^{-1}, and an increase in the intensity of the band at 1400–1440 cm^{-1} denoting a symmetrically chelated configuration (M):



(M)

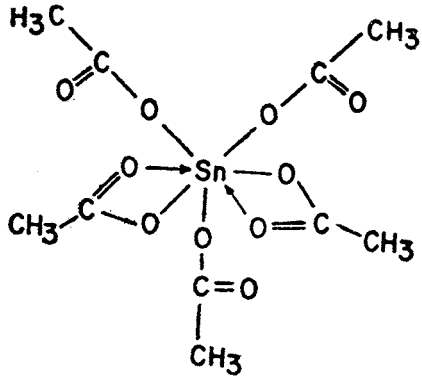
Binuclear tin complexes have also been studied (Croner & Waber, 1965; Kimura *et al.*, 1969; Bandoli *et al.*, 1971; Ho & Zuckerman, 1973; Graziani *et al.*, 1977; Calogero *et al.*, 1979; Mathiasch & Mitchell, 1980; and Calogero *et al.*, 1980). $(C_6H_5)_4Sn_2(OOCCH_3)_2$ contains (Bandoli *et al.*, 1971) tin-tin bond with a slightly distorted trigonal-bipyramidal configuration about each Sn atom. The compound crystallizes in the triclinic system with *a* 8.843, *b* 17.828, *c* 8.755Å, α 88.28Å, β 76.50Å, γ 98.57Å, $Z = 2$, space group *PT*.

IR spectra of tricarboxylates of organotin derivatives in CCl_4 solution, show coordinating COO stretching bands around 1570 cm^{-1} and 1420 cm^{-1} with weak to medium carbonyl absorption near 1700 cm^{-1}. The last band has been attributed to the partial hydrolysis. A seven coordinate structure (N) is proposed for the monoorganotin tricarboxylates:



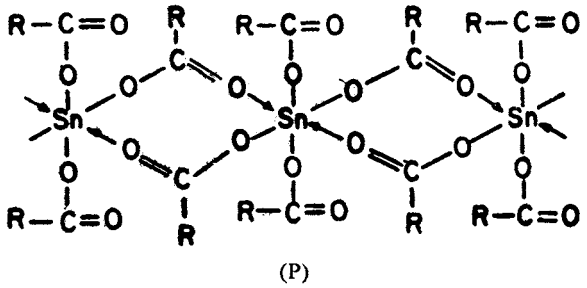
(N)

It is interestingly relevant to point out here that a seven coordinate environment for tin is also assigned for [(NMe_4) $Sn(OOCMe)_5$] by Alcock *et al.* (1976). The compound contains two bi- and three unidentate acetate groups. The IR spectrum shows ν_8 at 1635; ν_3 at 1310 and $\triangle\nu$ 325 cm^{-1}, corresponding to the unidentate acetate and ν_8 at 1570, ν_3 at 1430, $\triangle\nu$, 140 cm^{-1}, corresponding to the bidentate acetate. The X-ray crystallography also confirms this type of structure (O) (Alcock & Tracy, 1976):



(O)

Holliday and Henderson (1965) had also assigned a polymeric structure to tin tetracarboxylates, when they are considered in the solid state. However, in solution, a monomeric unit with four coordinate tin has been reported (P):



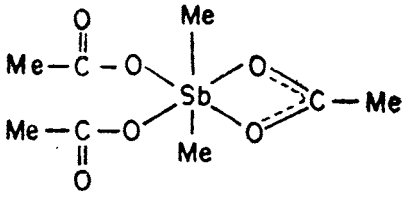
(P)

On the basis of crystal and molecular structure, it has been confirmed that the crystals of tin tetraacetate are monoclinic, possessing four independent acetate moieties, with dodecahedral geometry, but with variable Sn–O distances, because of over crowding (Sn–O mean 2.22Å, range 2.13 to 2.29 Å).

Free (ester like) as well as bridging carboxylate moieties have been observed in the IR spectra of the derivatives of $Sn(OOCCH_3)_4$ with mono and dicarboxylic acids (Mehrotra *et al.*, 1978*a*), β-diketones (Mehrotra *et al.*, 1978*b*), and thio and mercaptocarboxylic acids (Mehrotra *et al.*, 1980).

Diorganolead dicarboxylates (Cookson *et al.*, 1974), $Ph_2Pb(OOCR)_2$ ($R = C_6F_5$, *p*-$MeOC_6F_4$ or *p'*-$EtOC_6F_4$) have been assigned an associated structure with bridging bidentate carboxylate groups in the solid state and a monomeric with chelating carboxylate groups in the solution state. In D-pencillaminolead the amino acid acts as a tridentate chelating ligand with lead atom bonding both amino and carbonyl groups (Freeman *et al.*, 1974).

A hexacoordinated structure has been assigned (Meinema & Noltes, 1972) for $R_2Sb(OOCCH_3)_3$, (R = Me, Et, Pr, Bu) on the basis of IR, Raman and PMR spectroscopy. The structure (Q) depicts one bidentate and two monodentate acetoxy ligands occupying the equatorial positions and two methyl groups are assigned at the axial positions as follows:



(Q)

Two broad absorption bands one in the region 1680–1620 cm^{-1} and the other in the region 1600–1540 cm^{-1} are observed in the IR spectra of $R_2Sb(OOCR)_3$ Free ester type carboxylate appears between 1700–1600 cm^{-1}. A trigonal bipyramidal geometry has been assigned for Me_3Sb and Ph_3Sb carboxylates (Doak *et al.*, 1965; Goel *et al.*, 1970, 1971; Goel & Ridley, 1972; and Shindo & Okawara, 1966) on the basis of spectral analysis. IR spectra of tetraphenylantimony carboxylates, $Ph_4Sb(OOCR')$ ($R' = CH_3$, CCl_3, CF_3) showed that in the solid state, the tetraphenylantimony acetate has a 6-coordinate structure (Goel, 1969). However, the trichloro and trifluoro acetates have penta coordinate structures. In solution, all these derivatives appear to possess penta coordinate structures.

The crystal structure of tetraphenylantimony(V) formate shows a trigonal bipyramidal geometry (Bone & Sowerby, 1979). The formate moiety is behaving as unidentate ligand. A slight distortion of the angles between the equatorial groups has been attributed to residual intramolecular interaction between the non-bonded oxygen of unidentate formate groups and the antimony atom.

Similarly, crystal structure of triphenylantimony(V) acetate (Sowerby, 1979) indicates a distorted trigonal bipyramidal geometry. This has also been explained as due to the weak intramolecular interaction between the non-bonded oxygen atoms of the unidentate acetate groups and the central Sb atom.

Goel and Prasad (1970) studied IR spectra and carried out conductance measurements for triphenylbismuth (V) carboxylates. The results indicate non-ionic five coordinate structure. The carboxylate frequencies [ν_{asym}(COO–1592 cm^{-1}; ν_{sym}(COO)–1335 cm^{-1}] in $Ph_3Bi(OOCR)_2$ (R = CH_3, $CHCl_2$, CH_2Cl, CF_3 and CCl_3) are indicative of the presence of unidentate carboxylate groups. The presence of a doublet in the spectra of mono and disubstituted acetates can be attributed to the presence of conformational isomers as observed for the organotin halo acetates. (Simons & Graham, 1967*b*).

B. NMR Spectra

Several workers have studied the ^1H NMR spectra of Tl(Kurosawa & Okawara, 1967, 1970; Abe *et al.*, 1970; Lee, 1975; Kurosawa *et al.*, 1968, 1969; Tanaka *et al.*, 1969, 1970; and Fukumoto *et al.*, 1970), Si(Alcock *et al.*, 1976), Ge(Drake & Hemmings, 1973; and Barker *et al.*, 1974), Sn(Ford *et al.*, 1969; Garner & Hughes, 1974; Wang & Shreeve, 1970, 1972; Cohen & Dillard, 1970; Honnick & Zuckerman, 1978, 1979; Maeda *et al.*, 1966; Maeda & Okawara, 1967; Deacon & Farquharson, 1977; Frankel *et al.*, 1965; Ho & Zuckerman, 1973 *a*, *b*; Hall & Zuckerman, 1977; Habeeb & Tuck, 1974; and Simons & Graham, 1967*a*, *b*), Pb(Alcock *et al.*, 1976), Sb(Meinema & Noltes, 1972; Matsumura *et al.*, 1971; and Havranek *et al.*, 1978) and Te (Pant, 1972, 1974; and Pant *et al.*, 1973) derivatives of organometallic carboxylates.

The ^1H NMR spectra of monoalkylthallium derivatives of the type, $RTl(OOCR^1)_2$ (R = CH_3, C_2H_5; R^1 = CH_3, C_2H_5) show much larger J(Tl–H) values than those for dialkylthallium compounds (Kurosawa & Okawara, 1967*a*, *b*). This was qualitatively interpreted as due to increase in both the s-character in the Tl–C bond and the effective nuclear charge of the thallium atoms. Similarly, the chemical shifts of methyl protons (δ = 1.87 ppm) which are directly attached to Tl atom of $MeTl(OOCCH_3)_2$ is 0.7 ppm lower than that of $Me_2Tl(OOCCH_3)$ protons. This can be understood in terms of difference in electronegativity (Kurosawa & Okawara, 1967*a*).

Since the coupling constant J(^{119}Sn–CH_3 or ^{117}Sn–CH_3) provides uniquely valuable information concerning the hybridization and coordination number of the tin atom (Holmes & Kaesz, 1961; and Maddox *et al.*, 1965), it has been extensively employed in the studies of carboxylate derivatives also.

Simons and Graham (1967*a*, *b*) studied the effect of concentration, temperature and added complexing agents on NMR spectra of $Me_3Sn(OOCR)$, (R = H, CH_3, CH_2Cl, $CHCl_2$, CCl_3). The results suggest an equilibrium in solution between monomeric and associated forms. In the case of $Me_3Sn(OOCH)$, when the concentration is varied in $CdCl_3$ solution at constant temperature, values of *J* range from 62.7 cps at the lowest concentration to 67.4 cps at the highest. These values

indicate that four and five coordinate trimethyltin formate species are in rapid equilibrium and the proportion of the five coordinate form relative to four coordinate form increases with concentration.

These conclusions are based on the fact that for four coordinate tin compound, $J = 54.0$ to 58.5 cps and for five coordinate compounds, $J = 67.0$ to 70.0 cps (Holmes & Kaesey, 1961; Maddox *et al.*, 1965). In contrast to trimethyltin formate, the J values suggest that very little five coordinate tin is present in solution even at 30 °C in case of the corresponding acetate derivatives. Trimethyltin chloroacetates are essentially monomeric (four coordinate tin) in $CHCl_3$ and very slightly associated in CCl_4. The ^1H NMR spectra of dialkyltin diacetate (Maeda *et al.*, 1966; and Maeda & Okawara, 1967) in 20 per cent CCl_4 solution and in the liquid state at 85 °C, show that the values of J $^{119}Sn-CH_3$ are 82.5 and 81.7 cps for the respective states. It has been concluded that the ratio of *S*-character in the Sn—C bonds is about 40 per cent and C—Sn—C skeleton may not be linear.

In the diorganotin halide carboxylates, $R_2ClSn(OOCR')$ ($R' = CH_3$, CH_2Cl, $CHCl_2$, CH_2Br or CH_2I, CCl_3, CF_3, CF_2Cl and $CFCl_2$), the chemical shifts have been examined as a function of the screening constant of OOCR′ protons, which decrease with increasing number of halosubstituents. ^{119}Sn-proton coupling constants (Wang & Shreeve, 1970, 1972; Cohen & Dillard, 1970; Honnick & Zuckerman 1978, 1979) for these carboxylates fall in the range 73–77 cps in $CHCl_3$ solution, indicating that the tin atom is penta coordinated.

The three monodentate acetate groups in compounds of the type, $R_2Sb(OOCCH_3)_3$, occupy the equilateral positions, forming a rigid trigonal bipyramidal geometry. All acetate moieties have been shown to be magnetically and chemically equivalent (Meinema & Noltes, 1972).

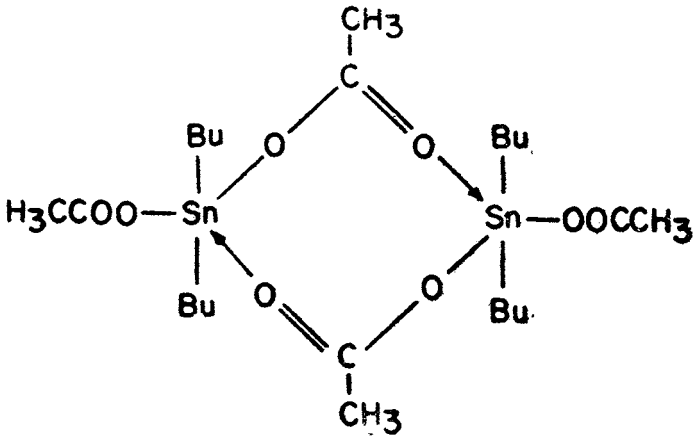
The ^{13}C NMR spectra of alkyl (aryl) thallium carboxylates (Kitching *et al.*, 1975; and Hoad *et al.*, 1977), diorganotin dicarboxylates (Mitchell, 1973), diorganotin halo-carboxylates (Honnick & Zuckerman, 1978, 1979), organolead carboxylates (Vos *et al.*, 1979) and organobismuth carboxylates (Ouchi *et al.*, 1975) have been analyzed by several workers.

The ^{13}C NMR spectrum of pure dibutyltin diacetate observed by Mitchell (1973), shows a value of $J(^{119}Sn-^{13}C)$ of 630 Hz. This value is very close to the value found for the dimethoxide (642 Hz) in which tin is pentacoordinated. The spectra shows only one carbonyl resonance at 181 ppm, indicating that the carbonyl group has some anionic character. On the basis of IR bands (bridging, 1570 cm^{-1} and non-bridging carboxylates, 1605 cm^{-1}) and ^{13}C NMR spectra, a five coordinate environment is assigned for tin in these derivatives [*see* (R)].

IR, ^{13}C, ^1H NMR and Sn Mössbauer data for diorganotin halide carboxylates, thio-carboxylates, halide haloacetates (Honnick & Zuckerman, 1978, 1979) have been interpreted in terms of acetoxy bridged trigonal bipyramidal tin in the solid phase and partial depolymerization occurring in solution state.

C. Mössbauer Spectra

Among Mössbauer parameters, the isomer shift (IS or δ), quadrupole splitting (QS or $\triangle$) and half widths (τ_1, τ_2) are important for the determination of the coordination



(R)

number of organotin (Herber *et al.*, 1965; Henderson & Stockler, 1966; Stockler *et al.*, 1967; Ford *et al.*, 1968; Goldanskii *et al.*, 1968; Podar & Sams, 1969, 1970, 1971; Zuckerman, 1970; Debye *et al.*, 1971; Platt & Maddock, 1971; Herber, 1971; Delmas *et al.*, 1971; Davies *et al.*, 1971; Calogero *et al.*, 1977; Allen *et al.*, 1978; Calogero *et al.*, 1979; 1980) and organoantimony (Goel *et al.*, 1975) carboxylates.

Mössbauer spectral (Herber *et al.*, 1965) data of solid, polymeric trialkyl (aryl) tin carboxylates has been used to determine the coordination number for tin. When the ratio of the quadrupole splitting to the isomer shifts has a value, in general, larger than 2.10, it indicates (Herber *et al.*, 1965; and Zuckerman, 1970), a penta coordination, or in other words, a coordination number greater than four at tin, i.e., a sp^3d hybridized state. While ρ values in the range 0 to 1.80 are associated with tetrahedral (sp^3 hybridized) tin atoms. Herber *et al.* (1965) calculated ρ for the trimethyltin derivatives and found that there are larger (2.37–2.52) than that found in the *n*-butyl (2.26) or cyclohexyl (2.01–2.18) analogues. For $Me_3SnOOCMe$, IS = 1.34, QS = 3.47 and for $Neo_3SnOOCMe$(Neo = $PhCMe_2CH_2$), IS = 1.35 and QS = 2.45 mm/sec, the large difference in the QS value is attributed to the fact that the tin atom is in a trigonal bipyramidal environment in $(CH_3)_3Sn$ series, whereas in the trineophyltin compounds, the tin atom is in a tetracoordinate state, because of the bulky neophyl groups.

Ford *et al.* (1969) reported Mössbauer parameters for a number of triphenyl tin carboxylates, having chain length varying from one to eighteen carbon atoms. Contrary to the assumption that lengthening the carboxylate chain might prevent polymerization, Ford *et al.* (1969) observed large values of QS ($\sim$ 3.4 mm/sec) in these derivatives indicating the presence of penta coordinate environment for tin. However, Ford and Sams (1970) observed that branching in the carboxylate chain might prevent polymerization. For example, $Ph_3SnOOCCMe_3$, $Ph_3SnOOCCMe{=}CH_2$ and $Ph_3SnOOCCHEtBu$ are tetra coordinated monomers. These compounds show IS of 1.21 mm/sec. and QS varies in the range 2.26–2.40 mm/sec. It has however, been observed that triphenyltin acrylates of the type

$Ph_3SnOOCR$ [R = $(CH_2)_3CHMe_2$, $(CH_2)_2CHMe_2$, $CH_2CHMeEt$, $CHMePr$, $CHMe_2$ and $(CH = CH_2)$] are polymeric and the quadrupole splittings are essentially constant and lies in the range 3.37 $\pm$ 0.05 mm/sec.

The QS value for Ph_3 $SnOOCCCl_3$ (2.97) is far below the value (3.9 mm/sec) anticipated for a penta coordinated structure (Ford & Sam, 1971). These data are consistent with monomeric tetra coordinated species in the solid state, though QS value in this case is larger than those found for non-halogenated monomeric analogue, $Ph_3SnOOCCMe_3$ (Ford & Sam, 1970) (QS = 2.40 mm/sec.). This is in accord with the general trends observed in the penta coordinate species, where QS for $Ph_3SnOOCCHCl_2$ is greater (3.81 mm/sec.) than that for $Ph_3SnOOCCHMe_2$ (3.32 mm/sec.).

Mössbauer data (QS > 3.6 mm/sec.) (Honnick & Zuckerman, 1978, 1979) indicate that the derivatives of the type, $(CH_3)_2ClSnOOCR$ are penta coordinate and are probably polymeric in the solid state. Similarly, the large QS values ($\sim$ 3.4 mm/sec.) observed in the spectra of trialkyltin carboxylates suggest the presence of five coordinate tin atoms (Ford *et al.*, 1969; and Ford Sams, 1970, 1971).

Mössbauer spectra (Ho & Zuckerman, 1973, *a*, *b*; and Hall & Zuckerman, 1977) of nitrogen coordinated trialkyltin amino acid derivatives, R_3SnAA, exhibit the value of QS in the range 3.2 $\pm$ 0.1 mm/sec. and the ratio QS/IS to be greater than 2.1; these suggest a five coordinate, bridged polymeric structure, through intermolecular coordination of the amino group. On the other hand, the cyclohexyl derivatives, Cyh_3SnAA, which are not nitrogen coordinated exhibit QS values below 1.8, indicating four coordination. The derivative, tricyclohexyltin glycylglycine behave differently.

Mössbauer studies for antimony carboxylates (Goel *et al.*, 1975) have been reported. On the basis of IS and QS values, a trigonal bipyramidal geometry with essentially planar C_3Sb groups has been assigned for bis(halogenoacetato) trimethylantimony derivatives. Comparison of these parameters with those reported for $Me_3SnOOCR$ (Podar & Sams, 1969) reveal a number of linear correlations (Goel *et al.*, 1975).

D. Mass Spectra

The peaks corresponding to the presence of dimer as well as of single monomeric units in the mass spectrum of dimethylindium acetate (Habeeb & Tuck, 1973) suggest polymerization in the solid state. Other molecular ions are also observed at 393 $[Me_3In_2(OOCCH_3)_2^+]$ and at 319 $[Me_2In_2(OOCCH_3)^+]$ with a series of lower intensity peaks representing masses between these values and monomeric species below *m/e* 204, indicating the presence of dimeric species in the gas phase.

From the mass spectra of aminocarboxylic acid derivatives, (Ho & Zuckerman, 1973), it has been found that the $P-R^+$ ion peaks (P = parent ion; R = Me, Cyh) have been found to be useful in determining the identity of the compounds.

The mass spectra (Adley *et al.*, 1975) of diorganotellurium dicarboxylates and trimethylene tellurium diacetate and dibenzoate indicate that the ease of the cleavage of groups bonded to Te atoms decreases in the order

$$CH_3COO > C_6H_5COO > C_2H_5OC_6H_4 \sim CH_3OC_6H_4 \sim C_6H_5.$$

Applications

Organometal carboxylates are widely used in industries as well as in biological systems. Among the metal carboxylates of main group elements, organotin (Bongisvanni, 1969; Sawyer 1971; Reifenberg & Gitlit, 1973; Yokoo, 1973; Polyateov *et al.*, 1973; Strapfer, 1974; Ittusukaichi *et al.*, 1975; Abeler, 1976; Van der Kerk, 1976; Dworkin & Ejk 1977; Elliott & Aldridge, 1977; and Farrow & Dawson, 1978), organosilicon (Bulten, 1978; Ayrey *et al.*, 1979; Motohashi *et al.*, 1979; Troitskaya *et al.*, 1978; and Kozuka *et al.*, 1978) and organo lead compounds (Walden *et al.*, 1968; Gras & Boucard, 1978; Grafer & Grasl 1969, Gorrich, 1974 *a*, *b*; Skinner, 1974; Weldon & Lund, 1973; and Kronstein, 1973) found much applications. They have been used as insecticides, herbicides, fungicides, pesticides and as bacteriocides (Sawyer, 1971). The use as stabilizer (Abeler, 1976; Van der Kerk, 1976; and Dworkin & Ejk, 1977) for polyvinylchloride resins and other compounds is the most important application of tin derivatives. Organolead carboxylates (Walden, 1968; Gras & Boucard, 1968; Graber & Gras, 1969; Gorrich, 1974*a*, *b*; Skinner, 1974; Weldon & Lund, 1973; and Kronstein, 1973) are also used as wood preservatives (Gorrisch, 1974; Skinner, 1974; Weldon & Lund, 1973; and Walden & Allen, 1968) as toxicants (Gras & Boucard, 1968), and in solvent dispersions of synthetic rubbers. Organoaluminium (Matsumura & Fukumoto, 1969; and Warner, 1978) derivatives also find applications in the textile industries.

Acknowledgement

Financial help from PL-480 grant is gratefully acknowledged.

References

Abe, T., Kurosawa, H., and Okawara, R. (1970) Preparation and reactions of methyl(allyl) thallium (III) derivatives. *J. organometal. Chem.*, **25**, 353.

Abeler, G. (1976) Diorganotin maleinates. *Ger. Offen.*, 2,549,332; *Chem. Abstr.*, **85**, 143300 p.

Abraham, M. H., Dadjour, D. F., Gielen, M., and Poorter, B. D. (1975) The cleavages of a series of alkyl tri-isopropyltins by mercury acetate in methanol. *J. organomental Chem.*, **84**, 317.

Abraham, M. H., Dadjour, D. F. and Holloway, C. J. (1973) The mechanism of reaction of tetraalkyltins with mercuric carboxylates in methanol. *J. organometal. Chem.*, **52**, C 27.

Abraham, M. H., Dadjour, D. F., and Sedaghat-Herati, H. R. (1977) Substitution at saturated Carbon. Part 22 Rate constants for the substitution of tetraethyltin by mercury(II) carboxylates in *t*-butylalcohol, acetonitrile, acetone and ethylacetate. *J. Chem. Soc., Perkin II*, 1225.

Adley, T. J., Pant, B. C., and Rye, R. T. B. (1975) Mass spectra of organotellurium compounds. I. diorganotellurium dicarboxylates. *Can J. Spectrosc.*, **20**, 71.

Alcock, N. W., and Timms, R. E. (1968*a*) Organotin acetates. Part II. The crystal and molecular structure of tricyclohexyltin acetate. *J. Chem. Soc.*, 1876.

——— (1968*b*) Organotin acetates. Part I. The crystal and molecular structure of tribenzyltin acetate. *J. Chem. Soc.*, 1873.

Alcock, N. W., and Tracy, V. L. (1976) Acetates and acetato complexes spectroscopic studies. *J. Chem. Soc. Dalton*, 2246.

Alcock, N. W., Waddington, T. C., and Tracy, T. L. (1976) Acetates and acetato-complexes. Part-2; *J. Chem. Soc. Dalton*, 2243.

Allen, D. W., Brooks, J. S., Formstone, R., Growe, A. J., and Smith, P. J. (1978) The preparation and tin 119-*m*-Mössbauer spectra of tri-*n*-butylstannyl esters of heterocyclic and substituted aromatic carboxylic acids. *J. organometal. Chem.*, **156**, 359.

Alleston, D. L., Davies, A. G., Hancock, M., and White, R. F. M. (1963) Organotin chemistry, Part II. Compounds of the composition, $R_4Sn_2X_2O$. *J. Chem. Soc.*, 5469.

Anderson, H. H. (1957) Reactions of triethylgermanium hydride with salts of transitional elements and with organic haloacids. *J. Am. Chem. Soc.*, **79**, 326.

——— (1962) Dealkylation of di-*n*-amyldimethyltin, di-*n*-butyl-, dimethyltin and tetraethyltin with perfluoro acids, inorganic halides and carboxylates. *Inorg. Chem.*, **1**, 647.

——— (1964) Volatile *n*-butyltin and phenyltin tricarboxylates: organotin oxymonocarboxylates. *Inorg. Chem.*, **3**, 912.

Andrianov, K. A., and Astakhin, V. V. (1963) Reaction of organocyclosilazanes with saturated monobasic acids. *Izv. Akad. Nauk SSSR Ser. Khim*, **12**, 2206; (1964) *Chem. Abstr.*, **60**, 9305*e*.

Andrianov, K. A., Dabagova, A. K., Shokino, V. V., and, Knunyants, I. L. (1974) Reaction of carboxylic acid fluorides and perfluoropropylene oxide with (acyloxymethyl) dimethyl ethoxysilanes. *Izv. Akad. Nauk SSSR Ser. Khim*, **9**, 2063; (1975) *Chem. Abstr.*, **82**, 43505*d*.

Andrianov, K. A., Igonina, S. A., and Sixorov, V. I. (1977) On the reactions of trialkyl (aryl) hydrosilanes with trifluoroacetic acid. *J. organometal. Chem*, **128**, 43.

Andrianov, K. A., Igonina, S. A., Sidorov, V. I., Eaborn, C., and Jackson, P. M. (1976) Novel cleavages of benzyl- and *m*-methoxybenzyltrimethylsilane by trifluoroacetic acid. *J. organometal. Chem.*, **110**, 39.

Angus, P. C., and Stobart, S. R. (1975) Interconversion of derivatives of germane using heavy metal salts: synthesis of germyl carboxylates. *J. Chem. Soc. Dalton*, 2342.

Aritomi, M., Hashimoto, K., and Kawasaki, Y. (1975) Interaction of dimethyllead(IV) benzoato complexes with some donor molecules in solution. *J. organometal. Chem.*, **93**, 181.

Armitage, D. A., and Sinden, A. W. (1975) Exchange reactions between oxygen and sulpher derivatives of germanium, tin and lead. *J. organometal. Chem.*, **90**, 285.

Armitage, D. A., and Tarassoli, A. (1973) Oxygen-halogen exchange between silicon, germanium, and tin. *Inorg. nucl. chem. Lett.*, **9**, 1225.

Ayrey, G., Man, F. P., and Poller, R. C. (1979) Mechanism of thermal stabilization of PVC by organotin compounds: scavenging of chlorine atoms. *J. organometal. Chem.*, **173**, 171.

Babak, Z., and Siskova, A. (1969) IR spectroscopic study of the reaction of dibutyltin oxide with carboxylic acids. *Chem. Prun.*, **19**, 509.

Bajpai, K., Singhal, R., and Srivastava, R. C. (1979) Studies on triarylantimony dicarboxylates. *Indian J. Chem.*, A, **18**, 73.

Bandoli, G., Clemente, D. A., and Panaltoni, C. (1971) Crystal structure of a binuclear tin complex with a Sn-Sn bond. *J. Chem. Soc., Chem. Commun.*, 311.

Barker, G. K., Drake, J. E., and Hemmings, R. T. (1974) Characterization of monohalogen and monopseudohalogen derivatives of dimethylgermane. *Can. J. Chem.*, **52**, 2622.

Beattie, I. R., and Gilson, T. (1961) The occurrence of organotin cation. *J. Chem. soc.*, 2585.

Bell, H. C., Kalman, J. R., Pinhey, J. T., and Sternhell, S. (1974*a*) Aryllead(IV) tricarboxylates. *Tetrahedron Lett.*, 3391.

——— (1974*b*). Aryllead(IV) tricarboxylates. *Tetrahedron Lett.*, 853.

——— (1979*a*) The chemistry of aryllead(IV) tricarboxylates, synthesis. *Aust. J. Chem.*, **32**, 1521; (1980) *Chem. Abstr.*, **92**, 6628*g*.

Bell, H. C., Penhey, J. T., and Sternhell, S. (1979*b*). The chemistry of aryllead(IV) tricarboxylates. Reaction with phenols. *Aust. J. Chem.*, **32**, 1551; (1980) *Chem. Abstr.*, **92**, 110609*n*.

Belyakova, Z. V., Pomerantieva, M. G., and Gulubtsov, S. A. (1974) Addition of methyldichlorosilane to allyltin fluoroacetate in the presence of chloropiatinic acid. *Zh. Obshch. Khim.*, **44**, 1780; (1975) *Chem. Abstr.*, **82**, 16885*w*.

Biserni, G. S., and Peruzzo, V. (1974) Monomeric and associated forms of trivinyltin formate in solution. *J. organometal. Chem.*, **67**, 265.

Bloodworth, A. J., Davies, A. G., and Vashistha, S. C. (1967) Organometallic reactions. VII. Further addition reaction of tributyltin methoxide and of bis (tributyltin oxide). *J. Chem. Soc.*, (*C*), 1309.

Boboli, E., Malasnicki, W. L., Kowalski, M., Sosinska, H., and Lato, C. (1978) Dialkyltin maleates. *Pol.*, **97**, 171; (1979) *Chem. Abstr.*, **91**, 91771*v*.

Bone, S. P., and Sowerby, D. B. (1979) The crystal structure of tetraphenylantimony(V) formate. *J. chem. Res., Synop.*, **3**, **82**,; (1979) *Chem. Abstr.*, **91**, 140925*j*.

Bongisvanni, G. C. (1969) Experimental results obtained in 1958–68 with tin compounds and new organic fungicides for combating sugar beet Cercospora. *Ind. Sac. Ital.*, **62**, 237; (1970) *Chem. Abstr.* **72**, 131396*t*.

Bradely, D. C., Gaur, D. P., and Mehrotra, R. C. (1978) *Metal Alkoxides*. Academic Press, London.

Brook, A. G. (1955) Thermal rearrangements of organosilicon and organogermanium compounds. *J. Am. Chem. Soc.*, **77**, 4827.

Bulten, E. J. (1978) Fungicidal and bactericidal organotin compounds. *Ger. Offen.*, **2**, 801, 700; *Chem. Abstr.*, **89**, 180157*a*.

Buschhoff, M. (1971*a*). Triorganolead acylates, *Ger. Offen.*; 2, 032, 299; (1972) *Chem. Abstr.* **76**, 59754*w*.

Buschhoff, M. (1971*b*). Trialkyllead acetates. *Ger. Offen.*, 2, 032, 426; (1972) *Chem. Abstr.*, **76**, 59756*y*.

Cadogan, J. I. G., and Gosney, I. (1974) Formation of triphebyl arsinimines—preparation of diacetoxy-triphenyl arsonane. *J. Chem. Soc. Perkin I*, 466.

Cahours, A. (1960) *Ann. Chem.*, **114**, 354.

Calogero, S., Clemente, D. A., Peruzzo, V., and Tagliavini, G. (1979) Crystal structure of trichloro methyl acetato trivinyltin and Mössbauer spectroscopic characterization of trivinyl- and divinyl-*n*-butyltin carboxylates. *J. Chem. Soc. Dalton*, 1172.

Calogero, S., Furlan, P., Peruzzo, U., and Tagliavini, G. (1977*a*) Mössbauer study of some disubstituted distannoxanes. *J. organometal. Chem.*, **128**, 177.

Calogero, S., Furlan, P., Peruzzo, V., and Plazzogna, G. (1977*b*) Preparation of polymeric organotin carboxylates and organostannoxanes. Mössbauer and IR characterization. *Inorg. Chim. Acta*, **22**, 55.

Calogero, S., Ganis, P., Peruzzo, V., and Tagliavini, G. (1980) X-ray crystal analysis of tricyclohexyltin trifluoroacetate and Mössbauer data for R′ = dichloromethyl, trichloromethyl and trifluoromethyl, methyl and chloromethyl derivatives of $(Cyclo\text{-}C_6H_{11})_3SnO_2CR'$. *J. organometal. Chem.*, **191**, 381.

Cassellato, U., Vigato, P. A., and Vidali, M. (1978) Actinide complexes with carboxylic acids. *Coord. Chem. Rev.*, **26**, 85.

Catterick J., and Thornton, P. (1977) Structures and physical properties of polynuclear carboxylates. *Adv. inorg. Chem., Radiochem.*, **20**, 291.

Chow, Y. M., and Britton, D. (1975) Crystal structures of dimethylthallium acetate, tropolonate, acetylacetonate and dibenzoylmethide. *Acta Cryst.*, **B31**, 1929.

Christen, U., and Neumann, W. P. (1972) Acylation of Sn during the reaction from Sn–H, Sn–C, Sn–Sn and Sn–O groups with tetraacetate. *J. organometal. Chem.*, **39**, C58.

Clark, H. C., and Pickard, A. L. (1967) Organoindium chemistry. A convenient preparation of dimethylindium (III) *J. organometal. Chem.*, **8**, 427.

——— (1968) Organoindium chemistry II. Derivatives of dimethylindium(III) and methylindium (III). *J. organometal. Chem.*, **13**, 61.

Coates, G. E., and Hayter, R. G. (1953) Trimethylgallium (II) reactions with hydroxy and similar compounds. *J. Chem. Soc.*, 2519.

Cohen, A. D., and Dillard, C. R. (1970) Exchange reactions of organotin carboxylates. *J. organometal. Chem.*, **25**, 421.

Cookron, P. G., Deacon, G. B., Felder, P. W., and Farquharson, G. J. (1974) Organolead compounds. II. Structures and thermal decomposition of some diphenyllead bis(polyfluorobenzoates). *Aust. J. Chem.*, **27**, 1895.

Cragg, R. H., and Lappert, M. F. (1966) Amino derivatives of metals and metalloids, Part IV. Aminosilylation and amino phosphination of some unsaturated substrates. *J. Chem. Soc.*, A, **82**.

Croner, D. T., and Waber, J. T. (1965) Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Cryst.*, **18**, 104; *Chem. Abstr.*, **62**, 4712.

Cummins, R. A., and Dunn, P. (1964) Organotin carboxylates. *Aust. J. Chem.*, **17**, 185; *Chem. Abstr.*, **60**, 9303*b*.

Cummins, R. A., Dunn, P., and Oldfield, D. (1971) Preparation, properties and structure of some organotin acrylates. *Aust. J. Chem.*, **24**, 2257; *Chem. Abstr.*, **75**, 151884*r*.

Davies, A. G., and Harrison, P. G. (1967) Organometallic reactions VIII. Addition reactions of dibutyltin dimethoxide and related compounds. *J. Chem. Soc.*, (C), 1313.

Davies, A. G., Les Smith, Smith, P. J., and McFarlane, W. (1971) Organotin chemistry, IX. Investigations of the structure of some 1, 3-difunctional tetraalkyl distannoxanes by Mössbauer spectroscopy and ^{119}Sn heteronuclear double magnetic resonance. *J. organometal. Chem.*, **29**, 245.

Deacon, G. B. (1967) Organothallium compounds IV. Carboxylato bis(pentafluorophenyl) thallium(III) compounds and their complexes with 1,10-phenanthroline and 2,2′-bipyridyl. *Aust. J. Chem.*, **20**, 459.

Deacon, G. B. (1970) Synthesis of organometallic compounds by thermal decarboxylation. *Organometal. Chem. Rev.*, **A5**, 355.

Deacon, G. B., and Felder, P. W. (1970) Preparation and properties of triphenyllead carboxylates. *Aust. J. Chem.*, **23**, 1359.

Deacon, G. B., Farquharson, G. J., and Phillips, R. J. (1976) New decarboxylation syntheses of polyfluorophenyl organometallic compounds. *J. Fluorine Chem.*, **8**, 545.

Deacon, G. B., and Farquharson, G. J (1977) Decarboxylation syntheses of some polyfluorophenyltin and germanium compounds. *J. organometal. Chem.*, **135**, 73.

Deacon, G. B., and Green, J. H. S. (1968) Vibrational spectra of organometallic compounds. II. Dialkyl-and diphenylthallium(III) compounds. *Spectrochim. Acta, Part A*, **24**, 885.

Deacon, G. B., Green, J. H. S., and Nyholm, R. S. (1965) The chemistry of organothallium compounds, Part I. The preparations and properties of bis(pentafluorophenyl) thallium(III) compounds. *J. Chem.*, 3411.

Deacon, G. B., and Phillips, R. J. (1978) Organothallium compounds XIV. Thermal decomposition of some polyfluorobenzoato bis(polyfluorophenyl) thallium(III) compounds. *Austr. J. Chem.*, **31**, 1709.

Deacon, G. B., and Smith, R. N. M. (1980) The effect of Lewis acids on the thallation of polyfluoroarenes. *J. Fluorine Chem.*, **15**, 85 **92**, 181250*z*.

Debye, N. W. G., Fenton, D. E., Ulrich, S. E., and Zuckerman, J. J. (1971) ^{119}Sn Mössbauer and NMR study of trialkyltin acetates *J. organometal. Chem.*, **28**, 339.

Delmas, M., Maire, J. C., Richard, Y., Plazzogna, G., Peruzzo, V., and Tagliavini, G. (1971) Mössbauer spectroscopic studies of the compounds of tin. *J. organometal Chem.*, **30**, C101.

Doak, G. O., Long, G. G., and Freedman, L. D. (1965) IR spectra of some phenyl substituted pentavalent antimony compounds. *J. organometal. Chem.*, **4**, 82.

Doedens, R. J. (1976) Structure and metal-metal interactions in copper(II) carboxylate complexes. *Progr. Inorg. Chem.*, **21**, 209.

Domazetis, G., Magee, R. J., and James, B. D. (1978) ^{13}C NMR spectroscopy on butyltin compounds containing nitrogen, oxygen and sulphur ligands. *J. organometal. Chem.*, **148**, 339.

Donaldson, J. D., Knifton, J. F., and Ross, S. D. (1964) The fundamental vibrational spectra of the formates of the main group elements. *Spectrochim. Acta*, **20**, 847.

Drake, J. E., and Hemmings, R. T. (1973) Preparation and characterization of pseudohalogeno (methyl) germanes and related compounds. *Can. J. Chem.*, **51**, 302.

Drake, J. E., Hemmings, R. T., and Henderson, H. E. (1976) Silyl and germyl derivatives of thiolacetic acid. *Inorg. nucl. Chem. Lett.*, **12**, 563.

Drake, J. E., Henderson, H. E., and Hemmings, R. T. (1977) Silyl and germyl derivatives of trifluoroacetic and trichloroacetic acids. *Inorg. Chem.*, **16**, 1682.

Duncanson, L. A., Gerrard, W., Lapert, M. F., Pyszera, H., and Shafferman, R. (1958) IR spectra and structures of some acyloxy derivatives of boron. *J. Chem. Soc.*, 3652.

Dworkin, R. D., and Ejk, A. J. (1977) Diorganotin carboxylates. *Ger. Offen.*, 2, 626, 554; *Chem. Abstr.*, **86**, 140253*k*.

Eigenberger, E. (1940) *Fett. Scifen.*, **40**, 505.

Einstein, F. W. B., Gilbert, M. M., and Tuck, D. G. (1973) Crystal structure of acetato (dimethyl) indium (III). *J. Chem. Soc. Dalton*, 248.

Eisch, J. J., and Foxton, M. W. (1968) The carbonation of unsaturated organoaluminium compounds. *J. organometal. Chem.*, **11**, p. 7, *Chem. Abstr.*, **68**, 86695*u*.

Elliott., B. M., and Aldridge, N. N. (1977) Binding of triethyltin to cat hemoglobin and modification of the binding sites by diethyl pyrocarbonate. *Biochem. J.*, **163**, 583.

Ernst, L. (1974) Carbon-13 nuclear magnetic resonance spectra of arylthallium(III) bis(trifluoroacetates). *Org. Magn. Reson*, **6**, 540; (1975) *Chem. Abstr.*, **82**, 154639*v*.

Farrow, B. G., and Dawson, A. P. (1978) Investigation of the interaction of triethyltin with rat liver mitochondria using binding studies and Mössbauer spectroscopy. *Eur. J. Biochem.*, **86**, 85.

Ford, B. F. E., Liengme, B. V., and Sams. J. R. (1968) Mössbauer and IR evidence for the structures of triphenyltin carboxylates. *J. Chem. Soc., Chem. Commun.*, 1333.

——— (1969*a*). Organotin carboxylates : Mössbauer and IR study of triphenyltin carboxylates and novel compounds. *J. organometal. Chem.*, **19**, 53.

——— (1969*b*) Organotin carboxylates. Mössbauer and IR study of bonding differences in trimethyltin haloacetates. *J. organometal. Chem.*, **19**, 67.

Ford, B. F. E., and Sams, J. R. (1970) Organotin carboxylates. Mössbauer study of tetra and penta coordination in branded chain triphenyltin carboxylates. *J. organometal. Chem.*, **21**, 345.

——— (1971) Organotin carboxylates. Mössbauer and IR spectroscopy of some triphenyltin haloacetates and the test of point charge model. *J. organometal. Chem.*, **31**, 47.

Frankel, M., Gertner, D., Wagner, D., and Zilkha, A. (1965) Organotin esters of amino-acids and their use in peptide syntheses. *J. org. Chem.*, **30**, 1596.

——— (1967) Use of the interfacial polymerization method for the preparation of organotin esters. *J. organometal. Chem.*, **9**, 83.

Freeman, J. P. (1958) Carbonyl stretching frequencies of certain carboxylic acid derivatives. *J. Am. Chem. Soc.*, **80**, 5954.

Freeman, H. C., Stevens, G. N., and Taylor, I. F. (1974) Metal binding in chelation therapy: the crystal structure of D-penicillaminatolead(II). *J. Chem. Soc., Chem. Commun.*, 367.

Fukumoto, T., Kurosawa, H, and Okawara, R. (1970) Preparation of monomethyl- and monoethyl thallium compounds by means of some methyl and ethyl tin derivatives, *J. organometal. Chem.*, **22**, 627.

Galigne, J. L., Mouvert, M., and Falqueirettes, F. (1970) New determination of the crystalline structure of lithiumacetate dihydrate. *Acta Crystal. Sect.*, **B 26**, 368.

Garner, C. D., and Hughes, B. (1974) Divinyltin bis(trifluoroacetate) and its reactions with sodium slats of metal-carbonyl anions. *J. Chem. Soc., Dalton*, 1306.

——— (1975) Inorganic compounds containing the trifluoroacetate group. *Adv. inorg. Chem., Radiochem.*, **17**, 1.

Garner, C. D., Hughes, B., and King, T. J. (1975) Inorganic compounds containing trifluoroacetate group (III). Reactions of bis(trifluoroacetate) divinyltin with N-, O-, or N- and O-donor ligands and the crystal structure of 2, 2¹- bipyridyl bis(trifluoroacetato)divinyltin carboxylates. *J. Chem. Soc., Dalton*, 562; (1976) Preparation and characterization of the cyclodistannoxane $(CH_2 = CH)_4Sn_2$ $(OOCCF_3)_2O_2$. *Inorg. nucl. Chem. Lett.*, **12**, 859.

Gerrard, W., Lappert, M. F., and Shafferman, R. (1958) The chemistry of certain acyloxy boron compounds and boron chelates. *J. Chem. Soc.*, 3648.

Gilman, H., and Yablunky, H. L. (1941) Reactions of organobismuth compounds in liquid ammonia. *J. Am. Chem. Soc.*, **63**, 212.

Gilman, H., and Yale, H. L. (1951) Some new pentavalent salts of triarylbismuth compounds. *J. Am. Chem. Soc.*, **73**, 4470.

Glockling, F. (1969) *The Chemistry of Germanium.* Academic Press, London and New York.

Glushkova, V. P., and Kocheshkov, K. A. (1957*a*) Phenylthallium dicarboxylates. New method of synthesis of organothallium compounds of class $ArTlX_2$ *Dokl. Akad. Nauk. SSSR*, **116**, 233; (1958) *Chem. Abstr.*, **52**, 6236*i*.

——— (1957*b*) Reaction of direct substitution of hydrogen in organic compounds by thallium (thallation). *Izv. Akad. Nauk. SSSR Otdl Khim; Nauk.*, 1186 (1958) *Chem. Abstr.*, **52**, 6238*d*.

Goel, R. G. (1969) Organoantimony compounds. II : studies on tetra phenylantimony (V) derivatives. *Can. J. Chem.*, **47**, 4607.

Goel, R. G., Maslowsky, E. Jr., and Senoff, C. V. (1970) Far-infrared and Raman spectra of triorganoantimony (V) derivatives, R_3SbX_2. *Inorg. nucl. Chem. Lett.*, **6**, 833.

——— (1971) Organoantimony compounds (III) : Far infrared and Raman spectroscopic studies on triorganoantimony(V) derivatives, R_3SbX_2. *Inorg. Chem.*, **10**, 2572.

Goel, R. G., and Prasad, H. S. (1970) Studies on triphenylbismuth(V) derivatives, Ph_3BiX_2. *Cand. J. Chem.*, **48**, 2488.

Goel, R. G., and Ridley, D. R. (1972) Organoantimony compounds (V) Trimethyl-and triphenyl-antimony (V) derivatives of haloacetic acids. *J. organometal. Chem.*, **38**, 83.

Goel, R. G., Ruddick, J. N. R., and Sams, J. R. (1975) Antimony 121-Mössbauer spectroscopic study of bis(halogenoacetato) trimethylantimony derivatives. *J. Chem. Soc., Dalton* 67.

Goldanskii, V. I., Kharapov, V. V., Okhlobystin, O. Yu., and Rochev, V. Ya. (1968) *Chemical Applications of Mössbauer Spectroscopy.*, Ch. 6. (*Eds.* : Goldanskii, V. I., & Herber, R. H.). Academic Press, New York.

Goldanskii, V. I., Makarov, E. F., Stukant, R. A., Trukhtanov, V. A., and Khrapov, V. V. (1963) Study of the structure of polymeric organotin oxides, by the Mössbauer effect. *Dokl. Akad. Nauk. SSSR*, **151**, 357.

Gol'din, G. S., Averbakh, K. O., Yusim, M. A., Fedotov, N. S., and Kukyanova, I. A. (1973) Synthesis of organosilicon esters of hydrazino carboxylic acids. *Zh. Obshch. Khim.*, **43**, 781; *Chem. Abstr.*, **79**, 53417*d*.

Gorsich, R.D. (1974*a*) Trialkyllead acetates. U. S., 3, 824, 265; *Chem. Abstr.*, **81**, 91731*a*.

——— (1974*b*) Triaryllead acetates. *U. S.*, 3, 824, 187; *Chem. Abstr.*, **81**, 91730*z*.

Grab, G., and Boucard, M. (1968) Acute toxocity of some dialkyllead diacetates. *C. R. Soc. Biol.*, **162**, 1456; *Chem. Abstr.*, (1969), **70**, 104724*a*.

Graber, M., and Gras, G. (1969) Effect of a new organometallic compound, dibutyllead diacetates against tapeworms. II. Ovine taeniasis. *Rev. Elev-Med. Vet-Pays. Trop*, **22**, 85; *Chem. Abstr.*, **71**, 111307*r*.

Graddon, D. P., and Rana, B. A. (1977*a*) Lewis acidity of organotin carboxylates, isocyanates. *J. organometal. Chem.*, **136**, 19.

——— (1977*b*) Lewis acidity of organosilicon acetates. *J. organometal. Chem.*, **136**, 315.

Gray, V. R., and Alexander, A. E. (1949) Aluminium soaps. I. Viscosity and streaming bire fringence of aluminium soap solutions. *J. Phys. Coll. Chem.*, **53**, 23; *Chem. Abstr.*, **43**, 3688*e*.

Graziani, R., Bombieri, G, Forsellini, E., Furlan, P., Peruzzo, V., and Tagliavini, G. (1977) A tetranuclear complex of tin : crystal structure of $[\{(n\text{-}C_4H_9)_2Sn-OOCCCl_3\}_2O]_2$ and related properties in solution. *J. organometal. Chem.*, **125**, 43.

Grenie, Y., and Garrigon-Lagrange, C. (1972) Infrared spectra of glycine isotopic species isolated in an argon or nitrogen matrix. *J. Mol. Spectrosc.*, **41**, 240.

Grigore'v, A. I. (1963) Infrared absorption spectra of acetates of elements in groups I and II of the periodic system. *Russ. J. inorg. Chem.*, **8**, 409.

Habeeb, J. J., and Tuck, D. G. (1973) Coordination compounds of indium, Part XXI. Some compounds derived from Indium (III) acetate, including indium diacetate. *J. Chem. Soc., Dalton*, 243.

Habeeb, J. J., and Tuek, D. C. (1974) Stepwise elimination of methane in the reaction of dimethylindium (III) compounds with dibasic acids. *J. organometal. Chem.*, **82**, C25.

Hall, W. T., and Zuckerman, J. J. (1977) Tin(II) and dimethyltin(IV) derivatives of amino acids. *Inorg. Chem.*, **16**, 1239.

Hara, M. O., and Okawara, R. (1965) The preparation of trialkyltin hydrides by thermal decomposition of formates. *J. organometal. Chem.*, **3**, 484.

Harrison, P. G. (1970) Organobismuth chemistry. *Organometal. Chem. Rev., A.*, **5**, 183.

Hausen, H. D. (1972) Diethylindium acetate, preparation and structure. *J. organometal. Chem.*, **39**, C37.

Hausen, H. D., and Schwering, H. U. (1973) Dimethyl (or ethyl) indium acetates-preparation, properties and structure. *Z. anorg. allg. Chem.*, **398**, 119; *Chem. Abstr.*, **79**, 66443*g*.

Hausen, H. D., Sille, K., Wwidlein, J., and Schwarz, W. (1978) Methylgallium diacetate-preparation, properties and crystal structure. *J. organometal. Chem.*, **160**, 411.

Havranek, J., Mleziva, J., and Lycka, A. (1978) Triphenylantimony diester preparation. *J. organometal. Chem.*, **157**, 163.

Henderson, A., and Holliday (1965) Properties of tin(IV) tetracarboxylates. *J. organometal. Chem.*, **4**, 377.

Henderson, A., and Stockler, H. A. (1966) *Applications of the Mossbauer Effect in Chemistry and Solid State Physics* : *Tech. Rept. Ser.*, IAEA, Vienna, **50**, 110.

Herber, R. H. (1971) Mössbauer spectroscopy of organometallics : lattice dynamics and structure of butyltin compounds. *J. chem. Phys.*, **54**, 3755; *Chem. Abstr.*, **74**, 132485*z*.

Herber, R H., Stockler, H A., and Reichle, W. T. (1965) Systematics of Mössbauer isomer shifts of organotin compounds. *J. chem. Phys.*, **42**, 2447.

Hester, R. E, (1970) Synthesis of some trivinyltin carboxylates. *J. organometal. Chem.*, **23**, 123.

Hester, R. E., and Mascord, D. (1973) Vibrational spectra and structure of some trivinyltin carboxylates. *J. organometal. Chem.*, **51**, 181.

Ho, B. Y. K., Zubieta, J. A., and Zuckerman, J. J. (1975) X-ray crystal and molecular structure of trimethyltin glycinate, a polymeric, trigonal bipyramidal tin compound. *J. Chem. Soc., Chem. Comn.*, 88.

Ho, B. Y. K., and Zuckerman, J. J. (1973*a*) Structural variations in trimethyl- and tricyclohexyltin derivatives of amino acids- preference for association by nitrogen bringing. *Inorg. nucl. Chem. Lett.*, **9**, 849.

——— (1973*b*). Trialkyltin derivatives of aminoacids and dipeptides. *Inorg. Chem.*, **12**, 1552.

——— (1973*c*) Structural organotin chemistry. *J. organometal. Chem.*, **49**, 1.

Hoad, C. S., Mathews, R. W., Thakur, M M., and Gillies, D. G. (1977) Thallium-205, carbon-13 and proton NMR parameters for some monomethyl hallium(III) derivatives. *J. organometal. Chem.*, **124**, C31.

Holmes, J. R., and Kaesz, H. D. (1961) Tin-proton spin-spin coupling in methyltin halides and related compounds. *J. Am. Chem. Soc.*, **83**, 3903.

Honnick, W. D., and Zuckerman, J. J. (1978) Diorganotin halide carboxylates, thio carboxylates and halide naloacetates. *U. S. Announce. Index*, **79**, 87; (1979) *Chem. Abstr.*, **90**, 16862*j*.

——— (1979) Diorganotin halide carboxylates, triscarboxylates and halide haloacetates. *J. organometal. Chem.*, **178**, 133.

Hota, N. K., and Willis, C. J. (1968) Studies on trifluoroacetoxy germanes. *Can. J. Chem.*, **46**, 3921.

Inoue, S., and Yokov, Y. (1971) *V. Int. Conf. on organometal Chem.*, **1**, Moscow, 289.

Itoh, K., and Bernstein, H. J. (1956) *Can. J. Chem.*, **34**, 170.

Ittsukaichi, Y., Kawai, M., and Kondo, T. (1975) Dialkyltin S, O-β-mercaptopropionate. *Japan Kokai*, **75**, 112; (1976) *Chem. Abstr.*, **84**, 122039*z*.

Jelen, A., and Lindqvist, O. (1969) The crystal structure of potassium triformato stannate (II) $KSn(HCOO)_3$. *Acta Chem. Scand.*, **23**, 3071.

Jones, L. H., and McLaren, E. (1954) Infrared spectra of CH_3COONa and CD_3COONa and assignments of vibrational frequencies. *J. chem. Phys.*, **22**, 1976.

Kaez, H. D., and Stone, F. G. A. (1960) *Organometallic Chemistry* (*Ed*: Leiss, H.). Reinhold, New York, 1239.

Kalsotra, B. L., Multani, R. K., and Jain, B. D. (1971) Carboxylato complexes of tricyclopentadienylcerium(IV) chloride and bis(indenylcerium)(IV) dichloride. *J. Chin. Chem. Soc.*, (*Taipei*), **18**, 189.

Khudobin, Yu. I., and Kharitonov, N. P. (1975) Reaction of triethylsilane with unsaturated mono- and di-carboxylic acids. *Izv. Akad. Nauk. SSSR, Ser Khim.*, **3**, 701; *Chem. Abstr.*, **83**, 58924*j*.

Kimura, T., Ueki, T., Yasuoka, N., Kasai, N., and Kakudo, M. (1969) The crystal and molecular structure of the high melting point isomer of bis(1,2-diethoxy carbonyl-ethyl) tin dibromide. *Bull. Chem. Soc. Jpn.*, **42**, 2479.

Kitching, W., Moore, C. J., Doddrell, D., and Alcock, W. (1975) ^{13}C NMR spectra of arylthallium trifluoroacetates. *J. organometal. Chem.*, **94**, 469.

Knips, U., and Huber, F. (1976) Dimethyl-thallium, tin and lead compounds preparation by anion exchange with thallium(I) salts. *J. organometal. Chem.*, **107**, 9.

Kocheshkov, K. A., Panovaev, E. M., and Zemlyanskii, N. N. (1961) Stepwise formation of an element-oxane chain in the presence of diazomethanes. *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.*, 2255.

Kohama, S., and Matsumoto, S. (1974) Organoacetoxy silanes. *Kagaku To Kogyo* (*Osaka*), **48**, 308; *Chem. Abstr.*, **82**, 57798*p*.

Kolosova, N. D., Zemlyanskii, N. N., Azizov, A. A., Zakharov P. I., Ustynyuk, Yu. A., Barminova, N. P., and Kocheshkov, K. A. (1974) Synthesis of cyclopentadienyltin triacylates and dicyclopentadienyltin (chloro) acetate. *Dokl. Akad. Nauk SSSR*, **218**, 350; *Chem. Abstr.*, **82**, 43551*r*.

Kozuka, Ko., Kurioka. S., Yasumoto, T., Kobayashi, S., Otoshi, N., and Kubota, A. (1978) Acrylic fibers. *USSR*, 629, 891; (1979) *Chem. Abstr.*, **90**, 40109*g*.

Kozuka, S., and Nakagami, J. I. (1977) The reaction of benzyol peroxide with trimethyl-phenyl tin. A polar mechanism of formation of trimethyltin benzoate. *J. organometal. Chem.*, **135**, CI.

Kronstein, M. (1973) Organolead antifoulants. Zeroing in on marine fouling. *Paint Varn. Proc.*, **63**, 47; (1974) *Chem. Abstr.*, **80**, 1648*y*.

Kudo, T., and Nose, A. (1975) Reaction of trialkylborane, III: Reaction of trialkyl borane with carbonylcompounds. *Yakugaku Zasshi*, **95**, 1411; (1976) *Chem. Abstr.*, **84**, 90200*b*.

Kuivila, H. G. (1964) *Adv. organometal. Chem.*, **1**, 47.

Kurosawa, H., Fukumoto, T., and Okawara, R. (1969) A new route to methylthallium compounds in an aqueous solution. *Inorg. nucl. Chem. Lett.*, **5**, 473.

Kurosawa, H., and Okawara, R. (1967*a*). The existence of monomethyl thallium(III) species. *Inorg nucl. Chem. Lett.*, **3**, 21 and 93.

——— (1967*b*) Preparation and properties of monoalkyl thallium derivatives. *J. organometal. Chem.*, **10**, 211.

——— (1969) Existence of two types of Tl–OAc bands (Thallium-acetate) in the far infrared spectra of some alkylthallium (Ph, Me) acetate derivatives. *J. organometal. Chem.*, **19**, 253.

Kurosawa, H., and Okawara, R. (1970) Recent advances in organothallium chemistry. *Organometal. Chem. Rev.*, A, **6**, 65.

Kurosawa, H. Tanaka, M., and Okawara, R. (1968) Some methyl (phenylethylnyl) and methyl (cyano)thallium derivatives. *J. organometal. Chem.*, **12**, 241.

Lappert, M. F. (1962) Co-ordination compounds having carboxylic esters as ligands, Part II. Relative acceptor strengths of some group III and IV halides. *J. Chem. Soc.*, 542.

Lee, A. G. (1970*a*) Organothallium chemistry. *Q. Rev. Chem. Soc.*, **24**, 310.

——— (1970*b*) Derivatives of phenylthallium(III). The preparation and properties of phenylthallium(III) compounds. *J. organometal. Chem.*, **22**, 537.

——— (1975) *Organometallic Reactions* (*Eds.* : Becker, E. I. & Tsutsui, M.). Wiley-Interscience, New York, **5**.

Leebrick, J. R., Eilender, A. L., and Veliz, R. G. (1969) Paracetic acid route to triphenyllead acetate from hexaphenyl dilead. *J. organometal. Chem.*, **18**, 370.

Lesbre, M., Mazerolles, P., and Satge, J. (1971) *The Organic Compounds of Germanium.* John Wiley & Sons, London.

Lisovin, E. G., and Komarov, N. V. (1978) Reaction of vinyloxy organosilanes with carboxylic acids. *Zh. Obshch. Khim.*, **48**, 856; (1978) *Chem. Abstr.*, **89**, 43590*x*.

Lohmann, D. H. (1965) Ethyltin compounds, infrared spectra in the region 2–45μ. *J. organometal. Chem.*, **4**, 382.

Luijten, J. G. A., van der Kerk, G. J. M., and Janseen, M. J. (1963) Organotin compounds; structures of trialkyltin acylates. *Rec. Trav. Chim. Pays-Bas*, **82**, 90; *Chem. Abstr.*, **59**, 406*h*.

Luneva, L. K., Lezhava, L. D., Vasneva, N. A., Sladkov, A. M., and Korshak, V. V. (1975) Synthesis of organosilicon and organogermanium 2-acetylene compounds with difunctional oxygen containing groups. *Tezisy, Dokl. Vses. Konf Khim Alsetilene*, 185; (1978) *Chem. Abstr.*, **89**, 129613*u*.

Maddox, M. L., Flitcroft, N., and Kaesz, H. D. (1965) Proton magnetic resonance and IR spectral parameters for the Sn-H bond in some alkyl- and phenyl-stannes. *J. organometal. Chem.*, **4**, 50.

Maeda, Y., Dillard, C. R., and Okawara, R. (1966) Dimethyltin diacetate and its configuration. *Inorg. nucl. Chem. Lett.*, **2**, 197.

Maeda, Y., and Okawara, R. (1967) Studies on dialkyltin diacetate derivatives. *J. organometal. Chem.*, **10**, 247.

Magnuson, J. A., and Knaub, E. W. (1965) Determination of alkoxy and mercapto germanes by acetylation and with hydrogen bromide. *Anal. Chem.*, **37**, 1607.

Mathiasch, B., and Mitchell, T. N. (1980) Tetramethylditin complexes : a general method for the preparation of a class of compounds with an unusual tin-tin bond. *J. organometal. Chem.*, **185**, 351.

Mathur, S., and Mehrotra, R. C. (1967) Organic derivatives of germanium (IV). Reactions of organogermanium alkoxides with carboxylic acids. *J. organometal. Chem.*, **7**, 227.

Matsuda, S., Matsuda, H., Yamaji, Y., and Ninomiya, K. (1970*a*) Organometallic compounds; thermal decomposition of dialkyltin dicarboxylates. *Kogya Kagaku. Zasshi.*, **73**, 1007; *Chem. Abstr.*, **73**, 87983*b*.

Matsuda, H., Moriguchi, J., and Yamaji, Y. (1970*b*) Thermal decomposition of dialkyltin bis-substituted carboxylates. *Kogya Kagaku Zasshi*, **73**, 1013; *Chem. Abstr.*, **73**, 87985*d*.

Matsumura, K., and Fukumoto, O. (1969) Organoaluminium compounds. *Japan*, 6926, 451; (1970) *Chem. Abstr.*, **72**, 21778*m*.

Matsumura, Y., Shindo, M., and Okawara, R. (1971) Preparation and properties of triorganoantimony thioglycolates and glycolates. *J. organometal. Chem.*, **27**, 357.

Mayerle, E. A. and Craig, R. L. (1969) Trialkyllead acetates. *U. S.*, 3, 450, 734; (1969*b*) *Chem. Abstr.*, **71**, 50224*n*.

Mc Gee, C. G. (1949) Aluminium mono laurate and proposed structures for aluminium soaps. *J. Am. Chem. Soc.*, **71**, 278.

McKillop, A., Ford, M. E., and Taylor, E. C. (1974) A comment on the acetoxy thallation-induced lactonization of 2- endonorborene carboxylic acids. *J. org. Chem.*, **39**, 2434.

McKillop, A., Fowler, J. S., Zelesko, M. J., Hunt, J. D., Taylor, E. C., and McGillivray, G. (1969) Thallium in organic synthesis. IX. Facile thallation of aromatic compounds with thallium(III) trifluoroacetate. *Tetrahedron Lett.*, **29**, 2424.

——— (1971) Thallium in organic synthesis. XXII. Electrophilic aromatic thallation using thallium(III) trifluoroacetate. A simple synthesis of aromatic iodides. *J. Am. Chem. Soc.*, **93**, 4841.

McWhinnie, W. R., Danie, N. S., and Pant, B. C. (1973) Organotellurium carboxylates and related compounds—structural and synthetic consideration. *J. organometal. Chem.*, **63**, 305.

Mehrotra, R. C. (1953) Preparation of aluminium tri soaps, *Nature*, **172**, 74.

——— (1965) Synthesis and properties of heavy metal soaps—preliminary lecture delivered at 6th International symposium on lubricants and lubrication technology. *Wissenchaftliche Zeitschrift der Friedriche-Schiller-Univ. gend Mathamatich-Natur. Wisseno Raftliche-Reiche* Heft 2 Jahrgard, **14**, 171.

Mehrotra, R. C., Bohra, R., and Gaur, D. P. (1978) *Metal-β-Diketones and Allied Derivatives.* Academic Press, London.

Mehrotra, R. C., and Pant, B. C. (1963) Organic derivatives of silicon. Part III—silicon and organosilicon derivatives of mandelic acid. *Indian J. Chem.*, **1**, 380.

Mehrotra, R. C., Rai, A. K., Singh, A., and Bohra, R. (1975) Oxime and hydroxylamine derivatives of metal and metalloids. *Inorg. Chem. Acta. Rev.*, **13**, 91.

Mehrotra, R. C., Srivastava, G., and Vasanta, E. N. (1978*a*) Synthesis and reactions of tin tetracarboxylates. *Inorg. Chim. Acta.*, **26**, 47.

——— (1978*b*) Reactions of tin tetracarboxylates with β-diketones. *Inorg. Chim. Acta*, **30**, 23.

——— (1980) Reactions of tin tetraacetate with sulphur ligands. *Inorg. Chim. Acta*, **47**, 125.

Meinema, H. A., and Marten, H. F. (1977) Preparation of ^{14}C labelled tributyltin acetate and dibutyltin dichloride. *Synth. React. Inorg. Metal. Org. Chem.*, **7**, (5), 455.

Meinema, H. A., and Noltes, J. G. (1972) Investigations on organoantimony compounds VI. Preparation and properties of thermally stable dialkylantimony(V) compounds of the types, $R_2Sb(OR)_3$, $R_2Sb(OAC)_3$, $R_2Sb(O)OH$. *J. organometal. Chem.*, **36**, 313.

Melnichenko, L. S., Zemlyanskii, N. N., Kolosova, N. D., and Kocheshkov, K. A. (1971) Radical rearrangement in a series of acyl derivatives of tin. *Dokl. Akad. Nauk., SSSR* **198**, 1348; *Chem. Abstr.*, **75**, 118388*e*.

Melnichenko, L. S., Zemlyanskii, N. N., Samurskaya, K. A., and Kocheshkov, K. A. (1970) Synthesis of tin and germanium tetraacylates. *Dokl. Akad. Nauk. SSSR*, **190**, 351; *Chem. Abstr.*, **73**, 3436*h*.

Mitchell, T. N. (1973) Carbon-13. NMR investigations on organotin compounds. *J. organometal. Chem.*, **59**, 189.

Morikawa, T. (1975) Thermal decomposition and stabilization of poly(vinylchloride). IR absorption spectra of alkyltin carboxylates. *Kagaku. To Kogyo (Osaka)*, **49**, 98; (1976) *Chem. Abstr.*, **84**, 5795*g*.

Morris, M. L., and Bush, D. H. (1956) Properties and infrared absorption spectra of complexes of cobalt (III) with pentadentate ethylenediaminetetraacetic acid and hydroxy ethylene diamine triacetic acid. *J. Am. Chem. Soc.*, **78**, 5178.

Motohashi, A., Sayama, S., and Kishihara, T. C. (1979) Bis(tributylstannyl) benzene dicarboxylic acid salts. *Japan*, 7, 961, 154; *Chem. Abstr.*, **91**, 140998*k*.

Nakamura, K. (1958) Normal vibrations of an acetate ion and a deuterated acetate ion. *Bull. Chem. Soc. Japan*, **79**, 1411 and 1420; (1959) *Chem. Abstr.*, **53**, 6768*c*.

Nakamura, K. (1963) *IR Spectra of Inorganic and Coordination Compounds.* Wiley & Sons, New York

Narain, R. P., and Kaur, A. J. (1978) Reactions of methyltrimethoxy- and methyldiethoxysilanes with salicylic, lactic, mandelic and benzilic acids. *Indian J. Chem. Soc.*, **A16**, 355.

Nesmeyanov, A. N., and Kocheshkov, K. A. (1960) *Methods of Elemental Organic Chemistry.* North Holland, Amsterdam, 410.

Neth. Appl. (1964) New organobismuth compounds6, 405, 309; (1964). *Chem. Abstr.*, **62**, 16300*e*.

Novikova, Z. S., Skorobogatore, Ya. S., Prishchenko, A. A. and Lusteenko, I. F. (1976) Synthesis of diphosphorus substituted esters of acetic acid. *Zh. Obsch. Khim.* **46**, 571 and 576; *Chem. Abstr.*, **85**, 5797*e*.

Okada, T., and Okawara, R. (1972) The reaction of triphenylphospine with some organometal haloacetates. *J. organometal. Chem.*, **42**, 117.

——— The pyrolysis of some trimethyltin bromoacetates and related methyl metal acetate derivatives. *J. organometal. Chem.*, **54**, 149.

Okawara, R. (1965) Chemical structure of organotin compounds. *Nippon Kagaku Zasshi*, **86**, 543.

Okawara. R., and Hara, M. O. (1963) Presence of a low polymer of triethyltin formate in solution. *Bull. Chem. Soc. Japan*, **36**, 623.

——— (1964) The IR and far IR of trialkyltin formates. *J. organometal. Chem.*, **1**, 360.

——— (1971) *Organotin Compounds*, Vol. II (*Ed.* : A. K. Sawyer, New York). Marcell *Dekker*, 253.

Okawara, R., and Wada, M. (1967) Structural aspects of organotin compounds. *Adv. organometal. Chem.*, **5**, 137.

Okawara., R., Webster, D. E., and Rochow, E. G. (1960) IR spectra, of methylacetoxysilanes and some methyltin carboxylates. The configuration of trimethyltin and dimethyltin cations. *J. Am. Chem. Soc.*, **82**, 3287.

Ol'dekop, Yu. A., Maier, N. A., and Shirokiev, V. L. (1979) Acylates of mercury (I) oxide in an anion exchange reaction synthesis of tin tetracylates and some organometallic acylates. *Vestri. Akad. Nauk. SSSR, Ser. Khim. Nauk*, **4**, 128; *Chem. Abstr.*, **91**, 175460.

Oldham, C. (1968) Complexes of simple carboxylic acids. *Progr. inorg. Chem.*, **10**, 223.

Ouchi, A., Uehiro, T., and Yoshino, Y. (1975) ^{13}C NMR of some triaryl and trialkylantimony and bismuth derivatives. *J. inorg. nucl. Chem.*, **37**, 2347.

Pande, K. C., and Winstein, S. (1964) Oxymercuration and oxythallation of norbornadiene and related olefins (I). *Tetrahedron Lett.*, **46**, 3393.

Pant B. C. (1972) Synthesis of organotelluriumacetates. *Letrahedron Tett.*, **47**, 4779.

——— (1974) Diaryltellurium diacetates : preparations, reactions and spectral studies. *J. organometal. Chem.*, **65**, 51.

Pant, B. C., Davidson, W. E., and Henry, M. C. (1969) Acetylenic derivatives of lead. *Org. Prep. Proc.*, **1**, 29.

Pant, B. C., McWhinnie, W. R., and Dance, N. S. (1973) Structural and synthetic consideration of organotellurium carboxylates and related compounds. *J. organometal. Chem.*, **63**, 305.

Peruzzo, V., Plazzogna, G., and Tagliavini, G. (1969*a*). Electrochemical preparation of trimethyltin carboxylates. *J. organometal. Chem.*, **18**, 89.

——— (1969*b*) Preparing a soluble form of trimethyltin acetate. *J. organometal. Chem.*, **16**, 500.

——— (1970) Preparation and properties of some trivinyltin carboxylates. *J. organometal. Chem.*, **24**, 347.

——— (1972) The preparation and properties of some allyltin carboxylates. *J. organometal. Chem.*, **40**, 121.

Peruzzo, V., Plazzogna, G., and Tagliavini, G. (1974*a*) Preparation and characterization of tetra vinyl 1,3-diacyloxy and tetra vinyl-l-acyloxy-3-hydroxy-di-stannoxanes. *Grazz. Chim. Ital.*, **104**, 767.

Peruzzo, V., and Tagliavini, G. (1974*b*). The cleavage of tin-allyl bonds in $R_2(CH_2{=}CH{-}CH_2)_2Sn$ substrates as a route to organostannoxanes. *J. organometal. Chem.*, **66**, 437.

Pestunovich, V. A., Albanov, A. I., Larin, H. F., Ignateva, L. P., and Voronkov, M. G. (1978) Complexes of organyl triacyloxysilanes with acetic and trifluoroacetic acid salts. *Izv. Akad. Nauk. SSSR Ser Khim.*, **9**, 2185; (1979) *Chem. Abstr.*, **90**, 23160z.

Platt, R. H., and Maddock, A. G. (1971) Mössbauer spectra and structures of organotin compounds. The relationship between quadrupole splitting and intermolecular association. *J. Chem. Soc., A*, 1191; *Chem. Abstr.*, **75**, 4899w.

Plazzogna, G., Peruzzo, V., Furlan, P., and Tagliavini, G. (1975) The preparation of distannoxanes, $(R_2SnO_2CMPh_3)_2O$ with R=n—butyl, phenyl, vinyl, allyl and M=carbon, silicon and germanium. *Gazz. Chim. Ital.*, **105**, 1233; (1976) *Chem. Abstr.*, **85**, 21563f.

Plazzogna, G., Peruzzo, V., and Tagliavini, G. (1970) The configuration of some 1, 1, 2, 2-tetraphenyl-1,2-diacyloxyditin-compounds in solution. *J. organometal. Chem.*, **24**, 667.

Podar, C., and Sams, J. R. (1969). Organotin carboxylates. (Mössbauer and IR study of bonding differences in trimethyltin haloacetates). *J. organometal. Chem.*, **19**, 67.

Poller, R. C. (1965) Coordination in organotin chemistry. *J. organometal. Chem.*, **3**, 321.

Poller, R. C. (1970) *The Chemistry of Organotin Compounds.* Logos Press, London; Newmann, W. P. (1970) *The Organic Chemistry of Tin.* John Wiley & Sons, London.

Poller, R. C., Ruddick, J. N. R., Taylor, B., and Tolley, D. L. B. (1970) Mössbauer spectra of organotin compounds. III. Compounds showing Mössbauer effects at room temperature. *J. organometal. Chem.*, **24**, 341.

Polyakov, V. S., Sul'zhenko, N. K., and Zuev. L. G. (1973) Petroleum oil base grease. *USSR*, 392, 086; *Chem. Abstr.*, (1974)., **81**, 5233k.

Pope, C. (1881) *Ber.*, **14**, 1875.

Razuvaev, G. A., Mitrofanova, E. V., Dadonov, A. A., and Mol'kova, L. N. (1970) Synthesis and some reactions of diethyl (α—(tertbutylperoxy) ethoxy) thallium. *Izv. Akad. Nauk. SSSR Ser V. Khim*, (2), 465; *Chem. Abstr.*, **73**, 3971k.

Reichle, W. T. (1966) Tetra neophyltin and its derivatives: the effects of steric hindrance in organotin chemistry. *Inorg. Chem.*, **5**, 87.

——— (1969) Pyrolysis of phenyltin benzoates and related substances. *J. organometal. Chem.*, **18**, 105.

Reifenberg, G. H., and Gitlitz, M. H. (1973) Organotin bromides and chlorides. *S. Africa*, **72**, 02, 018; *Chem. Abstr.*, **79**, 18853w.

Reinheckel, H., Haage, K., and Ludwig, H. (1975) Reactions with aluminium alkyls, XVI : conversion of phenylethylaluminium dichlorides with some carboxylic derivatives. *J. prakt. Chem.*, **317**, 359; *Chem. Abstr.*, **83**, 114535x.

Robert, D., and Adam, E. J. (1976) Diorganotin carboxylates. *Ger. Offen.*, 2, 554; 626, (1977) *Chem. Abstr.*, **86**, 140253k.

Robiette, A. G., and Thompson, J. C. (1965) The infrared spectra of some silyl esters. *Spectrochim. Acta*, **21**, 2023.

Rosenberg, S. D., Ingham, R. K., and Gilman, H. (1960) Organotin compounds. *Chem. Rev.*, **60**, 459.

Sartori, P., and Adelt, H. (1973) Reactions of perfluoro carboxylic acids. Preparation and properties of tetrafluoroisonicotinic acid derivatives of Group II B. *J. Fluorine Chem.*, **3**, 275; (1974) *Chem. Abstr* , **80**, 59813x.

Sartori P., and Frohn, H. J. (1974) Perfluoro dicarboxylic acids. V. Thermal decarboxylation of tetrafluoro terephthalic acid salts of group II B. *Chem. Ber.*, **107**, 1195; *Chem. Abstr.*, **81**, 78273h.

Sartori, P., and Weidenbruch, M. (1967) Reactions of metal halides with perfluoromonocarboxylic acids, (V). Preparation and properties of perfluoroacyloxy compounds of group IV elements. *Chem. Ber.*, **100**, 2049; *Chem. Abstr.*, **67**, 32301y.

Sawyer, A. K. (1971) *Organotin compounds*, Vol. III. (*Ed.*: Sawyer, A. K.) Marcell Dekker, New York.

Sawyer, A. K., and Kuivila, H. G. (1960) 1,2-Diacyloxyditins. *J. Am. Chem. Soc.*, **82**, 5958.

——— (1962) 1,2-diacyloxyditins : a new class of organotin compound and mechanistic aspects of the reaction of di-*n*-butyltin dihydride with acetic acid. *J. org. Chem.*, **27**, 610 & 837.

Schmidbauer, V. H., Mitschke, K. M., and Weidlein, J. (1971) Tetramethylantimony acetate and related compounds. *Z. anorg. allg. Chem.*, **386**, 147.

Seifullina, I. I., Verbetskaya, T. G., Kravchenko, T. P., and Skryler, L. D. (1978) New complexes of a series of salts of bivalent metals with acetic and formic acids. *Chugaev. Sovesh ch po Khimi Kompleks, Soedin*, 354, Ref. *Zh. Khim.*; (1979) *Chem. Abstr.*, **90**, 33302*m*.

Semenova, N. V., and Komarov, N. V. (1972) Vinyl esters of β-silicon containing carboxylic acids. *Izv. Akad. Nauk SSSR Ser Khim*, 185; *Chem. Abstr.*, **77**, 19721*x*.

Seyferth, D., Armbrecht, F. M. Jr., Prokai, B., and Cross, R. J. (1966) Halogenated organotin compounds as CX_2 transfer agents. *J. organometal. Chem.*, **6**, 573.

Seyferth, D., Prokai, B., and Cross, R. J. (1968) The thermal decomposition of organometallic heavy metal trihaloacetates in the presence of olefins. *J. organometal. Chem.*, **13**, 169.

Seyferth, D., Tronich, W., and Armbrecht, F. M. (1969) Halomethylmetal compounds. XXVI concerning the mechanism of dichlorocarbene transfer from trimethyltin trichloroacetate to olefines. *J. Am. Chem. Soc.*, **91**, 3218.

Shapiro, H., and Frey, F. W. (1968) *The Organic Compounds of Lead.* John Wiley & Sons, New York, 295 pp.

Shevchenko, L. L. (1963) Infrared spectra of slats and complex compounds of carboxylic acids and some of their derivatives. *Russ. Chem. Rev.*, **32**, 201; *Chem. Abstr.*, **59**, 4676*f*.

Shindo, M., and Okawara, R. (1966) The IR study of trimethylantimony (V) derivatives containing Sb-O bonds. *J. organometal. Chem.*, **5**, 537.

Simons, P. B., and Graham, W. A. G. (1976*a*) Studies of organotin chemistry I. Preparation and properties of new, soluble forms of trimethyltin formate and acetate. *J. organo.netal. Chem.*, **8**, 479.

——— (1976*b*) Trimethyltin chloroacetates: IR and NMR spectroscopic study. *J. organometal. Chem.*, **10**, 457.

Singh, A., Srivastava, G., Gupta, V. D., and Mehrotra, R. C. (1974) Organometallic hydroxylamines and oximes. *J. organometal. Chem. Rev.*, **64**, 145.

Skinner, C. E. (1974) Organolead compounds as paint biocides. *Paint Varn. Procd.*, **64**, 43; *Chem. Abstr.*, **81**, 171405*n*.

Smith, L., and Smith, P. J. (1975) Organotin compounds and applications. *Chem. Brit.*, **11**, 208, 226; *Chem. Abstr.*, **83**, 79306*z*.

Smith, P. J., Hyams, R. L., Brooks, J. S., and Clarkson, R. W. (1979) Synthesis of air stable triorganotin derivatives of aminoacids. *J. organometal. Chem.*, **171**, C29.

Sowerby, D. B. (1979) The crystal structure of triphenylantimony diacetate. *J. chem. Res. Synop.*, **3**, 80; *Chem. Abstr.*, **91**, 123816*g*.

Spinner, E. (1964) The vibration spectra of some substituted acetate ions. *J. Chem. Soc.*, 4217.

Srivastava, T. N., and Bhattacharya, S. N. (1968) Some triaryltin acetates. *J. Indian Chem. Soc.*, **45**, 764.

Srivastava, T. N., Griffiths, J. E., and Onyszchuk, M. (1962) Derivatives of monogermane II. Preparation and properties of germyl pseudo halides and related compounds. *Can. J. Chem.*, **40**, 739.

Srivastava, T. N., and Onyszchuk, M. (1963) Organogermanium compounds IR spectra of some acetoxy germanes. *Can. J. Chem.*, **41**, 1244

Srivastava, T. N., and Tandon, S. K. (1967) Triaryl-germanium derivatives. *Z. anorg. allg. Chem.*, **353**, 87; *Chem. Abstr.*, **67**, 90895*f*.

Stapfer, C. H., Dworkin, R. D., and Weisfeld, L. B. (1970) Diorganotin oxide/carboxylic ester reactions. *J. organometal. Chem.*, **24**, 355.

Stapfer, C. H. (1974) Organotin mercaptocarboxylates. *U.S.*, 3, 846, 459; (1975) *Chem. Abstr.*, **82**, 86416*t*.

Stockler, H. A., Sano, H., and Herber, R. H. (1967) Temperature dependence of the Mössbauer recoils fraction in organotin compounds. *J. Chem. Phys.*, **47**, 1567.

Syutkina, O. P., Panov, E. M., and Kocheshkov, K. A. (1973) Preparation of diaryllead diacylates. *Zh. Obshch. Khim*, **43**, 6,1322; *Chem. Abstr.*, **79**, 66498*f*.

Talbot, J. H., Van Nie Kerk, J. N., and Schoening, F. R. L. (1953) Crystal structure of $Zn(CH_3COO)_2 . 2H_2O$. *Acta cryst.*, **6**, 720 (1954) *Chem. Abstr.*, **48**, 19*b*.

Tanaka, T. (1970) Vibrational spectra of organotin and organolead compounds. *Organometal. Chem. Rev., A*, **5**, 1.

Tanaka, M., Kurosawa, H., and Okawara, R. (1969) Preparation of mixed diorganothallium (III) isobutyrates and their replacement reaction with tetramethyltin. *J. organometal. Chem.*, **18**, 49.

——— (1970) Redistribution reaction of some dialkyl thallium (III) compounds. *J. organometal. Chem.*, **21**, 41.

Taylor, E. C., Kienzle, F., Robey, R. L., McKillop, A., and Hunt, J. D. (1971) Thallium in organic synthesis XXIII. Electrophillic aromatic thallation. Kinetics and applications to orientation control in the synthesis of aromatic iodides. *J. Am. Chem. Soc.*, **93**, 4845.

Taylor, E. C., Attland, H. W., and McKillop, A. (1975) Thallium in organic synthesis, XL: preparation and synthetic utility of diaryl thallium trifluoroacetates. *J. org. Chem.*, **40**, 2351.

Topchiev, A. V., Paushkin, Ya. M., Prokhorova, A. A., Kurashev, M. V. (1959) Boron compounds–reactivity of triallyl boron. *Dokl. Akad. Nauk. SSSR*, **128**, 110; (1960) *Chem. Abstr.*, **54**, 1268*i*.

Toporcer, L. H., Dessy, R. E., and Green, S.I.E. (1965) A kinetic and mechanistic study on the cleavage of the carbon-carbon bond. The importance of coordination. *J. Am. Chem. Soc.*, **87**, 1236.

Triotskaya, L. S., Denisova, V. N., and Zakharova, R. P. (1978) Synthesis of sillicon containing organotin derivatives of maelic and thioglycolic acids and study of their stabilizing activity in the thermal degradation of poly(vinyl chloride). *Fiz-Khim osn sent pererab Polini*, **3**, 28; *Chem. Abstr.*, **91**, 157827*b*.

Tzschach, A., and Voigtlander, We. (1973) Organoarsenic compounds, XX: synthesis and reactivity of diphenylarsinocarboxylic acids. *Z. anorg. allg. Chem.*, **396**, 39.

Uemura, S., Miyoshi, H., Okano, M., Morishima, I., and Inubushi, T. (1979) Oxythallation of norbornene derivatives with thallium(III) acetate in methanol. *J. organometal. Chem.*, **165**, 9.

Uemura, S., Miyoshi, H. Tara, H., Okano, M., and Tohikawa, K. (1976) Acetoxy thallation of terminal acetylenes. *J. Chem. Soc., Chem. Commun.*, **6**, 218.

Uemura, S., Miyoshi, H., Wakasurguli, M., Okano, M. Itoh, O., Izumi, T., and Ichikawa, H. (1980) Phenyltolyl thallium(III) bis(trichloroacetates) preparation and reactions. *Bull. Chem. Soc. Japan*, **53**, 553.

Van Beelen, D. C., Vos, D de, Bots, G. J. M., Van Doorn, L. J., and Wolters, J. (1976) ^1H and ^{13}C – NMR of compounds–$(CH_3CH_2)_n$ Pb $(OAc)_{4-n}$($n = 2 - 4$). *Inorg. nucl. Chem. Lett.*, **12**, 581.

Van den Berghe, E. V., Van der Kelen, E. V., and Albert, G. P. (1968) Study of the structure of trimethyltin haloacetates by NMR and IR. *Inorg. Chim. Acta*, **2**, 89.

Van der Kerk, G. J. M. (1976). Organotin chemistry; past, present and future. *Adv. Chem. Ser.*, 157; (1977) *Chem. Abstr.*, **86**, 106688*w*.

Vilarem, M., and Maire, J. C. (1966) Structure of tributyltin salts. Study by IR spectroscopy. *C. r. Ser. C.*, **262**, 480; *Chem. Abstr.*, **64**, 18697*b*.

Voronkov, H. G., D'yakov, V. M., and Gubanov, L. I. (1979) Trifluoroacetoxy methyl trialkoxy (alkyl) silanes. *USSR*, 574, 929; *Chem. Abstr.*, **90**, 204244*a*.

Voronkov, M. G. Mirskov, R. G., Cherkova, V. G., and Shochilova, L. V. (1972) Triethylstannyl derivatives of alkanoic acids. *Dokl. Vses Konf. Khim Atsetilene*, **2**, 193; (1993) *Chem. Abstr.*, **79**, 78903*x*.

——— (1974) Trialkylstannyl haloacetylene carboxylates. *USSR*, 427, 944; *Chem. Abstr.*, **81**, 49833*k*.

Voron Kov, M. G., Yarosh, O. G., Shchukina, L. V., and Tatarinova, A. A. (1976) Acetoxy derivatives of trans-1,2-disilylethylene and their hydrolysis. *Izv. Akad. Nauk SSSR Ser. Khim*, 1395; *Chem. Abstr.*, **85**, 143178*c*.

Vos, D. De, Van Beelen, D. C., Van Der Kooi, H. O., and Wolters, J. (1975) Facile introduction of an acetate group in organolead compounds. *Recl. Trav. Chim, Pays-Bas*, **94**, 100; *Chem. Abstr.*, **83**, 164316*x*.

Vos D. De, Van Beelen, D. C., and Wolters, J. (1979) Aromatic lead(IV) compounds., ^{1}H and ^{13}C NMR spectroscopy of compounds Ar_n Pb $(OOCCH_3)$ $(n = 1–4)$. *J. organometal. Chem.*, **172**, 303.

Vos, D. De., and Wolters, J. (1972) Aromatic lead (IV) compounds, II. PMR spectroscopy of some aryllead tricarboxylates. *J. organometal. Chem.*, **39**, C63.

——— (1978) I_{π} and ^{13}C NMR spectroscopy of compounds Ar_n Pb $(OOCCH_3)$ $4–n$ $(n = 1 - 4)$. *Recl. Trav. Chim. Pays-Bas*, **97**, 219.

Vos, D. De, Wolters, J., and Van der Gen, A. (1973) Aromatic lead(IV) compounds. Direct plumbylation of monohalogen substituted benzenes; *Recl. Trav. Chim. Pays-Bas*, **92**, 701; *Chem. Abstr.*, **79**, 32125*s*.

Vostokov, I. A. (1978) Silylation of aminoacetic acid derivatives. *Zh. Obshch. Khim.*, **48**, 2140; (1979). *Chem. Abstr.*, **90**, 38985*w*.

Vyazankin, N. S., and Bychkov, V. T. (1965) Some reactions of organotin compounds. *Zh. Obshch. Khim.*, **35**, 684; (1966) *Chem. Abstr.*, **36**, 1684.

Wade, M., Shindo, M., and Okawara, R. (1963) Preparation and properties of dialkyltin chloride carboxylates. *J. organometal. Chem.*, **1**, 95.

Walden, C. C.. and Allen, I. V. F. (1968) Use of organic lead compounds in wood preservation. *Indian Vernice*, **22**, 16; *Chem. Abstr.*, **71**, 48636*c*.

Wang, C. S. C., and Shreeve, J. M. (1970) Diorganochlorotin perfluoro carboxylates. *J. Chem. Soc., Chem. Commun* , 151.

——— (1972) Preparation and spectral studies of dimethylchlorotin carboxylates. *J. organometal. Chem.*, **38**, 287.

Warner, G. H. (1978) Aluminium compounds. Aluminium carboxylates. *Kirk-Othmer Encycl. Chem. Tech.*, 3rd edn., **2** 202, *Chem. Absir.*, **89**, 45715*r*.

Weber, S., and Becker. E. I. (1962) Reactions of triphenyltin hydride with thiophene compounds and certain carboxylic acids. *J. org. Chem.*, **27**, 1258.

Weidlein, J. (1969) Cleavage of aluminium- and gallium-carbon bonds with carbon-di-oxide. *J. organometal. Chem.*, **16**, 33; *Chem. Abstr.*, **70**, 9634.

——— (1970) Carbon-di-oxide insertion reactions with aluminium, gallium and indium alkyl compounds. *Z. anorg. allg. Chem.*, **378**, 245; (1971) *Chem. Abstr.*, **74**, 31795*r*.

Weldon, D., and Lund, A. E. (1973) Organolead wood preservatives. *Proc. Am. Wood Preservn. Assoc.*, **69**, 47; (1974). *Chem Abstr.*, **80**, 61227*c*.

Wieberg, E , and Behringer, H. (1964) *Z. anorg. allg. Chem.*, **329**, 290.

Willemsens, L. C. (1964) *Organolead Chemistry*. Int. Lead, Zinc. Res. Organisation, Utrecht.

Willemsens. L. C., Vos, D. De, Spierenburg, J., and Wolters, J. (1972) Aromatic lead (IV) compounds. The plumbylation of some aromatic ethers. *J. organometal. Chem.*, **39**, C61.

Wilmshurst, K. J. (1965) Vibrational assignment for sodium acetates. *J. chem. Phys.*, **23**, 2463.

——— (1957) Vibrational spectroscopy. *I. mol. spectrosc.*, **1**, 201

Wirth, H. O., Maul, R., and Friedriich, H. H. (1969) One quicker method for the preparation of triorganolead acetate from hexaorganodilead compounds. *Tetrahedron Lett.*, 2959.

Yarosh, O. G., and Voronakov, M. G. (1974*a*) Ethynylacetoxysilanes. *Izv. Akad. Nauk. SSSR Ser Khim*, **7**, 1635; *Chem. Abstr.*, **81**, 120740*k*.

——— (1974*b*). Exchange of acetoxy for alkoxy groups on silicon in ethynylsilanes. *Izv. Akad. Nauk. SSSR Ser Khim*, **81**, 1635.

Yasuda, K., Matsumoto, H., and Okawara, R. (1964) Preparation and properties of dialkyltin nitrate derivatives. *J. organometal. Chem.*, **6**, 528.

Yokoo, T. (1973) Octaalkylcyclostannoxane derivatives as polymerization catalysts. *Japan*, 7330, 154; (1974) *Chem. Abstr.*, **80**, 96613*c*.

Yurtanov, A. I., Davidovich, Yu. A., Rogozhin, S. V. (1978) Study of the aminolysis of activated esters of N-protected amino acids by trimethylsilyl derivatives of amino compounds. *Izv. Akad. Nauk SSSR Ser Khim*, 1022; *Chem. Abstr.*, **89**, 180322*a*.

Zachariasen, W. H. (1940) The crystal structure of sodium formate, $NaHCO_2$. *J. Am. Chem. Soc.*, **62**, 1011.

Zachariasen, W. H., and Plettinger, H. A. (1959) Crystal chemical studies of the 5f-series of elements, XXV. The crystal structure of sodium uranyl acetate. *Acta Cryst.*, **12**, 526–530; *Chem. Abstr.*, **53**, 18588*a*.

Zemina, G. V., Sheverdina, N. T., and Kocheshkov, K. A. (1970) Acylates of aromatic organoaluminium compounds. *Dokl. Akad. Nauk. SSSR*, **195**, 96.

Zhivukhin, S. M., Dudikova, E. D., and Ter Sarkisyan, E. M. (1962) Synthesis and study of organostannoxanes. *Zh. Obshch. Khim.* **32**, 3059.

Ziegler, K. (1955) Aluminium inorganic chemistry. *Experientia Suppl.*, No. 2, 14; *Congr. int. Chem. pure et appl. Zurich*, 274–287; (1956) *Chem. Abstr.*, 14517.

Zubieta, J. A., and Zuckerman, J. J. (1978) Structural tin chemistry. *Progr. inorg. Chem.*, **24**, 251.

Zuckerman, J. J. (1970) *Adv. Organometal. Chem.* (*Eds.* Stone, F. G. A., West, R.). Academic Press, New Yok, **9**, 21.

——— (1976) *Advances in Chemistry Series*, **157**, *Organotin Compounds*: *New Chemistry and Applications*. ACS: Washington, D. C. 299.

Zvonkova, Z. V., Poveteva, Z. P., Vozzanikov, V. M., Glushkova, V. P., Jakovenko, V. I., and Khvatkina, A. N. (1966) *Acta. Cryst.*, *A*, **21**, 155.