VARIABLE-TEMPERATURE MÖSSBAUER SPECTROSCOPIC

STUDIES AND THE STRUCTURES OF ORGANOTIN(IV) COMPOUNDS

by

Kieran Quill

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Declaration

We, the undersigned, declare that this thesis represents the sole work of the author.

Koniels K. Quill

Kibran Molloy

K.C. Molloy

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Abbreviations used in this Thesis

| bipy | : | 2,2'-bipyridine |
|---------------------|---|---|
| ⁿ Bu | : | n-buty1 |
| t _{Bu} | : | t-butyl |
| Bz | : | benzyl |
| DMF | : | dimethylformamide |
| DMSO | : | dimethylsulphoxide |
| Et | : | ethyl |
| HMPA | : | hexamethylphosphoramide |
| Ме | : | methyl |
| Neo | : | neophyl |
| ⁱ Oct | : | iso-octyl |
| рс | : | phthalocyanine |
| Ph | : | phenyl |
| i _{Pr} | • | iso-propyl |
| n _{Pr} | : | <u>n</u> -propyl |
| pyz | : | pyrazine |
| ру | : | pyridine |
| salenH ₂ | : | N,N'-bis(salicylaldehyde)ethylenediimine |
| terpy | : | 2,2',2"-terpyridyl |
| TPP | : | $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine |
| Vin | : | viny1 |

Abstract

Organotin(IV) chemistry, with particular emphasis on solid-state structure and applications of ^{119m}Sn Mössbauer spectroscopy to structural characterisation, is briefly reviewed. The relevance of structure to the biocidal properties of organotin compounds is also discussed.

The results of variable-temperature ^{119m}Sn Mössbauer spectroscopic (v.t.M.s.) studies of a range of phenyl- and cyclohexyl-tin compounds are reported and analysed. This technique provides a measure of the vibrational freedom of the tin atoms in a lattice and the results are interpreted in terms of the potential of the technique for distinguishing between monomeric and polymeric lattices and between the different three-dimensional conformations of the polymer chains observed in organotin chemistry.

The solid-state structures of the pair of carboxylates triphenyltin acetate and triphenyltin formate have been determined by X-ray diffraction. In both compounds the carboxylates act as bridging groups to form infinite onedimensional polymeric chains with $trans-0_2 SnPh_3$ geometry at tin. However, in triphenyltin acetate, the carboxylate group, as well as coordinating intermolecularly, also weakly chelates intramolecularly to give a six-coordinate tin atom - an unusual coordination number for a triorganotin compound. The polymeric chains are helical for both

compounds, but a detailed consideration of their structures explains the observed significant difference in the v.t.M.s. behaviour of the two compounds.

The crystal and molecular structure of dicyclohexyltin dichloride has been solved by X-ray diffraction. The chlorine atoms act as bridging groups linking the molecules into a one-dimensional polymer, the local geometry at tin being a severely distorted $\underline{\mathrm{trans}}$ -R₂SnX₄ octahedron. The structure substantiates an initial prediction mode on the basis of the variable-temperature Mössbauer study of cyclohexyltins.

On the basis of v.t.M.s. and other spectroscopic data structural inferences are drawn for a number of crystallographically unconfirmed phenyl- and cyclohexyl-tin compounds. It is also suggested that for tricyclohexyltin compounds linear polymers rather than the more commonly observed zigzag or helical polymers are favoured because of the steric bulk of the cyclohexyl groups.

A preliminary v.t.M.s. study of tin-phthalocyanine complexes indicates that this technique can distinguish between a monomeric lattice and one in which the complexes are linked by strong covalent bonds. It may thus be a useful tool in the study of electroactive materials based on metallophthalocyanine species.

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Introduction

The determination of molecular structure is a problem of fundamental importance to the chemist. Knowledge of structure helps both the rationalisation of observed reactivity, physical and biological properties and the prediction of behaviour to be expected from novel systems.

For the solid state the most precise structural data are provided by diffraction techniques, X-ray diffraction by single crystals being the predominantly-used method. In the absence of definitive X-ray crystallographic information, the numerous spectroscopic probes available in modern chemistry must be The evidence thus provided in favour of one resorted to. structural arrangement as opposed to other possibilities can be very powerful, especially when several spectroscopic techniques are brought to bear on the problem, although the results thus obtained will inevitably be less quantitative and ambiguities For tin-containing materials ^{119m}Sn Mössbauer may arise. spectroscopy has established itself as an exceptionally useful non-destructive probe of both solid-state structure, even in non-crystalline materials, and the electronic environment at the tin sites.

This thesis reports, primarily, the results of a study of the solid-state structures of a number of organotin(IV) compounds by Mössbauer spectroscopy, concentrating on the biocidally important, although structurally not very well

characterised, phenyl- and cyclohexyl-tin classes of compound. As well as the more conventional singletemperature measurement of Mössbauer spectra at 78K, special emphasis is placed on the use of the temperature dependence of the recoil-free fraction as a probe of molecular and lattice structure. The crystal and molecular structures of several organotin(IV) compounds as determined by X-ray crystallography are also reported, as these provide points of quantitative reference for the temperature-dependence Mössbauer studies. A Mössbauer spectroscopic study of some tin-phthalocyanine complexes, which exemplify a class of compounds which has become important in recent years in the context of electroactive molecular systems, is also reported.

The Solid-State Structures of Organotin(IV) Compounds and the Use of ^{119m}Sn Mössbauer Spectroscopy in Structure Determination.

Tin is unmatched by any other heavy metal in the usefulness of its organoderivatives. By a happy coincidence, organotin compounds are also particularly suitable for the application of many important physical techniques which have been developed as probes of chemical structure and bonding. These two factors, together with very diverse reaction patterns and a wide variety of structural possibilities for the two stable formal oxidation states, make organotin chemistry a very attractive subject for the organometallic chemist and, indeed, since 1950 it has become one of the most intensively investigated areas of main group organometallic chemistry. The scale of this activity is reflected in the numerous reviews which have been published since then, beginning in 1960 with a review containing comprehensive tables of the compounds then known. Monographs by Neumann² and by Poller³ were published in 1970, and, shortly after, a three volumed work edited by Sawyer appeared 4. Advances during the next ten years have been reviewed by Davies and Smith². Synthetic methods are dealt with in a volume of Houben-Weyl⁶ and tetraorganotins⁷⁻⁹, organotin hydrides¹⁰, fluorides¹¹ and chlorides^{11,12} are covered in recent volumes of Gmelin. Structural Organotin chemistry has been reviewed¹³ and a comprehensive bibliography of X-ray diffraction studies published by the International Tin Research Institute in 1981¹⁴.

Applications of ^{119m}Sn Mössbauer spectroscopy to organotin chemistry were reviewed by Zuckerman in 1970, including extensive tables of isomer shift and quadrupole splitting data¹⁵, and by the same author in 1984¹⁶ and comprehensive tables of data were compiled by Ruddick in 1976¹⁷. Organotin compounds as reagents in organic synthesis are reviewed in Ref. 18.

The present work records some investigations into the solidstate structures of a number of biocidal and potentially biocidal organotin(IV) compounds in which Mössbauer spectroscopy, a spectroscopic technique especially suited to tin containing materials, has been extensively utilised. To put this work into perspective, the field of organotin (IV) compounds, with emphasis on structural chemistry and Mössbauer spectroscopy, is herein reviewed.

1.1. History

E. Frankland recorded the first preparation of an organotin derivative, diethyltin diiodide, in 1849¹⁹ and the subject developed continuously as a research topic during the following 100 years²⁰. However, research in, and practical applications of, organotin chemistry have increased dramatically since the 1950's, beginning with the work of van der Kerk and Luijten²¹ in Holland. Advances in X-ray crystallography and the emergence in the early 1960's of the specialised techniques of ^{119m}Sn Mössbauer and ¹¹⁹Sn nuclear magnetic resonance spectroscopies as powerful structural probes of the solid state and solution phase, respectively, have enormously facilitated this progress, and by 1980 it was estimated that about 1000 papers were published <u>per annum</u> in this area⁵.

Numerous commercial products based on organotin compounds have been developed and are marketed today in such areas as agrochemicals, wood preservation, antifouling paints and disinfectants; current production for these applications is estimated at some 10000 tonnes <u>per annum</u>²².

1.2. Solid-State Structures of Organotin(IV) Compounds

The general stoichiometric formula for an organotin(IV) compound may be written as $R_n Sn X_{4-n}$ (n = 1-4), where R is an unsubstituted or substituted alkyl or aryl group and X is an inorganic Lewis base group. Mixed organic and inorganic derivatives (e.g., of the type R'R₂SnX) have also been synthesised. Until an X-ray crystallographic confirmation of the presence of five-coordinate tin in the monopyridine adduct of trimethyltin chloride was reported,²³ organotin molecules were generally assumed to be tetrahedral, with four-coordinated tin atoms, but the wealth of crystallographic data available now reveal that many derivatives contain five-, six-, and seven-coordinate tin and that these higher coordinations can arise through intra- or intermolecular associations. Such structural information has proved invaluable in understanding the mode of action of these materials in their practical applications and toxicological behaviour.

1.2.1. Four-coordinate Structures

Tetraorganotin(IV) compounds are expected to be tetrahedral molecules with four-coordinate tin atoms. This has been demonstrated crystallographically for a number of such compounds, e.g., Ph_4Sn^{24} (regular tetrahedral), $(C_6F_5)_4Sn^{25}$ (distorted

tetrahedral), $(C_5H_5)_4 \text{Sn}^{26}$ (slightly distorted tetrahedral tin atom, σ -bonded to the four cyclopentadienyl groups), all of which are symmetrical tetraorganotins, and $Ph_3 \text{SnC}_7 H_7^{27}$ (a neartetrahedral triphenyltin unit σ -bonded to the cycloheptatriene ring, occupying an axial position at the methylene carbon), and $Ph_3 \text{SnCH}_2 I^{28}$ (near-regular tetrahedral geometry at tin) which are unsymmetrically substituted.

If an electronegative group, X, replaces one or more alkyl or aryl group in a tetraorganotin molecule, electron density will be drawn away from the central tin atom causing it to behave as a Lewis acid and so to have a marked tendency to increase its coordination number above four. However, despite any Lewis acidity which may be conferred on it under such circumstances, bulky organic or inorganic groups can prevent close enough approach of donor atoms to allow coordination expansion. Examples include $\{[(CH_3)_3Si]_2CH\}_3SnC1^{29}$ and $Ph_3SnSC_6H_4^{t}Bu-4$, ³⁰ both of which have near perfect tetrahedral geometry at tin with no close intermolecular contact distances or lengthening of Sn-X bonds. Bis(biphenylyl-2)tin dichloride is the only diorganotin dihalide known to form a monomeric solid,³¹ in which the molecules are well separated in space and no close intermolecular Sn----Cl contacts occur (notwithstanding the considerably enhanced Lewis acidity to be expected in a tin atom bonded to two electronegative chlorine atoms), but in which the tetrahedral geometry at tin is badly distorted. This has been attributed to the steric requirements of the two bulky organic ligands in which the C-Sn-C angle is opened to $130.8(3)^{\circ}$ and the C1-Sn-C1 angle correspondingly compressed [99.71(9)⁰] rather than to any extra coordination at tin.

The compounds $Ph_3SnXSnPh_3$ (X = 0, 32 , S^{33} , Te^{34} , Se^{35}) are all four-coordinate with regular or slightly distorted tetrahedral tin atoms, as is $Ph_3SnSPbPh_3$.³⁶ Diorganotin-chalogen compounds have invariably shown four-coordination, e.g., $(Me_2SnS)_3^{37}$ a sixmembered ring in the boat conformation, $({}^tBu_2SnX)_2$ (X = S^{38} , Se^{38}) with planar four-membered tin-chalogen rings, or $({}^{1}Pr_2SnS)_n^{39}$ which has a chain polymer structure. The diorganotin oxides di-t-butyltin oxide^{40,41} and di-t-amyltin oxide⁴¹ have also been shown to contain four coordinate tin with planar, six-membered tin-oxygen rings and no intermolecular association. $[(MeSn)_2X_3]_2$ (X = S^{42} , Se^{43}) both have an adamantane-type structure, again with tetrahedral geometry at tin.

Many organotin(IV)-transition metal complexes have been analysed by X-ray diffraction and most are four-coordinate. Small distortions from ideal tetrahedral geometry at tin are characteristic of such systems.¹³

Finally, many compounds containing tin-tin bonds or tin bonded to another group IV element have been characterised as four-coordinate in the solid state; examples include $(Ph_2Sn)_6^{44}$ (a six-membered ring in a chair conformation, with approximately tetrahedral geometry at tin), $Ph_3SnSnPh_3^{45}$ (slightly distorted tetrahedral), and $Ph_3SnPbPh_3$.⁴⁶

1.2.2. Five-coordinate Structures

This coordination number has been claimed for only one tetraorganotin (IV) species: the supposed 1:1 adduct of trimethyl(trifluoromethyl)tin with hexamethyl phosphoric triamide.⁴⁷

However, replacement of just one organic group in an R_4 Sn molecule by an electronegative group, X, increases the Lewis acidity behaviour of the metal atom, and five-coordinate complexes of tin are readily formed <u>via</u> intra- or intermolecular association. The geometry at tin in such complexes is invariably based on a trigonal bipyramid and the possible R_3 SnX₂ isomers are depicted schematically in Figure 1.1.



Figure 1.I.

Copious examples of the <u>trans</u>-X₂SnR₃ arrangement are available.¹⁴ It corresponds to the configuration most preferred by R₃SnX₂ molecules - the one in which the most electronegative atoms are occupying the axial positions of the trigonal bipyramid.¹³ $R_3SnX_2^-$ anions exclusively adopt this geometry, examples being $[Mo_3(h^5-C_5H_5)S_4]^+(Me_3SnCl_2)^-,^{48}$ and $(Ph_3AsCH_2.CO.Ph)^+(Ph_3SnCl_2)^-,^{49}$ and so do the cations $[Me_3Sn(HMPT)_2]^+$ (HMPT = hexamethylphosphoric triamide),⁵⁰ and $[Bu_3Sn(H_2O)_2]^+$.⁵¹ 1:1 adducts, R_3SnX_1 , always display a <u>trans</u> configuration, e.g., $(Me_3SnCl_pyridine)$, the first organotin compound to have been crystallographically confirmed as five-coordinate.²³ The 1:1 adduct of Me_3SnCl with $Ph_3P=CHCOMe$ has

the ylide residue bonded to the tin through the carbonyl oxygen to give a <u>trans</u>-OClSnC₃ geometry rather than using the carbanion carbon.⁵² In the complex $(Ph_3SnNO_3)_2$, $P(0)Ph_2(CH_2)_2Ph_2P(0)$, each tin atom achieves <u>trans</u>-O₂SnC₃ trigonal bipyramidal geometry through the diphosphine ligands bridging two axial sites <u>via</u> the oxygens and the other axial positions being occupied by the oxygen atoms of the unidentate nitrate groups.⁵³ A similar type of arrangement exists in $(Ph_3SnCl)_2$, $Ph_2As(0)(CH_2)_2(0)AsPh_2$.⁵⁴

Many triorganotins achieve five-coordination by intermolecular association and, without exception, the axially-most-electronegative motif is observed giving <u>trans-X</u>SnR₃ geometry at tin.¹⁴ In triphenyltin hydroxide, planar Ph₃Sn groups are joined by OH groups to give an infinite zigzag chain;⁵⁵ the bridging is asymmetric despite the planarity of the C₃Sn fragment (Figure 1.II(a)). Trimethyltin dicyanamide consists of infinite, one-dimensional chains in which planar N(CN)₂ groups bridge symmetrically planar organotin moieties,⁵⁶ (Figure 1.II(b)). Trimethyltin chloride consists of zigzag chains bent at chlorine but nearly linear at tin, in which the bridging is quite asymmetric and the Me₃Sn groups are non-planar.⁵⁷ Intermolecular bridging is a commonly observed theme in triorganotin carboxylates. 58 For example, in trimethyltin acetate⁵⁹ (Figure 1.II(c)) the organotin groups are spanned <u>via</u> the two oxygen atoms of the acetate group whereas in trimethyltin glycinate⁶⁰ the intermolecular coordination occurs through nitrogen (Figure 1.II(d)). There are some examples of a trans- X_2 SnR₃ geometry being generated by intramolecular coordination via an electronegative substituent on one of the organic groups: Figure 1.III illustrates two examples.



Figure 1.II. Some representative modes of polymer propagation.

ï



Compound (2) (Figure 1.III) is the first example of a diastereomerically pure chiral triorganotin halide, and has an $(S)_{C}(S)_{Sn}$ configuration.⁶²

The <u>cis</u>-R₃SnX₂ configuration is less common, Figure 1.1(b), occurring when a bidentate ligand chelates the tin atom, and never through intermolecular bridging. Occurences include R₃SnO.NPh.CO.Ph (R = Me⁶³, Ph⁶⁴), both of which have distorted <u>cis</u> R₃SnO₂ geometry, and Ph₃SnSC₆H₄NMe-2,⁶⁵ with the dimethylamino nitrogen and a phenyl group in the axial positions.

The <u>meridional-R</u> $_3$ SnX $_2$ arrangement, Figure 1.1(c), has yet to be demonstrated crystallographically.

In diorganotin(IV) molecules, $R_2 SnX_2$, the tin atom is more Lewis acidic than in $R_3 SnX$, five-coordination is less common, and saturation is usually reached with six-coordination. Nevertheless, many examples are now known, and contain two electronegative atoms in the axial sites of the trigonal bipyramid to give <u>cis-R_2SnX_3</u> geometry at tin, Figure 1.IV.



Examples include the anion of (Me₂SnCl,terpy)⁺(Me₂SnCl₃)^{-;66} Ph₂SnCl₂, (2-aminobenzothiazole),⁶⁷ in which the Sn-N bond is exceptionally long (2.548Å) (this together with the failure to obtain a 1:2 adduct was attributed to a combination of the large steric demand of the donor ligand and its weak donor capacity), ^tBu₂Sn(OCH₂CH₂)₂NMe and Me₂Sn(SCH₂CH₂)₂NMe⁶⁸ with R groups and N equatorial and BuPhSnCl(S.C.S.NEt₂)⁶⁹. Several compounds of the type XR, SnOSnR, X have been investigated by X-ray diffraction and shown to be centrosymmetric dimers with a nearly planar central SnOSnO ring in which the geometry at tin is very close to regular $\underline{cis}-R_2SnX_3$ trigonal bipyramidal and with the exocyclic tin atoms in a distorted <u>cis-R₂SnX₃</u> environment.¹⁴ An example is (Me₂Sn.OSiMe₃)₂0⁷⁰ whose dimeric ladder structure is illustrated in Figure 1.V.



Figure 1.V.

 $ClMe_2SnOSnMe_2Cl$ has a similar type of structure, but the dimeric units are held into a two-dimensional polymeric lattice by additional, very weak Sn----Cl bonds so that the geometries at both the endo- and exocyclic are distorted in an arrangement between five-coordinate <u>cis-R_2SnX_3</u> and six-coordinate <u>trans-</u> R_2SnX_4 octahedral.⁷¹ <u>cis-R_2SnX_3</u> geometry also occurs in the unique lattice structure of compound with the composition $Ph_2SnCl_2, \frac{3}{}$ pyrazine. The lattice is composed of alternating layers of polymeric chains $[Ph_2SnCl_2, pyz]_n$ with six-coordinate tins and of individual $(Ph_2SnCl_2)_2$, pyz molecules in which the tin atoms are close to trigonal bipyramidal <u>cis-R_2SnX_3</u>.⁷²

Monoorganotin species are known to form pentacoordinate complexes although six- and seven-coordination are much more common because of the strong electron-acceptor properties typical of the tin atom in such an environment. Electronegative atoms, rather than the organic group, always occupy the axial sites of the trigonal bipyramid in these compounds. Thus several 1:1 complexes of the type $[RSnX_3,L]$, with X = halide and L = monodentate ligand, are known, though these are less common than octahedral adducts with two such ligands. Examples are $(Ph_4As)^+(MeSnCl_4)^-$,⁷³ and MeSnBr₃,DMF.⁷⁴ A distorted trigonal bipyramidal RSnX₄ geometry also occurs in MeO.CO.CH₂CH₂SnCl₃⁷⁵ due to intramolecular coordination by the carbonyl group, Figure 1.VI, as it does in some tin-transition metal compounds, e.g., PhSn [Fe(CO)₂(h⁵-C₅H₅)](O.SO.Ph)(OH),⁷⁶ a hydroxy-bridged dimer, with a monodentate 0.SO.Ph group and a bridging hydroxide from the adjacent molecule occupying the axial sites.



Figure 1.VI

1.2.3. Six-coordinate Structures

Triorganotin(IV) molecules are relatively weak electron pair acceptors; in such compounds the tin atom prefers to increase its coordination number to five, and only one R_3SnX_3 complex has been confirmed. This is tris(pyrazolyl)borate(trimethyl)tin, in which the donor nitrogen atom in the uninegative tridentate ligand is ideally constrained to occupy three adjacent sites of an octahedral coordination sphere to give a <u>fac</u>- R_3SnN_3 geometry,⁷⁷ Figure 1.VII.



Figure 1.VII

Many diorganotin(IV) derivatives, R₂SnX₂, however, contain six-coordinate tin atoms, always based on an octahedral coordination sphere. Observed geometric isomers may be classified into two types, illustrated in Figure 1.VIII.



cis-R₂SnX₄

trans-R2 SnX4

Figure 1.VIII

The $\underline{\operatorname{cis}}_2 \operatorname{SnX}_4$ formation is often sterically favoured when two chelating bidentate ligands are present, e.g., the dithiocarbamate derivative $\operatorname{Ph}_2\operatorname{Sn}(\operatorname{S.CS.NEt}_2)_2$ in which the tin atom is occupying a distorted octahedral $\underline{\operatorname{cis}}_2\operatorname{SnS}_4$ geometry (<C-Sn-C = 101.4°).⁷⁸ A $\underline{\operatorname{cis}}_2\operatorname{SnX}_4$ arrangement also exists in $\operatorname{Ph}_2\operatorname{Sn}(\operatorname{NCS})$, bipy, in which the isothiocyanate groups are $\underline{\operatorname{trans}}$.⁷⁹

<u>Trans</u>-R₂SnX₄ geometries (usually distorted) are very common. Examples include $(Me_2SnCl_4)^{2-}(pyH^+)_2$,⁸⁰ and $[2-H_3NC_6H_4.CO.NH_2]_2^+$ $[Me_2SnCl_4]^{2-}(H_2O)_2$.⁸¹ In the monomeric molecule of $Cl_2Sn[C_6H_4(N=NPh)-2]_2$, a very distorted octahedral structure is adopted, with <u>cis</u>-chlorines, and <u>cis</u>-nitrogen atoms in the equatorial plane and distorted <u>trans</u>-organic groups (<C-Sn-C = 149.7°).⁸² Extensive series of the type $[R_2SnX_2, 2L]$ are known with <u>trans</u>-R groups, and the question arises of whether or not the all-<u>trans</u> isomer is adopted in a given complex, Figure 1.IX.



all-trans

cis-X₂L₂

Figure 1.IX

It has been predicted that a cis-donor atom arrangement (Figure 1.IX(a)) will be adopted if this is stereochemically possible,⁸³ whereas the all-<u>trans</u> one (Figure 1.IX(b)) will be forced by bulky ligands due to ligand-ligand repulsions. "Pointed" ligands such as O=ER in which the donor atoms are not substituted by organic groups can take the preferred cispositions but when the donor atom holds organic groups, :ER_, then ligand-ligand repulsions are greater and the alternative situation occurs.¹³ An example of the latter situation is [Me₂SnCl₂,2py]⁸⁴, while [Me₂SnCl₂,DMSO] represents the former.⁸⁵ [Me₂SnCl₂,2HMPA] also represents a stereochemically crowded complex and has an all-trans geometry very close to idealized octahedral.86 In polymeric [Bu₂SnCl₂,PhP(0)(CH₂)₂P(0)Ph] a distorted trans- $R_2 SnX_4$ geometry arises through intermolecular bridging of the diphosphine ligand, in which one P=O group is weakly coordinating, to give <u>cis</u>-chlorines and <u>cis</u>-oxygens.⁸⁷

Diorganotin(IV) derivatives, R_2SnX_2 , very commonly associate intermolecularly in the solid state to give, invariably, a <u>trans-R_2SnX_4</u> geometry. Me_SnF_2 has a lattice made up of infinite sheets of tin and fluorine atoms with each tin linearly bridged to its four neighbouring tins by symmetrically disposed fluorine atoms. The two methyl groups lie above and below the plane of the sheet to give a linear Me-Sn-Me unit, ⁸⁸ Figure 1.X.



Figure 1.X

The Sn-C bond length is very short (2.08\AA) , which was attributed to the ionic nature of the $(\text{SnF}_2)_{\infty}$ sheet in which the positive charge on the metal atoms leads to increased ionic character in the Sn-C bonds and hence a shortening relative to a normal covalent bond.⁸⁸ Me₂Sn(SO₃F)₂ has a similar polymeric structure with the tin atom in an almost regular octahedral <u>trans</u>-R₂SnO₄ geometry.⁸⁹

In dialkyltin dihalides and pseudohalides association between molecules is usually weaker than in Me_2SnF_2 , so that structures intermediate between four-coordinate tetrahedral and six-coordinate octahedral are obtained. This can be described as distorted <u>trans</u>-R₂SnX₄ geometry in which <C-Sn-C is less than 180° and the four inorganic groups lie in a plane including the central tin atom, but two pairs are at different distances from this atom. Thus, for example, dimethyltin dichloride,⁹⁰ diethyltin dichloride⁹¹ and diethyltin dibromide⁹¹ have the structure outlined in the diagram below, Figure 1.XI.



Figure 1.XI

Dimethyltin dichloride was the second dialkyltin dihalide (after Me_2SnF_2) to have its solid-state structure determined by X-ray diffraction, but its gas-phase structure was known from an earlier electron-diffraction experiment and was shown to be approximately tetrahedral.⁹² The considerable distortions from tetrahedral geometry in the solid state were attributed to association between neighbouring molecules rather than packing forces in the lattice.⁹⁰ Similarly, Et_2SnCl_2 , Et_2SnBr_2 and Et_2SnI_2 have been described as forming chains of interacting molecules with each tin atom in an environment intermediate between octahedral and tetrahedral.⁹¹

The crystallographic data for Ph₂SnCl₂⁹³ illustrate the often subjective nature of determining coordination number where interactions between atoms are weak. Data were first reported as representing tetrahedral molecules with no significant association.⁹³ In a later reinterpretation other workers offered an alternative view, in which the lattice consists of linear groups of four molecules with the two terminal tin atoms four-coordinate and the middle two six-coordinate. The terminal molecules are coordinated to the central pair by a Cl----Sn interaction of 3.78Å, while the bridging chlorines in the central Sn_2Cl_2 ring are 3.77Å from the neighbouring tins; both these distances are very long.³¹

Some monoorganotin compounds form octahedral six-coordinate complexes, although seven-coordination is more usual. A recent instance is BuSn(OMe)Cl₂.CoCl(salen) in which the tin atom is bonded to two <u>cis</u>-chlorines, one butyl group and threeoxygen atoms. Two of the oxygens come from the salen ligand, and the third oxygen, that of the methoxy, is <u>trans</u> to the butyl group and also bridges the cobalt intermolecularly.⁹⁵

1.2.4. Seven-coordinate Structures

This coordination number at tin has been observed for monoand diorganotin(IV) derivatives, with the geometry at the tin always based on a pentagonal bipyramid. In diorganotins, the hydrocarbon groups always occupy the axial positions.¹³ Examples include:

$$({}^{n}Pr_{2}SO)Ph_{2}Sn(NO_{3}).0.CO.CO.O.SnPh_{2}(NO_{3})({}^{n}Pr_{2}SO),{}^{96}$$

 $[Ph_2Sn(NO_3), 3DMSO]^+NO_3^- 97$ and $[Ph_2Sn(NO_3)_2, Ph_3AsO].^{98}$

Seven coordination occurs in some monoorganotins, e.g., $MeSn(NO_3)_3^{99}$ (Figure 1.XII), and $^nBuSn(S.CS.NEt_2)_3$.¹⁰⁰



Figure 1.XII

1.3. Mössbauer Spectroscopy and Organotin(IV)

Compounds

Determination of molecular and lattice structures is a matter of basic concern to the organotin chemist. For the solid state, the most definitive and quantitative data are given by X-ray diffraction, but for materials which cannot be obtained in a crystalline state, or in situations in which disorder or crystal twinning occurs, a wide range of physical techniques can be brought to bear on the structural problem. These techniques, especially when considered together, can constitute compelling evidence for one scenario as against alternative arrangements. Furthermore, in many organotin crystal structures, the question of coordination number at tin cannot be unequivocally decided.¹³ This is especially the case when inter- or intramolecular interaction is relatively weak and observed distortions from the regular geometries may be largely due to crystal packing, steric, or electronic (isovalent rehybridisation) forces (c.f. refs. 31 and 93), and again ancillary spectroscopic data can help resolve ambiguities.

In particular, the parameters which can be measured by ^{119m}Sn Mössbauer spectroscopy can be very informative in regard to the bonding situation at tin, both within the first coordination sphere and the overall lattice structure. Analysis of the Mössbauer spectra of model compounds, whose solid-state structures have been substantiated crystallographically, has resulted in the development of powerful methodologies for the structural characterisation of novel organotin materials.

1.3.1 Background

Mössbauer spectroscopy has its origin in the resonant absorption and emission of γ -rays arising from nuclear excited states (with half-lives typically in the range 10^{-6} to 10^{-10} s) in a solid matrix without degradation by recoil or thermal broadening, to give an energy distribution according to the Heisenberg uncertainty principle. Spectra are obtained by measuring resonance absorption as a function of γ -ray energy.

After ⁵⁷Fe, the most extensively investigated M8ssbauer nuclide is ¹¹⁹Sn. The γ -ray transition is the 23.875keV decay from the first excited nuclear state. This is a $^{3}/2 \rightarrow ^{1}/_{2}$ magnetic dipole transition, so that the hyperfine properties are similar to those of ⁵⁷Fe. ¹⁰¹ The range of D8ppler velocities required is also similar, so that the much larger natural (Heisenberg) linewidth for ¹¹⁹Sn ($\Gamma_{\rm H}$ = 0.626mms⁻¹ for ¹¹⁹Sn and 0.192mms⁻¹ for ⁵⁷Fe) reduces the resolution of energy differences for tin. No stable organotin compounds are paramagnetic; external magnetic fields of about 5T must be applied to produce Zeeman splitting, and few experiments of this kind have been reported. The effective Debye temperature of most organotin compounds is low which means that measurements must be made at low temperatures, and the great majority of the reported data refer to liquid nitrogen temperature (78K). No known compound has failed to give a spectrum at this temperature.

1.3.2. The hyperfine Interactions

The two most important quantities measured by the singletemperature experiment (78K) in the absence of an external magnetic field are the isomer shift, IS, (also called chemical shift) and the quadrupole splitting, QS. These hyperfine interactions arise from the interactions of the nuclear charge distribution and extranuclear electric fields and they have been extensively used to characterise the chemical bonding and structure at the Mössbauer atom site.

Because the Mössbauer effect produces mono-energetic γ -radiation of extremely high precision (of the order of 1 part in 10¹²) it can be used to probe the very small differences in energy separation between the nuclear ground and excited states, as one moves from compound to compound, resulting in a slight shift in the position of the observed resonance line.

The total interaction Hamiltonian for the tin atom can be expressed as:

$$H = H_0 + E_0 + M_1 + E_2$$
Eqn. 1.1

where H_0 stands for all terms in the Hamiltonian except the hyperfine interactions under discussion; E_0 is the Coulombic (electrostatic) interaction between nucleus and the electrons; M_1 is the magnetic dipole hyperfine interaction; and E_2 represents the electric quadrupole interactions.

 E_o gives rise to the observed IS and has its origin in the overlap of electron density with nuclear charge density. The electron density in question is that of s-electrons as only they have a finite probability of existing in the nuclear region (at least to a very good approximation). An expression for the IS may be derived from classical electrostatic considerations.¹⁰² Assuming that the nucleus is a uniformly charged sphere of radius R and that s-electron density at the nucleus, $[\Psi(0)_s]^2$, is a constant over nuclear dimensions, the IS is given by:

IS =
$$K(R_e^2 - R_g^2) \{ [\Psi(0)_s]_a^2 - [\Psi(0)_s]_s^2 \}$$
Eqn. 1.II

where K is a nuclear constant for ¹¹⁹Sn; e and g refer to the first excited and ground nuclear states; and a and s refer to the absorber and source of γ -radiation. Because the difference between R_e and R_p is very small, the relationship can also be expressed as

IS =
$$2KR^2(\delta R/R) \{ [\Psi(0)_s]_a^2 - C \}$$
Eqn. 1.III

where $\delta R = R_e - R_g$ and C is a constant characteristic of the source used. Since the source is usually a standard material (e.g., Ca^{119m}SnO₃), the actual numerical value of IS is with respect to the reference source material used. Thus, IS for a compound depends on a nuclear factor δR and an extranuclear factor $[\Psi(0)_g]_a^2$. For a given nuclide, such as¹¹⁹Sn, δR is a constant so that IS is directly proportional to s-electron density at the nucleus. Since $\delta R/R$ is positive for ¹¹⁹Sn an increase in s-electron density at the nucleus is signalled by a more positive IS. $\delta R/R$ is not known very accurately, so s-electron densities calculated from IS values are not reliable.¹⁰² Figure 1.XIII illustrates diagramatically the origin of the isomer shift.



Figure 1.XIII

S-electron density at the nucleus is often sensitive to pand d-electron density: Hartree -Fock calculations indicate that $\left[\Psi(0)_{s}\right]^{2}$ decreases as p- or d-orbital density increases. Thus with a positive $\delta R/R$ an increase in p- or d-electron density will decrease IS. An expression for IS (relative to Mg₂Sn) has been derived¹⁰³ which gives it as a function of the number of 5s and 5p electrons:

IS =
$$-2.36 + 3.01n_s - 0.20n_s^2 - 0.17n_{sp}^{n} (mms^{-1})$$

Though of doubtful accuracy, this suggests that the isomer shift should be much more sensitive to s-electron density than that of p electrons, so that it (for tin species) may be expected to increase (i.e. become more positive) in the order:

ionic
$$Sn(IV)(4d^{10}) < covalent Sn(IV)(5s^{1}5p^{3}) < Sn(II)(5s^{2-x}5p^{x}).$$

The second hyperfine parameter, QS, arises from an electric quadrupole interaction and generates some of the most important information in Mössbauer spectroscopy. Any nucleus with spin quantum number $I > \frac{1}{2}$ has a non-spherical charge distribution, the magnitude of whose deviation from spherical symmetry is given by the nuclear quadrupole moment, Q. This is a signed quantity: when the nucleus is flattened along the spin axis Q is negative, and when the nucleus is elongated along that axis Q is positive. This non-spherical charge will interact with a non-spherically symmetric electric field at the nucleus, such as exists in most compounds due to asymmetry in the electron density distribution, so that the degeneracy of the nuclear levels is lifted (see Figure 1.XIII).

The moment, Q, may be regarded as arising from an elliptic charge distribution in the nucleus. Suppose that the distribution is elongated and acted upon by ligands A_1 and A_2 with A_1 more negative than A₂, Figure 1.XIV.



Figure 1.XIV.

Situation (b) has lower energy since positive nuclear charge is closer to the more negative external charges. These two orientations correspond to two different sets of m_I values. For the very important case of a γ -ray transition between states with I = $^3/2$ and I = $^1/2$ (including 119 Sn and 57 Fe) the nucleus can take just two orientations, $m_I = ^{\pm 1}/2$ and $^{\pm 3}/2$, when I = $^3/2$. The I = $^1/2$ level remains unsplit, so the spectrum comprises of two lines. The energy separation between the two levels (lines) is called the quadrupole splitting, QS, and is proportional to the electric quadrupole moment and the Z-component (Z = principal axis) of the electric field gradient at the nucleus, q:

QS \propto qQEqn. 1.IV This is a product of a nuclear factor, Q, which is a constant for a given nucleus, and q which depends on the chemical environment.
The electric field at the Mössbauer nucleus is the negative gradient of the electrostatic potential, V:

$$\underline{\mathbf{E}} = -\nabla \mathbf{V} = -(\underline{\mathbf{i}}\mathbf{V}_{\mathbf{x}} + \underline{\mathbf{j}}\mathbf{V}_{\mathbf{y}} + \underline{\mathbf{k}}\mathbf{V}_{\mathbf{z}})$$

where $V_x = \partial V / \partial x$, etc., so that the electric field gradient is the tensor quantity:

$$\overline{\nabla \underline{E}} = - \begin{bmatrix} \overline{\nabla}_{xx} & \overline{\nabla}_{xy} & \overline{\nabla}_{xz} \\ \overline{\nabla}_{yx} & \overline{\nabla}_{yy} & \overline{\nabla}_{yz} \\ \overline{\nabla}_{yx} & \overline{\nabla}_{yy} & \overline{\nabla}_{yz} \\ \overline{\nabla}_{zx} & \overline{\nabla}_{zy} & \overline{\nabla}_{zz} \end{bmatrix}, \text{ where } \overline{\nabla}_{xy} = \partial^2 \nabla / \partial x \partial y, \text{ etc.}$$

Assuming that the electric field gradient (e.f.g.) is generated by point charges Z_i , the contribution one point charge makes to each component of the e.f.g. tensor is given by the expressions: ¹⁰²



$$V_{xx} = Z_{i}er^{-3}(3sin^{2}\thetacos^{2}\theta-1)$$

$$V_{yy} = Z_{i}er^{-3}(3sin^{2}\thetasin^{2}\theta-1)$$

$$V_{zz} = Z_{i}er^{-3}(3cos^{2}\theta-1)$$

$$V_{xy} = V_{yx} = Z_{i}er^{-3}(3sin^{2}\thetasin\phicos\phi)$$

$$V_{xz} = V_{zx} = Z_{i}er^{-3}(3sin\thetacos\thetacos\phi)$$

$$V_{yz} = V_{zy} = Z_{i}er^{-3}(3sin\thetacos\thetasin\phi)$$

The total value of each component is the algebraic sum of each contribution.

A coordination system (X, Y, Z) can often be found in which the off-diagonal components of the e.f.g. are zero and $|V_{ZZ}| \ge |V_{YY}| \ge |V_{XX}|$. Then the e.f.g. can be specified by three components which are interdependent through the (Laplace) condition

that $V_{XX} + V_{YY} + V_{ZZ} = 0$. It follows that there are only two independent parameters usually chosen to be V_{ZZ} and $\eta \equiv (V_{XX} - V_{YY})/V_{ZZ}$, the asymmetry parameter. These conditions constrain η to lie in the range $0 \le \eta \le 1$. If the off-diagonal elements are non-zero, the tensor must be diagonalised before the diagonal components are chosen as above. Often the Z axis of the e.f.g. is coincident with the highest symmetry axis of the molecule or crystal. The quadrupole splitting is then given, in terms of these parameters, by:

$$QS = \frac{1}{2}e^2 qQ(1 + \eta^2/3)^{\frac{1}{2}}$$

with $q \equiv V_{ZZ}^{\prime}/e$. V_{ZZ}^{\prime} is the negative of the Z component of the e.f.g.

The e.f.g. arises from both the valence electrons of the Mössbauer atom and the surrounding ligand charges Z_i , and q can be divided into two components:¹⁰¹

 $q = (1-R)q_{valence} + (1-\gamma_{\infty})q_{lattice}$

with $q_{lattice}$ being given by $(1/e) [\sum_{i} 2r_{i}er_{i}^{-3}(3cos^{2}\theta_{i}-1)]$ and $q_{valence}$ by $\langle \psi | (3cos^{2}\theta-1)/r^{3} | \psi \rangle = \Sigma \langle 3cos^{2}\theta-1 \rangle \langle r^{-3} \rangle$. The valence term is generally the major contributor to the e.f.g. unless the ion has S symmetry, in which case the lattice term dominates.

Both of these terms are difficult to calculate, and the value of Q is not accurately known for ¹¹⁹Sn, so that <u>a priori</u> calculations of QS for a compound are usually not realistic and semi-empirical rationalisations of observed quadrupole splittings are used almost exclusively for molecular compounds like organotins.

1.3.3. The Recoil-Free Fraction

A third Mössbauer parameter, the recoil-free fraction, which determines the intensity of the spectrum, has become important in structural organotin chemistry.

The size of the recoil-free fraction, f, is given by:

$$f = \exp\left(\frac{-4\pi^2 \langle x^2 \rangle}{\lambda^2}\right) = \exp\left(\frac{-E_{\gamma}^2 \langle x^2 \rangle}{(hc)^2}\right) \qquad \dots Eqn. \quad \forall$$

in which $\langle x^2 \rangle$ is the mean-square amplitude of vibration of the Mössbauer nucleus in the direction of the observed γ -ray and E_{γ} is the energy of the γ -ray photons. No condition of periodicy is required by this equation, so that Mössbauer spectra can be recorded for amorphous solids or frozen solutions as well as crystalline materials. The value of $\langle x^2 \rangle$ is of fundamental importance; it must be small compared to λ , the wavelength of the γ -photon, and thus the Mössbauer effect is undetectable in gases or non-viscous liquids. The temperature dependence of f affords an important method of studying lattice dynamics of the solid.

A fully realistic model of the vibrational modes of a crystal is beyond present methods and the Debye model of solids is the one most often used for interpretation of Mössbauer behaviour. It approximates the solid as an assembly of harmonic oscillators whose vibrational frequencies form a continuum from zero to a maximum value $\omega_{\rm D}$ with a distribution N(ω) = constant x ω^2 , see Figure 1.XV



Figure 1.XV

A quantity, θ_D , with the dimensions of temperature, is defined by: $\omega_D = k\theta_D$, and the average frequency for the assembly is given by $\overline{\omega} = \frac{3}{4} \omega_D$. Values of θ_D are strictly valid only for solids which closely resemble a Debye solid, and even many pure metals deviate greatly from the conditions, so that for molecular solids values derived can only be considered as rough indicators of lattice properties and are not to be taken too quantitatively.

The model leads to an expression for the recoil-free fraction as a function of temperature:¹⁰¹

$$f(T) = \exp\left[\frac{-6E_R}{k\theta_D}\left\{\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta/T} \left(\frac{xdx}{e^x-1}\right)\right\}\right] \qquad \dots Eqn. 1.VI$$

When

 $T << \theta_D$ this becomes:

$$f(T) = \exp \left[\frac{-E_R}{\overline{k \theta_D}} \left\{ \frac{3}{2} + \frac{\pi^2 T^2}{\theta_D^2} \right\} \right],$$

and in the high temperature limit $T \geq \frac{1}{2}\theta_{D}$,

$$f(T) = \exp\left[\frac{-6E_R}{k \theta^2}\right], \quad T \ge \frac{1}{2}\theta_D \qquad \dots Eqn. \ 1.VII$$

Hence, if a solid can be approximated by the Debye model, lnf(T) becomes a linear function of T, at least over a certain temperature range. In practice lnf(T) is not always linear due to vibrational anharmonicity, i.e., the Debye model is not always valid.

1.3.4. Applications of ^{119m}Sn Mössbauer Spectroscopy to Chemical Problems in Organotin Chemistry

The Mössbauer parameters discussed above, IS, QS, and f, are sensitive to the electronic and molecular structures and lattice dynamics of a compound, and the types of application which can be exploited fall into two broad categories: (a) finger-printing, and (b) characterisation of bonding and structure.

Finger-printing is the more straightforward area of application, being based on the simple assumption that identical macroscopic systems will behave in identical ways. Analyses of Mössbauer spectra for this purpose are greatly facilitated by the fact that line shapes are usually very well behaved Lorentzians, so that partially overlapping lines can often be readily identified. This approach can help in determining: (a) oxidation state of the tin atom (or atoms); (b) purity; (c) proof that one compound has a different structure from another of the same composition; (d) proof that two or more atoms in a structure are not in equivalent environments; (e) identification of the species in a physical mixture.

Identification of oxidation state is, perhaps, the most common of these uses, and as indicated above, the two oxidation states of tin, Sn(II) and Sn(IV) have IS values in two different regions, with Sn(II) > Sn(IV) in terms of Döppler velocity. It has been suggested¹⁰⁴ that the diamond-type lattice of α -Sn is constituted of tin atoms at the limit of the use of four valenceshell electrons, so that its IS value, 2.10mms⁻¹ (with respect to SnO₂), should be taken as the reference crossover point between Sn(II) and Sn(IV) and Zuckerman also argued in favour of this reference point.¹⁶ However, the value for β -Sn (2.56mms⁻¹) is also widely quoted¹⁰⁵ as the dividing line between oxidation states.

An important general principle which must be applied when using the other finger-printing applications listed above is that only positive evidence should be considered when drawing conclusions on questions of purity, non-equivalence of atoms etc., because many examples are known in which the Mössbauer parameters are not sensitive to chemical differences between the tin atoms in a compound or mixture, a situation exacerbated by the broad lines of the ¹¹⁹Sn resonance. For example, in the salt $[Me_2SnCl,terpy]^+[Me_2SnCl_3]^-$, one of the Sn(IV) atoms is cationic and six-coordinate, while the other is anionic and five-coordinate, ⁶⁶ and yet both tin atoms give identical Mössbauer parameters in a perfectly overlapping pair of doublets [IS = 1.38, QS = 3.31, $\Gamma_1 = 1.12$, $\Gamma_2 = 1.20$ mms⁻¹ (Γ = full width at half height for a resonance line)]¹⁰⁶ A second example is the two types of tin site in [Ph₂SnCl₂, ‡pyrazine] (see above, Section 1.2.2.), which also gives just one doublet in its spectrum.⁷²

Interpretations of Mössbauer parameters in terms of electronic structure, molecular geometry and lattice properties raise many difficulties. This follows from the nature of the fundamental equations for IS and QS, which involve variables representing valence-orbital electronic populations of tin atoms, the electronic properties and positions of ligands, and the value of Q the nuclear quadrupole moment of ¹¹⁹Sn, none of which are, in general, well determined. The quantitative interpretation of the Mössbauer fraction, f, requires a realistic model for the lattice dynamics (vibrational modes) of molecular solids, a very difficult and, so far, unattained goal.

Because organotins are molecular, diamagnetic and highly covalent the amount of information derivable from the Mössbauer experiment is restricted compared with paramagnetic iron complexes. Magnetic hyperfine interactions do not exist because there is no net electronic spin moment; close-lying electronic states are not present, so that temperature-dependent QS values are not observed; and extensive ligand participation in bonding makes estimations of electric field gradients and s-electron populations difficult, unlike classical iron complexes, in which d orbitals retain their identity, and ligand field theory can be fruitfully employed. Thus, interpretations have been of a semi-empirical nature.

Isomer shift values, beyond their use in distinguishing oxidation states, have proved singularly difficult to explain in detail in organotin compounds and much more attention has been focussed on the rationalisation of QS values.

As already mentioned, q_{valence} is the major contributor to q (the principal component of the e.f.g.) and it in turn is dominated by the covalent electronic distribution due to overlap of ligand and tin orbitals. QS values therefore do not depend significantly on temperature and any small variations are due to small changes in tin-ligand bond lengths.

The main approach to rationalisation of observed QS data has been the point-charge model, in which partial quadrupole splittings (p.q.s.) have been assigned to ligands and additivity of the p.q.s. values assumed. Observed QS values are then functions of the ligands and their distribution about the tin atom.

An early additivity model assumed that the same partial QS values (p.q.s.) could be used for a ligand in either four-, five-, or six-coordination Sn(IV) compounds.¹⁰⁷ Each ligand L was regarded as a point charge Z_L and the point-charge expressions for V_{ZZ} , V_{XX} , and V_{YY} used. A quantity called the partial quadrupole splitting of the ligand L was defined according to:

$$(p.q.s.)_{\tau} = \frac{1}{2}e|Q|[L]$$
Eqn. 1.VIII

with $[L] = Z_L/r_L^3$, the partial field gradient of ligand L, and analytic expressions for the contributions of each L to the total e.f.g. for each geometry (tetrahedral, trigonal bipyramidal, and octahedral) evaluated (see Table 1.I for these expressions). The inorganic anion $SnCl_5^-$ of known trigonal bipyramidal geometry was chosen to obtain the value of [C1]. It has an observed QS of $-0.63mms^{-1}$, thus:

 $-0.63 \text{mms}^{-1} = \frac{1}{2} e^2 (V_{ZZ}/e) Q(1 + \eta^2/3)^{\frac{1}{2}}$

Since $V_{ZZ}/e = Z_{C1}/r^3 = \{C1\}$ assuming the same p.q.s. for axial and equatorial positions, and $\eta = 0$,

 $-0.63 \text{mms}^{-1} = \frac{1}{2} e^2 [C1]Q$

Q is negative for 119 Sn, so that

 $(p.q.s.)_{c1} \equiv \frac{1}{2}e^{2}[C1]|Q| = +0.63 \text{ mm s}^{-1}$

This value having been chosen as the standard reference point, other p.q.s. values could then be calculated. Thus, a p.q.s. value for R = Me or Et was determined from the average QS value for a series of trigonal bipyramidal compounds $R_3 SnCl_2$ and intermolecularly associated $R_3 SnCl$ compounds (R = Me, Et). P.q.s. values for other ligands can be computed in a similar manner.

The point-charge model can rationalise the main trends in QS values in terms of the known structural types. For example, for SnA_2B_4 octahedral systems, the quadrupole splitting in the trans-isomer is expected to be twice that for the <u>cis</u>-isomer; SnAB_5 should have the same QS as <u>cis</u>-SnA₂B₄, and tetrahedral SnA_2B_2 should display a QS 1.6 times that of SnAB_3 .¹⁰⁸ The



100

Point-Charge Expressions for Some Common Structures

semi-empirical method¹⁰⁷ yields quantitative predictions of the quadrupole splittings to be expected for known types of geometry about the tin atom and indicates that QS should decrease in the order: <u>trans</u>-octahedral > five-coordinate trigonal bipyramidal > <u>cis</u>-octahedral \approx four-coordinate tetrahedral \approx RSnX₅²⁻. Agreement between calculated and observed QS is generally fair to good,^{107,109} but poor agreements also occur, for example: Ph₃SnCl(tetrahedral), observed -2.54mms⁻¹, predicted -1.66mms⁻¹; Ph₃SnBr(tetrahedral), observed -2.50mms⁻¹, predicted -1.60mms⁻¹.

A more sophisticated parameterization was arrived at by obtaining separate p.q.s. values for ligands in different coordination environments and also separate p.q.s. for the axial and equatorial ligands in the trigonal bipyramidal coordination On the basis of molecular orbital calculations, polyhedron. these were computed for four-(tetrahedral) and six-coordinate (octahedral) geometries.¹¹⁰ Predicted quadrupole splittings, in most instances, agreed with experimental values to within $\frac{+}{-}$ 0.4mms⁻¹, and it was suggested that disagreements greater than this could be used as evidence for large distortions from ideal geometry or incorrect assignment of structure.¹¹⁰ Other results were that (a) for a given L, $(p.q.s.)_{L}^{oct} \simeq 0.67(p.q.s.)_{L}^{tet.}$; (b) $QS(R_3SnX_2) \simeq 1.33QS(R_3SnX)$, with R = alkyl group; and (c) π bonding, in which electrons are donated to the tin atom's 5d orbitals, should have no effect on the quadrupole splitting, so that variations in the quadrupole splitting and partial quadrupole splitting values are due solely to σ bonding. Extensions of the

molecular-orbital model¹¹¹⁻¹¹³ allowed p.q.s. values to be derived for trigonal bipyramidal coordination, with different partial quadrupole splittings being assigned for the axial and equatorial positions.

There are limitations, however. Ideal geometries are assumed in these calculations although most actual structures are distorted. Such distortions could increase QS even when no intermolecular association is present. Also, although intermolecular bonds, Sn----X, are usually about 1Å longer than a normal Sn-X covalent bond, both X groups are assigned the same p.q.s.

The size of the ratio $\rho = QS/IS$ for systems which show resolvable splitting was proposed very early on as a test for coordination number at tin(IV).¹¹⁴ A ρ value greater than 2.1 (when IS is measured relative to SnO₂) appears to occur only when a higher-than-four coordination is present; $\rho < 1.8$ signals four coordination. This is because in moving from four to higher coordination IS generally decreases (increased screening of 5s by p and d electrons) whilst QS generally increases. The criterion appears to hold well experimentally.¹⁶

For one class of organotins, the six-coordinate diorganotin(IV) derivatives, point charge calculations are capable of predicting quantitatively the C-Sn-C bond angle. With the assumption that only the two organic ligands contribute significantly to the quadrupole splitting,¹¹⁵ the point charge model predicts that the

magnitude of QS obeys the relationship¹¹⁶:

$$|QS| = 4[R] (1-3\sin^2\theta\cos^2\theta)^{\frac{1}{2}}$$
Eqn. 1.IX

where [R] is the p.q.s. for the organic group R, and $(180-\theta)^{\circ}$ is the C-Sn-C angle. This relationship seems to agree quite well with crystallographic data for Me₂Sn(IV) and Ph₂Sn(IV) derivatives, with |QS| increasing smoothly from <u>ca</u>. 2mms⁻¹ for <u>cis-R₂Sn(IV)</u> to about 4mms⁻¹ for <u>trans-R₂Sn(IV)</u>. Compounds in which the model yields incorrect values have been reported, e.g., Me₂Sn(NO₃)₂,¹¹⁵ and |QS| values greater than those calculated for a linear C-Sn-C group have been observed.¹⁶

Finally, the recoil-free fraction, measured in terms of its temperature dependence, is becoming exploited as a structural probe because the extent of intermolecular association in an organotin solid may influence the magnitude of f and its temperature dependence. In equation 1.V, f is written as a reciprocal exponential function of $\langle x^2 \rangle$ the mean-square vibrational amplitude of the Mössbauer atom in the direction of the Y-ray, a quantity which in turn is proportional to how tightly bound $\langle x^2 \rangle$ increases with increasing the atom is in its lattice. temperature (and hence f decreases) but may be expected to do so more slowly when vibrational freedom of the Mössbauer atom is restricted in one or more directions by its incorporation into a polymeric network than in solids where the forces holding the lattice together are relatively weak.

If the recoil-free fraction of an absorber decreases only slowly with increasing temperature then the probability of recoiless absorption of the γ-radiation at room temperature could be high enough to give a marked resonance effect at that temperature. Early observation of ^{119m}Sn spectra at room temperature led to the generalization that this phenomenon could be correlated with the presence of polymeric structures¹¹⁷ and theoretical work lent support to this by showing that Debye temperatures for polymeric tin compounds should be appreciably higher than for monomeric solids.¹¹⁸ A study of thirty organotin(IV) compounds which, from evidence such as high melting point, insolubility, QS values and infrared spectra, were considered to be polymeric all gave significant room-temperature resonances.¹¹⁹

Bancroft et al.¹²⁰ pointed out, however, that a roomtemperature spectrum for at least one monomeric compound, Ph₄Sn, had been obtained and also that a number of known polymeric structures do not exhibit a spectrum at this temperature. Easily observable room temperature spectra were also obtained for a number of other Sn(IV) compounds known crystallographically not to be polymeric, including, for example, Ph₃SnC1.

A more quantitative approach to measuring the degree of intermolecular association is suggested by equation 1.VII. Lnf(T) is a linear function of temperature, T, in the hightemperature limit in the Debye model and this has been found to be so for many systems despite the limitations of the model used. Evaluation of reliable absolute f values is not

straightforward, however, due to the need for knowledge of absorber and source linewidths, but if a "thin" sample is used then the relative percentage area under the resonance envelope, A(T), will be directly proportional to f so that one may write:

$$A(T) \propto f(T) = \exp\left[\frac{-6E_R \cdot T}{k\theta_D^2}\right], \quad T \ge \frac{1}{2}\theta_D \qquad \dots \dots Eqn. 1.X$$

and a plot of lnA(T) versus T should give a straight line with a (negative) slope which is a measure of the rate of decay of the resonance effect.

Such slope values have been used by a number of workers to investigate intermolecular association. It has been proposed that relatively shallow slopes are characteristic of polymeric lattices in which the tin atom cannot vibrate with a large amplitude along the direction or directions of polymer propagation.¹²¹ Large (steep) slopes, in this theory, signal monomeric solids whose lattices are assembled from discrete, non-interacting (except for vander Waals forces) molecules. A study of a series of organic and inorganic tin compounds of known lattice structure showed that slopes were a useful guide to lattice structure and slope/structure systematics were proposed. Thus molecular, non-interacting lattices had a values (a being defined as $\underline{a} = -dlnA(T)/dT$ of \underline{ca} . 1.8 x $10^{-2}K^{-1}$ no matter what the coordination at tin, e.g. Me₃SnONPh.CO.Ph, Ph₃ONPh.CO.Ph, and Me₂Sn(ONMe.CO.Me)₂. The magnitude of the slope decreased progressively for a series of related triorganotin oxygen-bonded derivatives, $R_n Sn(OE)_{4-n}$ (R = Me, Ph, n = 2, 3), in which the

lattices are progressively stiffened by stronger intermolecular forces: [Me₃SnO₃SPh,H₂O] consists of chains of molecules held together by only weak hydrogen bonds and shows a slight decrease in its a value (1.71 x 10^{-2} K⁻¹), but [Me₃Sn(picolinate), H₂0] which has a more complex, three-dimensional network of hydrogen bonds exhibited a considerably reduced value of 1.27 x 10^{-2} K⁻¹ and a lattice formed by very strong hydrogen bonds, Me₂Sn(ONH.CO.Me)₂, gave only $0.92 \times 10^{-2} \text{K}^{-1}$. Similar, and lower, values were obtained for one-, two- and three-dimensional polymeric lattices: $Me_3SnON=C_6H_{10}$, $Sn(0_2CH)_2$ and Me_2SnO , <u>ca</u>. 0.9 x $10^{-2}K^{-1}$. $SnCl_2$ gave a similar value, 0.92 x $10^{-2}K^{-1}$ and SnO, which was assumed to be ionic, gave a very shallow slope, 0.23 x 10^{-2} K⁻¹. This correlation of <u>a</u> with structure was used to infer that $Ph_3SnON=C_6H_{10}$ is unassociated (a = 1.825 x $10^{-2}K^{-1}$) and that the ethyl- and n-propylhomologues (a = 1.16, 1.43 x $10^{-2} K^{-1}$, respectively) adopt structures of intermediate rigidity between the known one-dimensional polymer of the trimethyltin homologue and the inferred monomeric structure of the phenyl derivative. A compound containing tin in both its stable oxidation states, [Sn(IV)Sn(II)(02CPhN02-0)40,THF]2 gave significantly different slopes for the two types of tin, reflecting the relative tightness with which the two atoms are bound in the tetranuclear molecules. The triorganotin derivative $[Ph_3Sn(C_6H_4CHCH_2)]_n$ has a polymeric lattice, ¹²³ but the Ph₃Sn is four-coordinate and pendant to the polymer chain; its slope of 2.30 x 10^{-2} K⁻¹ indicates that the tin atom has vibrational freedom akin to that of monomers. 124

Complications exist, however. The compound $Ph_2 Sn[S_2P(0^{i}Pr)_2]_2$ gives a shallow slope, 1.06 x $10^{-2}K^{-1}$, ¹²⁵ nevertheless, it is known to be monomeric. ¹²⁵ The molecules pack very regularly and tightly in their lattice as chelated monomers (a bridged, associated form would be expected to have the same dimensions and density) and because of its variable temperature Mössbauer behaviour the compound has been termed a "virtual polymer". ¹²⁵

A model has been developed which links the temperature dependence of the recoil-free fraction and low energy (< 200 cm^{-1}) lattice-mode frequencies in the Raman spectrum to calculate a value for the mass of the vibrating unit in the lattice.¹²⁶ In the equation $dlnf/dT = -6E_R/k\theta_M^2$, θ_M is a characteristic temperature which is, for an ideal, monoatomic, isotropic, cubic solid, equivalent to the Debye temperature $\boldsymbol{\theta}_{D}$ calculated from lowtemperature specific-heat data. From conservation of momentum considerations dlnf/dT =-3E $^{2}_{\gamma}/M_{eff}C^{2}k\theta^{2}_{M}$, so that M_{eff} is the "effective" recoiling mass which contains the Mössbauer active Because, to a first approximation, inter- and intraatom. molecular motions do not couple in a molecular solid the lattice can be regarded as an assembly of hard, spherical particles which interact within the unit cell by van der Waals intermolecular Raman spectroscopy in the low energy region (< 200 cm⁻¹) forces. can probe such intra-unit-cell vibrations of the molecules against each other, and if one of these lattice modes corresponds to the unique intermolecular, intra-unit cell vibration of two molecules against each other then the frequency of this mode, $\boldsymbol{\omega}_{_{\!\boldsymbol{T}}}$, can be used to calculate an effective Debye temperature:

$$\theta = h\omega/k$$

so that:
$$\frac{d \ln f}{dT} = \frac{d \ln A}{dT} = \frac{-3E^2 k}{\gamma k}$$
Eqn. 1.XI

and a value, M_{eff}, can be calculated. Therefore the temperature dependence of the resonance area can be used to distinguish between monomers, dimers, trimers and other low-molecularweight polymeric units. This model has been tested for a number of geometries and coordination numbers of tin¹²⁷ and appears to be valid for structures in which the tin atom is or is not at the centre of mass of the molecule, consistent with the predictions of the model.

1.4. Biocidal Activity of Organotin(IV) Compounds

The control of pest organisms is a technological problem of the highest importance. To date the most effective agents have been chemical pesticides, and among these are a wide variety of organo derivatives of heavy main-group metals especially organoarsenic, organomercuric and organotin compounds. Tin has a crucial advantage over mercury and arsenic in these applications because organotins are easily degraded to non-toxic tin under environmental conditions such as U.V. irradiation and microbial attack.⁵ No evidence for biomethylation of organic tin in the natural environment has been found¹²⁸ though Brinckman et al. obtained evidence of biomethylation of SnCl₄ to a dimethyltin species by <u>Pseudomonas</u> bacteria in the laboratory.¹²⁸ In the series $R_n SnX_{4-n}$ (n = 1 through 4) the triorganotins are by far the most active biologically. Biological behaviour of $R_3 SnX$ species shows a marked species dependence of the R group as summarised below:

| Species | Most active R in R ₃ SnX |
|-------------------------|---|
| Insects, mammals | Ме |
| Mammals | Et |
| Gram-negative bacteria | n-Pr |
| Gram-positive bacteria, | |
| fungi, and molluscs | n-Bu |
| Fish, fungi, molluscs | Ph |
| Mites | $\left(\begin{array}{c} cyclo-C_{6}^{H} \\ 11 \end{array} \right)$ |
| | Neophyl |

It has generally been reported that within a particular series of R₃SnX, variation of the inorganic group, X, has very little effect on the biological activity.⁵ However, in practical applications in a natural environment X may affect physical properties such as volatility and solubility and hence the mobility of an R₃Sn species in the environment and within the target organism. Moreover, several instances of X making a significant direct difference to the toxicity of trioorganotin compounds have been documented. In general the biological activity of R₃SnX molecules is attributed to exchange of anionic X with the active sites on proteins⁵ which are thought to be histidine residues¹²⁹ and sulphydryl groups¹²⁸ consistent with activity being independent of X. It has also been demonstrated that residues of triphenyltin acetate on glass, formed by evaporation

of acetone solutions of the compound, were, on contact with houseflies, less toxic with increasing concentration and, since triphenyltin acetate was thought to be polymeric in the solid state and in concentrated solutions, it was proposed that the four-coordinate monomer, which exists in dilute solutions, is toxic to insects, whereas the polymer is non-toxic. 5,130 The reduced activity is thought to arise because the polymeric form is less likely to exchange its X group. It was also observed that the tributyltin derivative, Bu₃SnOCHPhCH₂NEt₂, which has an intramolecularly chelating anionic ligand with cis-R₃SnX₂ geometry was only one-eighth as toxic orally to mice as fourcoordinated bis(tributyltin)oxide. 130 This has been ascribed to a lack of affinity of the chelated molecule for the active sites on proteins.¹³⁰ Similarly, 4-hydroxybutyldibutyltin acetate, in which the hydroxyl group may coordinate intramolecularly to the tin was found to be only half as toxic to mice as fourcoordinate Bu₃SnC1.^{5,131}

A series of triorganotins (R = Ph, Cyh, Neo) which are known to have chelated $\underline{\operatorname{cis}}_3 \operatorname{SnX}_2$ structures were tested for miticidal and fungicidal activity compared with tricyclohexyltin hydroxide and triphenyltin acetate and it was found that intramolecular coordination to the tin reduced miticidal activity, but fungicidal effectiveness was more variable.¹³⁰

Toxicological data for dialkyltin derivatives imply formation of octahedral complexes in which vicinal dithiol groups on certain enzymes associated with α -keto acid oxidation act as neutral bidentate ligand ⁵ or can combine with R₂SnX₂ with elimination of HX, Figure 1.XVI.



Figure 1.XVI

Unlike the behaviour of trialkyltin compounds, there is marked dependence of toxicity on the inorganic ligand X^5 . For example, Me₂SnCl₂ is moderately toxic for mammals (as measured by acute oral toxicity in rats)¹³² and would be expected to readily complex with the dithiol groups, whereas Me₂Sn(SCH₂CO₂ⁱOct)₂ in which substitution by less electronegative sulphur ligands occurs, is essentially non-toxic.¹³²

Thus, both lattice structure and local coordination number at the tin atom have an important influence on the practical applications of organotin species, and an accurate understanding of structure/activity relationships with concomittant advances in such physical probes of structure as variable-temperature Mössbauer spectroscopy are a pre-requisite for continued progress in this field.

Chapter 2

A Variable-Temperature MBssbauer Study of

Phenyltin(IV) Compounds

2.1. Introduction

Triphenyltin(IV) compounds (R₃SnX) show important biocidal properties and a number have reached commercialisation. Thus the first organotins commercially marketed (in the early 1960's) were the agrochemicals triphenyltin acetate (Brestan^R, Hoechst A.G.) and triphenyltin hydroxide (Duter^R, Philips Duphar N.V.). These two compounds continue to be widely used as fungicides, and have also been shown to function as insect "antifeedants", and may in addition act as chemosterilants for insects²². In recent years several triphenyltins have been further commercialised as toxicants in marine anti-fouling paints. 133,134,135 It is therefore, perhaps, rather surprising that comparatively little structural information and especially crystallographic data are available for this class of organotin, particularly the important coordination polymer arrangements. As part of the present work, therefore, a range of triphenyl- and diphenyltin(IV) derivatives have been studied by means of Mössbauer spectroscopy, and the X-ray structures of two important compounds, triphenyltin acetate and triphenyltin formate, determined.

The use of ^{119m}Sn M&ssbauer spectroscopy as a solid-state structural probe has played a very important role in supporting and supplementing structural insights which have accrued from the key technique of X-ray diffraction analysis. Summarising the discussions in Chapter 1, the single-temperature experiment, usually at 78K, supplies reliable information on the oxidation state of the tin through the isomer shift and on the coordination number and isomeric arrangement of ligands about the tin by means of both the isomer shift and quadrupole splitting values. Analysis of the rate of decay of the resonance area A(T) with increasing temperature (variable-temperature Mössbauer spectroscopy, v.t.M.s.) based on the equations:

$$d\ln A(T)/dT = d\ln f(T)/dT = -6E_{R}T/k\theta_{D}^{2} = -3E_{\gamma}^{2}/M_{eff}C^{2}k\theta_{D}^{2}$$

gives information on the question of association (i.e., intermolecular bonding) in the solid. Detailed correlations between A(T) and the bonding at tin in the solid would require independent data on θ_{D} and M_{eff}, but even without these, generalisations can be made concerning the magnitude of the temperature dependence of A(T) and the question of intermolecular association in the solid for molecules of similar molecular weights. 122,136 Slope/structure systematics may thus be developed for a class of compound (e.g., methyltin derivatives or phenyltin derivatives, etc.) based on a foundation of secure crystallographic data. Such systematics can then be used to explore structural trends in series of related compounds: the slope value can be used to support inferences drawn from IS and QS values as to the existence of intermolecular association. In some instances, e.g., for two alternative geometries of a triorganotin derivative of a bidentate ligand (Figure 2.1) the QS values for the two geometric isomers may be too close to permit unambiguous resolution, especially when distortions from ideal geometries occur.



cis-R₃SnL₂

trans-L₂SnR₃

Figure 2.I

QS values alone cannot distinguish between true polymers (Figure 2.I, n up to ∞) and short-chain or cyclic oligomers (n up to <u>ca</u>. 10), an example of the latter situation being {Ph₃SnOP(0)(OPh)₂}.¹³⁷ As well as helping to establish the existence or not of association between molecules, such systematics can be used to estimate the relative strengths and extent of association. Of course, it is important to keep in mind that, like any indirect technique, Mössbauer spectroscopic evidence of necessity is circumstantial and best considered in conjunction with other observations pertaining to possible intermolecular interactions, such as solubility, melting point, infrared and Raman spectroscopies, mass spectrometry and relation to compounds of known structure.

Crystallographic characterisation of organotin(IV) compounds is most developed for methyltin derivatives¹⁴ and <u>a</u>/structure systematics (<u>a</u> =-dlnA(T)/dT) have been broadly established for this class. Much less diffraction information is available for phenyltin derivatives and v.t.M.s. data are also less common, so correlation with structure is less securely based.

The strategy of the present work has been to examine by v.t.M.s. a range of phenyltins of known lattice structure and, on the basis of the results obtained, and by consideration of data reported in the published literature, to propose a correlation of <u>a</u> values with lattice structure. Conclusions from this study have also been used to make structural predictions for a number of crystallographically uncharacterised phenyltins.

A general feature of the compounds under study which could, <u>a priori</u>, be anticipated to influence the v.t.M.s. data, and cause them to differ from those obtained from methyltins, is the nature of the phenyl ligand. This is structured and sterically bulky compared with the relatively small and spherical methyl group, and is electron withdrawing as opposed to the electronreleasing methyl group. Such electronic and steric properties can very significantly effect both the local coordination number at the tin atom and the overall packing of the molecules into the lattice.

It must also be recognised that determination of dlnf(T)/dTfrom the temperature dependence of A(T) is not entirely straightforward because (i) the systematics are based on the assumption that the Debye model of solids holds (at least approximately), and (ii) the fact that only when a thin absorber is used, so that saturation effects can be neglected, is A(T) directly proportional to f(T). Deviation of a sample from either, or both, of these conditions (of which, of course, condition (i) is entirely beyond the experimenter's control) may lead to curvature of the ln A(T) vs. T plot. If the curvature is slight a range of equally valid "best straight lines" (as judged by the correlation coefficient, r, for each fit) can be made to fit the data and a range of slope values will be obtained. Deviations of data from a linear function were not uncommon in this work and are also evident in results reported from other laboratories (for example, ref. 138). Comparisons of data from a number of laboratories therefore have potential risks due to inevitable variations in sample thickness, and the subjectivity of what is an acceptable linear range for the data. The overall trends which can be discerned in the data are thus more important than minor variations Figure 2.II shows some representative variable-temperature in a. data, including varying degrees of curvature.

2.2. Experimental

Organotin reagents and ligands were purchased from normal commercial sources (usually Merck or Aldrich) and were used in syntheses without further purification. Samples of tetraphenyltin (Aldrich) and triphenyltin chloride (Merck) used for MBssbauer spectra were recrystallised from toluene or diethyl ether. Triphenyltin hydroxide and diphenyltin oxide were gifts from the International Tin Research Institute (Greenford); triphenyltin hydroxide was recrystallised from cold acetone. Diphenyltin dichloride (B.D.H.) was recrystallised from toluene.



Figure 2.II. Representative variable-temperature Mössbauer data: (\Box) , $(C_6H_{11})_3$ SnOH, linear over whole T range $(\underline{a} = 0.66 \times 10^{-2} \text{K}^{-1})$; (\blacksquare) , $(C_6H_{11})_3$ Sn(1,2,4-triazol-1-y1), showing mild curvature (78 -145K); the range of 'best straight lines' is given by - (1.31 x 10^{-2}K^{-1} , all data) and---(1.10 x 10^{-2}K^{-1} , three points); (•, o), Ph₃SnO₂PPh₂, showing a marked deviation from linearity over the whole T range. For the latter, data correspond to two separate data sets (•, 1 mg ¹¹⁹Sn per cm²; o, 4 mg ¹¹⁹Sn per cm²) collected over a time interval of 4 months. Normalisation of data to 78K is merely to facilitate inter-sample comparison, the point Δ (78,0.00) being common to all plots.

The pyrazine (pyz) adduct of diphenyltin dichloride precipitated from a 1:1 mixture of the reagents in light petroleum b.p. 40 - 60° C, and was recrystallised from the same solvent.⁷²

The remaining phenyltin compounds used in this study were prepared by standard metathesis reactions, involving either triphenyltin hydroxide and a protonated form of the ligand, with the water formed in the reaction removed azeotropically in a Dean and Stark apparatus (Route 1), or from triphenyltin chloride and an alkali-metal (Na or K) salt of the ligand (Route 2). Route 1 was employed to prepare the triphenyltin derivatives of 1,2,4-triazole, diphenylphosphinic, formic, and acetic acids. Triphenyltin fluoride and isothiocyanate were prepared by Route 2. Bis(triphenyltin) oxide was obtained by dehydration of Ph₃SnOH in boiling toluene under the conditions used in Route 1.

All the compounds subjected to variable-temperature Mössbauer spectroscopy analysis were confirmed by i.r. m.p. and (in most cases) C, H, and N microanalyses (microanalytical service, University College, Dublin) and the Mössbauer IS and QS data are in good agreement with published values (Table 2.I).

Samples were utilised as finely ground powders (to minimise orientation effects), with up to 2mg ¹¹⁹Sn per cm² to comply as fully as possible with the criteria for a "thin sample" while allowing good quality spectra to be accumulated within a

Table 2.I

| | Analytic | al Data for H | henyltin Compo | unds | | | |
|---|--|---|---|---|---|---------------------------------------|-----|
| | An | alysis (%) ^a | | | | | |
| Compound | C | H | N | M.p. (°C) ^b | IS ^c | QS ^c | |
| Ph ₄ Sn | | | | 224–226 (224–225) | 1.27(1.27) | 0.00 | |
| Ph ₃ SnF | 58.70(58.60) | 4.00(4.10) | | 320 (de comp.) (357, de comp.) | 1.30(1.25) | 3.62(3.53) | |
| Ph ₃ SnC1 | | | | 104-106(105.5-107) | 1.35(1.37) | 2.53(2.45) | |
| Ph ₃ SnNCS | 56.10(55.90) | 3.70(3.70) | 3.20(3.45) | 162-164 | 1.40(1.35) | 3.44(3.54) | |
| Ph ₃ SnOH | | | | 119-120(119-120) | 1.18(1.24) | 2.82(2.98) | |
| (Ph ₃ Sn) ₂ 0 | | | | 123-124(124) | 1.16(1.07) | 1.37(1.63) | 59. |
| Ph ₃ SnO ₂ CMe | 58.35(58.70) | 4.40(4.45) | | 120-121(121-122) | 1.28(1.28) | 3.35(3.36) | |
| Ph ₃ SnO ₂ CH | 57.60(57.75) | 4.00(4.10) | | 206–207 (201) ^d | 1.48(1.37) | 3.48(3.58) | |
| Ph ₃ Sn0 ₂ PPh ₂ | 63.15(63.55) | 4.70(4.45) | | 280(decomp.) | 1.23 | 3.33 | |
| Ph ₃ Sn(triaz) ^e | 56,50(57,45) | 3.75(4.10) | 9.90(10.05) | 306-308 | 1.25(1.29) | 2.89(2.76) | |
| Ph ₂ SnO | | | | | 0.89(0.95) | 1.90(1.87) | |
| Ph2SnC12 | | | | 42-44(42-44) | 1.41(1.40) | 2.85(2.80) | |
| Ph_2SnCl_2 . $\frac{3}{4}pyz^f$ | 44.40(44.60) | 3.25(3.25) | 5.15(5.20) | 114-115 | 1.37(1.32) | 3.08(3.00) | |
| ^a Required values otherwise state ^d B.F.E. Ford, B f pyz = pyrazine. | s given in paren ed. ^C Literatur .V. Liengme, and | theses. ^b Li e values (mms J.R. Sams, <u>J</u> | terature values ⁻¹) in parenthe . Organomet. Ch | s (in parentheses) are eses are taken from Re nem., 1961, <u>19</u> , 53. | e taken from H efs. 15 and 17 ² triaz = 1,2, | Ref. 1 unless 7. ,4-triazol-1-y | 1. |

reasonable time (ca. 12 hr). In certain instances quantities of absorber in excess of 2mg were used (up to a maximum of 4mg) usually at the higher temperatures for species with relatively non-rigid lattices, leading to a curvature in the lnA(T) vs. T plots because of absorption saturation. It was found that a range of equally valid best straight lines was possible depending on the temperature range over which the linear range was assumed to hold. In reporting these results, a single value for a is given for the complete data set, followed in parentheses by maximum and minimum slopes for segments of the data which could be considered to obey a linear relationship, and which do not show any significant reduction in correlation coefficient. Data for which only a single fit are given show no appreciable deviation from a linear relationship, from which it may be concluded that vibrational anharmonicity is also absent. The quoted correlation coefficients are related to the complete data set for a given compound.

2.3. Discussion

Of the phenyltin compounds studied by variable-temperature Mössbauer spectroscopy in the present work and by others (Table 2.II), those which are known to have lattices made up of non-interacting molecules comprise the monomers $(Ph_2Sn)_6$ (3),⁴⁴ $Ph_3SnSnPh_3$ (14)⁴⁵, $Ph_2Sn[S_2P(OEt)_2]_2$ (19),¹³⁹ $Ph_3SnON(Ph)C(0)Ph$ (21),⁶⁴ Ph_3SnC1 (31),¹⁴⁰ $(Ph_3Sn)_20$ (32),³² Ph_2SnC1_2 (33),⁹³ $Ph_3SnO_2CC_6H_4$ ($o-N_2R^4$) (R^4 = 2-hydroxy-5-methyl-

| Table 2.II | | | |
|------------|------|--|--|
| | 119m | | |

Variable-Temperature In Mossbauer Data for Phenyltin

| (| Compound | $10^{2} a/K^{-1}$ |
|------|--|------------------------------|
| (3) | (Ph ₂ Sn) ₆ | 2.80 ^b |
| (4) | $\{\operatorname{Ph}_{2}\operatorname{Sn}[(\operatorname{CH}_{2})C_{6}H_{4}(\operatorname{CH}_{2})_{2}]\}_{n}$ | 2.72 ^d |
| (5) | (Ph ₃ Sn) ₄ Sn | 2.42 ^b |
| (6) | $Ph_2Sn(C_6F_5)_2$ | 2.37 ^b |
| (7) | $[Ph_3Sn(C_6H_4CHCH_2)]_n$ | 2.30 ^d |
| (8) | $Ph_2Sn[S_2^P(OPr^n)_2]_2$ | 2.19 ^g |
| (9) | Ph2 ^{SnH} 2 | 2.19 ^b |
| (10) | $Ph_3Sn(C_6F_5)$ | 2.17 ^b |
| (11) | $Ph_{3}SnO_{2}C(CH_{2})_{2}C(O)Me$ | 2.17 ^b |
| (12) | $Ph_{3}SnO_{2}CC$ (Me) CH ₂ | 2.13 ^{b,i} |
| (13) | Ph ₃ SnO ₂ PPh ₂ | 2.09(2.09-1.43) ^j |
| (14) | Ph ₃ SnSnPh ₃ | 2.09 ^b |
| (15) | (Ph ₃ Sn) ₂ NCN | 2.08 ^k |
| (16) | Ph ₃ SnH | 2.01 ^b |
| (17) | PhSnCl ₃ | 1.97 ^b |
| | | |

Compounds

| -r(T range/K, points) | Structure |
|-----------------------|------------------------------------|
| | Monomer ^C |
| | Polymer (3 or 4) ^{d,e} |
| | Monomer |
| | Monomer |
| 0.991(77-130,14) | Polymer ^{d,f} |
| (78-110,5) | Monomer ^h ⁶¹ |
| | Monomer |
| | Monomer |
| | Polymer (3 or 4) ^{e,h} |
| | Monomer ^h |
| 0.985(78-150,12) | Polymer (3) |
| | Monomer ^C |
| | Polymer (4) ^e ,h |
| | Monomer |
| | Monomer ^h |
| | |

Table 2.II (contd)

| | Compound | $10^{2} \underline{a} / \mathrm{K}^{-1}$ |
|------|--|--|
| (18) | PhSnCl ₃ .H ₂ salen | 1.94 ¹ |
| (19) | $Ph_2Sn[S_2P(OEt)_2]_2$ | 1.92 ^g |
| (20) | Ph ₃ SnO ₂ CMe | 1.91 ^m |
| (21) | Ph ₃ SnON(Ph)C(0)Ph | 1.85 ⁿ |
| (22) | Ph ₃ SnNCS | 1.84 ^j |
| (23) | Ph ₃ SnONC ₆ ^H 10 | 1.82 ⁿ |
| (24) | Ph ₂ SnCl ₂ . ³ pyz | 1.79 ^j |
| | | |
| (25) | ${Ph_2Sn[OP(S)(OPh)_2]OH}_2$ | 1.76 [°] |
| (26) | Ph ₃ SnCN | 1.73 ^k |
| (27) | Ph ₂ SnOC ₆ H ₄ O | 1.73 ^b |
| (28) | $Ph_3SnO_2CC_6H_4(\underline{o}-N_2R^1)$ | 1.71 ^p |
| (29) | $Ph_3SnO_2CC_6H_4(\underline{o}-N_2R^2)$ | 1.60 ^p |
| (30) | $Ph_3SnO_2CC_6H_4(\underline{o}-N_2R^3)$ | 1.59 ^p |
| (31) | Ph ₃ SnC1 | 1.56(1.56-1.43) ^{j,q} |
| (32) | (Ph ₃ Sn) ₂ 0 | 1.56(1.56-1.38) ^j |
| (33) | Ph ₂ SnC1 ₂ | 1.54(1.54-1.39) ^{j,r} |
| | | |

-r(T range/K, points) 0.995 (78-115,4) (78 - 145, 8)0.998 (78-145,8) 0.997 (78-110.7) 0.998 (78-205,13) 0.995 (77-160,6) 0.998 (78-145,6) 0.996(78 - 145, 7)0.998 (78 - 145, 7)

Structure Polymer (3)^{e,h} Monomer^c Polymer (3)^{e,m} Monomer^C Polymer (3)^{c,e} Monomer^h 62. Monomer, polymer (2)^{c,e} Dimer^c Monomer^h Polymer (3 or 4)^{e,h} Monomer^h Monomer^h Monomer^h Monomer^C Monomer^C Monomer^c

Table 2.II (contd)

9-

| | Compound | $10^{2} \underline{a} / \mathrm{K}^{-1}$ |
|------|--|--|
| (34) | $Ph_3Sn0_2CC_6H_4(\underline{o}-N_2R^4)$ | 1.53 ^p |
| (35) | Ph ₃ SnF | 1.49 ^{j,s} |
| (36) | Ph ₃ SnS ₂ P(OEt) ₂ | 1.43 ^t |
| (37) | $Ph_3SnS_2P(0Pr^i)_2$ | 1.40 ^t |
| (38) | Ph ₄ Sn | 1.37 ^j |
| (39) | [Ph ₃ SnO ₂ P(OPh) ₂] ₆ | 1.37 ⁰ |
| (40) | Ph2 ^{SnCl} 2.H2 ^{salen} | 1.27 ¹ |
| (41) | Ph ₂ Sn(trop) ₂ | 1.20 ^u |
| (42) | Ph ₃ SnO ₂ CH | 1.15(1.15-1.03) ^j |
| (43) | Ph ₂ SnO | 1.15(1.15-0.94) ^j ,v |
| (44) | Ph ₃ SnOH | 1.10(1.10-1.08) ^j |
| (45) | $Ph_2Sn[S_2P(OPr^i)_2]_2$ | 1.06 ^g |
| (46) | Ph ₃ Sn(triaz) | 1.04 ^j |
| (47) | Ph2SnCl2.dppoe | 1.04 ^w |
| (48) | $Ph_2Sn[OP(S)(OMe)_2]_2$ | 0.97 ⁰ |
| (49) | PhSnCl ₃ .pyz | 0.90 ^x |
| | | |

| -r(T range/K,points) |
|----------------------|
| |
| 0.999 (78-160,13) |
| 0.999 (77-150,7) |
| 0.998 (77-155,9) |
| 1.000 (78-140,6) |
| 0.984 (77-170,6) |
| 0.995 (78-140,7) |
| |
| 0.997 (78-145,7) |
| 0.996 (78-200,8) |
| 0.998 (78-145,6) |
| (78-160,9) |
| 1.000 (78-145,6) |
| (77-110,6) |
| 0.972 (77-170,6) |
| 0.999 (79-150,5) |

Structure Monomer^p Polymer (2)^{e,h} Monomer^c Monomer^h Monomer^c Cyclic hexamer^C Polymer (2)^{e,h} 63 Monomer^h Polymer^h Polymer (2)^{e,h} Polymer (2)^{c,e} Monomer^C Polymer (2)^{e,h} Polymer (1)^{e,h} Monomer^h Polymer (1)^{e,h}
Table 2.II (contd)

^a Abbreviations: H_2 salen = N,N'-ethylenebis(salicylideneimine); pyz = pyrazine; R^1 = 4-hydroxynaphthyl; R^2 = 2-hydroxynaphthyl; R^3 = 4-dimethylaminophenyl; R^4 = 2-hydroxy-5-methylphenyl; trop = tropolonate (2-hydroxycyclohepta-2,4,6-trien-1-onate); triaz = 1,2,4-triazol-1-yl; dppoe = 1,2-bis(diphenylphosphoryl) ethane; ONC₆H₁₀ is cyclohexanone oximate.

^bRef. 159. ^c From X-ray crystallographic data (see Refs. 13 and 14 and Discussion section 2.3).
^d Ref. 123. ^e Figures in parentheses define the polymer class (see Figure 2.1II and Discussion section 2.3).
^f Ph₃Sn pendant to polymer chain. ^g Ref. 125. ^h On the basis of v.t.M.s. and other spectroscopic evidence.
ⁱ H. Sano and R. Kuroda, <u>Chem. Phys. Lett.</u>, 1971, <u>11</u>, 512. ^j This work. ^k Ref.156. ¹ Ref. 138. ^m This work, ^c
^k K.C. Molloy, T.G. Purcell, K. Quill, and I.W. Nowell, <u>J. Organomet. Chem.</u>, 1984, <u>267</u>, 237. Also reported as
2.17 x 10²K⁻¹ in Ref. 159. ⁿ Ref. 122. ^o F.A.K. Nasser and J.J. Zuckerman, <u>J. Organomet. Chem.</u>, 1983, <u>244</u>, 17.
^p Ref. 58. ^q Also quoted as 1.53 x 10⁻²K⁻¹ in Ref. 156. ^r Also quoted as 2.21 x 10⁻² K⁻¹ in Ref. 156.
^s Also quoted as 1.33 x 10⁻²K⁻¹ in Ref. 159. ^t Ref. 145. ^u A.J. Rein and R.H. Herber, <u>J. Chem. Phys.</u>, 1975, <u>63</u>, 1021. ^v Also quoted as 1.30 x 10⁻²K⁻¹ in Ref. 159. ^w Ref. 87. ^x E. Rivarola, A. Silvestri, and
R. Barbieri, Inorg. Chim. Acta, 1978, 28, 223.

phenyl) (34),⁵⁸ Ph₃Sn[S₂P(OEt)₂] (36),¹⁴¹ and Ph₄Sn (38),²⁴ the dimer $\{Ph_2Sn[OP(S)(OPh)_2]OH\}_2$ (25)¹⁴² and the cyclic hexamer $\{Ph_3Sn[0_2P(OPh)_2]\}_6$ (39) ¹⁴³ and on the basis of spectroscopic evidence also include (Ph₃Sn)₄Sn (5), $Ph_2Sn(C_6F_5)_2$ (6), $Ph_2Sn[S_2P(OPr^n)_2]_2$ (8), $Ph_3Sn(C_6F_5)$ (10), Ph₃SnH (16), Ph₃SnO₂CC₆H₄(\underline{o} -N₂R²) (R² = 2-hydroxynaphthy1) (29), $Ph_3SnO_2CC_6H_4(\underline{o}-N_2R^3)(R^3 = 4-dimethylaminophenyl)$ (30), and Ph₃Sn[S₂P(OPr¹)₂] (37). All these compounds give a large a value (1.37 - 2.80) x 10^{-2} K⁻¹ reflecting the relative vibrational freedom of the tin atom in each case. However. this range embraces (in part) data reported for compounds whose lattices are stiffened by intermolecular hydrogen bonding, 122 suggesting that molecules with regular, well-structured groups bonded to the tin atom, like the planar phenyl group, can pack efficiently in an interleaving fashion into the crystal so that molecular motion is restricted. The recoil-free fraction at a given temperature is then larger than for more typical, loosely packed, monomers and the fraction value decays more slowly with increasing temperature. Rationalisations along similar lines have been advanced by a number of previous authors. 144,145,58 A particularly striking example is the compound $Ph_2Sn[S_2P(OPr^i)_2]_2$ which is known crystallographically to be monomeric. 146 gave comparatively a very shallow slope of 1.06 x 10^{-2} K⁻¹ 125 which was explained by the very efficient packing of the chelated molecules to give a dense structure in which the isomeric doublybridged form could be equally well accommodated without change in cell dimensions, a situation the authors called a 'virtual polymer'.¹²⁵ One may also note that $Ph_{L}Sn$ (a = 1.37 x $10^{-2}K^{-1}$)

has a very high melting point for a monomeric organotin (224°C, Table 2.I), and shows a room-temperature M8ssbauer spectrum^{117,126(b)} both of which facts signal a high degree of cohesion between the molecules which must be attributable to the operation of relatively large (non-directional) packing forces for this cleanly monomeric (in the sense that no directed chemical bonds exist between the molecules) solid.

The variable-temperature Mössbauer experiment divides phenyltin compounds known crystallographically to have polymeric structures into two groups: on the one hand $Ph_3SnOH (44)^{55}$, $a = 1.1 \times 10^{-2} K^{-1}$, and on the other, $Ph_3SnO_2CMe (20)$ (this work, see Chapter 3), $Ph_3SnNCS (22)^{147}$ and $Ph_2SnCl_2.$ ³pyrazine (24),⁷² all with <u>a ca</u>. 1.80 $\times 10^{-2} K^{-1}$. The lower value of Ph_3SnOH relative to the non-associated lattices discussed above follows from the expected restrictions imposed on the vibrational motion of a tin atom when incorporated into a polymer chain. Such a straightforward explanation is clearly not valid for the second group of polymers, whose <u>a</u> values are all in the 'non-polymer' region of the systematics, and a more searching analysis of the structural factors which might affect vibration motion in a polymer is called for.

A clear understanding of the three-dimensional architectures of polymers is essential to this aim. In general, a structure may be thought of as having three layers of complexity: the <u>primary structure</u> which is the structure of the monomer from which the polymer is built, its coordination number, geometry, stereochemistry, etc.; the secondary structure, which is the

66.

dimensionality of the polymer, i.e., one-dimensional chain, two-dimensional sheet or three-dimensional network; and the <u>tertiary structure</u> which is the three-dimensional distribution in space of the secondary structure. Primary and secondary structure obviously play a major role in defining the properties of a polymer, but, in the light of the variable-temperature data, they do not, alone, necessarily impose an extra restriction on the vibrational amplitudes of the atoms incorporated into the polymer backbone, and the consequences of tertiary structure must be considered.

Some classification of known structures is useful in this regard and may be made on the basis of the relative spacial disposition of the R_nSn and bridging ligand, X, sub-units. For the purposes of the present work, leaving aside polymeric structures arising from hydrogen bonding due, for example, to the presence of lattice water, four classes of tertiary structure can be identified as a framework for analysis of polymers in which X is covalently bound to R_n Sn and bridges an adjacent R_n Sn moiety as depicted in Figure 2.III. Class 1 is a rod-like polymer [Figure 2.III(a)] in which all the Sn and X groups are co-linear. Examples are Me₃SnCN¹⁴⁸ and $(C_6H_{11})SnX$ [X = F, ¹⁴⁹ C1¹⁵⁰] which have one-dimensional secondary structures, and Me_2SnF_2 which is two-dimensional,⁸⁸ <SnFSn = 180°. Class 2 is a characteristic zigzag arrangement, Figure 2.III(b) exemplified by Ph₃SnOH⁵⁵ $(\text{SnOSn} = 137.8^{\circ}), \text{Me}_{3}\text{SnC1}^{57} (\text{SnC1Sn} = 150.3^{\circ}, \text{Me}_{2}\text{SnC1}_{2}^{90})$ and Bu₂SnO(CH₂)₃0,¹⁵¹ all of which are one-dimensional, the former two with single, the latter two with double bridges. If the



Figure 2.III. Schematic classification of organotin polymers: (a) Class 1 (rod), (b) Class 2 (zigzag),

(c) Class 3 ('S'), and (d) Class 4 (helical).

bridging group, X, contains several atoms the structure expands and should become more flexible to give a Class 3, 'S'-shaped tertiary structure, Figure 2.III(c). This classification is not meant to be objectively rigid in its distinctions, so that, for example, Ph₃SnNCS¹⁴⁷ is placed in Class 3 (Figure 2.IV) although, because the tin atoms remain co-linear, and the linear NCS group is rigid, the overall tertiary structure retains some Class 2 character.



Figure 2. IV

When a more flexible X group is present, and particularly when the tin atoms are not co-linear, the 'S'-shape becomes more pronounced, e.g. Ph_3SnO_2CMe discussed in Chapter 3, and $(C_6H_{11})_3SnO_2CMe^{152,58}$ both of which are one-dimensional, and $Me_2Sn(SO_3F)_2^{89}$ which is two-dimensional. Clearly helical structures are reached when the extent of coiling of the polymer increases further (Class 4 tertiary structure, Figure 2. III(d)), for example α -Me_3Sn[O_2P(Ph)OH]^{153} and Me_3Sn(O_2SMe). ¹⁵⁴ In such cases the bridging group may embody entire primary units, and the only tin atoms shown in Figure 2.III(d) are the starting points of the unique repeating coil section. The point of this classification is that as one moves from Class 1 through Class 4, that is, as the bridging mass is progressively displaced away from the Sn----Sn vector, the structure should become inherently less rigid from the point of view of the tin atom's motion (i.e., more 'springy' as the extent of coiling increases). The second factor contributing to lattice rigidity will be the strength of the bridging bond: the stronger the bond the stiffer the structure. In practice some combination of tertiary structure and bond strength will operate.

On the evidence of the v.t.M.s. experiment, a Class 2 zigzag tertiary structure is, in fact, effective in reducing the vibrational lattitude of the tin relative to non-interacting lattices, e.g. Ph_3SnOH . The more flexible Class 3 polymers Ph_3SnO_2CMe and Ph_3SnNCS on the other hand, allow a vibrational freedom of the same order as non-polymers.

In Ph₃SnO₂CMe, the Class 3 structure (Chapter 3) results in the bridging mass of the acetate group being concentrated away from the line joining adjacent tin atoms, so that the space between the metal atoms is largely a void and the bridging role of the carboxylate group is reduced to the long (intra) Sn-O(1) bond (see Chapter 3). The polymer thus has a 'concertina-like' flexibility and, unlike the situation in more linear Class 2 or 1 polymers in which the tin's motion is restricted along the direction of polymer propagation, the tin atom's vibration becomes anisotropic.

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Consistent with this is the absence of any observable temperature-dependent spectral line asymmetry (Gol'danski-Karyagin effect) which arises from the recoil-free fraction being different for γ -ray absorption along and perpendicular to the polymer chain direction due to anisotropic vibration of the tin (Figure 2.V). The behaviour of the acetate is in sharp contrast to that of the similar compound trimethyltin glycinate, the rigidity of whose lattice is reflected in its a value, $1.15 \times 10^{-2} K^{-1}.60$ This was attributed primarily to the C=0....H-N hydrogen bonds formed between the polymeric chains ^{6C} but must also derive a significant contribution from the polymer itself. This gives rise to a sizeable Gol'danski-Karyagin effect arising from anisotropic vibrations of the tin atoms, the majority of this motion occurring in the plane of the C₂Sn group and perpendicular to the O-Sn-N axis, and this anisotropy is also reflected in the thermal ellipsoids of the room-temperature X-ray structure.⁶⁰ The salient structural difference is that in the glycinate the bridging $O-C-CH_2-N$ unit lies between neighbouring tin atoms straddling the Sn----Sn vector to produce a linear polymer chain (i.e. approximates a Class 1type tertiary structure) rather than the Class 3 flattened helical construction of the acetate which leaves largely a void between tin atoms.

The behaviour of a methyltin derivative, α -Me₃SnO₂P(OPh)OH, which has also been studied as part of the present work¹⁵⁵ supports this rationale. It is known to consist of helices held together into two-dimensional sheets by a network of strong

71.



Figure 2.V. Plot of the temperature dependence of the Mössbauer doublet spectrum line asymmetry. A_{+} and A_{-} are the areas under the more positive and more negative velocity wings, respectively. The slope of the line is $1.28 \times 10^{-5} \text{K}^{-1}$.

hydrogen bonds (P=0----H=0), ¹⁵³ and has an <u>a</u> value in the range $(1.42-1.62) \ge 10^{-2} \text{K}^{-1}$ which on the basis of known systematics ^{122,136} merely reflects the contribution of the hydrogen bonds to the lattice rigidity. As with triphenyltin acetate, incorporation of tin into a helical polymer (Class 4 in this case) does little to inhibit further the vibrational freedom of the tin.

Compound (4), $\{Ph_2Sn[(CH_2)C_6H_4(CH_2)_2]\}_n$ which is polymeric shows a very high <u>a</u> value¹²³ (2.72 x $10^{-2}K^{-1}$), and in the light of the analysis presented here must be severely coiled (Class 4).

 Ph_2SnCl_2 , #pyrazine has a unique structure involving both monomeric units and polymeric chains in the crystal.⁷² The polymeric component of the lattice is a Class-2 type accentuated by the large, but rigid, pyrazine bridge. It is plausible that such a long bridge would increase the value of <u>a</u> from <u>ca</u>. 1.10 x $10^{-2}K^{-1}$ (the value for Ph_3SnOH) in its own right and, in any case, because the two types of tin site cannot be distinguished by their IS and QS, the experiment is measuring only the average rigidity of the two types of tin site and the observed value of <u>a</u> (1.79 x $10^{-2}K^{-1}$) is not anomalous.

Finally, as has been noted previously, 123,124 tin atoms in $[Ph_3Sn(C_6H_4CHCH_2)]_n$ (7), in which Ph_3Sn units are pendant to the polymer chain, have the vibrational properties characteristic of a monomer, irrespective of the tertiary structure of the polymer.

On the basis of these systematics values for lnA(T) vs. T slopes can be used to draw inferences about the structures of crystallographically unconfirmed lattices (Table 2.II), especially in conjunction with other spectroscopic (including Mössbauer IS and QS values), physical, and chemical properties.

Ph₃SnCN, $\underline{a} = 1.73 \times 10^{-2} \text{ K}^{-1}$, must be monomeric, because any lattice association would have to be of Class-1 type in accordance with the coordinating properties of the -CN: ligand. This is in contrast to the structures of Me_2SnCN^{148} and Et_2SnCN^{157} which are Class-1 polymers (the latter structure has only been partially determined¹⁵⁷) but is consistent with the relatively large steric demands of the phenyl groups. Ph_3SnF (a = 1.49 x 10^{-2} K⁻¹) has been assigned a polymeric structure on the basis of its QS value, 3.53 mms⁻¹, 107 which indicates a five-coordinate trans- X_2 SnR₃ geometry at tin. The size of <u>a</u> signals a Class 2, zigzag, structure and its comparatively high value for this polymer class must mean that the intermolecular bond is weak (anisobidentate bridging). A similar geometry occurs in Me₃SnF.¹⁵⁸ The two oxygen-bonded polymeric, diphenyltin compounds $Ph_2SnOC_5H_0O(27)$ (presumably of para stereochemistry) ($\underline{a} = 1.73 \times 10^{-2} \text{K}^{-1}$ 159) and $Ph_{2}Sn0$ (43) (a = 1.15 x $10^{-2}K^{-1}$) both exhibit higher a values than might have been expected on the basis of related compounds which are thought to have extensive Sn-O cross-links between chains.²² The former compound must belong to Class 3 or 4, facilitated by a tetrahedral geometry at tin, and the latter to Class 2, with little or no cross-linking between chains. Me, SnO is thought to consist of two-dimensional polymeric sheets 22 and

its low <u>a</u> value of $0.87 \times 10^{-2} \text{K}^{-1}$ is consistent with this, ¹²² but bulky groups on tin are known to reduce the degree of crosslinking between chains.²² In Ph₂SnO, therefore, the steric effect of the phenyl groups may result in a Class 2 polymer similar to that of ⁱPr₂SnS.³⁹ Ph₃Sn(1,2,4-triazole) can also be assigned a Class 2 polymer structure (<u>a</u> = 1.04 x 10^{-2}K^{-1}), supported by its quadrupole splitting (2.89mms⁻¹) and is isostructural with the crystallographically established (C₅H₁₁)₃Sn(1,2,4-triazole).¹⁶⁰

In a study of a series of triphenyltin arylazobenzoates, $Ph_3Sn[O_2CC_6H_4(N_2R')-o]$ (28), (29), (30), (34) recently reported,⁵⁸ triphenyltin o-(4-hydroxynaphthylazo)benzoate (28) is assigned a monomeric mer-C_3SnON geometry Figure 2.VI on the basis of the simultaneous occurrence of a large quadrupole splitting (3.06mms⁻¹) and a large a value (1.710 x $10^{-2}K^{-1}$).



Figure 2.VI

However, the fact that no crystallographic precedent for this geometry in organotin chemistry exists ^{13,14} and the acknowledged lack of rationale for the structural change from the established structure of triphenyltin (o-2-hydroxy-5-methylphenylazo)benzoate (34), which adopts a distorted <u>cis-C₃SnO₂</u> five-coordinate geometry, militate against this argument, and in the light of the results presented in this Chapter two alternative structural possibilities are reasonable. The first of these is a structure with trans- 0_2SnC_3 geometry and a Class 3 tertiary structure for the resulting polymer which is consistent with both QS and variable-temperature data (despite being discounted in the original report⁵⁸), and would follow the familiar structural theme found in associated organotin However, this would still fail to explain why the carboxylates. structure should be so different from that of (34). The second possibility is a highly distorted six-coordinate mer-C₃SnO₂(OH) geometry in which the only intermolecular interaction is a long Sn----OH bond which, in conjunction with a Class 2- or Class 3-type tertiary structure for the resulting polymer, would maintain a high a value. This latter bonding scheme is plausible in that in the 4-hydroxynaphthyl group the para positioned hydroxyl group would, on steric grounds be freed from the intramolecular hydrogen-bonding role played by the 2-hydroxyphenyl moiety in (34). On the whole the relevant data favour this second alternative bonding scenario. Its general features occur in the recently solved crystal structure of $Ph_3SnO_2CC_{6H_4}(OH-2)$, ¹⁶¹ discussed in the following section of this Chapter.

The variable-temperature Mössbauer data for Ph₃SnOP(0)Ph₂ give a markedly curved line over the entire temperature range, Figure 2.II, a situation which must presumably be due to vibrational anharmonicity (i.e., a breakdown of the Debye model Quadrupole splitting of magnitude 3.33mms⁻¹ implies of solids). a coordination number higher than four and the fact that the compound decomposes without melting at <u>ca</u>. 300⁰C suggests lattice Inclusion of the majority of the data points in a association. linear fit gives an approximate indication of the rate of decay of the resonance for comparison with other compounds, and gives an 'a' value of ca. 1.50 x $10^{-2} K^{-1}$. Thus the polymer probably has a Class 3 structure akin to that of Ph3Sn02CMe (Chapter 3), and is isostructural with Me₃SnOP(S)Me₂ and Me₃SnOP(0)Me.¹⁶²

2.4. Mössbauer Study of Triphenyltin Substituted Benzoates.

2.4.1. Introduction

The solid-state structures of the series Ph3SnO2CC6H4X $(X = NH_2-2, NMe_2-2, NH_2-4, OH-2, OMe-2, SMe-4)$ have in each case been analysed crystallographically and explained in terms of cis-Ph₃SnO₂ penta-coordination arising from weakly chelating carboxylate ligands. 161,163 The structural distortions observed in each were described as a displacement away from tetrahedral towards trigonal bipyramidal. Where the possibility of hydrogen bonding exists it is, in each compound, availed of. Thus intramolecular hydrogen bonding from an amino hydrogen to the coordinate carboxyl oxygen occurs in the $X = NH_2^{-2}$ molecule, while for the para isomer (X = NH_2 -4) hydrogen bonding is intermolecular to a 2, screw-related carboxyl oxygen atom, forming a helical, hydrogen-bonded polymer chain.¹⁶¹ The same solid-state intramolecular hydrogen-bonding theme occurs in the X = OH-2 molecule.¹⁶³

Consistent with formation of hydrogen bonds in the series with $X = NH_2^{-2}$, NH_2^{-4} , OH^{-2} is a lengthening of the intramolecular tin-to-chelating oxygen distance relative to the corresponding distances in the molecules where hydrogen bonding cannot occur ($X = NMe_2^{-2}$, OMe^{-2} , SMe^{-4}). There is also an additional, sixth, coordination interaction at tin in the X = OH^{-2} structure: the hydroxyl oxygen atom of a neighbouring <u>c</u>-glide related molecule weakly bonds intermolecularly to the tin atom by approaching the 'tetrahedral' face opposite that approached by the intramolecularly chelating oxygen to give a very distorted <u>mer</u>-C₃SnO₃ octahedron about tin, Figure 2.VII.



Figure 2. VII.

This intermolecular interaction was proposed¹⁶³ as the reason for the very small distortion of the $C_3 SnO(1)$ framework from tetrahedral geometry (sum of the equatorial angles = 328.6° <u>vs</u>. 328.40° for a tetrahedron). Infrared and ¹H NMR measurements were cited as evidence of five coordination <u>via</u> the preservation of carboxylate chelation in solution in a non-polar solvent (CC1₄).

As part of the present work, ¹¹⁹Sn NMR and Mössbauer spectroscopic data were recorded for the series of compounds $Ph_3SnO_2CC_6H_4X$ (X = H, Me-2, NH_2 -2, NMe_2 -2, C1-2, C1-3, C1-4, OH-2, SMe-4, OH-4, OMe-2) and $Ph_3SnO_2CC_{10}H_7$ -1 and the results,¹⁶⁴ in conjunction with infrared data for the solution phase (CC1₄) and solid (KBr discs) cast doubt on the original interpretations of the X-ray crystallographic data for $Ph_3SnO_2CC_6H_4X$ (X = NH_2 -2, NMe_2 -2, OH-2, OMe-2, SMe-4).^{161,163}

2.4.2. Experimental

¹¹⁹Sn NMR spectra were recorded at the International Tin Research Institute, Greenford, Middx., under nuclear Overhausersuppressed conditions, in 10mm tubes on a JEOL FX60Q spectrometer, with field frequency lock to external D_2^{0} . ¹¹⁹Sn chemical shifts (δ^{119} Sn) are relative to Me₄Sn and are accurate to \pm 0.1ppm.

Infrared spectra were recorded in the region 4000-200 cm⁻¹ on a Perkin Elmer 1330 spectrometer as KBr discs or CCl₄ solutions (0.2g/3.0 cm³). ^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor-controlled spectrometer with a 512 channel data store as described in more detail in a later Chapter (Experimental Procedures). The samples used in the v.t.M.s. experiment (X = OH-2, OMe-2) contained lmg ¹¹⁹Sn cm⁻² in order to minimise saturation effects, although for temperatures above 110K samples containing 1.5mg ¹¹⁹Sn cm⁻² were required to obtain good quality spectra in a reasonable time of <u>ca</u>. 12hr. However, the data for both temperature intervals coalesced into a single line which exhibited no systematic curvature, suggesting that vibrational anharmonicity within the lattice is also absent.

The compounds $Ph_3SnO_2CC_6H_4X$ (X = NH_2-2 , NMe_2-2 , OMe-2, SMe-4) were prepared by an azeotropic dehydration reaction between stoichiometric amounts of triphenyltin hydroxide and the appropriate arylcarboxylic acid, in refluxing toluene and using a Dean and Stark trap (reflux times ca. 2hr). $Ph_3SnO_2C_6H_4(OH-2)$ was prepared by refluxing together the reagents using acetone as the reaction solvent. Table 2.III gives recrystallisation solvents, m.p.'s and analytical data for each compound.

2.4.3. Discussion

The structural possibilities of the series are represented by (I)-(VI), Figure 2.VIII, and all were described in terms of (II). 161,163 119 Sn NMR data for these esters, measured in carbon tetrachloride, a non-coordinating solvent, definitively imply four-coordination at the metal in each case 164 (Table 2. IV). The chemical shifts were all in the range -96.2 to -124.5ppm relative to Me₄Sn. Previous work has associated a chemical

Table 2.III

| Analytical | Data for Triphenyltin | Derivatives of | Aryl-substitute | d Benzoic | Acids, Ph_SnO_CC_H_X |
|--------------------|--|--------------------|--------------------|--------------------|----------------------|
| х | M.p. (^o C) ^a | c ^b (%) | H ^b (%) | N ^b (%) | Sn ^b (Z) |
| NH2-2 | 110-112(108-109 ^c) ^d | 61.4(61.7) | 4.5(4.3) | 2.9(2.9) | 23.9(24.5) |
| NMe2 ⁻² | 80-82(79-80 ^e) ^f | 62.8(63.0) | 5.2(4.9) | 2.7(2.7) | 23.2(23.2) |
| ОН-2 | 122–124(123–124 ^g) ^h | 60.8(61.6) | 4.0(4.1) | | 24.4(24.4) |
| OMe-2 | 110-112(107-108 ^g) ⁱ | 62.3(62.3) | 4.5(4.4) | | 23.6(23.7) |
| SMe-4 ^j | 143–145 (141–143 ^g) ^f | 60.6(60.4) | 4.4(4.3) | | 23.4(23.0) |

^a Literature values in parentheses.

^b Calculated values in parentheses.

^c L.E. Khoo and F.E. Smith, <u>Inorg. Chim. Acta</u>, 1981, <u>53</u>, L83.
^d Recrystallised from diethyl ether/petroleum ether.
^e Ref. 163. ^f Obtained analytically pure after reaction solvent removed. ^g Ref. 161. ^h Recrystallised from petroleum ether.
ⁱ Recrystallised from toluene/petroleum ether.
^j Sulphur, Found: 6.1; Calcd.: 6.2%









(VI b)

ΧI

Figure 2.VIII. Structural possibilities for

 $Ph_3Sn0_2CC_{6}H_4X$ compounds.

shift range of -40 to -120ppm for Ph_3SnX compounds with tetra-coordination^{165,166} and reference measurements were made on $(Ph_3Sn)_2^0$ (-83.6ppm) which is definitely four-coordinate in the solid state³² and $Ph_3SnOC(Ph)CHCO(Ph)$ (-221.2ppm) which is unambiguously five-coordinate in the solid state with structure(II)¹⁶⁷; it is unlikely that the coordination number will change in either case upon dissolution.

The link between solution- and solid-phase structure is made by infrared spectroscopy. The data in the v_{asym} (C=O) region for both phases for each compound were essentially the same, Table 2. IV, and this strongly suggests that the carboxylate ligand is unidentate in the solid state also. This rules out structures (II), (III) and (V) for the solid state and hence the original interpretations of the crystal structures of Ph₃SnO₂CC₆H₄X (X = NH₂-2, NMe₂-2, OH-2, OMe-2, SMe-2)^{161,163}. Structure (IV) is unlikely in view of its ¹¹⁹Sn NMR spectrum, as the chelation should persist in solution, but the data could be consistent with (VI) as well as (I).

The MBssbauer quadrupole splitting parameter should be diagnostic here as structure (I) will only generate a sufficient electric field gradient to give a QS magnitude in the range 1.00-2.40mms⁻¹, while the range for <u>cis</u>-XYSnR₃ (VIa) is 1.70-2.40mms⁻¹ and for <u>trans</u> XYSnR₃ (VIb), 3.00 - 4.00mms⁻¹.²² QS values fell in the range 2.30 - 2.55mms⁻¹ except for X = 0H-2 (Table 2.V) and so, of the two alternatives I and VI, MBssbauer spectroscopy, in conjunction with infrared and ¹¹⁹Sn NMR is consistent only with (I).

| Table 2.IV | | | | | | | |
|---|--------------------------------|--|-----------------------|--|--|--|--|
| ¹¹⁹ Sn N.M.R. (ppm) ^a an | nd Infrared (c | m ⁻¹) ^b Spectroso | copic | | | | |
| Data for Ph ₃ S | Data for Ph_SnX | | | | | | |
| | | ν asym (| C=0) | | | | |
| х | δ^{119} Sn ^c | Solid ^d | Solution ^C | | | | |
| ⁰ 2 ^{CC} 6 ^H 4 ^{NH} 2 ⁻² | -119.5 | 1615 | 1622 | | | | |
| 0_2 CC $6H_4$ NMe 2^{-2} | -124.5 | 1613 | 1613 | | | | |
| ⁰ 2 ^{СС} 6 ^Н 4 ^{ОН-2} | -96.2 | 1629 | 1630 | | | | |
| $O_2 CC_6 H_4 OMe - 2$ | -121.9 | 1629 | 1628 | | | | |
| 0_2 CC $_6$ H $_4$ SMe - 4 | -115.6 | 1 62 8 | 1636 | | | | |
| OC (Ph) CHCO (Ph) | -221.2 ^e | | | | | | |
| 0SnPh ₃ | -83.6 | | | | | | |

| - | Relative to Me ₄ Sn. |
|---|--|
| Ъ | ± 3 cm ⁻¹ . |
| с | CC1 ₄ solution. |
| d | KBr disc. |
| e | The previously reported value of -82.2ppm (S.J. Blunden and |
| | P.J. Smith, J. Organomet. Chem., 1982, 226, 157) is incorrect |
| | and is believed to have been due to either Ph ₃ SnOH or |

(Ph₃Sn)₂0 (Ref. 164).

a

Table 2.V.

.

| | 119 ^m Sn | Mössbauer | Data for Ph | $3\frac{\text{SnO}_2\text{CC}_6\text{H}_4\text{X}}{6}$ | |
|-------|---------------------|-----------------|-----------------|--|------------------|
| х | | IS ^a | QS ^a | Γ ₁ ^b | г ₂ b |
| ОН−2 | | 1.34 | 2.97 | 1.01 | 1.01 |
| OMe-2 | 2 | 1.25 | 2.30 | 1.03 | 1.03 |
| SMe-4 | 4 | 1.27 | 2.42 | 1.02 | 1.01 |

 $a \pm 0.04 \text{mms}^{-1}$

^b Full width at half height

The <u>cis</u> $OXSnR_3$ geometry implied by structure (VIa) can be ruled out with a fair degree of certainty as intermolecular bonding invariably results in a <u>trans</u>- $OXSnR_3$ (VIb) structure in which the more electronegative atoms occupy the axial positions of the trigonal bipyramid.

The QS for $Ph_3Sn0_2CC_6H_4OH-2$ is significantly higher (2.97 ± 0.04) mms⁻¹, and signals a higher-than-four coordination number. A short intramolecular contact Sn----O=C exists at 3.071(2)Å, and an intermolecular Sn----OH one at 3.035(2)Å (Figure 2.VII). Since weak intermolecular interactions such as the latter will be absent in dilute solutions, the ¹¹⁹Sn NMR chemical shift (-96.2ppm) which is consistent only with four-coordination implies that the Sn---O=C contact at 3.071(2) A is fortuitous and does not represent a bonding interaction as claimed originally. The enhanced QS relative to the other (four-coordinate) analogues can be attributed to an intermolecular Sn----OH bond, corresponding to the 3.035(2) A contact, which results in coordination expansion to five and formation of a trans-0, SnR, geometry (VIb) and Figure 2.VII. The resulting trigonal bipyramid is quite distorted with the sum of the CSnC angles = 350.4° and a difference of 0.095 Å between the two axial Sn-O bond lengths. As discussed above, section 2.3, a similar intermolecular Sn----OH interaction probably occurs in $Ph_3SnO_2CC_6H_4(N_2C_{10}H_6^{-1}, OH^{-4})^{-2}$ which has $QS = 3.06 \text{mms}^{-1.58}$

Variable-temperature Mössbauer spectroscopy can potentially distinguish between coordination polymers such as $Ph_3SnO_2CC_6H_4(OH-2)$

and discrete monomers such as Ph₃SnO₂C₆H₄(OMe-2), but in fact, the two compounds give very similar slopes ($\underline{a} = 1.36 \times 10^{-2} \text{K}^{-1}$, X = OH-2; 1.46 x 10⁻²K⁻¹, X = OMe-2, Figure 2.1X) which are consistent with discrete molecules within the lattice and also in accordance with an approximately equal effective vibrating mass for the two compounds which is to be expected from the near The values are close to equality of their molecular weights. those obtained for Ph_4Sn and $Ph_3SnO_2CC_6H_4(\underline{o}-N_2R)$ (Table 2.11). It is not, perhaps, surprising that the variable-temperature experiment is insensitive to the intermolecular interaction in Ph3Sn02CC6H4(OH-2) given both the weakness of the bond formed, and the Class 3 tertiary structure of the polymer. The bridging unit $-0C.C_6^{H_4}O-$ lies off the Sn-Sn' vector to give a flattened helical mode of propagation (Figure 2.X) similar to Ph3Sn02CMe, and hence does not inhibit the vibrational motion of the tin atoms. This interaction does, however, produce a large electric field gradient at the metal atom's nucleus and so manifests itself in the QS rather than in the lattice dynamics.

This reclassification of the coordination situation at tin in these substituted triphenyltin benzoates emphasises the importance of spectroscopic methods in deciding between closely related coordination geometries and the necessity of considering bond distances and angles comprehensively and not selectively.

For example, in $Ph_3SnO_2CC_6H_4$ (NMe-2), while the Sn-O distances suggest chelation by the carboxylate group (2.115 and 2.564Å),



Figure 2.IX. Plot of ln (reduced area) vs T for $Ph_3SnO_2CC_6H_4X$ (X = OH-2, OMe-2). The slopes of the lines are 1.36 x $10^{-2}K^{-1}$ (r = 0.997, 8 points) and 1.46 x $10^{-2}K^{-1}$ (r = 0.993, 7 points).



Figure 2.X. Polymer propagation in $Ph_{3}SnO_{2}CC_{6}H_{4}(OH-2)$, shown as a projection of part of the cell contents onto the <u>bc</u> plane. Only atoms linking metal centres are included for clarity. Data taken from ref. 161.

the angles do not change systematically in the correct directions for the transition from a tetrahedron to a trigonal Thus the "equatorial" angles should all change from bipyramid. 109° 28' towards 120°, but are in fact 122.1(3)°, 112.6(3)°, and $104.9(3)^{\circ}$, while the angles subtended at tin between the "axial" α -carbon of the phenyl ring and the equatorial atoms should change from 109° 28' towards 90°, but are 92.9(3)°, 108.4(3)° and 114.8(3)°. Many (but in fairness not all!) of these angular variations are in accord with the expected rehybridisation within a tetrahedral framework, which concentrates p-character in the bond to the more electronegative oxygen, hence naturally closing from 109° 28' angles involving oxygen while opening those which only involve In short, interpretation of these data in terms of a carbon. coordination number of five at tin is tenuous, and underlines the need of ancillary spectroscopic data in such circumstances.

2.5. Conclusions

The variable-temperature Mössbauer spectroscopy systematics outlined for methyltin species are broadly applicable to a wide range of phenyltin species also, i.e. <u>a</u> (-dlnf/dT) values of about 1.80 x 10^{-2} K⁻¹ correlate with monomeric lattices but the onset of polymerisation due to intermolecular association can significantly inhibit the tin atoms vibrational motion to give, characteristically, an <u>a</u> value of <u>ca</u>. 1.0 x 10^{-2} K⁻¹. However, caution must be exercised in the interpretation of such data: (i) in organotins containing structured, well-ordered groups bonded to the tin such as the phenyl group, the molecules can sometimes pack very efficiently into the crystal so that even "non-interacting" (in the sense of directed chemical bonds) molecules can be locked in the crystal tightly enough to give a relatively low <u>a</u> value (<u>ca</u>. 1.30 x 10^{-2} K⁻¹), and (ii) when the tin is incorporated into a helical or coiled polymer chain its environment will be usually flexible enough for it to mimic typical monomers i.e. its <u>a</u> value will be <u>ca</u>. 1.80 x 10^{-2} K⁻¹. Consideration of the nature of the (potentially) bridging group(s) and the tertiary structure of viable polymeric arrangements together with other spectroscopic evidence (including Mössbauer isomer shift and quadrupole splitting) can, however, make v.t.M.s.

Chapter 3

The Crystal and Molecular Structures of Triphenyltin Acetate and Triphenyltin Formate

3.1. Introduction

Organotin carboxylates have been the subject of numerous structural studies both spectroscopic and crystallographic, largely because of the potentially chelating or bridging properties of the -OC(0)- group. For triorganotins, detailed studies of the $\nu(C=0)/\nu(CO_{\gamma})$ region of the infrared, and IS and QS values in Mössbauer spectra, have predicted that both trialkyl- and triaryltin carboxylates always exist as five-coordinate polymers in the solid state unless steric interactions between the alkyl or aryl groups on the tin and the α -carbon substituent of the carboxylate group prevent such polymerisation in which case monomeric, tetra-coordinate species in the solid state are formed. 168 Furthermore, a study of trimethyltin acetate and a series of trimethyltin haloacetates (all apparently polymeric) by infrared and (single-temperature) Mössbauer spectroscopy has predicted that as the pK_a of the parent carboxylic acid decreases the differences between the two Sn-O bond lengths in the polymer and the difference between the two C-O bond lengths should both increase. 169 For triphenyltin derivatives, the structure (polymeric or four-coordinate monomeric) adopted is conspicuously sensitive to steric factors. 168 Thus, Mössbauer evidence has shown that a sample of monomeric, four-coordinate Ph3Sn02CCC13, upon ageing (ca. 5 yr.), had partially converted to the five-coordinate form so that this compound represents a borderline case in which the tendency of the tin to increase

its coordination number to five is very nearly balanced by steric interactions operating in the opposite direction.¹⁷⁰

This Chapter presents the crystal and molecular structures of the two important compounds, triphenyltin acetate and triphenyltin formate. Though closely related, they show quite different lattice dynamics in the variable-temperature Mössbauer experiment [Table 2.II, (20) and (42)], and this behaviour is rationalised by consideration of the two structures within the framework of the tertiary-structure description of organotin polymers developed in Chapter 2. Compounds such as these, more especially when studied as a pair in which only one relatively small change is made in the molecule, as in the present case, are often used as model compounds in spectroscopic and other studies of structurally more complex systems. The two compounds are also key examples of the biocidally active triphenyltin family of Triphenyltin acetate itself has been in use since the organotins. early 1960's as the active ingredient in Brestan^R (Hoechst A.G.) which is used to combat early blight in potatoes (caused by the organism Phytophthora infestans), and the compound is as effective against a range of fungi as conventional copper-based formulations, but at one-tenth the dose. 171

3.2. Experimental

3.2.1. Syntheses

Recrystallisation of the product of the reaction between triphenyltin hydroxide and the betaine $(HOOCCH_2 \dot{N}C_5 H_4 C_5 H_4 \dot{N}CH_2 COOH) \cdot 2C1^{-1}$ from acetic acid/methanol (20/80)

93.

yielded triphenyltin acetate as the only identifiable product.¹⁷² Further recrystallisation from the same solvent mixture afforded crystals of suitable quality for X-ray analysis. The melting point of a mixture of the material used in the variabletemperature Mössbauer study (Chapter 2, Table 2.1) and that used in the crystallographic study showed no depression.

The sample of triphenyltin formate used for v.t.M.s. (Chapter 2, Table 2.I) was prepared by route 1 (see Chapter 2, Section 2.2) using benzene as the refluxing solvent. Recrystallisation of the product from hot toluene yielded crystals suitable for X-ray analysis.

3.2.2. Crystal Data

(a) Triphenyltin acetate:

 $C_{20}H_{18}O_{2}Sn$, M = 409.1, monoclinic P2₁/c, <u>a</u> 8.969(4), <u>b</u> 10.146(5), <u>c</u> 19.540(7)Å, β 93.70(4)^o, <u>U</u> 1774.5Å, Z = 4, <u>D</u> 1.53, <u>D</u> 1.51Mgm⁻³, μ (Mo-K_{α}) 1.32mm⁻¹, <u>F</u>(000) = 816.

(b) Triphenyltin formate:

 $C_{19}H_{16}O_{2}Sn$, M = 395.0, monoclinic $B2_{1}/c$ (a non-standard setting of $P2_{1}/c$), <u>a</u> 20.176(8), <u>b</u> 15.539(6), <u>c</u> 21.952(10)Å, β 90.30(6)^o <u>U</u> = 6882.2Å³, Z = 16 (two independent molecules in the asymmetric unit), D_c 1.53, D_m 1.54Mgm⁻³, μ (Mo-<u>K</u>_{α}) 1.36mm⁻¹, <u>F</u>(000) 3136

3.2.3. Data Collection and Reduction

(a) Triphenyltin acetate:

A crystal of approximate dimensions $0.13 \times 0.14 \times 0.35$ mm was used for data collection and was mounted with the <u>b</u> axis coincident with the rotation (ω) axis of a Stöe Stadi-2 two-circle diffractometer. 2163 unique reflections were collected, of which 1841 had I \geq 3 σ (I) and were considered as observed and used for subsequent analysis. Corrections were made for Lorentz and polarisation effects, but no corrections were applied for absorption.

(b) Triphenyltin formate:

A crystal of approximate dimensions 0.10 x 0.30 x 0.35mm was used for data collection and was mounted with the <u>b</u> axis coincident with the rotation (ω) axis of a StBe Stadi-2 twocircle diffractometer. 4282 unique reflections were collected, of which 3413 had I \geq 3 σ (I) and were considered as observed and used for subsequent analysis. Corrections were made for Lorentz and polarisation effects, but no corrections were applied for absorption.

3.2.4. Structure Determination and Refinement

(a) Triphenyltin acetate:

The approximate position of the tin atom was calculated using a three-dimensional Patterson synthesis. The remaining atoms were located from successive difference Fourier maps. The hydrogen atoms were located, but given ideal geometry (C-H 1.08Å). Scattering factors were calculated using an analytical approximation¹⁷³ and the weighting scheme adopted was $w = 1.2022/[\sigma^2(F_0) + 0.003(F_0)^2]$. The phenyl and methyl hydrogen atoms were given common isotropic temperature factors which refined to respective final values of U = 0.091(5), $0.177(17)Å^2$. All other atoms were given anisotropic temperature factors and full matrix least-squares refinement gave final values of R = 0.022 and R' = 0.023. Table 3.I gives the final positional parameters, and Table 3.II gives bond distances

| Table | 3. | Ι |
|-------|----|---|
|-------|----|---|

C(34)

C(35)

| Triphenyltin | Acetate: Fractio | nal Positional Pa | rameters |
|--------------------------|-------------------------------|-------------------|----------|
| (x 10 ⁵ for S | n; x 10 ⁴ for rema | ining atoms) with | e.s.d.'s |
| for Non-Hydro | ogen Atoms in Pare | ntheses | |
| | | | |
| Atom | x | У | Z |
| Sn | 91578(3) | 30183(2) | 76237(1) |
| 0(1) | 9523(3) | -121(3) | 7720(1) |
| 0(2) | 7950(3) | 1382(3) | 8060(1) |
| C(1) | 8492(5) | 232(4) | 8081(1) |
| C(2) | 7846(6) | -680(4) | 8587(2) |
| C(11) | 7618(4) | 4343(3) | 8033(2) |
| C(12) | 6277(5) | 4651(5) | 7673(2) |
| C(13) | 5274(5) | 5527(6) | 7936(3) |
| C(14) | 5568(5) | 6079(5) | 8572(3) |
| C(15) | 6887(5) | 5795(4) | 8931(2) |
| C(16) | 7905(5) | 4944(4) | 8666(2) |
| C(21) | 11045(4) | 2613(4) | 8316(2) |
| C(22) | 10748(5) | 2353(4) | 8996(2) |
| C(23) | 11906(7) | 2123(4) | 9485(2) |
| C(24) | 13357(7) | 2147(5) | 9318(3) |
| C(25) | 13672(6) | 2393(6) | 8661(3) |
| C(26) | 12516(5) | 2631(5) | 8154(3) |
| C(31) | 8578(4) | 2616(4) | 6569(2) |
| C(32) | 8471(5) | 1356(4) | 6299(2) |
| C(33) | 7983(5) | 1159(5) | 5617(2) |

7553(5)

7635(6)

2202(5)

3455(5)

5202(2)

5467(2)

Table 3.I (contd).

| Atom | x | У | z |
|--------|---------|---------|--------------|
| C(36) | 8141(5) | 3663(5) | 6145(2) |
| H(111) | 8394 | -1625 | 8563 |
| H(112) | 6664 | -800 | 8462 |
| H(113) | 8022 | -281 | 9098 |
| H(12) | 6014 | 4192 | 7182 |
| H(13) | 4259 | 5786 | 7639 |
| H(14) | 4760 | 6719 | 8790 |
| H(15) | 7140 | 6243 | 9426 |
| H(16) | 8953 | 4742 | 8950 |
| H(22) | 9601 | 2331 | 9134 |
| H(23) | 11652 | 1931 | 10008 |
| H(24) | 14247 | 1960 | 97 05 |
| H(25) | 14819 | 2410 | 8523 |
| H(26) | 12766 | 2831 | 7630 |
| H(32) | 8766 | 526 | 6627 |
| H(33) | 7937 | 171 | 5411 |
| H(34) | 7164 | 2038 | 4674 |
| H(35) | 7303 | 4285 | 51 46 |
| H(36) | 8200 | 4650 | 6352 |

| Table 3.II | | | | | | |
|-------------------------|---|-------------------------|----------|--|--|--|
| Triphenyltin Acet | Triphenyltin Acetate:Bond Distances(A) and Angles (⁰) with | | | | | |
| e.s.d.'s in Paren | theses. Symme | etry Code None x, y, z; | | | | |
| (') $2-x$, $0.5 + y$, | 1.5-z; (") 2 | 2-x, -0.5 + y, 1.5-z | | | | |
| Bond distances | | | | | | |
| Sn-0(1) | 3,206(3) | C(16)-C(11) | 1,388(5) | | | |
| Sn-0(1') | 2.349(3) | C(21)-C(22) | 1.397(6) | | | |
| Sn-0(2) | 2.185(3) | C(22)-C(23) | 1.385(7) | | | |
| Sn-C(11) | 2.120(4) | C(23)→C(24) | 1.362(8) | | | |
| Sn-C(21) | 2.138(4) | C(24)-C(25) | 1,356(9) | | | |
| Sn-C(31) | 2.133(4) | C(25)-C(26) | 1.408(7) | | | |
| 0(1)-C(1) | 1.251(5) | C(26)-C(21) | 1.377(6) | | | |
| 0(2)-C(1) | 1.263(5) | C(31)-C(32) | 1,384(6) | | | |
| C(1)-C(2) | 1.497(6) | C(32)-C(33) | 1,391(6) | | | |
| C(11)-C(12) | 1.390(6) | C(33)-C(34) | 1.374(6) | | | |
| C(12)-C(13) | 1.387(7) | C(34)-C(35) | 1.372(7) | | | |
| C(13)-C(14) | 1,373(8) | C(35)-C(36) | 1.389(6) | | | |
| C(14)-C(15) | 1.366(7) | C(36)-C(31) | 1.387(6) | | | |
| C(15)-C(16) | 1.381(6) | | | | | |
| | | | | | | |

Bond angles

| 0(1)-Sn-0(1') | 139.8(1) | Sn-C(11)-C(16) | 121.8(3) |
|----------------|----------|-------------------|----------|
| 0(1)-Sn-0(2) | 43.4(1) | C(12)-C(11)-C(16) | 117.2(4) |
| 0(1)-Sn-C(11) | 132,4(1) | C(11)-C(12)-C(13) | 121.2(4) |
| 0(1)-Sn-C(21) | 72.4(1) | C(12)-C(13)-C(14) | 120.3(4) |
| 0(1)-Sn-C(31) | 83.4(1) | C(13)-C(14)-C(15) | 119.2(5) |
| 0(1')-Sn-0(2) | 173.6(1) | C(14)-C(15)-C(16) | 120.7(4) |
| 0(1')-Sn-C(11) | 87.2(1) | C(11)-C(16)-C(15) | 121.3(4) |

Table 3.II (contd)

Bond angles contd.

| 0(1')-Sn-C(21) | 86.7(1) | Sn-C(21)-C(22) | 116.5(3) |
|----------------|----------|-------------------|----------|
| 0(1')-Sn-C(31) | 88.5(1) | Sn-C(21)-C(26) | 125.6(3) |
| 0(2)-Sn-C(11) | 89.0(1) | C(22)-C(21)-C(26) | 117.8(4) |
| 0(2)-Sn-C(21) | 90.0(1) | C(21)-C(22)-C(23) | 120.5(4) |
| 0(2)-Sn-C(31) | 97.8(1) | C(22)-C(23)-C(24) | 121.2(5) |
| C(11)-Sn-C(21) | 113.0(1) | C(23)-C(24)-C(25) | 119.4(5) |
| C(11)-Sn-C(31) | 111.2(1) | C(24)-C(25)-C(26) | 120.6(5) |
| C(21)-Sn-C(31) | 135.2(1) | C(21)-C(26)-C(25) | 120.6(5) |
| Sn-0(1)-Sn" | 146.4(1) | Sn-C(31)-C(32) | 123.4(3) |
| Sn-0(1)-C(1) | 70.9(1) | Sn-C(31)-C(36) | 118.1(3) |
| Sn"-0(1)-C(1) | 142.7(2) | C(32)-C(31)-C(36) | 118.1(3) |
| Sn-0(2)-C(1) | 121.0(2) | C(31)-C(32)-C(33) | 120.5(4) |
| 0(1)-C(1)-O(2) | 122.9(4) | C(32)-C(33)-C(34) | 120.9(4) |
| 0(1)-C(1)-C(2) | 121.8(4) | C(33)-C(34)-C(35) | 119.0(4) |
| 0(2)-C(1)-C(2) | 115.3(4) | C(34)-C(35)-C(36) | 120.5(4) |
| Sn-C(11)-C(12) | 121.0(3) | C(31)-C(36)-C(35) | 121.0(4) |
and angles.

(b) Triphenyltin formate:

The atoms of the two independent molecules in the asymmetric unit were located in a similar manner to triphenyltin acetate. All the hydrogen atoms were located and the phenyl hydrogens given ideal geometry (C-H 1.08Å) while the formyl hydrogen positions were not refined. Scattering factors were calculated with the same analytical expression¹⁷³ and the weighting scheme adopted was $w = 3.9417/[\sigma^2(F_o) + 0.0002(F_o)^2]$. The phenyl and formyl hydrogen atoms were given common isotropic temperature factors which refined to final values of U = 0.144(16) and 0.041(22)Å², respectively. All the other atoms were given anisotropic temperature factors and least-squares refinement gave final values of R = 0.047 and R['] = 0.047.

Table 3.III gives final positional parameters for nonhydrogen atoms, and Table 3.IV lists bond distances and angles.

3.3. Discussion

3.3.1. Triphenyltin acetate

The compound forms polymeric chains in the lattice, in which essentially planar Ph_3Sn units are bridged by acetate groups. The acetates are disposed in the usual <u>syn</u>, <u>anti</u> conformation¹⁷⁴ with respect to pairs of tin atoms, but the bridging is anisobidentate, with one shorter tin-oxygen bond [Sn-O(2) 2.185(3)Å] and another [Sn-O(1') 2.349(3)Å] relatively long (Figures 3.I and 3.II). The syn, anti conformation,

| Table 3.III | | | | | | | |
|--|-----------------------|----------------------|---------------|--|--|--|--|
| Triphenyltin Formate: Fractional Positional Parameters | | | | | | | |
| <u>(x 10⁵ f</u> | for Sn; $\times 10^4$ | for remaining Atoms) | with e.s.d.'s | | | | |
| in Parer | theses | | | | | | |
| A. M. a | | | | | | | |
| ALOM | X 0.0(07(0) | y 21022 (1) | Z | | | | |
| Sn(1) | 33627(3) | 24029(4) | 32243(3) | | | | |
| Sn(2) | 41378(3) | 23073(4) | 6976(2) | | | | |
| 0(1) | 2841(3) | 2321(4) | - 910(3) | | | | |
| 0(2) | 3705(3) | 2329(4) | - 283(2) | | | | |
| 0(3) | 4638(3) | 2406(4) | 1597(3) | | | | |
| 0(4) | 3816(3) | 2206(4) | 2267(2) | | | | |
| C(1) | 3107(5) | 2251(7) | - 395(4) | | | | |
| C(2) | 4371(5) | 2447(6) | 2108(4) | | | | |
| C(11) | 2433(4) | 2203(5) | 2807(3) | | | | |
| C(12) | 1878(5) | 2713(7) | 2947(5) | | | | |
| C(13) | 1266(5) | 2519(8) | 2673(6) | | | | |
| C(14) | 1206(6) | 1864(8) | 2249(6) | | | | |
| C(15) | 1733(6) | 1379(8) | 2121(5) | | | | |
| C(16) | 2346(5) | 1531(7) | 2402(5) | | | | |
| C(21) | 3805(4) | 3627(5) | 3192(4) | | | | |
| C(22) | 4303(5) | 3872(7) | 3590(5) | | | | |
| C(23) | 4570(7) | 4720(9) | 3534(7) | | | | |
| C(24) | 4323(9) | 5264(8) | 3088(7) | | | | |
| C(25) | 3845(7) | 5041(7) | 2703(6) | | | | |
| C(26) | 3587(5) | 4210(6) | 2753(5) | | | | |
| C(31) | 3818(5) | 1238(5) | 3529(4) | | | | |
| C(32) | 3519(5) | 771(6) | 3989(5) | | | | |
| C(33) | 3801(8) | 19(8) | 4205(6) | | | | |

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| Atom | x | У | Z |
|-------|----------|----------|-----------------|
| C(34) | 4386(7) | - 276(7) | 3963(7) |
| C(35) | 4697(7) | 191(7) | 3519(6) |
| C(36) | 4403(5) | 928(6) | 3298(5) |
| C(41) | 5057(4) | 2648(5) | 289(3) |
| C(42) | 5647(4) | 2426(6) | 550(4) |
| C(43) | 6249(5) | 2573(6) | 289(5) |
| C(44) | 6267(5) | 3026(7) | - 252(5) |
| C(45) | 5685(5) | 3256(6) | - 540(5) |
| C(46) | 5081(4) | 3079 (6) | - 266(4) |
| C(51) | 3447 (4) | 3283(5) | 924(4) |
| C(52) | 3578(5) | 4129(7) | 785(5) |
| C(53) | 3109(7) | 4752(7) | 914(7) |
| C(54) | 2532(7) | 4555(7) | 11 80(5) |
| C(55) | 2396(5) | 3737(8) | 1334(5) |
| C(56) | 2856(4) | 3086(6) | 1213(4) |
| C(61) | 3893(4) | 988(5) | 761(4) |
| C(62) | 3656(6) | 633(6) | 1282(5) |
| C(63) | 3483(7) | - 274(7) | 1300(7) |
| C(64) | 3562(8) | - 728(8) | 788(8) |
| C(65) | 3827 (9) | - 398(9) | 289(7) |
| C(66) | 3968(8) | 470(7) | 254(5) |

| Table 3.IV | | | |
|------------------------|---------------------------|------------------|-----------|
| Triphenyltin Formate: | Bond Distance | s (A) and Angles | (°) with |
| e.s.d.'s in Parenthese | es. ^a Symmetry | Code None x, y, | z; |
| (') x, 0.5-y, 0.5+z | | | |
| Bond distances | | | |
| Sn(1)-0(1') | 2.219(6) | Sn(2) = 0(3) | 2.219(6) |
| Sn(1)-0(4) | 2.317(6) | Sn(2)-0(2) | 2.318(5) |
| Sn(1)-0(2') | 3.372(6) | Sn(2)-0(4) | 3.513(6) |
| Sn(1)-C(11) | 2.105(8) | Sn(2)-C(41) | 2.131(8) |
| Sn(1)-C(21) | 2.102(9) | Sn(2)-C(51) | 2.121(9) |
| Sn(1)-C(31) | 2.136(9) | Sn(2)-C(61) | 2.113(8) |
| C(1)-O(1) | 1.253(11) | C(2)-O(3) | 1.248(11) |
| C(1)-H(1) | 1.077 | C(2)-H(2) | 0.876 |
| C(1)-O(2) | 1.235(11) | C(2)-O(4) | 1.232(12) |

n = 1 2 3 4 5 6 C(n1)-C(n2) 1.409(13) 1.382(14) 1.384(13) 1.365(12) 1.376(13) 1.360(14) C(n1)-C(n6) 1.381(13) 1.393(14) 1.375(14) 1.391(12) 1.387(12) 1.382(14) C(n2)-C(n3) 1.404(15) 1.429(18) 1.383(16) 1.364(13) 1.384(16) 1.452(15) C(n3)-C(n4) 1.383(18) 1.385(21) 1.374(21) 1.383(15) 1.341(20) 1.338(22) C(n4)-C(n5) 1.335(17) 1.324(22) 1.370(19) 1.378(14) 1.344(17) 1.325(23) C(n5)-C(n6) 1.399(15) 1.396(15) 1.376(16) 1.388(14) 1.398(15) 1.379(18)

Bond angles

| 0(4)-Sn(1)-0(1') | 173.6(2) | 0(2)-Sn(2)-0(3) | 173.1(2) |
|-------------------|----------|------------------|----------|
| 0(4)-Sn(1)-0(2') | 144.9(2) | 0(2)-Sn(2)-0(4) | 147.2(2) |
| 0(4)-Sn(1)-C(11) | 86.6(3) | 0(2)-Sn(2)-C(41) | 86.0(3) |
| 0(4)-Sn(1)-C(21) | 85.4(3) | 0(2)-Sn(2)-C(51) | 87.8(3) |
| 0(4)-Sn(1)-C(31) | 90.1(3) | 0(2)-Sn(2)-C(61) | 89.3(3) |
| 0(1')-Sn(1)-0(2') | 40.5(2) | 0(3)-Sn(2)-O(4) | 38.3(2) |
| 0(1')-Sn(1)-C(11) | 88.6(3) | 0(3)-Sn(2)-C(41) | 88.0(3) |

Bond angles (contd)

| 0(1')-Sn(1)-C(21) | 93.3(3) | 0(3)-Sn(2)-C(51) | 92.2(3) |
|--------------------|----------|-------------------|----------|
| 0(1')-Sn(1)-C(31) | 95.8(3) | 0(3)-Sn(2)-C(61) | 96.5(3) |
| 0(2')-Sn(1)-C(11) | 128.2(3) | 0(4)-Sn(2)-C(41) | 126.1(3) |
| 0(2')-Sn(1)-C(21) | 80.6(3) | 0(4)-Sn(2)-C(51) | 71.2(3) |
| 0(2')-Sn(1)-C(31) | 73.4(3) | 0(4)-Sn(2)-C(61) | 81.3(3) |
| C(11)-Sn(1)-C(21) | 119.8(3) | C(41)-Sn(2)-C(51) | 119.7(3) |
| C(11)-Sn(1)-C(31) | 113.1(3) | C(41)-Sn(2)-C(61) | 118.2(3) |
| C(21)-Sn(1)-C(31) | 126.5(3) | C(51)-Sn(2)-C(61) | 121.6(3) |
| Sn(1)-O(1')-C(1') | 125.9(6) | Sn(2)=O(3)=C(2) | 127.3(6) |
| Sn(1)-0(2')-Sn(2') | 168.0(1) | Sn(2)=0(4)=Sn(1) | 163.6(1) |
| Sn(1)-0(2')-C(1') | 67.9(6) | Sn(2)=0(4)=C(2) | 62.3(6) |
| 0(1)-C(1)-H(1) | 111.4 | O(3)-C(2)-H(2) | 110.5 |
| 0(1)-C(1)-O(2) | 125.8(9) | 0(3)-C(2)-O(4) | 129.6(9) |
| O(2)-C(1)-H(1) | 121.2 | O(4)-C(2)-H(2) | 115.9 |
| Sn(1)-C(11)-C(12) | 122.0(6) | Sn(2)-C(41)-C(42) | 121.3(6) |
| Sn(1)-C(11)-C(16) | 120,1(6) | Sn(2)-C(41)-C(46) | 121.6(6) |
| Sn(1)-C(21)-C(22) | 122.4(7) | Sn(2)-C(51)-C(52) | 120.2(7) |
| Sn(1)-C(21)-C(26) | 118.7(7) | Sn(2)-C(51)-C(56) | 121.1(7) |
| Sn(1)-C(31)-C(32) | 119.0(7) | Sn(2)-C(61)-C(62) | 122.2(7) |
| Sn(1)-C(31)-C(36) | 123.3(7) | Sn(2)-C(61)-C(66) | 119.1(7) |
| | | | |

Table 3.IV (contd)

| | n=1 | 2 | 3 | 4 | 5 | 6 |
|-------------------|-----------|-----------|-----------|-------------------|-----------|-----------|
| C(n6)-C(n1)-C(n2) | 117.8(8) | 119.0(9) | 117.7(9) | 117.0(8) | 118.7(9) | 118.7(9) |
| C(n1)-C(n2)-C(n3) | 119.0(9) | 118.2(10) | 120.8(11) | 123.9(8) | 119.3(10) | 120.2(11) |
| C(n2)-C(n3)-C(n4) | 121.3(10) | 119.3(12) | 120.1(12) | 118.3(9) | 121.7(10) | 117.4(13) |
| C(n3)-C(n4)-C(n5) | 119.4(11) | 123.3(12) | 119.7(11) | 120.0(9) | 120.2(11) | 122.6(13) |
| C(n4)-C(n5)-C(n6) | 121.0(11) | 117.6(11) | 119.7(12) | 119.8(9) | 120.0(10) | 120.6(13) |
| C(n1)-C(n6)-C(n5) | 121.4(9) | 122.6(10) | 121.9(16) | 120.7(8) | 120.0(9) | 120.1(11) |

a No errors included for bond distances and angles involving the formyl hydrogens, whose positions were not refined.



Figure 3.1. The coordination about tin in Ph₃SnO₂CMe showing atomic labelling. The symmetry code for (') and (") atoms is given in Table 3.11.



Figure 3.II. A segment of the Ph_3SnO_2CMe polymer viewed perpendicular to the <u>a b</u> cell face.

combined with the crystallographic 2, screw axis coincident with the b axis (the axis of polymer propagation) leads to a one-dimensional polymeric structure which can be described as a 'stretched S'-shaped or flattened helix (Figure 3.II) corresponding to a Class 3-type polymer architecture in the classification introduced in Chapter 2. As a consequence of this polymeric, helical, construction, the tin atoms are not co-linear, rather they are positioned alternately either side of the 21 axis coincident with b, and the direction in which the polymer is building at a tin atom is not along <u>b</u> but at approximately 60° to it, based on the general orientation of the nearly linear O(1')-Sn-O(2) fragment. As discussed in Chapter 2, section 2.3, these features concentrate the bridging mass of the acetate group away from space between adjacent tin atoms so that this space is largely a void and the polymer has a spring-like flexibility from the point of view of the vibrational motion of the tin atom.

The two tin-oxygen bonds involved in the bridge are not unusual compared with the corresponding bonds in related compounds (Table 3.V), although the covalent, ester Sn-O(2) bond $[2.185(3)^{A}]$ lies towards the long end of the range $[2.07 - 2.21^{A}]$ while the bridging Sn-O(1') dative linkage $[2.349(3)^{A}]$ is at the shortest end of the observed range for this bond type.

The polyhedron of atoms about the central tin atom is, to a first approximation, a distorted trigonal bipyramid in which the oxygen atoms (the more electronegative atoms) occupy the axial positions and the α -carbons of the phenyl rings form the equatorial girdle (Figure 3.1). The SnC₃ group of atoms is very nearly

Table 3.V

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| Collect | ted Structur | al Data for | Organotin Carb | oxylates ^{a,b} | | |
|--|----------------------|----------------------|----------------------|---|--|------------|
| Compound | Sn-0(2) (Å) | Sn-0(1') inter(Å) | Sn-0(1) intra(Å) | C-Sn-C ^C ([°]) | 0(2)-C(1)-0(1) (Å) | Reference |
| Ph ₃ SnO ₂ CMe | 2.185(3) | 2.349(3) | 3.206(3) | 135.2(1) | 1.263(5), 1.251(5) | This work |
| Ph ₃ Sn0 ₂ CH | 2.219(6) 2.219(6) | 2.317(6) 2.318(5) | 3.372(6) 3.513(6) | 126.5(3) 121.6(3) | 1.253(11),1.235(11) 1.248(11),1.232(12) | This work |
| Ph ₃ Sn0 ₂ CC ₆ H ₄ x ¹ | 2.043(3) | - | 2.823(3) | 108.8(2) | 1.310(5), 1.237(5) | 163 |
| Ph ₃ SnO ₂ CC ₆ H ₄ x ² | 2.115(6) | - | 2.564(7) | 112.6(3) | 1.272(9), 1.22(1) | 163 |
| Ph ₃ SnO ₂ CC ₆ H ₄ x ³ | 2.072(2) | - | 2.629(2) | 118.3(1) | 1.306(4), 1.236(4) | 163 |
| Ph ₃ SnO ₂ CC ₆ H ₄ X ⁴ | 2.083(2) | - | 3.071(2) | 121.0(1) | 1.301(3), 1.232(3) | 161 |
| $Ph_3SnO_2CC_6H_4x^5$ | 2.054(3) | - | 2.781(3) | 119.9(1) | 1.321(5), 1.214(5) | 161 |
| Ph ₃ SnO ₂ CC ₆ H ₄ X ⁶ | 2.060(2) | - | 2.783(3) | 118.5(1) | 1.310(4), 1.232(4) | 161 |
| $Ph_3SnO_2C_6H_4(N_2R)-2$ | 2.070(5) | - | 2.463(7) | 11 7. 0(2) ^d | 1.296(8), 1.224(8) | 58 |
| Me ₃ SnO ₂ CMe | 2.205(3) | 2.391(4) | 3.23 | 121.9(2) | 1.269(5), 1.240(6) | 59 |
| Me ₃ SnO ₂ CCF ₃ | 2.177(14) | 2.458(15) | 3.30 | 122.9(10) | 1.28(2), 1.21(2) | 59 |
| $Me_3SnO_2CCH_2NH_2$ | 2.21(1) | - | 3.23(3) | 121.8(11) | 1.34(3), 1.23(3) | 60 |
| Me3Sn02CR' | 2.19(1) 2.17(1) | 2.46(2) 2.44(2) | 3.16 3.12 | 124.9 123.6 | 1.27(3), 1.22(3) 1.28(3), 1.28(3) | Footnote e |



| ClMe2SnO2CMe | 2.165(6) | 2.392(7) | 2.782(7) | 140.9(6) | 1.260(9), 1.262(10) | 178 |
|---|----------|----------|-----------|-----------|---------------------|-----|
| Vin ₃ SnO ₂ CMe | 2.20(1) | 2.33(1) | not given | 134.6(14) | Not given | 179 |
| Vin ₃ SnO ₂ CCH ₂ C1 | 2.21(1) | 2.34(1) | not given | 124.4(6) | Not given | 179 |
| Vin ₃ Sn0 ₂ CCC1 ₃ | 2.17(2) | 2.49(1) | 3.30 | 124.8(5) | 1.25(2), 1.21(2) | |
| Vin ₃ SnO ₂ C(Fer) | 2.12(1) | 2.42(1) | 3.21 | 127(1) | 1.27(1), 1.21(2) | 180 |
| Bz ₃ SnO ₂ CMe | 2.14(2) | 2.65(2) | 3.23(3) | 123.8(14) | 1.31(4), 1.21(4) | 152 |
| Cyh ₃ SnO ₂ CMe | 2.12(3) | 3.84 | 2.95(4) | 113(1) | 1.39(8), 1.25(9) | 191 |
| Cyh ₃ SnO ₂ CCF ₃ | 2.08(4) | 3.70 | 3.11 | 122 | 1.28(4), 1.20(5) | f |

^a Atomic numbering as in Figure 3.1. ^b Abbreviations: Vin = $CH_2=CH$, $Bz = C_0H_5CH_2$, $Cyh = C_0H_{11}$, Fer = $C_5H_4FeC_5H_5$, R = 2-hydroxy-5-methylphenyl, $R' = CH_2CO_2SnMe_3$, $X^1 = NH_2-2$, $X^2 = NMe_2-2$, $X^3 = NH_2-4$, $X^4 = OH-2$, $X^5 = OMe-2$, $X^6 = SMe-4$. ^c C-Sn-C angle closest in proximity to O(1). ^d cis-Ph_3SnX_2 geometry. ^e U. Schubert, <u>J. Organomet. Chem.</u>, 1978, <u>155</u>, 285. ^f S. Calergo, P. Eanis, V. Peruzzo and G. Tagliavini, <u>J. Organomet.Chem</u>. 1980, <u>191</u>, 381. planar (sum of CSnC angles = 359.4°) and all the OSnC angles are within 3.5° of a right angle except O(2)-Sn-C(31) which is $97.8(1)^{\circ}$.

However, an additional weak Sn----O interaction occurs between the central tin atom and the acyl, bridging oxygen, O(1), so that this atom plays an intermolecularly bridging and intramolecularly chelating role simultaneously (Figure 3.I). Although the interatomic distance of 3.206(3) A is long compared with both the covalent and bridging Sn-O bonds, it is well within the sum of the two van der Waals radii (3.70Å) and severely distorts the equatorial C(21)-Sn-C(31) bond angle (which is closest to the direction of O(1)'s intramolecular approach to the tin) from the regular trigonal bipyramidal angle of 120° to 135.2°. Further evidence for a bonding interaction is found in a consideration of the two C-O bond distances in the acetate group. In an acetate group which is involved in a purely bridging role, equality of the two C-O distances would only occur if the bridging was isobidentate, that is, if both the Sn-O bonds were equal, so that the π electrons are symmetrically delocalised over the O-C-O framework. In all the organotin carboxylates for which data are available bridging is anisobidentate, and for most species the two C-O bond lengths are unequal, because the majority of double bond character is localised along one C-O axis (Table 3.V) corresponding to the oxygen engaging in the bridging, dative, bond to the neighbouring In the title compound, however, the two C-O distances tin atom. are very similar [C(1)-O(1) 1.251(5), C(1)-O(2) 1.263(5)Å], a

situation which is consistent with electron density being drawn away from the acyl C(1)-O(1) bond along the O(1)-Sn vector concomitant with the formation of the chelating Sn-O(1) interaction. A similar argument has been used to rationalise the bifurcated Sn-S-Sn bonding in the dimer $\{Sn[S_2P(OPh)_2]_2\}_2$.¹⁷⁵ The coordination sphere is thus best described as a distorted <u>mer-R_3SnX_3</u> octahedron.

Only one other example of a six-coordinate triorganotin compound has been substantiated crystallographically, namely, trimethyltin tris-(pyrazolyl)borate, in which the donor nitrogen atoms in the uninegative tridentate ligand are ideally constrained to occupy three adjacent sites of an octahedral coordination sphere in such a manner as to give a distorted fac-R₃SnX₃ octahedron.⁷⁷ 1:1 Adducts of Me₃SnCl with 2,2'-bipyridyl and Me₃SnNCS with 1,10 phenanthroline have been interpreted in terms of sixcoordination at tin on the basis of infrared studies,¹⁷⁶ and tricyclohexyltin glycylglycinate, on the basis of infrared and Mössbauer evidence, was assigned a mer-C₃SnO₂N local geometry in either a monomeric chelated structure or a polymeric or oligomeric arrangement,¹⁷⁷ but no X-ray confirmation of any of these systems is available to date.

The diorganotin derivative, $\text{ClMe}_2 \text{SnO}_2 \text{CMe}$ has also been interpreted as being six-coordinate at \tan^{178} with the coordination system arising in a similar way to that of $\text{Ph}_3 \text{SnO}_2 \text{CMe}$ to give a distorted octahedron. The chelating interaction Sn-O(1) [2.782(7)Å] is much stronger in the chlorotin acetate and is manifested in both a greater opening of the C-Sn-C angle in the region of this interaction $[140.9(6)^{\circ}]$ and the equalising of the C-O bond lengths [1.260(9)Å, 1.262(10)Å] despite anisobidentate bridging [Sn-O(2) 2.165(6), Sn-(0') 2.392(7)Å].

The crystallographic data for organotin carboxylates, presented in Table 3.V, suggest that the Lewis acidity of the tin(IV) atom may be the factor which determines the coordination number adopted, at least when steric factors can be discounted. Steric effects have been invoked to explain the absence of intermolecular bridging in triphenyltin o-(2-hydroxy-5-methylphenylazo)benzoate⁵⁸ but the issue is complicated by the relevant oxygen atom's involvement in an intramolecular trifurcated hydrogen bond. In both ClMe₂SnO₂CMe and Ph₃SnO₂CMe the tin is directly bonded to electronegative atoms, chlorine in the former and the α -carbons of the phenyl groups in the latter, and this enhanced Lewis acidity favours additional coordination and a final coordination number of six. The same factor might be expected to operate in trivinyltin In trivinyltin acetate¹⁷⁹ a <CSnC is reported to carboxylates. be 134.6(14)Å, close to the value in the present compound, but other relevant data (bond lengths) are not given in the report so that a detailed comparison cannot be made. In $(CH_2=CH)_3SnO_2C(C_5H_4FeC_5H_5)^{180}$ the relevant angle is 127(1)°, an opening in the right direction for a very weak chelating Sn-O(1) interaction, but too small to be definitive.

The Mössbauer quadrupole splitting value (3.36 ± 0.03) mms⁻¹ is consistent with both a five-coordinate <u>trans</u>-R₃SnX₂ geometry at tin¹⁶⁸ or a <u>mer</u>-R₃SnX₃,¹⁸¹ both of which are predicted to give <u>ca</u>. 3.50mms⁻¹ by point-charge calculations.

In the Ph₃SnO₂CMe structure the three phenyl groups are essentially planar, and adopt a propellor-like conformation about the tin. The operation of the 2₁ symmetry results in the tin-phenyl bonds being staggered along the chain. All the Sn-C and C-C bond lengths are normal.

3.3.2. Triphenyltin formate

The asymmetric unit of triphenyltin formate consists of two independent molecules but the differences between these are small and, to a first approximation, the structure adopted in the solid state is very similar to that of triphenyltin acetate: it is polymeric due to formate bridging, with the chain propagating along the <u>c</u> axis. The geometry at tin is distorted trigonal bipyramidal with the oxygen atoms in the axial sites, the α -carbons of the phenyl groups forming the equatorial girdle, and near planar SnC₃ groups (Σ CSnC = 359.4°). Figure 3.111 shows the local geometry at the two tin atoms in the asymmetric unit, and Figure 3.1V the polymeric chain. The overall three-dimensional structure of the polymer chain is, again, a flattened helix.

The formate ligands bridge in an anisobidentate fashion: Sn(1)-O(1') 2.219(6), Sn(2)-O(2) 2.318(5)Å and Sn(2)-O(3) 2.219(6), Sn(1)-O(4) 2.317(6)Å for the two molecules. These bond lengths are notable because they represent the least anisobidentate



Figure 3.III.

The coordination about the two tin atoms in the asymmetric unit of Ph_3SnO_2CH .



(a)

(b**)**

Figure 3.IV. (a) A segment of the Ph_3SnO_2CH polymer viewed perpendicular to the <u>ac</u> cell face

0(1')

0(1)

(b) Unit cell viewed along <u>b</u> showing the nature of polymer propagation.

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(i.e., most symmetrical) carboxylate bridging in any of the associated triorganotin carboxylates (Table 3.V). The pattern of Sn-O bonds in the formate and acetate is illustrated schematically in Figure 3.V.

The problem of a weak intramolecular interaction between tin and the oxygen atom involved in the intermolecular bridge arises again. However, in the formate, the oxygen in question lies significantly further from the central tin atom: Sn(1)....0(2') 3.372(6), Sn(2)....0(4) 3.513(6)^A for molecules 1 and 2, compared with Sn....0(1) 3.206(3) A for the acetate. Moreover, the <CSnC in the region of the Sn....0(2',4) axis in each molecule is not significantly opened: C(21)-Sn(1)-C(31)126.5(3)°, C(51)-Sn(2)-C(61) 121.6(3)°, so that any interaction is minimal and the tin atoms are five-coordinate. Distances within the formate group are consistent with the absence of a sixth coordination. In molecule 1 the shorter C-O bond is only 98.6% of the longer bond, in molecule 2, 98.7%, whereas in the acetate the shorter bond is 99.0% of the longer despite the bridging being more anisobidentate than in the formate.

The formate shows a larger QS than the acetate (3.48, 3.35mms⁻¹, respectively). This is in line with trends observed in trimethyland triphenyltin haloacetates^{168,169} in which an increase in QS occurs with increasing strength of the carboxylic acid. It has been suggested that this trend arises from an increasing asymmetry of the two Sn-O bonds with increasing σ^* (Taft inductive factor)









of the (halo) acetate group, i.e. increasing acid strength, and that the Me3Sn or Ph3Sn fragment should remain unaffected. This is not the case here, however. Though HO₂CH is a stronger acid than HO_2CCH_3 (pK = 3.75, 4.76, respectively) the two Sn-O bonds are more symmetrical in the formate. Moreover, the electron density in the Ph₂Sn fragment of the acetate must be different from that in the formate because of the sixth coordination It is possible that the more symmetrical transinteraction. 0, SnPh, trigonal bipyramidal geometry in the formate results in increased withdrawal of p-electron density into the Sn-O bonds with concomittant increase in the s-electron density in the Sn-C bonds, [i.e., an sp³ (C_{3v} symmetry) \rightarrow sp², p_z (D_{3h} symmetry) rehybridisation], and this increased imbalance in p-electron distribution increases QS. The IS values of the compounds support this idea: the larger IS for the formate reflects the larger s-electron density at the tin nucleus, this density being deshielded by the p-electron withdrawal.

3.3.3. Variable-Temperature Mössbauer Behaviour

Triphenyltin formate shows a distinctly more rigid lattice $(\underline{a} = 1.15 \times 10^{-2} \text{K}^{-1})$ than its acetate homologue $(\underline{a} = 1.91 \times 10^{-2} \text{K}^{-1})$ (Table 2.II). This is perhaps rather surprising in view of the close similarity of the two molecules and a comparison of the two structures provides an interesting and illuminating example of how sensitive the variable-temperature Mössbauer experiment can be to a cross-over from one tertiary structure to another, as represented by this pair of compounds. As discussed above, in the formate the intermolecular, bridging, bond is shorter than the corresponding bond in the acetate and the carboxylate is more

symmetrically placed between neighbouring tin atoms. Furthermore, an extra stabilisation of structure by formation of a weak intramolecular Sn-O bond to give mer-R₃SnO₃ primary structure in the acetate does not occur in the formate. As a result the direction along which the polymer is building at the tin atom makes an angle of only ca. 30° with respect to the c axis, based on the general orientation of the near-linear 0(2)-Sn(2)-O(3) group [<0Sn0 = 173.1(2)⁰], whereas the corresponding angle in the acetate is approximately 60°. The bridging mass in the formate is therefore much closer to the Sn....Sn vector than the corresponding mass in the acetate and the combination of this more linear (Class 2) polymer architecture and the stronger bridge leads to a more rigid structure, as reflected in the lower a value. Figure 3.VI illustrates this point. Both structures are drawn to the same scale and the distinctly more linear formate polymer backbone compared with that of the acetate is clearly visible, with the dotted lines indicating the 'linearity' of the two polymers. A priori the differences between the two structures adopted by this pair of compounds must depend only on the different properties of carboxylate substituents hydrogen and methyl. Formic acid is a stronger acid than acetic acid which might be expected to lead to greater asymmetry in the Sn-O bond lengths for the formate^{59,169} but the opposite is the case and the large steric bulk of CH, relative to H must be the dominating The Sn-O-C angles give a measure of these steric factor. interactions, Figure 3.VII.

120.



Figure 3.VI

Comparison of the tertiary structures of the polymer chains in Ph_3SnO_2CH and Ph_3SnO_2CMe .

121.



Ph, SnO, CR'

Figure 3.VII

The angle β about the bridging interaction (anti-oxygen), is a measure of the steric repulsions between the R' group and the phenyl groups on the tin atom Sn(2) (Figure 3.VII).⁵⁹ The more bulky R' the greater must be the β angle to minimize the repulsion interaction and/or the bridge must lengthen, and as β becomes larger (with a remaining approximately constant as, in fact, it does for the known associated triorganotin carboxylates, see Table 3.VI) the bridging mass is displaced further from the This can be easily seen in Figure 3.VI. Sn.....Sn vector. The steric bulk differences between the methyl and hydrogen substituents, as reflected by β , can thus account for a change from a Class 3-type polymer to a Class 2-type. The small steric demand of the hydrogen substituent also allows a stronger intermolecular bridging bond to be formed (compared to the acetate) with

Collected Structural Data for Carboxylate Bridges

in Triorganotin Carboxylates



| R | R' | Sn-0(1) | Sn-O(2) | α | β | Ref. |
|--------------------------------|---|----------|----------|----------|----------|------------|
| Me | Ме | 2.205(3) | 2.391(4) | 122.5(3) | 136.6(3) | 59 |
| Me | CF3 | 2.18(1) | 2.46(2) | 121(1) | 147(1) | 59 |
| Me | CH ₂ CO ₂ SnMe ₃ | 2.19(1) | 2,46(2) | 121(1) | 152(1) | footnote a |
| | | 2.17(1) | 2.44(2) | 121(1) | 139(1) | |
| Vin | Me | 2.20(1) | 2.33(1) | 119 | 138 | 179 |
| Vin | CH ₂ C1 | 2.21(1) | 2.34(1) | 119 | 137 | 179 |
| Vin | cc1 ₃ | 2.17(2) | 2.49(1) | 122.8(8) | 157.4(7) | |
| Vin | Fer | 2.12(1) | 2.42(1) | 123(1) | 156(1) | 180 |
| Ph | н | 2.219(6) | 2.318(5) | 125.9(6) | 123.1 | This work |
| | | 2.219(6) | 2.317(6) | 127.3(6) | 125.5 | |
| Ph | Me | 2.185(3) | 2.349(3) | 121.0(2) | 142.7(2) | This work |
| PhCH ₂ | Me | 2.14(2) | 2.65(2) | 123.9 | 131.7 | 152 |
| C ₆ H ₁₁ | Me | 2.12(3) | 3.84 | 124.9 | 146.9 | 191 |
| C6H11 | CF 3 | 2.08(4) | 3.70 | 122(2) | 159 | |

^aU Schubert, <u>J. Organomet. Chem.</u>, 1978, <u>155</u>, 285

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concomittant lengthening of the Sn-O ester bond, rather than stabilization (to satisfy the Lewis acidity of the tin atom) <u>via</u> intramolecular coordination.

Chapter 4

<u>A Variable-Temperature Mössbauer Study of Cyclohexyltin Compounds</u> 4.1. Introduction

Cyclohexyltin derivatives have emerged as an important class of biocidally active organotin compounds 182-184 yet structural information is quite meagre.^{13,14} Thus, many tricyclohexyltins are highly active as acaricides but have low mammalian toxicity and a favourable environmental degradation pathway resulting ultimately in SnO,, and two members of this class, tricyclohexyltin hydroxide (Plictran.^R Dow) and tricyclohexyltin 1,2,4-triazol-l-yl (Peropal^K, Bayer) are commercial agrochemicals. The control of phytophagous mites is a worldwide problem of increasing acuteness because of the propensity of these organisms for developing resistance to established organophosphorous pesticides.¹⁶⁰ Thus, the much needed requirement for substitute treatments is being met by tricyclohexyltins and continuing commercial attention is likely to be focussed on such compounds in the future.

Systematic progress in the practical application of cyclohexyltin derivatives should be considerably aided by a better understanding of their structural chemistry. Extrapolation of the relatively well developed area of solid-state methyltin chemistry can only be, at best, tentative because of the unpredictable effects of the sterically bulky cyclohexyl groups. This steric factor is also of theoretical importance because cyclohexyltins frequently lie at the cross-over point between the tendency to associate intermolecularly and the

retention of discrete tetrahedral molecules with four-coordinate tin^{186,187}.

Thus these compounds form a pertinent subject for variabletemperature Mössbauer studies. As for phenyltins (Chapter 2), compounds of known structure provide points of reference for interpretation of data for structurally unsubstantiated lattices, though the range of structurally established compounds is even more restricted than in the case of phenyltins. The systematics thereby outlined can then be used to draw inferences on the solidstate structures of crystallographically uncharacterised species.

4.2. Experimental

Tricyclohexyltin hydroxide was obtained as a gift from the International Tin Research Institute, Greenford. Tetracyclohexyltin was prepared from cyclohexylmagnesium chloride and tin(IV) chloride in dried diethyl ether.¹⁸⁸ The crude product was recrystallised from toluene. The percentage yield of pure product was 9%. Dicyclohexyltin dichloride was obtained by a redistribution reaction between tetracyclohexyltin and tin(IV) chloride (1:1 molar ratio) according to a literature method¹⁸⁹ in which the reagents are heated (without solvent) at 200°C for 7 hr. Yield of crude product was 30%, and this was purified by recrystallisation from diethyl ether. Route 1 (see Chapter 2, section 2.2) was used to prepare the tricyclohexyltin derivatives of 1,2,4-triazole, diphenylphosphinic, formic, acetic, hydrochloric and indol-3-ylacetic¹⁹⁰ acids. Tricyclohexyltin fluoride and dicyclohexyltin difluoride were prepared by route 2 (Chapter 2, section 2.2).

All the cyclohexyltin compounds studied by v.t.M.s. were confirmed by i.r., m.p. and C, H, and N microanalysis (microanalytical service, University College, Dublin), and Mössbauer IS and QS data are in good agreement with published values. Table 4.I gives analytical, melting point, IS and QS data for the cyclohexyltin derivatives used in this study. Variable-temperature data were collected as outlined previously (Chapter 2, section 2.2).

4.3. Discussion

Variable-temperature data obtained in the present study and those obtained by other workers are set out in Table 4.II. 0f the known cyclohexyltins, only two have clear-cut monomeric lattices: the two halides, $(C_6H_{11})_3$ SnBr and $(C_6H_{11})_3$ SnI.¹⁴⁹ Both show high a values $(\underline{ca}, 1.60 \times 10^{-2} \text{K}^{-1})$ consistent with their monomeric constitutions. The crystal structure of $(C_6H_{11})_3SnO_2CMe$ (a = 1.59 x $10^{-2}K^{-1}$) has been interpreted in terms of a monomeric lattice¹⁹¹ but it is now considered to be weakly polymeric 58,186,187 with a Class 3 's'-shaped tertiary structure on the basis of its QS value and systematic distortions of bond angles at tin towards trigonal bipyramidal. Both these factors (or even the tertiary structure alone) allow the tin atom vibrational freedom equivalent to that of a monomer. Tetracyclohexyltin, which must be monomeric on the grounds of its formulation and its lack of Mössbauer quadrupole splitting, gives

| | A | nalysis(%) ^a | | | | | |
|---|--------------|-------------------------|------------|--------------------------------|-----------------|-----------------|-----|
| Compound r | C | Н | N | M.p.(°C) ^b | IS ^C | QS ^C | |
| (C ₆ H ₁₁) ₄ Sn | 63.50(63.85) | 10.0(9.30) | | 263–264 (263–2 64) | 1.46(1.57) | 0.00 | |
| (C ₆ H ₁₁) ₃ SnF | 55.55(55.85) | 8.65(8.60) | | 310(decomp) (305, decomp) | 1.47(1.56) | 3.71(3.96 |) |
| (C ₆ ^H ₁₁) ₃ SnCl | 53,75(53,55) | 8.20(8.25) | | 127–129 (129–130) | 1.68(1.64) | 3.52(3.49 |) |
| (C ₆ ^H ₁₁) ₃ SnOH | 56.35(56.10) | 9.05(8.90) | | 198-202 (220-222) ^d | 1,41(1.40) | 2.99(2.99 |) |
| (C ₆ ^H ₁₁) ₃ SnO ₂ CMe | 56.45(56.25) | 8.45(8.50) | | 61-63(61-63) | 1.59(1.57) | 3.35(3.27 |) |
| (C ₆ ^H ₁₁) ₃ SnO ₂ CH | 55.25(55.25) | 8.65(8.30) | | 152-153 | 1.59 | 3.79 | |
| ^{(C} 6 ^H 11 ⁾ 3 ^{Sn(iaa)^e} | 62.20(62.00) | 7.75(7.65) | 2.50(2.60) | 150–152 | 1.54 | 3.00 | - |
| (C ₆ ^H ₁₁) ₃ SnO ₂ PPh ₂ | 61.50(61.55) | 7.45(7.40) | | 300 (decomp) | 1.56 | 3.93 | 28. |
| $(C_{6}^{H}_{11})_{3}^{Sn(triaz)}^{f}$ | 55.00(55.10) | 8.20(8.10) | 9.45(9.65) | 202–205(218) ^g | 1.51 | 3.26 | |
| (C ₆ ^H ₁₁) ₂ SnCl ₂ | 40.35(40.50) | 6.55(6.25) | | 88-89 (88-89) | 1.78(1.76) | 3.40(3.47 |) |
| $(C_{6}^{H}_{11})_{2}^{SnF}_{2}$ | 43.60(44.60) | 7.30(6.85) | | 275 (278) | 1.37 | 3.31 | |

 Table 4.I
 Analytical Data for Cyclohexyltin Compounds

^a Required values given in parentheses.
^b Literature values (in parentheses) are taken from ref. 1
^c Literature values (mms⁻¹) in parentheses are taken from refs. 15 and 17.
^d C.A. Kraus and R.H. Bullard, <u>J. Am. Chem. Soc.</u>, 1929, <u>51</u>, 3605.
^e iaa = indol-3-ylacetate.
^f triaz = 1,2,4-triazol-1-yl.
^g Ref. 160.

Table 4.II

| Varia | Variable-Temperature Sn Mössbauer Data for Cyclohexyltin Compounds | | | | | | |
|-------|--|------------------------------|------------------|---------------------------|--|--|--|
| | | | -r(T range/K | | | | |
| Compo | ound ^a | $10^{2} a^{b} / K^{-1}$ | points) | Structure ^C | | | |
| (50) | Cyh ₃ Sn(iaa) | 1.75(1.75-1.45) | 0.996(78-165,6) | Polymer(3) ^d | | | |
| (51) | Cyh ₃ SnBr | 1.64 ^e | 0.999(77-175,6) | Monomer ^f | | | |
| (52) | Cyh ₃ SnI | 1.60 ^e | 1.000(77-175,5) | Monomer ^f | | | |
| (53) | Cyh ₃ SnO ₂ CMe | 1.59 | 0.997(78-145,7) | Polymer(3) ^f | | | |
| (54) | Cyh ₃ Sn0 ₂ PPh ₂ | 1.58(1.95-0.82) | 0.988(78-200,8) | Polymer(3) | | | |
| (55) | Cyh ₃ SnCl | 1.40(1.40-1.28) ^g | 0.998(78-145,7) | Polymer(1) ^f | | | |
| (56) | Cyh ₃ SnNCS | 1.34 | | Polymer(2) ^{h,i} | | | |
| (57) | Cyh ₃ Sn(triaz) | 1.31(1.31-1.10) | 0.993(78-145,6) | Polymer(2) ^f | | | |
| (58) | $Cyh_3Sn0_2CC_6H_4(\underline{o}-N_2R)$ | 1.30 | (78-175,9) | Polymer(3) ^h | | | |
| (59) | Cyh ₂ SnF ₂ | 1.23 | 0.999(78-160,11) | Polymer(2) ^h | | | |
| (60) | Cyh ₄ Sn | 1.14 ^j | 0.996(78-165,9) | Monomer ^h | | | |
| (61) | Cyh ₂ SnCl ₂ | 1.13(1.13-0.94) | 0.996(78-160,7) | Polymer(2) ^h | | | |
| (62) | Cyh ₃ SnF | 0.91(0.91-0.79) | 0.996(78-145,6) | Polymer(1) ^f | | | |
| (63) | Cyh ₃ SnO ₂ CH | 0.93 | 0.992(78-150,10) | Polymer ^h | | | |
| (64) | Cyh ₃ SnOH | 0.66 | 0.999(78-135,6) | Polymer(1) ^h | | | |

^a Abbreviations: Cyh = cyclohexyl; iaa = indol-3-ylacetate;
triaz = 1,2,4-triazol-1-yl; R = 2-hydroxy-5-methylphenyl.
^b This work unless specified otherwise. ^c Figures in parentheses denote the polymer class (see Figure 2.III and Discussion section 4.3).
^d Ref. 190. ^e Ref. 149. ^f X-ray crystallographic data (see Refs. 13 and 14 and Discussion section 4.3). ^g Also quoted as 1.60 x 10⁻²K⁻¹,
Ref. 149. ^h On the basis of v.t.M.s. and other spectroscopic data.
ⁱ See below, section 4.4.2. ^j Quoted as 1.78 x 10⁻²K⁻¹ in Ref. 159.

a remarkably low <u>a</u> value $(1.14 \times 10^{-2} \text{K}^{-1})$. -dlnf/dT for this compound has also been quoted as $1.78 \times 10^{-2} \text{K}^{-1}$, ¹⁵⁹ but the lower value seems to be more consistent with the very high melting point of this compound (263°C) compared with the monomers $(C_{6}H_{11})_{3}$ SnBr $(\text{m.p. } 76^{\circ}\text{C})^{149}$ and $(C_{6}H_{11})_{3}$ SnI (m.p. $63^{\circ}\text{C})^{149}$ and parallels the example of Ph₄Sn. The molecules are held rigidly in their lattice through the operation of the strong crystal packing forces which must arise from very efficient packing of the molecules unlike the lattices of the two monomeric halides in which approximately spherical molecules are well separated from their neighbours.

Tricyclohexyltin indol-3-ylacetate is polymeric with the chain adopting a helical (Class 3) tertiary structure, but in this case the polymer arises from hydrogen bonding between -NH and C=0 units of adjacent molecules and the $(C_6H_{11})_3$ Sn units remain four-coordinate and pendant to the polymeric backbone.¹⁹⁰ The tertiary structure is reflected in the <u>a</u> value (1.75 x $10^{-2}K^{-1}$) and its slightly higher value relative to that of the true Class 3 polymer $(C_6H_{11})_3$ SnO₂CMe may be due to the pendant nature of the tin atom. This behaviour is comparable to that of [Ph₃Sn(C₆H₄CHCH₂)]_n, discussed in Chapter 2, section 2.3, where, again, the triorganotin moiety is pendant to the polymeric chain.

The triazole (57)¹⁶⁰ adopts a Class 2 polymeric structure with a corresponding decrease in <u>a</u> to 1.31 x 10^{-2} K⁻¹.

Crystallographic data for the complete series $(C_6H_{11})_3$ SnX $(X = F, {}^{149} C1, {}^{150} Br, {}^{149} I^{149})$ are available and all have been described as discrete, distorted tetrahedral molecules in the solid^{149,150} on the basis of the bond angles about tin and the intermolecular Sn----X distances (Sn----F, 3.32Å; Sn----C1, 3.30Å; Sn - - - Br, I, > 5A). The geometries and intermolecular separations are very similar for all four (e.g. the similar molar volumes) in spite of the relatively short Sn----X 'contact' distances for Almost identical <u>a</u> values (<u>ca</u>. 1.60 x 10^{-2} K⁻¹) X = C1, F.have been obtained for X = Cl, Br, $I^{149,150}$ but data obtained for the chloride and fluoride in the present work (Table 4.II) reflect a sequential stiffening of the lattice as one moves from the iodide and bromide to the chloride and fluoride. The unit cells of the isostructural pair X = Br, I contain the molecules in a random orientation relative to each other whereas in the two light halides an ordered array, suggestive of a Class 1 (rod -like) polymeric structure, is formed. The crystallographic data do not allow detailed assessments of intermolecular bond strengths to be made because of the large uncertainties in bond lengths arising from decomposition of the crystal in the X-ray beam in each case, resulting in R factors of the order of 10%. Nevertheless the variabletemperature Mössbauer data obtained for the chloride and fluoride are entirely consistent with the widely-held belief that the strength of an intermolecular bond should increase in parallel with the electronegativity of the bridging atoms because the increasing

polarity of the covalent Sn-X will increase the electrostatic interaction between the halide and the neighbouring tin atom. Melting points reflect the relative cohesion between molecules, and for the tricyclohexyltin halides these follow the order: $F(310^{\circ}C \text{ decomp.}) > C1(127^{\circ}C) > Br(76^{\circ}C^{149}) > I(63^{\circ}C^{149}).$ This sequence, together with the very similar molar volumes of each compound which means that similar packing forces operate in each lattice, also suggests increasing strength of intermolecular interaction via halide bridging in the lighter halides. The Mössbauer quadrupole splitting values compared with those of the analogous Me₂SnX and Neo₂SnX halides [Neo = MeCPh(Me)CH₂] have been interpreted in terms of a polymeric five-coordinate structure for $(C_{5}H_{11})_{3}$ SnX (X = F, C1) and structures intermediate between fourand five-coordinate for the corresponding bromide and iodide with weak but distinct intermolecular association. 186 The validity of this approach to the existence of intermolecular association seems, however, somewhat undermined by point-charge calculations which assume the chloride and fluoride to be four-coordinate but take the crystallographically observed angular distortions from regular tetrahedral into account. 149,150 Reasonable agreement between observed and calculated QS values is obtained by this approach, and the observed distortions can be attributed to intramolecular electronic factors (e.g., the coordination geometry at tin in the chloride is almost identical to that⁹² of Me₃SnCl in the gas phase). Thus, the variable-temperature Mössbauer experiment is a much more sensitive indicator of the presence of intermolecular association than the single-temperature experiment for this series. The very

shallow slope obtained for $(C_{6}H_{11})_{3}$ SnF suggests that a Class 1-type tertiary structure is indeed effective in producing quite a rigid lattice compared with similar Class 2 phenyl- and cyclohexyltin polymers.

The lattice of tricyclohexyltin hydroxide is even more rigid than that of the fluoride, in fact its <u>a</u> value (0.66 x 10^{-2} K⁻¹) is the lowest of all the compounds in Tables 2.II and 4.II. Its quadrupole splitting, 2.99mms⁻¹, is large enough to be the result of a trans-0, SnC, geometry, thereby implying a polymeric structure, and in comparison with the Class 2 polymer of Ph₃SnOH (<SnOSn = 137.8°; $\underline{a} = 1.10 \times 10^{-2} \text{K}^{-1}$ the lattice is significantly more rigid. Extrapolation of the crystallographic and variabletemperature Mössbauer data for $(C_6H_{11})_3$ SnCl and $(C_6H_{11})_3$ SnF suggests that $(C_{6}H_{11})_{3}$ SnOH is a Class 1 polymer in which \leq SnOSn is ca. 180°. This structure is consistent with the steric demands of the hydrocarbon groups pendant to the polymeric -Sn-O-Snbackbone which are likely to be greater for the chair-shaped cyclohexyl- group than the planar phenyl ring and Class 1 polymers may turn out to be a common feature of tricyclohexyltin chemistry.

The variable-temperature data for dicyclohexyltin dichloride imply that the tin atom is held in a lattice environment about as rigid as the tin environments in the associated Class 1 halides $(C_6H_{11})_3SnX$ (X = F or Cl) and more rigid than the lattices of $(C_6H_{11})_3SnX$ (X = Br, I). However, the bridging bonds in the fluoride and chloride are relatively long and therefore weak, so that if dicyclohexyltin dichloride were also a polymer of Class 1-type like Me₂SnF₂ $\frac{88}{100}$ it should have an <u>a</u> value rather lower than either triorganotin even if one or both of the bridging bonds were weak. Thus a zigzag, probably doublybridged (c.f. Me₂SnCl₂ ⁹⁰) Class 2 polymer architecture is the most likely structure from this spectroscopic evidence. The crystal stucture of this compound has been obtained as part of this work (Chapter 5) and substantiates this spectroscopic assignment. Dicyclohexyltin difluoride ($\underline{a} = 1.23 \times 10^{-2} \text{K}^{-1}$) must have a similar polymer construction though its a value is higher than might be expected on the basis of the results obtained for the tricyclohexyltin halides, and its QS (3.31mms⁻¹) is lower than that of $(C_6H_{11})_2SnCl_2$ $(3.40 \text{ mm s}^{-1}).$ These factors may reflect a coordination at tin intermediate between five and six, with weak intermolecular association.

The Mössbauer data for $(C_{6}H_{11})_{3}SnO_{2}CC_{6}H_{4}(\underline{o}-N_{2}R)$ (R = 2-hydroxy-5-methylphenyl) (QS = 3.35mms⁻¹; <u>a</u> = 1.30 x 10⁻²K⁻¹) have been explained by a <u>trans-O_{2}SnC_{3}</u> geometry arising from a weakly-bridged chain structure similar to that of $(C_{6}H_{11})_{3}SnO_{2}CMe$.⁵⁸ The <u>a</u> value however, seems too low for this rationale [c.f. $(C_{6}H_{11})_{3}SnO_{2}CMe$, <u>a</u> = 1.59 x 10⁻²K⁻¹] and the lattice may receive additional stability, possibly via intermolecular hydrogen bonds.

The diphenylphosphinate (54) behaves in a similar fashion to its triphenyltin analogue (13) (Table 2.II), giving a markedly curved lnA(T) vs. T plot over the whole temperature range, with an approximate slope of <u>ca</u>. 1.50 x 10^{-2} K⁻¹. This value along with a QS value of 3.93mms^{-1} and the fact that the compound decomposes without melting at <u>ca</u>. 300° C again suggests a polymeric Class 3 structure akin to Ph₃SnO₂CMe and isostructural with Me₃SnOP(S)Me₂ and Me₃SnO₂PMe₂.¹⁶²

Tricyclohexyltin formate shows a distinctly more rigid lattice than its acetate counterpart (a = $0.93 \times 10^{-2} K^{-1}$, 1.59 x 10^{-2} K⁻¹ respectively) which parallels the behaviour of the two triphenyltin analogues (Table 2.II). Again, the QS of the formate is enhanced relative to the acetate (3.79mms⁻¹, 3.35mms⁻¹ respectively) and it seems reasonable that a similar change from the Class 3 tertiary structure of $(C_6H_{11})_3SnO_2CMe$ to a more linear The steric bulk of the cyclohexyl groups may polymer occurs. cause the polymer chain to be even more linear than that of Ph_3SnO_3CH (by decreasing angle β and/or increasing α , Figure 3.VII), thus minimising repulsions between the cyclohexyl groups of one tin and those of its neighbour along the chain, and lowering the <u>a</u> value of tricyclohexyltin formate (0.93 x 10^{-2} K⁻¹) compared with the corresponding triphenyltin compound (1.15 x 10^{-2} K⁻¹).

Finally the v.t.M.s. behaviour of the carboxylate pair Me_3SnO_2CMe and Me_3SnO_2CH was investigated for comparison with their phenyl- and cyclohexyltin analogues. The data for the entire series is presented in Table 4.III. The behaviour of Me_3SnO_2CH <u>vis</u> <u>a vis</u> Me_3SnO_2CMe is strikingly different from that
Table 4.III

Collected Variable-Temperature Mössbauer Data^a for Triorganotin Acetates and Formates

| Compound | $10^{2} a/K^{-1}$ |
|---|-------------------|
| Ph ₃ Sn0 ₂ CMe | 1.91 |
| Ph ₃ SnO ₂ CH | 1.15 |
| (C ₆ H ₁₁) ₃ SnO ₂ CMe | 1.59 |
| (C ₆ H ₁₁) ₃ SnO ₂ CH | 0.93 |
| Me3Sn02CMe | 1.62 |
| MeaSnOaCH | 1.89 ^b |

a All this work

^b Also quoted as 2.15 x 10^{-2} K⁻¹ in ref. 159

of the other two acetate/formate pairs. Me_3SnO_2CMe is polymeric with a Class 3 helical tertiary structure⁵⁹ and its <u>a</u> value $(1.62 \times 10^{-2} \text{K}^{-1})$ is consistent with this, although rather lower than might be anticipated from the value for Ph₂SnO₂CMe. To the extent that this difference is significant, it may be due to the somewhat more 'linear' polymer chain as measured by the α and β angles (see Figure 3.VII) which are respectively 122.5(3)° and 136.6(3)° in Me₃SnO₂CMe compared with $121.0(2)^{\circ}$ and $142.7(2)^{\circ}$ in Ph₃SnO₂CMe. The behaviour of $R_3 SnO_2 CH$ (R = Ph or $C_6 H_{11}$) in the v.t.M.s. experiment strongly suggests that if Me₃SnO₂CH is polymeric it too should show a distinctly more rigid lattice than its acetate counterpart. In fact its a value is significantly higher The resolution of this paradox must lie in the (Table 4.III). observation that solid trimethyltin formate can exist in two markedly different forms: one form is virtually insoluble in organic solvents while the second form is very soluble, ca. 200mg/ml in chloroform. 192,193 Both forms are sublimable in a It has been proposed 193 high vacuum without interconversion. that the soluble form exists in solution (e.g., chloroform, cyclohexane) in a cyclic, associated form in equilibrium with free monomer, and that the cyclic form, such as the cyclic trimer depicted in Figure 4.I, persists in the solid state.



Figure 4.I

A linear polymeric structure, on the other hand, was attributed to the insoluble form (Ref. 193, and references therein) and an incomplete X-ray structure for trimethyltin formate¹⁹⁴ shows planar trimethyltin groups and formoxy groups arranged alternately along a helical chain. The sample of trimethyltin formate used in the present v.t.M.s. experiment was very readily soluble in chloroform at room temperature, and, on the basis of v.t.M.s. systematics for methyltin compounds, its high a value is entirely consistent with the hypothesis that the soluble form exists as small cyclic systems in the solid state. Trimethyltin acetate has also been observed in two forms, one relatively insoluble, the other soluble, in organic solvents such as chloroform. 193 The sample examined in the present study was only sparingly soluble in chloroform and thus probably had the one-dimensional, helical polymeric structure reported in the crystallographic study⁵⁹ discussed above.

The insoluble form of Me₃SnO₂CH was prepared by mixing stoichiometric quantities of Me₃SnOH and formic acid and purified by sublimation, ^{192,193} and was converted to soluble trimethyltin formate by heating in a sealed ampoule with cyclohexane at 90 $^{\circ}$ for 12 - 24 hr. 193 The material used in the present study was prepared by refluxing reagents in toluene in a Dean and Stark The formation of small cyclic systems is favoured apparatus. because of increase in entropy and is free to occur at higher temperature preparations as in the literature method¹⁹², or the preparation used herein (refluxing toluene). Me_Sn0_CMe was obtained in its insoluble and soluble forms in the same manner as the formate, ^{192,193} and the material in the present study was prepared from aqueous solutions of sodium acetate and trimethyltin chloride at room temperature followed by recrystallisation from toluene. It would seem reasonable to assume that the low-temperature route to Me3SnO2CMe used in this study would parallel the mixing of neat reagents and yield the insoluble (polymeric) form of the compound.

It seems likely, however, that the favourable entropy change associated with ring formation in $R_3 SnO_2 CR'$ is offset by energy (steric repulsion) factors when bulky R and/or R' groups are involved, so that polymeric rather than ring structures are obtained for $(C_6H_{11})_3SnO_2CR'$ (R' = H, CH₃, CF₃) and Ph₃SnO₂CR' (R' = H, CH₃). 4.4. ¹¹⁹Sn, ¹⁴N N.M.R. and ^{119m}Sn Variable-Temperature <u>Mössbauer Spectroscopic Study of Tricyclohexyltin</u> <u>Isothiocyanate including the First Observation of</u> <u>resolved</u> ¹¹⁷, ¹¹⁹Sn-¹⁴N Coupling in an Organotin <u>Compound.</u>

4.4.1. Experimental

Tricyclohexyltin isothiocyanate, $(C_6H_{11})_3$ SnNCS, was prepared by mixing equimolar quantities of tricyclohexyltin hydroxide and ammonium isothiocyanate in methylcyclohexane and heating the mixture under reflux for 7hr, as described previously¹⁹⁵ The solvent was removed under vacuum and the white solid recrystallised from dry toluene. Found: C, 53.32; H, 7.89; N, 3.43%. Calculated for $C_{19}H_{33}$ NSSn: C, 53.54; H, 7.80; N, 3.29%. m.p. 119-121°C (lit. 123°C).¹⁹⁵

119 14 Sn and N n.m.r. spectra were recorded in 10mm tubes at 30°C on an JEOL FX60Q spectrometer, at the International Tin Research Institute, Greenford, with field frequency lock to external ¹¹⁹ Sn spectra were recorded under nuclear Overhauser D_0. suppressed conditions, with chemical shifts relative to Me, Sn ¹⁴N chemical shifts are relative to and accurate to \pm 0.1ppm. nitromethane and are accurate to ± 0.5ppm. A finely powdered sample containing 1.5mg 119 Sn per cm² was used for the collection of M8ssbauer spectra in the temperature range 78 - 153K; temperature stability was ± 0.1K over the period of data collection at each temperature value (ca. 12hr). Despite the relative "thickness" of the sample, the lnA(T) vs. T plot is linear over the range 78 - 135K, with mild curvature of the plot at higher temperatures. This suggests that a Debye model for

the lattice of the title compound is acceptable, at least up to 135K, and the data have been fitted to a straight line with slope $\underline{a} = -dlnf/dT = 1.34 \times 10^{-2} K^{-1}$ (correlation coefficient, r =-0.998 for 8 points). No attempt was made to account for deviations from linearity of the plot in the high-temperature region (T>135K) in terms of a model incorporating anharmonic oscillators.

4.4.2. <u>Results and Discussion</u> (a) ¹¹⁹Sn, ¹⁴N n.m.r.:

Figure 4.II shows the ¹¹⁹Sn n.m.r. spectrum of a 0.15M solution of $(C_{6}^{H}_{11})_{3}$ SnNCS in toluene. The chemical shift of -3.2ppm is consistent with a four-coordinate geometry about tin in solution, in accord with observations on related systems. Thus, for example, the ¹¹⁹Sn chemical shift for $[(C_{\tilde{b}}H_{11})_3Sn]_2$ 0 is -7.9ppm.¹⁹⁶ The fine structure of the spectrum consists of a triplet of (within experimental error) equal intensities and linewidths (ca. 14Hz after allowance for exponential broadening) which arises from coupling of ¹¹⁹Sn and ¹⁴N nuclei (I = $\frac{1}{2}$ and 1, respectively) with ¹J(¹¹⁹Sn-¹⁴N) = This is the first observation of resolved coupling between 136Hz, these two nuclei in an organotin compound, and can only be compared directly with one other report of such an interaction, namely, the anion $Sn(NCS)_{6}^{2-}$ which gave ${}^{1}J({}^{119}Sn-{}^{14}N) = 150Hz.$ ¹⁹⁷ In addition, indirect comparison can be drawn with about a dozen citings of $^{1}J(^{119}Sn-^{15}N)$ data (Ref. 197, and references therein) using reduced coupling constants which normalise the effects of a different magnetogyric ratio for each of the two nitrogen isotopes [the reduced coupling constant K(Sn-N) is defined as



Figure 4.II. ¹¹⁹Sn n.m.r. spectrum of $(C_{\tilde{o}}H_{11})_{3}$ Sn NCS (0.15M in toluene).

 1 J(Sn-N)4 π^{2} /h_Y(Sn)_Y(N), Y= magnetogyric ratio]. The reduced coupling constant for the title compound (42nm⁻³) is only exceeded by that for the above anion (46.3nm⁻³) and (n-C₄H₉)₃SnNCS (68.5nm⁻³)¹⁹⁷.

The ¹⁴N n.m.r. spectrum of the same solution, Figure 4.III, clearly shows ^{117,119}Sn satellites, and although the individual couplings to each tin isotope are not resolved, the measured average ¹J(Sn-¹⁴N) coupling of 133Hz can be scaled up to a value of 136Hz for ¹J(¹¹⁹Sn-¹⁴N), and is entirely consistent with the ¹¹⁹Sn spectrum. The ranges of ¹⁴N chemical shifts for thiocyanate (M-SCN) and isothiocyanate (M-NCS) compounds are -100 to -150ppm and -200 to -300ppm respectively, ¹⁹⁸ and on the basis of these systematics the direct linkage between tin and nitrogen is confirmed by the observed ¹⁴N shift of -264.2 ppm for the title compound. The ¹⁴N linewidth of 9Hz (after correction for exponential broadening) implies a minimum spin-lattice relaxation time, T₁, of 0.035s, a value which indicates a significant contribution to the observed ¹¹⁹Sn linewidth from scalar coupling between the two nuclei.

Spectra in which coupling between ^{117,119} Sn and ¹⁴N is not observed are generally attributed to the presence of one (or more) of the following phenomena:

(i) ¹⁴N quadrupole relaxation which is fast compared to the coupling constant,

(ii) fast tin relaxation, and

(iii) exchange.

In the present case both conditions (i) and (ii) must not be satisfied, while the observed 119 Sn and 14 N linewidths indicate that possible contributions from exchange mechanisms are, if at all,



Figure 4.III. ¹⁴N n.m.r. spectrum of $(C_6H_{11})_3$ SnNCS (0.15M) in toluene.

minimal. ¹⁴N spectra are usually most readily observed in compounds in which the electric field gradient at nitrogen is small or absent, e.g., NH_4^+ , and it would appear that this is also fortuitously the case in $(C_6^{H_{11}})_3$ SnNCS.

(b) Mössbauer Spectroscopy:

While the ¹¹⁹Sn n.m.r. shift data indicate a four-coordinate, tetrahedral geometry about the metal in solution, M8ssbauer data (IS = 1.66mms^{-1} , QS = 3.78mms^{-1} at 78K) indicate a coordination number of five in the solid state. Furthermore, the magnitude of QS indicates a <u>trans-X2SnR3</u> trigonal bipyramidal geometry at tin, which in this case can only arise from intermolecular association whereby isothiocyanate groups link adjacent tin atoms, with N and S atoms occupying axial sites on the polyhedron of ligands about the tin.

The variable-temperature Mössbauer spectroscopic data for both $(C_6H_{11})_3$ SnNCS and Ph₃SnNCS (see Table 2.II) are illustrated in Figure 4.IV as lnA(T) <u>vs</u> T plots; the <u>a</u> values are, respectively, 1.34 x 10⁻² and 1.84 x 10⁻²K⁻¹. As already discussed (Chapter 2, section 2.3), Ph₃SnNCS is a Class 3 polymer with a local geometry identical to that inferred for $(C_6H_{11})_3$ SnNCS described above, and is illustrated in Figure 2.IV, Chapter 2, section 2.3. Its <u>a</u> value is consistent with this polymer architecture, but the significantly lower value for $(C_6H_{11})_3$ SnNCS indicates a more rigid lattice. Although other factors such as the strength of the intermolecular bond (Sn-S in this case) will also influence the value of <u>a</u>, the data suggest that polymeric $(C_6H_{11})_3$ SnNCS is





more linear in character and represents a transition from Class 3 towards Class 2 tertiary structure. Again, this is plausible in view of the steric bulk of the chair conformation of the cyclohexyl group compared with the planar phenyl ring: a Class 2 polymer more readily accommodates the steric requirements of the $C_{0}H_{11}$ groups bonded to adjacent tin atoms, and the situation recalls the Class 3 + Class 2-type conversion in the pair of carboxylates $Ph_{3}SnO_{2}CR'$ ($R' = CH_{3}$, H) described in Chapter 2, and the lower <u>a</u> value for $(C_{6}H_{11})_{3}SnO_{2}CH$ (0.93 x $10^{-2}K^{-1}$) compared with $Ph_{3}SnO_{2}CH$ (1.15 x $10^{-2}K^{-1}$) may also reflect this steric factor.

4.5. Conclusions

The variable-temperature MBssbauer data for cyclohexyltin compounds can be interpreted in a similar fashion to those of the The tertiary structure of a polymeric phenyltin compounds. species appears to be an important determinant of lattice dynamics, with a values in the order: Class 3/4 and monomers > Class 2 > Class 1-type tertiary structures are likely to be a Class 1. Figure 4.V collates common feature of tricyclohexyltin chemistry. the available data for both cyclohexyl- and phenyl-tin compounds. The ranges in a values for each class will undoubtedly change as further crystallographic and v.t.M.s. data become available, and in any case judgment of where the cross-over between an ordered array of non-interacting units and a weakly associated polymer can be drawn inevitably contains a subjective element.





Chapter 5.

The Structure of Dicyclohexyltin Dichloride

5.1. Introduction

Organotin halides are of central importance in organotin chemistry, both as the starting point for most synthetic work in the field and as structural models for other more complex systems. X-ray diffraction studies of these materials have in some cases revealed structures in which the existence or not of bridging halogen-tin systems have been contentious issues (see Chapter 1). The halides have also figured prominently as model compounds in ^{119m}Sn Mössbauer spectroscopy, for example in the development of point charge models for the rationalisation of quadrupole splitting values as outlined in Chapter 1.

Relatively little structural information is available for cyclohexyltin compounds, despite their biocidal potential. To complement the X-ray diffraction studies on the complete range of tricyclohexyltin halides^{149,150} this Chapter reports the results of an X-ray diffraction study of dicyclohexyltin dichloride, a compound which was also the subject of a variable-temperature ⁻ Mössbauer study as reported in Chapter 4.

5.2. Experimental

5.2.1. Synthesis

Dicyclohexyltin dichloride was prepared by a redistribution reaction between equimolar quantities of tetracyclohexyltin and stannic chloride. Suitable crystals for X-ray diffraction were obtained by slow evaporation of a diethyl ether solution. Analysis: Found, C, 40.36; H, 6.55; C₁₂H₂₂Cl₂Sn calcd.: C, 40.50; H, 6.23%. M.p. 88 - 89°C, lit.¹⁸⁹ 88 - 89°C.

5.2.2. Crystal Data

 $C_{12}H_{22}Cl_{2}Sn$, M = 355.9, orthorhombic Pbcm, <u>a</u> 6.671(5), <u>b</u> 9.445(6), <u>c</u> 24.203(12)Å, <u>U</u> 1525.0Å³, Z = 4, D_c 1.55Mgm⁻³, μ (Mo-K_a) 18.4mm⁻¹, <u>F</u>(000) 712.

5.2.3. Data Collection and Reduction

A crystal of approximate dimensions 0.42 x 0.35 x 0.24mm was used for data collection. 1722 unique reflections were collected on a Stöe Stadi-2 two-circle diffractometer, of which 1527 were considered observed [I \geq 3 σ (I)] and used for subsequent analysis. Corrections were made for Lorentz and polarisation effects; no absorption corrections were included due to the low μ (Mo-K $_{\alpha}$) coefficient.

5.2.4. Structure Determination and Refinement

Structure analysis was initially conducted in the noncentrosymmetric space group $Pca2_1$, $[\underline{a} \ 9.445(6)$, $\underline{b} \ 6.671(5)$, $\underline{c} \ 24.203(12)^{\text{A}}]$. The structure was solved using conventional Patterson and Fourier methods to final value of R = 0.046 and R' = 0.054. However, the presence of an apparent mirror plane perpendicular to \underline{c} through the Sn and Cl atoms (relating the two cyclohexyl groups) led to the imposition of exact mirror symmetry and the structure was refined in the centrosymmetric space group Pbcm (Z = 4). The final R values were marginally higher (R = 0.047, R' = 0.058) but this is to be expected given that imposition of exact mirror symmetry reduces the number of independent variables. However, refinement in Pbcm did lead to a significant improvement in the bond distances and angles associated with the cyclohexyl group and hence the centrosymmetric space group seems to be the more appropriate. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were localised in ideal positions and given a common isotropic temperature factor which finally refined to U 0.131(9)Å². Scattering factors were calculated using an analytical expression¹⁷³ and the weighting scheme employed was w = $1.0000/[\sigma^2(F_0) + 0.007(F_0)^2]$.

The final positional parameters for the non-hydrogen atoms are given in Table 5.I, bond distances and angles in Table 5.II. Figure 5.I shows the asymmetric unit with atomic labelling.

5.3. Discussion

The structure of dicyclohexyltin dichloride consists of subunits intermediate in geometry between $\underline{\operatorname{cis}}_2\operatorname{SnCl}_3$ and $\underline{\operatorname{trans}}_2\operatorname{SnCl}_4$ linked by chlorine bridges into a one-dimensional polymer. The complexities of this arrangement can be considered in two parts: the intramolecular geometry about tin and the spacial distribution of monomers from which the polymer is built. The local geometry about tin can be best understood in terms of a two-step reaction Table 5.I

| Dicyclohexyltin | Dichloride: | Fractional Positi | onal Parameters |
|----------------------------|-------------|---------------------------------|-----------------|
| (x 10 ⁵ for Sn; | otherwise x | 10 ⁴) with e.s.d.'s | in Parentheses |
| | | | |
| Atom | x | У | Z |
| Sn | 7507(6) | 14109(4) | 25000 |
| C1(1) | 2404(2) | 3676(2) | 2500 |
| C1(2) | -2522(2) | 2391(2) | 2500 |
| C(11) | 1388(7) | 651(5) | 3319(2) |
| C(12) | 193(13) | 1483(8) | 3753(3) |
| C(13) | 631(2) | 911(4) | 4336(3) |
| C(14) | 2889(13) | 874(10) | 4458(3) |
| C(15) | 3991(9) | 73(1) | 4033(3) |
| C(16) | 3618(8) | 595(7) | 3447(2) |

7

| Table 5.II | | | |
|-----------------|-------------|--------------------------------|-------------|
| Dicyclohexyltin | Dichloride: | Bond Distances (A) and | Angles (°) |
| | with e.s.d. | 's in Parentheses ^a | |
| | | | |
| Bond distances | | | |
| Sn-C1(1) | 2.407(2) | C(12)-C(13) | 1.540(10) |
| Sn-C1(2) | 2.371(1) | C(13)-C(14) | 1.535(10) |
| Sn-Cl(1') | 3.332(2) | C(14)-C(15) | 1.473(11) |
| Sn-C1(2') | 3.976(1) | C(15)-C(16) | 1.523(8) |
| Sn-C(11) | 2.151(4) | C(16)-C(11) | 1.520(7) |
| C(11)-C(12) | 1.535(7) | | |
| | | | |
| Bond angles | | | |
| C1(1)-Sn-Cl(1') | 168.1(1) | C(12)-C(13)-C(1 | 4) 111.7(6) |
| C1(1)-Sn-C1(2) | 94.3(1) | C(13)-C(14)-C(1 | 5) 111.6(7) |
| C1(1)-Sn-C1(11) | 101.9(1) | C(14)-C(15)-C(1 | 6) 113.7(6) |

| C1(1)-Sn-C1(2) | 94.3(1) | C(13)-C(14)-C(15) | 111.6(7) |
|-------------------|----------|-------------------|----------|
| C1(1)-Sn-C1(11) | 101.9(1) | C(14)-C(15)-C(16) | 113.7(6) |
| C1(2)-Sn-C1(1') | 73.8(1) | C(15)-C(16)-C(11) | 111.2(5) |
| C1(2)-Sn-C(11) | 108.2(1) | C1(2')-Sn-C1(1) | 135.5(1) |
| C1(1')-Sn-C(11) | 82.3(1) | C1(2')-Sn-C1(2) | 130.3(1) |
| Sn-C(11)-C(12) | 110.9(3) | C1(2')-Sn-C1(1') | 56.5(1) |
| Sn-C(11)-C(16) | 113.1(3) | C1(2')-Sn-C(11) | 67.8(1) |
| C(12)-C(11)-C(16) | 112.8(5) | C(11)-Sn-C(11") | 134.4(2) |

C(11)-C(12)-C(13) 110.4(5)

^a Primed atoms are related to their unprimed counterparts (x, y, z) by: (') - x, y - 0.5, z; (") x, y, 0.5 - z

153.



Figure 5.1. Part of the polymeric structure of $(C_0H_{11})_2SnCl_2$, showing atomic labelling. Hydrogen atoms have been omitted for clarity. Primed and double-primed atoms are related to their unprimed counterparts by the symmetry operations -x, y-0.5, z and x, y, 0.5-z, respectively. between a tetrahedral $(C_6 H_{11})_2$ SnC1₂ molecule and two chlorine atoms, Figure 5.II. The first step is the intermolecular approach of Cl(1') towards the C(11), C(11"), Cl(2)-triangular face of the tetrahedron, producing a cis-R₂SnCl₃ trigonal bipyramidal (tbp) geometry at tin with Cl(1) and Cl(1') in the axial positions. This arrangement implies a closing of the angles between Cl(1) and each of C(11), C(11") and Cl(2) from 109° 28' towards the ideal tbp value of 90° [101.9(1), 101.9(1) and 94.3(1), respectively]. The corresponding angles involving Cl(1') are all less than 90° [82.3. (1), 82.3(1), 73.8(1)]. The magnitude of the C1(1'): \longrightarrow Sn attraction [3.332(2)Å], while relatively weak compared with normal covalent bonds, is clearly significant. Indeed, in comparison with Sn-Cl bond lengths in other diorganotin dichloride structures ^{90,91,93,94} (Table 5.III), the intra- and inter-molecular Sn-Cl(1') bonds [2.407(2), 3.332(2)Å] are the longest and shortest respectively of their types yet reported. Only in solid Me₂SnCl are the two analogous bonds more similar in length [2.430(2), 3.269(2)Å]. Further comparison for this primary mode for coordination expansion at tin in $(C_6H_{11})_2SnCl_2$ can be made with $(C_{6}H_{11})_{3}$ SnCl, ¹⁵⁰ in which the stereochemical arrangement of tin and chlorine atoms along c is suggestive of lattice association. The two Sn-Cl bond lengths in this latter compound [2.407(5), 3.30A] are almost identical with those in the In each of these organotin chlorides, the title compound. arrangement of bond lengths (and angles, see below) is totally consistent with a re-distribution of the chlorine bonding electrons between two bonds to tin, rather than one, and the intramolecular



Figure 5.11. The formation of the coordination sphere about tin, depicted schematically in terms of the sequential approach of chlorine atoms to an initially tetrahedral $(C_6H_{11})_2SnCl_2$ molecule.

| Tab | le | 5. | II | I |
|-----|----|----|----|---|
| | | | | _ |

| Compara | tive Structura | al Data for Organot | tin Chlorides | | |
|---|--|----------------------|----------------------------------|------------------------|-----------|
| Compound | Sn-C1 (Å) | SnC1(Å) | <c-sn-c(<sup>0)</c-sn-c(<sup> | Structure ^b | Ref. |
| (C ₆ H ₁₁) ₂ SnC1 ₂ | 2.407(2) 2.371(1) | 3.332(2) 3.976(1) | 134.4(2) | 5.IIIc | this work |
| (CH ₃) ₂ SnC1 ₂ | 2.40(4) | 3.54(5) | 123.5(4.5) | 5.IIId | 90 |
| (C ₂ H ₅) ₂ SnCl ₂ | 2.385(3) 2.384(3) | 3.483(4) 3.440(3) | 134.0(6) | 5.IIId | 91 |
| (C1CH ₂) ₂ SnC1 ₂ | 2.37(2) | 3.71 | 135.0(6) | 5.IIIc | 94 |
| (C ₆ H ₅) ₂ SnCl ₂ | 2.336 [°] 2.355 [°] | 3.77 | 125.5 ^c | 5.IIIa ^d | 93 |
| (2-C ₆ H ₅ C ₆ H ₄) ₂ SnCl ₂ | 2.391(2) 2.381(3) | | 130.8(3) | tetrahedral | 31 |
| (CH ₃) ₃ SnC1 | 2.351(7) ^e 2.430(2) | 3.269(2) | 114.9(1.6) 117.1 ^f | tetrahedral tbp | 57 |
| (C ₆ H ₅) ₃ SnC1 | 2.32 | | 112.3 | tetrahedral | 140 |
| R ₃ SnC1 ^g | 2.380(3) | | 114.4 ^f | tetrahedral | 29 |
| (C ₆ H ₁₁) ₃ SnCl | 2.407(5) | 3.30 | 115.0(6) 119.0(5) | tbp | 150 |

^a X-ray diffraction unless stated otherwise. ^b See Figure 5.III for representations of 5.IIIa-d. ^c Mean value for two molecules in the asymmetric unit. ^d See also ref. 94. ^e Gas phase electron diffraction data: R.F. Zahrobsky, <u>J. Solid State Chem.</u>, 1973, <u>8</u>, 101. ^f Mean value of the three independent C-Sn-C angles. ^g R = {[(CH₃)₃Si]₂CH}. Sn-Cl bond is always longer than in tetrahedral $(C_6H_5)_3$ SnCl $[2.32\text{\AA}]^{140}$ or tetrahedral $[(Me_3Si)_2CH]_3$ SnCl $[2.380(3)\text{\AA}].^{29}$

The second intermolecular tin-chlorine interaction, step two of the reaction shown in Figure 5.II, is markedly weaker and more subjective in its significance. C1(2') approaches tin in the plane of the metal and the three halogen atoms, from below the equatorial plane of the tbp and between the two carbon atoms C(11) and C(11"). The final intermolecular Sn-Cl(2') distance is long[3.976(1)Å] and in excess of the sum of van der Waals radii (3.85Å)¹⁹⁹ generally taken as the limit of meaningful electronic interactions between these atom types. The proximity of C1(2') to tin does, however, cause angular distortions about that atom which are consistent with a very weak attraction. The most relevant of these angular changes occurs at C(11)-Sn-C(11") which is opened to 134.4(2)^o, and C(11)-Sn-Cl(2), C(11th)-Sn-Cl(2) which close to 108.2(1)°, all three of which would be 120° in a regular tbp geometry and all of which have altered in a manner consistent with the formation of a distorted six-coordinate octahedral trans-R₂SnCl₄ geometry at tin in which the idealised angles would be 180° and 90° for each of the two angular types. It is notable that in $(C_2H_5)_2SnI_2$ the intermolecular Sn-I interaction at 4.284(5) A is also in excess of the sum of the tin and iodine van der Waals radii (4.08Å)¹⁹⁹ but still results in a <C-Sn-C of 130.2(11)⁰.⁹¹ Thus it seems preferable to describe the structure of $(C_{6}H_{11})_{2}SnCl_{2}$ in terms of distortions of an octahedral rather trigonal bipyramidal geometry, a distinction which has chemical and not merely semantic significance. The angular

distortions from the presumably near-tetrahedral arrangement of bonds at tin which would exist in the isolated gas phase molecules of (C₆H₁₁)₂SnCl₂ (cf. Me₂SnCl₂) are larger than in any of the other $R_2 SnX_2$ (X = C1, Br, I) cases in which the geometry has been explained in terms of halogen bridging (Table 5.IV), although the observed distortions in the title compound could also have contributions from both isovalent rehybridisation, which would close<Cl-Sn-Cl from the ideal tetrahedral angle and open <C-Sn-C, and steric repulsion of the bulky cyclohexyl groups which would open up <C-Sn-C similar to the situation in monomeric $(2-C_{6}H_{5}C_{6}H_{4})_{2}SnCl_{2}$. The values of the two trans angles C1----Sn-C1 are quite different: < C1(1)-Sn-C1(1') = 168.1(1)^o, <Cl(2)-Sn-Cl(2') = 130.3(1)°. The near-linear angle corresponds to the relatively strong bridging interaction and is an example of a situation called 'secondary bonding' by Alcock²⁰⁰ in which the secondary bond is formed in an approximately linear relation with a primary bond. The bond in the Cl(1)-Sn-Cl(1') fragment can be qualitatively described as a 3-centre 4-electron covalent bond. The angle is comparable to the corresponding angles in Me₃SnCl⁵⁷ $[<C1-Sn-C1 = 176.85(6)^{\circ}]$ or $(C_2H_5)_2SnC1_2^{91}$ [173.0(1)°, The weakness of the Cl(2')----Sn bridge is reflected $172.0(1)^{\circ}$]. in the large deviation from linearity of the trans bond and may be compared with the angle $\langle I-Sn---I in (C_2H_5)_2SnI_2 [158.0(1)^{\circ}]$.

The second structural feature of interest is the stereochemical relationship of bonds which give rise to polymer formation. The various known scenarios on this theme in diorganotin dihalide

| | Tab | le | 5. | IV |
|--|-----|----|----|----|
|--|-----|----|----|----|

| Structural Data ^a for $R_2 SnX_2$ (R = organic group, X = halide) Units | | | | | | |
|--|-------------------------------|------------------------------------|-----------------------------------|--------------------------|-----------|--|
| R ₂ SnX ₂ | <c-sn-c(<sup>0)</c-sn-c(<sup> | <c-sn-cl(°)<sup>b</c-sn-cl(°)<sup> | <c1-sn-c1(<sup>°)</c1-sn-c1(<sup> | Structure | Ref. | |
| (C ₆ H ₁₁) ₂ SnC1 ₂ | 134.4(2) | 105.1 | 94.3(1) | 1-d polymer | this work | |
| (CH ₃) ₂ SnC1 ₂ | 123.5 | 109.0 | 93.0 | 1-d polymer | 90 | |
| (C ₂ H ₅) ₂ SnCl ₂ | 134.0(6) | 105.8 | 96. 0(1) | 1-d polymer | 91 | |
| (C2H5)2SnBr2 | 135.9(10) | 97.5(9) | 98.5(1) | l-d polymer | 91 | |
| (C ₂ H ₅) ₂ SnI ₂ | 130.2(11) | 105,6(8) | 104.0(2) | 1-d polymer | 91 | |
| $(C_6H_5)_2SnCl_2$ | 125.5 ^c | 107.2 ^c | 99.8 ^C | tetrahedral ^d | 93 | |
| (C1CH ₂) ₂ SnC1 ₂ | 135(6) | 105(2) | 97(2) | 1-d polymer | 94 | |
| $(2-C_6H_5C_6H_4)_2SnCl_2$ | 130.8(3) | 105.6 | 99.7(9) | tetrahedral | 31 | |
| (CH ₃) ₂ SnCl ₂ ^e | not given | 109.8 | 107.5 | tetrahedral | 92 | |

^a X-ray diffraction unless stated otherwise. ^b Mean value. ^c Mean value for two molecules in the asymmetric unit. ^d See also ref. 94. ^e Gas phase electron diffraction data.

chemistry are depicted in Figure 5.III, while the nature of the polymer architecture for $(C_6H_{11})_2$ SnCl₂ can be seen in the simplified diagram of cell contents in Figure 5.IV. In addition to a tetrahedral monomer (Figure 5.IIIa) such as $(2-C_6H_5C_6H_4)_2SnCl_2^{31}$ or, arguably, $Ph_2SnCl_2^{93,94}$ three types of polymer are known which embody a trans-R, SnX, geometry at tin. In the unique example of Me₂SnF₂ (Figure 5.IIIb), all the Sn-F bonds are equivalent, the polymer is two-dimensional and the Sn-F-Sn residue is linear,⁸⁸ a situation corresponding to a Class 1 type polymer in the terminology of Chapter 2. Two other arrangements are known: both incorporate two distinct types of Sn-X bond, and the spacial disposition of the Sn-X-Sn unit is zigzag or Class 2, i.e., less rigid as seen in the variable-temperature M8ssbauer experiment. The halogens which form the longer, bridging, bonds to tin can be from the same molecule [Figure 5.IIIc; e.g. $(C_2H_5)_2SnI_2^{91}$] or different molecules (Figure 5.IIId; e.g., $Me_2SnCl_2^{90}$). The title compound adopts a Figure 5.IIIc type structure with the C1(1')-Sn(1')-C1(2') unit both bridging and chelating Sn(1), although the mode of chelation It has been tentatively suggested is markedly anisobidentate. that the chelating bridge mode will be adopted by longer, weaker bonds⁹¹ but in the present compound one of the bridging bonds is shorter (and therefore stronger) than in any of the other reported polymeric diorganotin chlorides (Table 5.III). The lattice structure of dicyclohexyltin dichloride thus substantiates the prediction that a Class 2 rather than Class 1 polymer is adopted, based upon the variable-temperature Mössbauer studies reported in Chapter 4,



Figure 5.III. Structural variations in diorganotin dihalide chemistry: (a) tetrahedral monomer, (b) 2-d polymer, (c) 1-d polymer with bridging/chelating chlorine atoms and (d) 1-d polymer with purely bridging chlorine atoms. For each of structures (b) - (d), the R groups lying above and below the polymer plane have been omitted for clarity.



Figure 5.IV. Unit cell of $(C_{6}H_{11})_{2}SnCl_{2}$ viewed along <u>c</u>, showing the nature of polymer propagation. Only the α -carbon of the $C_{6}H_{11}$ ring above the polymer plane has been included for clarity.

although such studies cannot distinguish between the two types of Class 2 polymer. A distorted octahedral structure has also been predicted on the basis of the compounds quadrupole splitting by comparison with QS data for other dialkyltin dihalides.

Finally, the present structure provides a test for the relationship between QS and the C-Sn-C angle derived from a point-charge model^{115,116} discussed in Chapter 1. Using Equation 1.IX, $|QS| = 4[R] (1-3\sin^2\theta\cos^2\theta)^{\frac{1}{2}}$ and $[R] = -1.03 \text{mms}^{-1}$ for C_6H_{11} and an experimentally observed QS value of 3.40mms^{-1} (Table 4.I), the calculated <C-Sn-C (=20) is 139° . This is in good agreement with the observed value of $134.4(2)^{\circ}$, particularly in the light of the assumptions made in the model, namely that the electric field gradient at the tin nucleus is generated very largely by the R_2 Sn fragment, the contributions of the other ligands being negligible.

Chapter 6.

A Variable-Temperature Mössbauer Study of some (Phthalocyaninato)tin Complexes.

6.1. Introduction

A considerable amount of research effort has been directed in recent years towards the synthesis of organic and metal-organic molecular systems which have metal-like electrical,magnetic and optical properties, and towards an understanding of how these properties arise and how they can be controlled. The general feature of all such quasi-metallic substances is that they consist of linear rows of closely-spaced atoms or molecules which allow the formation of delocalized orbitals in the direction of the row. If the energy band so formed is incompletely filled near the Fermi surface, the crystal can conduct electricity along the direction of the row, this anisotropic conductivity being of the order of $10^{-4}-10^2\Omega^{-1}cm^{-1}$ at room temperature (c.f. $\sigma_{R.T.}$ $10^{-10}\Omega^{-1}cm^{-1}$ for most pure organic materials).²⁰¹

Although the best-known examples of such compounds are the so-called "organic metals", e.g., tetrathiafulvalene -tetracyanoquinodimethane (TTF-TCNQ), which are charge-transfer complexes, and polymeric tetracyanoplatinate complexes, e.g., K_2 [Pt(CN)₄]Cl_{0.32}, ^{2.6H}₂⁰, in which the conducting pathway is formed from direct overlap of metal d₂ orbitals along the spine of metal atoms, one-dimensional conductors formed from closely stacked, in crystallographically similar sites, square-planar metal complexes with highly delocalized, polarizable, macrocyclic ring systems have recently come to the fore.

Among the known classes of suitable metallomacrocycles, the metalloporphyrins and metallophthalocyanines stand out in terms of their chemical flexibility, robustness, and chargecarrier properties.²⁰² Metallophthalocyanine (pcM) compounds themselves are known to have semiconductor properties (e.g., refs. 203 and 204, and references therein). When pcM compounds or metal-free phthalocyanine are partially oxidized by a halogen (typically I₂), they may become conducting solids in which chains of polyhalide ions (e.g., I_3^{-}) occupy the channels formed by the spaces between stacks of planar pcM units, e.g., (pcNi)1.^{202,205} Partial oxidation by a halogen results in a fractional charge on the PcM units of the stack, so that charge transport involves movement of positive 'holes' between isoenergetic configurations and electrical conduction along the pathway formed by the closely stacked planar units (i.e., the required incompletely filled band) is facile. 206 In principle non-integral oxidation states could also be achieved by partial reduction.

An important goal is the control of and improvement in the metal-like properties of these pcM systems through rational chemical synthesis. As has been pointed out by Marks²⁰⁷ and others, halogen doping has the disadvantage that the crucial criterion of stacking is dependent upon the unpredictable and largely uncontrollable intermolecular packing forces which determine whether or not stacks are formed, the stacking repeat distance, the redox donor-acceptor orientations, and the relative orientations of pcM units in a stack. One important method for controlling stacking architecture is to link pcM units to each

other by strong covalent bonds. Thus, linear, polymeric, phthalocyanines, pcML, with bridging ligands L such as F, O, N, C_2^{2-} , CN⁻, pyrazine, 4,4'-pyridine which link covalently the metallomacrocycle in a face-to-face orientation have been synthesised and shown to be semiconductors, and can be converted to conductors by halide doping.²⁰⁴ Indeed if the bridging ligand forms a rigid group with one or two m-systems, continuous conjugation is possible along the entire polymer chain through suitable metal orbitals and perhaps those of pc^{2-} , and a suitable energy-band structure for electrical conduction is possible even without partial oxidation or reduction.²⁰¹ Electrical properties of such pcM and polymeric pcML species, both doped and undoped with oxidizing (or reducing) agents, may be expected to depend inter alia on such structural parameters as inter-ring distances along the stack, deviation of the stacking direction from the molecular symmetry axis and rotation of neighbouring rings producing deviation from ideal eclipsed stacking and also on electronic properties such as oxidation state of the central atom.

Recently extensive studies have been made of tin and other Group IVB complexes of phthalocyanine especially from the point of view of synthesizing molecular conductors with controlled properties (e.g., refs. 207-210). Numerous phthalocyanine complexes of tin are known, including (phthalocyaninato)tin(II)(pcSn), (phthalocyaninato)tin(IV) dichloride (pcSnCl₂), and bis(phthalocyaninato)tin(IV) (pc₂Sn), all of which have been established by Linstead <u>et al.</u>,²¹¹ and pcSnX₂ (X = F, Br, I, and OH).²¹² PcSn(OH)₂ can be condensed to give a polymeric, crystalline (pcSnO)_n (n <u>c</u>.100) species²⁰⁹ consisting of cofacially joined pcSn units of the type required as precursors for electrically conducting polymers (see Figure 6.1). Analogous complexes of both transition metal and main-group metals and metalloids including tin in which the phthalocyanine ring is peripherally substituted by organic groups have been prepared.²¹³ Such compounds, e.g., t-Butyl-substituted species, have the advantage of being more soluble in organic solvents than their unsubstituted counterparts so that chemical purity is more readily achieved, and homogeneous doping with iodine can be carried out.

As part of the analysis of electroactive polymers in which desired structural features are brought about by structure-enforcing linkages, variable-temperature Mössbauer studies of Mössbaueractive metallo-phthalocyanine complexes suggest themselves as a potentially very useful indicator of lattice structure. This chapter reports the results of a preliminary study of the use of this technique as applied to tin-phthalocyanine compounds.

6.2. Experimental

6.2.1. General

The solvents quinoline (B.D.H.) and 1-chloronaphthalene (B.D.H.) were vacuum-distilled from BaO before use. Pyridine was dried over sodium hydroxide pellets and distilled under dry nitrogen. Anhydrous stannous chloride was used as obtained in its commercial form (B.D.H.). 4-Tert-butyl-o-xylene (2) was prepared by the alkylation of o-xylene (1) with t-butylchloride and ferric chloride as reported previously²¹⁴ (see Figure 6.II).







OH

OH

 $(t-Bu)_{4}^{1} pcSn(OH)_{2} \stackrel{6}{\simeq}$

[(t-Bu) pcSnO] 7

Reactions: $1 \longrightarrow 2$, Ref. 214

 $2 \longrightarrow 3 \longrightarrow 4 \longrightarrow 5$, Ref. 215

Figure 6.II. Preparation of tin-phthalocyanine complexes: Synthetic routes. However, instead of recovering the desired product by means of a vacuum distillation (which proved to be very difficult due to 'bumping'), o-xylene was removed from the brown-green organic phase by distillation at atmospheric pressure through a fractionating column (a 15cm-length air-condenser filled with glass rings). The remaining brown-green liquid was distilled at atmospheric pressure without a fractionating column, the product, a colourless liquid, coming over at ca. 208°C. This was identified as 4-tert-butyl-o-xylene by means of its ¹H n.m.r. spectrum which was consistent with the desired butylated compound. The percentage yield was 52 %. Compound (4) was obtained as outlined in Figure 6.II, based on a literature method.²¹⁵ As the synthetic procedures in the present work included some modifications of this literature method the details are presented as follows: 4-tert-butyl-o-xylene (2) (32.8g, 0.20mol) was oxidized by potassium permanganate (169.5g, 1.07mol) in a mixture of pyridine (244cm³) and distilled water (81.5cm³). Potassium permanganate was added in portions to the organic/water system, which was at reflux temperature and stirred mechanically. The resulting reaction, upon addition of each portion of KMnO4, was sufficiently exothermic to maintain reflux without further external heating. The total time for addition of KMnO4 was 1.5hr. Following this, the system was heated at reflux with stirring for a further 30min. Then ethanol (30cm³) was added to the hot solution. The resulting brown solution contained a large amount of brown sediment, presumably manganese dioxide. After allowing to cool to room temperature, a

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slightly pink, clear, solution was separated by suction filtration through a sintered-glass frit. On standing, the solution turned slightly brown, and a colourless, clear, liquid was separated by filtration. The volume was reduced to one-third, and then slowly treated with concentrated hydrochloric acid (82 cm^3) . A white precipitate and an aqueous/oily phase were The organic layer was removed by several washings with formed. diethyl ether, the washings combined and washed with distilled The ether layer was dried over anhydrous magnesium water. sulphate, filtered, and evaporated to yield a very viscous oil. When a hot 1:1 mixture of chloroform and light petroleum (b.p. 60 - 80° C) (30cm³) was added to this oil a white solid separated from the solution. The mixture was placed in a freezer for lhr and filtered to give a white powder (21.5g). The filtrate was evaporated to give a waxy solid. A small amount of hot 1:1 $CHC1_3/light petroleum (60-80^{\circ})$ was added to this and further white solid recovered (3.1g). Thus the total amount of product was 24.6g (55% yield). The mass spectrum of this material was consistent with the desired compound 3. Compound 3. (24.6g, 0.11mol) was added to acetic anhydride (70 cm^3) and the mixture heated at The solid soon dissolved to give a straw-yellow reflux for lhr. solution. The solution was cooled to room temperature, filtered through a sintered glass frit and the volume reduced to ca. 20 cm^3 . When placed in a freezer a white solid was precipitated which was Further solid was obtained when the recovered by filtration. filtrate was further concentrated and a small quantity of the white solid added to initiate crystallization. Attempts to recrystallize the solid from methanol, light petroleum (60 - 80° C b.p.) or acetic anhydride failed, giving a light-yellow oil.

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However, the solid sublimed readily in a static vacuum (<u>ca. 1mmHg</u>) at <u>ca.</u> 80° C to give colourless crystals. The yield of sublimate was essentially 100%. This was identified as 4-t-butylphthalic acid anhydride (<u>4</u>) by ¹H n.m.r. spectroscopy, mass spectrometry and infrared spectroscopy. Total yield was 16g (71% based on weight of 3 used).

Phthalocyanine-tin complexes were identified by microanalysis in most cases (microanalytical service of University College, Dublin, except when otherwise stated), by infrared spectroscopy,^{209,215} and Mössbauer IS and QS values.¹⁷ Samples for Mössbauer spectroscopy were prepared as finely-ground powders and contained 1.0mg ¹¹⁹Sn per cm² except for the case of poly(2,9,16,23-tetra-t-butylphthalocyaninato)stannoxane, in which the sample contained 0.5mg ¹¹⁹Sn per cm².

6.2.2. Syntheses

(a) (Phthalocyaninato)tin dichloride $(pcSnCl_2)$: This compound was prepared according to the method of reference 209. Anhydrous stannous chloride (18g, 0.10mol) and o-phthalonitrile (40g, 0.31mol) were added to 1-chloronaphthalene (1L), the solution brought to reflux over a period of 1hr and then maintained at reflux for 3hr. The dark solution was allowed to cool to room temperature and then filtered to yield a purple, crystalline, solid which was washed with toluene in a Soxhlet extractor for 24hr. Analysis: Found, C, 52.04; H, 2.14; N, 15.64; $C_{32}H_{16}Cl_2N_8$ Sn calcd.: C, 54.79; H, 2.30; N, 16.00%. The infrared spectrum of this material was recorded as a nujol mull, and agreed well with literature data.²⁰⁹

(b) (Phthalocyaninato)tin(II) (pcSn):

PcSn was prepared by the method of ref. 212, in which pcSnCl₂ is reduced by SnCl₂. PcSnCl₂ (3.0g) and anhydrous stannous chloride (3.0g) (3.7:1 mole ratio) were heated at reflux (238°C) in guinoline (150cm³) for 2hr. The experiment was performed under nitrogen, as pcSn is reported as being susceptible to oxidation at elevated temperatures.²¹² The mixture thus obtained was allowed to cool to room temperature and then filtered. The dark-blue solid was washed with toluene and diethyl ether, extracted with refluxing quinoline in a Soxhlet apparatus under a nitrogen atmosphere, and the resulting solution cooled to yield the product which was again washed with toluene and diethyl ether. Mössbauer spectroscopy showed the presence of an Sn(IV) impurity accounting for 7% of the total absorption spectrum. Infrared data were consistent with the presence of a phthalocyanine system, and the Mössbauer parameters at 78K for the Sn(II) absorption are in good agreement with literature values (Table 6.I).

(c) (Phthalocyaninato)tin diiodide (pcSnI₂):

A procedure based on that of Kroenke and Kenney²¹² was followed. PcSn (1.0g) and I₂ (0.51g) (1:1.3mole ratio) were heated in 1-chloronaphthalene at reflux under N₂ for 6 min. The dark green solution was allowed to cool to room temperature, and the precipitate recovered by filtration. The crystalline solid was washed successively with 1-chloronaphthalene, toluene, and ethanol, and air dried. The yield was 1.0g of dark-blue crystalline solid. Analysis (Microanalytical service, School of Chemistry, University of Bath): Found, C, 43.53; H, 1.89; N, 12.46; C₃₂H₁₆I₂N₈Sn calcd.: C, 43.43; H, 1.82; N, 12.65%.

(d) (2,9,16,23-Tetra-t-butylphthalocyaninato)tin dichloride
 (t-Bu)₄pcSnCl₂:

This peripherally-substituted phthalocyanine complex was prepared by the method of Hanack et al.²¹⁵. A mixture of 4-t-butylphthalic acid anhydride (9.0g), urea (8.91g), anhydrous stannous chloride (2.23g) and ammonium molybdate (0.065g) in dried 1-chloronaphthalene (30 cm^3) was heated slowly from room temperature to 250° C under nitrogen, with mechanical stirring. The mixture was maintained at this temperature for 4hr, turning dark blue-green. After cooling, under nitrogen, to room temperature and addition of light petroleum b.p. 60 - $80^{\circ}C$ (30cm³) the mixture was cooled in a freezer for several hours, and, upon filtering, a blue-green This was washed, under nitrogen, for 7hr powder was obtained. with diethyl ether by means of a Soxhlet apparatus. The initial colour of the extracting solvent was dark green, but this turned to a very pale green towards the end of the 7hr period. The remaining solid in the thimble was then extracted with dry chloroform at reflux under nitrogen to give a dark blue-green microcrystalline solid. Analysis: Found, C, 59.1; H, 5.32; N, 11.6; C48H48C12N8Sn calcd.: C, 62.22; H, 5.22; N, 12.09%

(e) (2,9,16,23-Tetra-t-butylphthalocyaninato)tin dihydroxide
 (t-Bu)₄pcSn(OH)₂:

A sample of $(t-Bu)_4 pcSnCl_2$ in aqueous NaOH and ethanol (2.4g NaOH in 50cm³ water and 10cm³ ethanol)was heated at reflux for 6hr and the dark blue solid recovered by filtration. This was dissolved in dry chloroform and the deep blue solution washed several times with distilled water. The organic layer was separated, dried over anhydrous sodium sulphate and the microcrystalline blue solid product was recovered by evaporation of the solvent. Analysis: Found, C, 64.20; H, 5.69; N, 11.59; $C_{48}H_{50}NO_{7}Sn$ calcd.: C, 64.81; H, 5.67; N, 12.60%.

(f) Poly(2,9,16,23-tetra-t-butylphthalocyaninato)stannoxane
[(t-Bu),pcSn0];

A sample of $(t-Bu)_4 pcSn(0H)_2$ was heated under dynamic vacuum at 330[°]C for 30min. The powder obtained was washed with dry chloroform until the washings were colourless. The black microcrystalline solid remaining was insoluble in organic solvents.

6.3. Discussion

6.3.1. Synthesis and Characterization

The syntheses of pcSnCl₂ and (t-Bu)₄pcSnCl₂ in the present work follow the usual procedure in synthesizing phthalocyanine complexes whereby the complex is formed from molecular fragments of phthalocyanine, which could be phthalonitrile, Figure 6.III (a); phthalimide, Figure 6.III (b); phthalic anhydride, Figure 6.III (c); diiminoisoindoline, Figure 6.III (d) or some other derivative of o-phthalic acid, in the presence of a metal ion source e.g. chlorides,





Thus pcSnCl₂ was formed from <u>o</u>-phthalonitrile and stannous chloride, while the peripherally-substituted phthalocyanine complex, (t-Bu)₄pcSnCl₂, was synthesized using 4-t-butylphthalic anhydride (compound 4, Figure 6.II) as the starting material. The great chemical and thermal stability of the phthalocyanine ring system allows the preparation of a wide variety of tin-phthalocyanine complexes from pcSnCl₂ and (t-Bu)₄pcSnCl₂ including reactions involving reduction and oxidation of the tin atom.

The low solubilities of $pcSnX_2$ and pcSn in organic solvents makes the purification of these compounds difficult as reflected in the microanalysis results for $pcSnCl_2$ and the presence of an

acetates, metal oxides or free metals. 203(b)

Sn(II) impurity in the Mössbauer spectrum of $pcSnCl_2$ accounting for 10% of the total absorption (IS = 3.0, QS = 4.2mms⁻¹) and an Sn(IV) impurity in pcSn accounting for 7% of the total absorption (IS = -0.1, full width at half height 1.14mms⁻¹). In such cases infrared spectroscopy and Mössbauer isomer shift and quadrupole splitting parameters are important methods of characterization.

The high solubilities of both $(t-Bu)_4 pcSnCl_2$ and $(t-Bu)_4 pcSn(OH)_2$ in organic solvents, especially chloroform, allows increased standards of purity as reflected in the microanalysis data and the absence of visible impurity absorptions in the Mössbauer spectra. The infrared spectrum of (t-Bu), pcSnCl, showed absorptions due to the tert-butyl groups (2900 - 2700cm⁻¹) and at 300cm⁻¹, characteristic ofv(Sn-C1).²¹⁵ The UV/vis spectrum of this compound, recorded from 300nm to 800nm in chloroform agreed well with the literature data.²¹⁵ The proton n.m.r. data are consistent with the expected spectrum: δ(p.p.m.) 9.7, 8.5, 1.8(respective ratios 8:4:35). Α solution obtained by heating, at reflux, a sample of the solid in aqueous NaOH (0.25g cm^{-3}), when filtered and acidified with concentrated nitric acid gave a white precipitate on addition of a few drops of dilute aqueous silver nitrate. For the corresponding dihydroxide, $(t-Bu)_{\mu}pcSn(OH)_{2}$, the v(Sn-C1) absorption in the infrared is absent and a band has grown in at <u>ca</u>. 560 cm^{-1} . The absorption at 562cm⁻¹ in pcSn(OH), has been assigned to the antisymmetric Sn-0 stretch.²⁰⁹ The spectrum is otherwise very

similar to that of (t-Bu), pcSnCl₂. The insoluble polystannoxane [(t-Bu)₄pcSnO]_n showed an Sn(II) impurity in its Mössbauer spectrum accounting for 10% of the total absorption (IS = 3.05 $OS = 1.71 \text{mms}^{-1}$). Good quality infrared spectra (KBr disc or nujol mull) could not be obtained; however, the spectra show absorptions due to the tert-butyl groups and the absorption at 560cm⁻¹ has disappeared. The pattern of the other absorptions are very similar to those of $(t-Bu)_{L}pcSnX_{2}$ (X = C1, OH). Thus apart from insolubility in organic solvents and disappearance of the strong absorption at 560 cm^{-1} it is difficult to distinguish [(t-Bu) pcSnO] from (t-Bu) pcSn(OH). Figure 6.IV shows the infrared spectra of $(t-Bu)_{2}pcSnX_{2}$ (X = C1, OH) and $[(t-Bu)_{4}pcSnO]_{n}$ in the v(Sn-0) region, and the corresponding region in $pcSnX_2$ $(X = C1, OH)^{209}$ and $[pcSn0]_{n}^{209}$.

6.3.2. Variable-Temperature Mössbauer Spectroscopy

Table 6.I presents the Mössbauer spectroscopic data for the phthalocyanine complexes. Isomer-shift values for the $pcSnX_2$ series decrease with increasing electronegativity of the X group: O>Cl>I. The same pattern has been observed for a series of $pcSnX_2$ and TArPSnX₂ (TArP = tetraarylporphine) complexes²¹⁶ and indicates that increasing electronegativity of the ligand X results in increasing s-electron density being attracted away from the tin atom into the Sn-X bond. The magnitude of the quadrupole splitting also decreases with increasing electronegativity. This trend reflects the approach towards octahedral electronic symmetry at the tin site with decreasing electronegativity



(From ref. 209)

Figure 6.IV. Infrared spectra for tin phthalocyanine complexes in the v(Sn-0) region.

Table 6.I

| | Mössbauer | Data for | Tin-Ph | thalocyanine | Complexes ^a | |
|------------|-------------------------------------|-----------------|-----------------|--------------------|------------------------|-------------------|
| | | | | | | |
| Compou | ind | IS ^b | qs ^b | Γ ₁ b,c | Γ ^{b,c} 2 | $10^{2} a/K^{-1}$ |
| pcSnCl | L_2^{d} | 0.26 | 0.90 | 0.53 | 0.60 | 1.10 |
| pcSnI | е 2 | 0.45 | 1.21 | 0.63 | 0.585 | 0.67 |
| $pcSn^{f}$ | | 2.80 | 1.425 | 0.64 | 0.63 | 1.40 |
| (t-8u) | 4 ^{pcSnC1} 2 | 0.25 | 0.89 | 0.50 | 0.55 | 1.055 |
| (t-Bu) | 4 ^{pcSn(OH)} | 0.18 | 0.64 | 0.51 | 0.60 | 1.15 |
| [(t-B | 1) ₄ pcSnO] _n | 0.10 | 0.67 | 0.49 | 0.685 | 0.36 |
| TPPSn | (OH) ₂ .solv | g | | | | 1.19 ^h |

a All this work unless stated otherwise.

^b At 78K, mms⁻¹.

^c $\Gamma_{1,2}$ = half-width at half-height of lower and higher velocity absorption respectively.

- d Literature (ref. 17) : IS, 0.28; QS, 0.99 mms⁻¹.
 e Literature (ref. 17) : IS, 0.45; QS, 0.99 mms⁻¹.
 f Literature (ref. 17) : IS, 2.78; QS, 1.40 mms⁻¹.
- ^g α, β, γ, δ-tetraphenylporphinato-dihydroxytin-bis(chloroform)-bis (carbon tetrachloride) solvate.
- ^h Ref. 218

difference between the equatorial (nitrogen) atoms and the axial X atoms. The IS and QS parameters for $pcSnCl_2$ and $(t-Bu)_4pcSnCl_2$ are the same within experimental error, showing, reasonably, that peripheral substitution by alkyl groups has no appreciable effects on the electronic environment at the tin nucleus. The marginally larger IS of $[(t-Bu)_4pcSnO]_n$ compared with $(t-Bu)_4pcSn(OH)_2$ may be attributed to the higher electronegativity of the oxygen atoms in the polymeric compound.

The variable-temperature Mössbauer data for the series (Table 6.I) imply that the tin atom vibrates with similar freedom in each lattice (a ca. 1.0 x $10^{-2} K^{-1}$) except for pcSn and [(t-Bu),pcSnO],. The crystal structure of pcSnCl, has been determined²¹⁶ and it consists of essentially discrete pcSnCl₂ units in which the octahedral geometry at tin corresponds very closely to a regular square bipyramid although the octahedron is tilted with respect to the general plane of the stepped-deformed, and distended, phthalocyanine ring - both the tilting and ring deformation being due to the Sn(IV) atoms being somewhat too large to fit directly into the macrocyclic hole. There is also, apparently, a chain of intermolecular hydrogen bonds linking each chlorine with the hydrogen atom on a carbon of an isoindole unit of the neighbouring $pcSnCl_2$ molecule (C1....H 2.70Å). This will stiffen the lattice and hence constrain the vibrational freedom However, such hydrogen bonds are expected to be of the tin atom. weak compared with 0....H hydrogen bonds.²¹⁷ One other v.t.M.s. study of a tin-macrocycle has been reported, that of $(\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato)tin dihydroxide [TPPSn(OH)₂] as

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its bis(chloroform)-bis(carbon tetrachloride) solvate²¹⁸, which consists of discrete TPPSn(OH)₂ molecules in the solid state²¹⁸, and it gives an <u>a</u> value in the same region (1.193 x $10^{-2}K^{-1}$). Thus it seems likely that the significant reduction in the value of <u>a</u> for these systems relative to values characteristic of non-interacting organotins and organotins held together by one-dimensional chains of hydrogen bonds (i.e., <u>a</u> > 1.4 x $10^{-2}K^{-1}$) can be attributed mainly to a "macrocyclic effect" in which the tins motion is restricted by its situation within the cavity of the bulky macrocyclic system. A mass effect may also be operating to produce the low <u>a</u> value observed for pcSnI₂ (<u>a</u> = 0.67 x $10^{-2}K^{-1}$).

The solid-state structure of pcSn is known.²¹⁹ The covalent radius of the Sn(II) atom is so large that the metal lies 1.11Å above the plane of the four isoindole nitrogens, and the macrocycle is slightly deformed away from the tin atom to a "saucer" shape, and the SnN₄ group thus forms a square pyramid. Such an environment for the metal atom, in which the tin is "sitting-atop" the macrocycle, reduces the "macrocyclic effect" as reflected in the relatively high <u>a</u> value of 1.40×10^{-2} K⁻¹.

The insoluble polymeric material $[(t-Bu)_4 pcSn0]_n$ has a considerably more rigid lattice than any of the others (<u>a</u> = 0.35 x $10^{-2}K^{-1}$) showing that the formation of strong covalent single-atom linkages between tin-phthalocyanine complexes to form a cofacially-stacked polymer chain has a large effect on the variable-temperature M8ssbauer behaviour of the tin. This a value may

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thus represent a useful reference value for variabletemperature Mössbauer studies of other polymeric macrocycles in which the important parameter of intra-chain ring-ring distance is systematically increased by the use of longer, multiatom, linking ligands. The mode of polymer propagation of the present complex (Figure 6.I) corresponds to a Class 1-type tertiary structure and hence probably exemplifies the more rigid limit of v.t.M.s. behaviour, analogous to the Class 1 behaviour of $(C_6H_{11})_3$ SnOH <u>vis-à-vis</u> triorganotins (Chapter 4).

Appendix

Al. Synthesis of Trimethyltin acetate and Trimethyltin formate:

(a) Trimethyltin acetate: A solution of sodium acetate (2.50g) in deionised water (25 cm^3) was added to a solution of trimethyltin chloride (5.50g) in deionised water (50 cm^3). The resulting solution, on stirring, turned cloudy white. The precipitate was recovered by filtration, yielding 4.10g of white powdered solid. Crystalline needles were obtained on recrystallisation from hot toluene. This product was quite insoluble in toluene at room temperature but near the boiling point it dissolved and crystallised rapidly on cooling. Analysis: Found: C, 27.08; H, 5.34. $C_5H_{12}O_2$ Sn calcd.: C, 26.95; H, 5.43% m.p. 193-195^OC. Mössbauer data: IS, 1.34 (11t¹⁷ 1.30); QS, 3.58 (11t¹⁷ 3.57) mms⁻¹.

(b) Trimethyltin formate: Formic acid (1.0 cm^3) was added to trimethyltin hydroxide (2.30g) in dry toluene (80 cm^3) . The system was then heated at reflux in a Dean and Stark apparatus for 1 hr, then filtered while still hot. 1.47g of crystalline fine needles precipitated on cooling to room temperature. Analysis: Found: C, 22.89; H, 4.84. $C_4H_{10}O_2$ Sn calcd.: C, 23.01; H, 4.83%. m.p. 140-150°C (11t¹⁹³ 147-148°C). Mbssbauer data: IS, 1.32; QS, 3.59 mms⁻¹. Infrared spectra (KBr discs) for both the acetate and formate were consistent with the presence of bridging carboxylate groups.

A2. Drying of Laboratory Solvents:

(a) Toluene: Anhydrous toluene for Dean and Stark experiments was prepared by storing laboratory toluene over sodium wire.

(b) Diethyl ether: Anhydrous ether was prepared by storing laboratory ether over sodium wire and then distilling it over sodium wire in the presence of sodium benzophenone.

A3. Mössbauer Spectroscopy:

Mössbauer spectra were recorded on a constant acceleration Mössbauer spectrometer (Cryophysics) fitted with a room temperature 5mCi calcium stannate-119m source (Amersham Int.) and operated in a sawtooth wave mode. Temperature control of the sample was achieved using a continuous-flow liquid nitrogen cryostat linked to a DTC-2 digital variable-temperature controller (Oxford Instruments). Temperature stability was ± 0.1K of the desired temperature throughout spectral accumulation. Samples were prepared as finely ground powders to avoid orientation effects and generally contained 1-2mg 119 Sn per cm² in a disc of area ca. 0.75 cm². Velocity calibration measurements were periodically carried out using natural iron (in conjunction with a 57Co source) and β -tin. Spectra were curve-fitted using conventional leastsquares techniques to standard Lorentzian line shapes, with prior data correction for parabolic background curvature.

Conclusions

The variable-temperature MBssbauer spectroscopy (v.t.M.s.) systematics which have previously been outlined for methyltin species are also broadly applicable to a wide range of phenyltin species. Thus $\underline{a} = -d \ln f/dT$ values of \underline{ca} . 1.80 x 10^{-2}K^{-1} correlate with monomeric lattices but the onset of polymerisation due to intermolecular association (usually by the bridging of neighbouring tin atoms by the inorganic ligand/s) can significantly inhibit the vibrational freedom of the tin atoms to give, typically, an \underline{a} value of \underline{ca} . 1.0 x 10^{-2}K^{-1} . The data for cyclohexyltin compounds can be interpreted in a similar fashion to those of phenyltin compounds.

However, rationalisation of v.t.M.s. behaviour in terms of the extent of polymerisation is not as straightforward as appeared to be the case from earlier work, which has been based, for the major part, on results obtained for methyltins: (i) Noninteracting molecules (in the sense of directed chemical bonds) containing structured, well-ordered groups bonded to the tin, such as phenyl or cyclohexyl, can sometimes pack very efficiently into the lattice in an interleaving fashion to produce a rigid environment for the tin and hence a relatively low a value (ca. 1.30 x 10^{-2} K⁻¹). (ii) For polymeric organotins, in addition to the strength of the intermolecular interactions, the tertiary structure of the polymeric backbone appears to be an important determinant of lattice dynamics. Thus when the tin is incorporated into a helical or coiled polymer chain its environment will usually be flexible enough for it to mimic

typical monomers i.e., its <u>a</u> value will be <u>ca</u>. 1.80×10^{-2} K⁻¹. Linear (rod -like) and zigzag polymers do however, significantly reduce <u>a</u>. In this regard, it is useful to divide organotin polymers into four classes, and, other things being similar, <u>a</u> values will tend to be in the order: Class 4 (coiled polymers), Class 3 (helical and 'S'-shaped polymers) and monomers > Class 2 (zigzag polymers) > Class 1 (rod-like polymers). Although Class 1 polymers are not a common feature of organotin structural chemistry, they are likely to be a more frequently occurring theme in tricyclohexyltin chemistry where the combined steric bulk of the three hydrocarbon groups may be small enough to allow intermolecular association but large enough to force a linear, rod-like tertiary structure.

A Class l-type tertiary structure will also be adopted when metallophthalocyanine complexes are cofacially linked by short covalent bridges between the central metal atoms, and a study of tin-phthalocyanines shows that this type of polymeric arrangement also results in a considerable reduction in <u>a</u> relative to monomeric phthalocyanine lattices.

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ORGANOTIN BIOCIDES

I. THE STRUCTURE OF TRIPHENYLTIN ACETATE

K.C. MOLLOY *, T.G. PURCELL, K. QUILL,

School of Chemical Sciences, National Institute for Higher Education, Glasnevin, Dublin 9 (Ireland)

and I.W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB (Great Britain) (Received January 16th, 1984)

Summary

The crystal structure of triphenyltin acetate has been determined using heavy atom methods in conjunction with least squares refinement of data measured on a two-circle diffractometer. Crystals are monoclinic, space group $P2_1/c$, cell dimensions a 8.969(4), b 10.146(5), c 19.540(7) Å, β 93.70(4)°, U = 1774.5 Å³ and Z = 4. The structure was refined using 1841 observed reflections to give conventional discrepancy factors of R = 0.022 and R' = 0.023. The environment at tin is described in terms of a distorted, six-coordinate, *mer*-Ph₃SnO₃ geometry, the first six-coordinate triorganotin structure authenticated crystallographically. Carboxylate bridges link subunits together to form a flattened helical polymer. Variable temperature Mössbauer spectroscopy ($a = dln A(T)/dT = -1.91 \times 10^{-2} K^{-1}$) suggests that polymers of this type afford tin atoms the same vibrational freedom normally associated with non-interacting lattices.

Introduction

Organotin compounds are extensively used as biocides, with some 10,000 tonnes of these compounds currently in use [1]. This commercialisation reflects both the versatility of this class with respect to a variety of biocidal fields (agrochemicals, surface disinfectants, wood preservatives, marine anti-fouling paints [2]) and a favourable environment degradation pathway to non-toxic inorganic tin. This latter property in particular sets organotins apart from similarly used organoarsenic and

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^{*} Address for correspondence

organomercury compounds, whose environmental fate is less desirable due to the ease with which these elements are biomethylated to volatile, highly toxic methylmetals [3].

Triphenyltin acetate has itself been used since the early 1960's (Brestan[®], Hoechst A.G.) to control potato blight (*Phytophthora infestans*), and is as effective against a range of fungi as conventional copper-based formulations but at one-tenth the dose [4]. We initiate this series of studies into the synthetic and structural chemistry of organotins with known or potential biocidal properties by reporting the structure of this important agrochemical, as studied by both single crystal X-ray diffraction and variable temperature Mössbauer spectroscopy.

Experimental

Recrystallisation of the product of the reaction between triphenyltin hydroxide and the betaine (HOOCCH₂NC₅H₄C₅H₄NCH₂COOH) \cdot 2Cl⁻ from acetic acid/methanol (20/80) yielded triphenyltin acetate as the only identifiable product [5]. Further recrystallisation from the same solvent mixture afforded crystals suitable for X-ray study. The sample of Ph₃SnO₂CCH₃ used in the Mössbauer study was prepared by literature methods [6], and found to be analytically pure *. The melting point of a mixture of products from the two sources showed no depression.

Mössbauer Data

Mössbauer spectra were recorded on a constant acceleration Mössbauer spectrometer (Cryophysics) fitted with a room temperature 5 mCi calcium stannate-119m source (Amersham Int.) and operated in a sawtooth wave mode. Temperature control of the sample was achieved using a continuous flow, liquid nitrogen cryostat linked to a DTC-2 digital variable temperature controller (Oxford Instruments). Temperature stability was ± 0.1 K of the desired temperature throughout spectral accumulation. Samples were prepared as finely ground powders to avoid orientation effects. Velocity calibration was based on the spectrum of natural iron, and CaSnO₃ used as the zero velocity reference. Spectra were curve fitted using conventional least-squares techniques to standard Lorentzian line shapes, with prior data correction for parabolic background curvature.

Crystal data

 $C_{20}H_{18}O_2Sn$, M = 409.1, monoclinic $P2_1/c$, a 8.969(4), b 10.146(5), c 19.540(7) Å, β 93.70(4)°, U 1774.5 Å³, Z = 4, D_c 1.53, D_m 1.51 Mgm^{-3} , $\mu(Mo-K_{\alpha})$ 1.32 mm⁻¹, F(000) = 816.

Data collection and reduction

A crystal of approximate dimensions $0.13 \times 0.14 \times 0.35$ mm was used for data collection and was mounted with the *b* axis coincident with the rotation (ω) axis of a Stoe Stadi-2 two circle diffractometer. 2163 unique reflection were collected, of which 1841 had $I \ge 3\sigma(I)$ and were considered as observed and used for subsequent

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^{*} Found: C, 58.34; H, 4.39. C₂₀H₁₈O₂Sn calcd.: C, 58.72; H, 4.44%.

analysis. Corrections were made for Lorentz and polarisation effects, but no corrections were applied for absorption.

Structure determination and refinement

The approximate position of the tin atom was calculated using a three-dimensional Patterson synthesis. The remaining atoms were located from successive difference Fourier maps. The hydrogen atoms were located, but given ideal geometry

TABLE 1

FRACTIONAL POSITIONAL PARAMETERS ($\times 10^5$ for Sn; $\times 10^4$ for remaining atoms) WITH e.s.d.'s FOR NON-HYDROGEN ATOMS IN PARENTHESES

| Atom | X | У | Ζ | |
|--------|----------|----------|----------|--|
| Sn | 91578(3) | 30183(2) | 76237(1) | |
| O(1) | 9523(3) | -121(3) | 7720(1) | |
| O(2) | 7950(3) | 1382(3) | 8060(1) | |
| C(1) | 8492(5) | 232(4) | 8081(2) | |
| C(2) | 7846(6) | -680(4) | 8587(2) | |
| C(11) | 7618(4) | 4343(3) | 8033(2) | |
| C(12) | 6277(5) | 4651(5) | 7673(2) | |
| C(13) | 5274(5) | 5527(6) | 7936(3) | |
| C(14) | 5568(5) | 6079(5) | 8572(3) | |
| C(15) | 6887(5) | 5795(4) | 8931(2) | |
| C(16) | 7905(5) | 4944(4) | 8666(2) | |
| C(21) | 11045(4) | 2613(4) | 8316(2) | |
| C(22) | 10748(5) | 2353(4) | 8996(2) | |
| C(23) | 11906(7) | 2123(4) | 9485(2) | |
| C(24) | 13357(7) | 2147(5) | 9318(3) | |
| C(25) | 13672(6) | 2393(6) | 8661(3) | |
| C(26) | 12516(5) | 2631(5) | 8154(3) | |
| C(31) | 8578(4) | 2616(4) | 6569(2) | |
| C(32) | 8471(5) | 1356(4) | 6299(2) | |
| C(33) | 7983(5) | 1159(5) | 5617(2) | |
| C(34) | 7553(5) | 2202(5) | 5202(2) | |
| C(35) | 7635(6) | 3455(5) | 5467(2) | |
| C(36) | 8141(5) | 3663(5) | 6145(2) | |
| H(111) | 8394 | -1625 | 8563 | |
| H(112) | 6664 | -800 | 8462 | |
| H(113) | 8022 | 281 | 9098 | |
| H(12) | 6014 | 4192 | 7182 | |
| H(13) | 4259 | 5786 | 7639 | |
| H(14) | 4760 | 6719 | 8790 | |
| H(15) | 7140 | 6243 | 9426 | |
| H(16) | 8953 | 4742 | 8950 | |
| H(22) | 9601 | 2331 | 9134 | |
| H(23) | 11652 | 1931 | 10008 | |
| H(24) | 14247 | 1960 | 9705 | |
| H(25) | 14819 | 2410 | 8523 | |
| H(26) | 12766 | 2831 | 7630 | |
| H(32) | 8766 | 526 | 6627 | |
| H(33) | 7937 | 171 | 5411 | |
| H(34) | 7164 | 2038 | 4674 | |
| H(35) | 7303 | 4285 | 5146 | |
| H(36) | 8200 | 4650 | 6352 | |

(C-H 1.08 Å). Scattering factors were calculated using an analytical approximation [7] and the weighting scheme adopted was $w = 1.2022/[\sigma^2(F_o) + 0.003(F_o)^2]$. The phenyl and methyl hydrogen atoms were given common isotropic temperature factors which refined to final values of U = 0.091(5), 0.177(17) Å². All other atoms were given anisotropic temperature factors and full matrix least-squares refinement gave final values of R = 0.022 and R' = 0.023. The final positional parameters are given in Table 1, bond distances and angles in Table 2. The coordination about tin

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES. SYMMETRY CODE NONE x, y, z, (') 2-x, 0.5+y, 1.5-z; ('') 2-x, -0.5+y, 1.5-z

| Bond distances | | | |
|-------------------|----------|--------------------|----------|
| Sn-O(1) | 3.206(3) | C(16)-C(11) | 1.388(5) |
| Sn-O(1') | 2.349(3) | C(21)-C(22) | 1.397(6) |
| Sn-O(2) | 2.185(3) | C(22)-C(23) | 1.385(7) |
| Sn-C(11) | 2.120(4) | C(23)-C(24) | 1.362(8) |
| Sn-C(21) | 2.138(4) | C(24)-C(25) | 1.356(9) |
| Sn-C(31) | 2.133(4) | C(25)-C(26) | 1.408(7) |
| O(1)-C(1) | 1.251(5) | C(26)-C(21) | 1.377(6) |
| O(2) - C(1) | 1.263(5) | C(31)-C(32) | 1.384(6) |
| C(1)–C(2) | 1.497(6) | C(32)-C(33) | 1.391(6) |
| C(11)-C(12) | 1.390(6) | C(33)-C(34) | 1.374(6) |
| C(12)-C(13) | 1.387(7) | C(34)-C(35) | 1.372(7) |
| C(13)-C(14) | 1.373(8) | C(35)-C(36) | 1.389(6) |
| C(14)-C(15) | 1.366(7) | C(36)-C(31) | 1.387(6) |
| C(15)-C(16) | 1.381(6) | | |
| Bond angles | | | |
| O(1)-Sn-O(1') | 139.8(1) | Sn-C(11)-C(12) | 121.0(3) |
| O(1) - Sn - O(2) | 43.4(1) | Sn-C(11)-C(16) | 121.8(3) |
| O(1) - Sn - C(11) | 132.4(1) | C(12)-C(11)-C(16) | 117.2(4) |
| O(1)-Sn-C(21) | 72.4(1) | C(11)-C(12)-C(13) | 121.2(4) |
| O(1)-Sn-C(31) | 83.4(1) | C(12)-C(13)-C(14) | 120.3(4) |
| O(1')-Sn-O(2) | 173.6(1) | C(13)-C(14)-C(15) | 119.2(5) |
| O(1')-Sn-C(11) | 87.2(1) | C(14)-C(15)-C(16) | 120.7(4) |
| O(1')-Sn-C(21) | 86.7(1) | C(11)-C(16)-C(15) | 121.3(4) |
| O(1')-Sn-C(31) | 88.5(1) | Sn - C(21) - C(22) | 116.5(3) |
| O(2)-Sn-C(11) | 89.0(1) | Sn-C(21)-C(26) | 125.6(3) |
| O(2)-Sn-C(21) | 90.0(1) | C(22)-C(21)-C(26) | 117.8(4) |
| O(2) - Sn - C(31) | 97.8(1) | C(21)-C(22)-C(23) | 120.5(4) |
| C(11)-Sn-C(21) | 113.0(1) | C(22)-C(23)-C(24) | 121.2(5) |
| C(11)-Sn-C(31) | 111.2(1) | C(23)-C(24)-C(25) | 119.4(5) |
| C(21)-Sn-C(31) | 135.2(1) | C(24)-C(25)-C(26) | 120.6(5) |
| Sn-O(1)-Sn" | 146.4(1) | C(21)-C(26)-C(25) | 120.6(5) |
| Sn-O(1)-C(1) | 70.9(1) | Sn-C(31)-C(32) | 123.4(3) |
| Sn''-O(1)-C(1) | 142.7(2) | Sn-C(31)-C(36) | 118.1(3) |
| Sn-O(2)-C(1) | 121.0(2) | C(32)-C(31)-C(36) | 118.1(3) |
| O(1)-C(1)-O(2) | 122.9(4) | C(31)-C(32)-C(33) | 120.5(4) |
| O(1)-C(1)-C(2) | 121.8(4) | C(32)-C(33)-C(34) | 120.9(4) |
| O(2)-C(1)-C(2) | 115.3(4) | C(33)-C(34)-C(35) | 119.0(4) |
| | | C(34)-C(35)-C(36) | 120.5(4) |
| | | C(31)-C(36)-C(35) | 121.0(4) |

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Fig. 1. The coordination about tin in $(C_6H_5)_3SnO_2CCH_3$ showing atomic labelling. The symmetry code for (') and ('') atoms is given in Table 2.

together with atomic labelling is shown in Fig. 1. Lists of structure factors and thermal parameters are available on request from the authors (I.W.N.).

Discussion

The structure

The structure of triphenyltin acetate consists of polymeric chains in which essentially planar triorganotin moieties are bridged by carboxylate groups. The nature of this bridging is anisotropic, in which tin forms one short (Sn-O(2) 2.185(3))A) and one relatively long (Sn-O(1') 2.349(3) Å) bond to oxygen. The acetate groups are disposed in the usual syn, anti-fashion [8] with respect to pairs of tin atoms [9-18], which, coupled with a 2₁ axis coincident with the b axis of propagation, leads to a polymer which can alternatively be described as being of "flattened helical" or "stretched-S" construction (Fig. 2). This structure dominates the structural chemistry of organotin carboxylates (Table 3), and to which even the proposed monomers $(C_6H_{11})_3$ SnO₂CCH₃ [16] and $(C_6H_{11})_3$ SnO₂CCF₃ [17] have recently been reclassified [9]. Excluding bis(trimethyltin) malonate which is three dimensional by virtue of the bifunctional ligand [12], only three compounds deviate from this structure, triphenyltin o-(2-hydroxy-5-methylphenylazo)benzoate [9], trimethyltin glycinate [11] and tricyclohexyltin indole-3-acetate [19], and in each case the acyl oxygen is involved in hydrogen bonding. This feature appears enough to preclude polymer formation through carboxylate bridges, although chelation remains as a bonding option [9,19].

The two tin-oxygen bonds are comparable with the analogous bonds in related compounds (Table 3), although the covalent, ester Sn-O(2) bond (2.185(3) Å) lies towards the long end of the range found for such interactions (2.07–2.21 Å), while the formally coordinate, bridging Sn-O(1') linkage (2.349(3) Å) is the shortest of its type yet reported.

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Fig. 2. A segment of the $(C_6H_5)_3$ SnO₂CCH₃ polymer viewed perpendicular to the *a b* cell face.

The local geometry at tin is quite complex. Ostensibly, the coordination about the metal is a *trans*- R_3SnX_2 arrangement, in which the axial positions of the trigonal bipyramid are occupied by the more electronegative oxygens, while the α -carbons of the phenyl groups form the equatorial girdle (Fig. 1). There is, however, an additional weak Sn–O interaction arising from the acyl, bridging oxygen, which simultaneously chelates the tin from which the ligand emanates (Sn–O(1) 3.206(3) Å). Although long by comparison with both covalent or bridging coordinate Sn–O

TABLE 3

COLLECTED STRUCTURAL DATA FOR ORGANOTIN CARBOXYLATES 4.4

| Compound | Sn-O(2) | Sn-O(1') inter | Sn-O(1) intra | C-Sn-C ' | O(2)-C(1)-O(1) | Reference |
|---|-----------|-------------------|------------------|-----------|---------------------|-----------|
| Ph ₃ SnO ₂ CCH ₃ | 2.185(3) | 2.349(3) | 3.206(3) | 135.2(1) | 1.263(5), 1.251(5) | This work |
| $Ph_3SnO_2CC_6H_4(N_2R)-o^d$ | 2.070(5) | - | 2.463(7) | 117.0(2) | 1.296(8), 1.224(8) | [9] |
| Me ₃ SnO ₂ CCH ₃ | 2.205(3) | 2.391(4) | 3.23 | 121.9(2) | 1.269(5), 1.240(6) | [10] |
| Me ₃ SnO ₂ CCF ₃ | 2.177(14) | 2.458(15) | 3.30 | 122.9(10) | 1.28(2), 1.21(2) | [10] |
| Me ₃ SnO ₂ CCH ₂ NH ₂ | 2.21(1) | - | 3.23(3) | 121.8(11) | 1.34(3), 1.23(3) | [11] |
| Me ₃ SnO ₂ CCH ₂ CO ₂ SnMe ₃ | 2.19(1) | 2.46(2) | 3.16 | 124.9 | 1.27(3), 1.22(3) | [12] |
| | 2.17(1) | 2.44(2) | 3.12 | 123.6 | 1.28(3), 1.28(3) | |
| Me ₂ (Cl)SnO ₂ CCH ₄ | 2.165(6) | 2.392(7) | 2.782(7) | 140.9(6) | 1.260(9), 1.262(10) | [13] |
| Vin SnO,CCCl | 2.17(2) | 2.49(1) | 3.30 | 124.8(5) | 1.25(2), 1.21(2) | [14] |
| Vin ₃ SnO ₂ C(Fer) | 2.12(1) | 2.42(1) | 3.21 | 127(1) | 1.27(1), 1.21(2) | [15] |
| Bz ₃ SnO ₂ CCH ₃ | 2.14(2) | 2.65(2) | 3.23(3) | 123.8(14) | 1.31(4), 1.21(4) | [16] |
| Cyc ₁ SnO ₂ CCH ₁ | 2.12(3) | 3.84 | 2.95(4) | 113(1) | 1.39(8), 1.25(9) | [17] |
| Cyc ₃ SnO ₂ CCF ₃ | 2.08(4) | 3.70 | 3.11 | 122 | 1.28(4), 1.20(5) | [18] |

"Atomic numbering as in Fig. 1. ^b Abbreviations: $Ph = C_6H_5$, $Me = CH_3$, $Vin = CH_2=CH$, $Bz = C_6H_5CH_2$, $Cyc = C_6H_{11}$, $Fer = C_5H_4FeC_5H_5$. ^c C-Sn-C angle closest in proximity to O(1). ^d R = 2-hydroxy-5-methylphenyl. ^c cis-Ph₃SnX₂ geometry.

bonds, it is well within the sum of the two Van der Waals' radii (3.70 Å), and, moreover, severely distorts the equatorial C(21)-Sn-C(31) bond angle (135.2°) which is closest to the direction of O(1) approach to tin. Further evidence supporting the reality of this chelating interaction can be found from inspection of the two C-O distances within the ligand. Considering only the bridging role of the carboxylate, equality of the two C–O bonds will only arise when the two Sn–O bonds are equal i.e. bridging is isobidentate and the π -bond is symmetrically delocalised over the O-C-O framework. Such a situation generally does not occur in polymeric organotin caryboxylates, the bridging is anisobidentate and the majority of double bond character is localised in one C-O bond, manifesting itself in dissimilar C-O bond lengths (Table 3). In the title compound, however, despite a difference of ca. 0.164 A in the two tin-oxygen bonds, the carbon-oxygen bonds are remarkably close (C(1)-O(1) 1.251(5); C(1)-O(2) 1.263(5) Å), a situation which can be rationalised in terms of additional electron withdrawal from the acyl C(1)-O(1) bond concomitant with formation of the chelating Sn-O(1) interaction. A similar argument has been used to rationalise the bifurcated Sn-S-Sn bonding in dimeric $\{Sn[S,P(OPh)_2]_2\}_2$ [20].

The structure of triphenyltin acetate is thus best described in terms of a distorted $mer-R_3SnX_3$ geometry at tin, and represents the first crystallographically authenticated example of a six-coordinate triorganotin compound.

In related systems, $Cl(CH_3)_2SnO_2CCH_3$ has also been interpreted as being six-coordinate at tin [13] the coordination sphere about tin arising in exactly the manner described above for $(C_6H_5)_3SnO_2CCH_3$. Within the halotin acetate, the chelating Sn-O(1) bond is much stronger ([2.782(7) Å), manifesting itself in both a greater opening of the $\angle C$ -Sn-C in the region of this interaction (140.9(6)°) and an equalising of C-O bond lengths (1.260(9), 1.262(10) Å) despite inequalities in the primary Sn-O bonds (2.165(6), 2.392(7) Å).

Considering the data for triorganotin carboxylates as a whole, it would appear that a coordination number of six at tin only occurs in compounds in which the Lewis acidity of the metal is enhanced by direct bonding to electron-withdrawing groups, chlorine in the case of $(CH_3)_2CISnO_2CCH_3$ and three phenyl groups in the title compound. Trivinyltin derivatives might also be expected to show this tendancy, and a $\angle C-Sn-C$ of $127(1)^\circ$ in $(CH_2=CH)_3SnO_2C(C_5H_4FeC_5H_5)$ [15] suggests that this is possibly the case, although the phenomenon is clearly marginal.

Variable temperature Mössbauer study

Mössbauer data, embracing both the conventional isomer shift (IS) and quadrupole splitting (QS) parameters derived from the single temperature experiment, and more recent use of variable temperature studies to probe lattice dynamics [21, and ref. therein] have proved invaluable tools in the development of structural organotin chemistry. Key compounds such as triphenyltin acetate are often cited as reference points in the discussion of Mössbauer data of more esoteric compounds, and in the light of the current structure determination we present results of a variable temperature (78–145 K) study which highlight potential limitations in this area of Mössbauer methodology.

IS and QS values from the present study (1.28, 3.36 ± 0.03 mm s⁻¹, respectively) are in excellent agreement with earlier reports [6]. The magnitude of QS has generally been cited as evidence for a *trans*-R₃SnX₂ geometry at tin, largely by







Fig. 4. Plot of the temperature dependence of the Mössbauer doublet spectrum line asymmetry. A_{+} and A_{-} are the areas under the more positive and more negative velocity wings, respectively. The slope of the line is 1.28×10^{-5} K⁻¹.

comparison with predictions from point charge calculations [22], and in the light of the secondary nature of the bond which increases the coordination number at tin in this compound to six (Sn-O(1) 3.206(3) Å) this appears to be largely justified. We do, however, note that predicted QS values for mer-R₃SnX₃ structures are also ca. 3.50 mm^{-1} [23] and are equally applicable in this instance.

The lattice structure of organotins is reflected in a, the temperature dependance of the ¹¹⁹Sn recoil-free-fraction [f(T)] which in turn is related to the experimentally more accessible parameter A(T), the area under the spectral envelope:

$$a = \frac{d[f(T)]}{dT} = \frac{d[A(T)]}{dT}$$
(1)

For a "thin absorber" ($N\sigma \le 1$; N = number of absorber resonant atoms per cm², $\sigma =$ resonant absorption cross-section of ¹¹⁹Sn [24]), *a* can further be expressed as:

$$a = \frac{d[\exp(-\langle x_{iso}(T) \rangle^2]}{dT}$$
(2)

$$a = \frac{d\left[\exp\left(-\frac{6E_{R}T}{k\theta_{M}}\right)\right]}{dT}$$
(3)

where $\langle x_{iso}(T) \rangle^2$ is the mean-square amplitude of vibration of the Mössbauer atom at temperature T, E_R is the Mössbauer recoil energy, and θ_M a characteristic temperature equivalent to the Debye temperature. Plots of $\ln A(T)$ vs. T should be linear and of slope a, and be characteristic of the tightness with which the Mössbauer atom is held in the lattice. For methyltins, values of -a ca. 1.8×10^{-2} K⁻¹ reflect non-interacting molecules, dropping to ca. 1.0×10^{-2} K⁻¹ and lower for one- and higher-dimensional polymers, respectively [25]. Transfer of these systematics to phenyltin derivatives is broadly acceptable, although we have found that packing of the structured hydrocarbon groups in the latter case often mimic hydrogen bonding between methyltin compounds, based on comparable a values [26].

The plot of the $\ln A(T)$ vs. T for the title compound is shown in Fig. 3. Although a non-thin sample was used to enable acceptable spectra to be accumulated within reasonable count times (ca. 12 h), no systemtic deviation from linearity in the plot is observed suggesting that lattice vibrational anharmonicity is also absent. The derived value of -a is 1.91×10^{-2} K⁻¹ (7 points; r = -0.998), which on the basis of the above systematics quite incorrectly predicts a monomeric rather than the observed 1-d polymeric lattice. Rationalisation of the data can be made in terms of the helical nature of the polymer, which has a two-fold effect on the distribution of atomic mass with respect to the direction of polymer propagation. Firstly, the tin atoms themselves do not lie along a single line, rather they are found alternatively either side of the 2_1 axis along b. Secondly, and more importantly, the direction in which the polymer is building at the tin is not along b, but approximately 60° to it based upon the general orientation of the O(1')-Sn-O(2) unit. These factors combine to concentrate the bridging mass away from a line joining adjacent tin atoms, such that the space between tins is largely a void, and the bridging role of the carboxylate group is reduced to the long Sn-O(1) bond. The polymer thus has a "concertina-like" flexibility that confers a vibrational freedom upon the tin which more linear polymers do not. The motion of the tin thus becomes isotropic, a fact endorsed by the absence of any observable temperature dependent spectral line asymmetry (Gol'danski-Karyagin effect; Fig. 4). This phenomenon is in sharp contrast to the related trimethyltin glycinate, in which tin atoms are O,N-bridged by the four atom backbone of the amino acid. The rigidity of this lattice is reflected in a value of $-a = 1.15 \times 10^{-2} \text{ K}^{-1}$, which in part arises from a network of hydrogen bonds approximately perpendicular to, and linking, adjacent polymer chains, but derives also a significant contribution from the polymer itself. This in turn is reflected in a sizeable Gol'danski-Karyagin effect arising from anisotropic vibrations of the tin, the majority of this motion occuring in the plane of the C₃Sn moiety and perpendicular to the O-Sn-N axis [11]. The structural variation which gives rise to these differences is that in the glycinate, the bridging O-C-C-N unit lies between tin atoms straddling the tin-tin vector to produce a linear extension of the chain, rather than the helical construction of the acetate which leaves largely a void between tin atoms.

We have found support for the above rationale in variable temperature Mössbauer studies of other polymeric systems. In particular, α -trimethyltin phenylphosphonate, $(CH_3)_3SnO_2P(C_6H_5)OH$, which is known to consist of helices held together into 2-d sheets by a network of strong hydrogen bonds [27], has -a in the range $1.42-1.64 \times 10^{-2} \text{ K}^{-1}$ [28], which on the basis of known systematics [25] merely reflects the contribution of the hydrogen bonds to lattice rigidity. As with triphenyltin acetate, incorporating the tin into a helical polymer does little (if anything) to inhibit vibrational motion of the tin, and it is only when helices are linked into sheets that such motion becomes anisotropic.

In conclusion, helical polymers are flexible enough to mimic non-interacting lattices with respect to the variable temperature Mössbauer experiment, and in instances where the bridging group is a multi-atom moiety, interpretation of data so derived must be tempered with caution.

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ORGANOTIN BIOCIDES

V*. THE STRUCTURE OF DICYCLOHEXYLTIN DICHLORIDE

K.C. MOLLOY **,

School of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY (Great Britain)

K. QUILL,

School of Chemical Sciences, National Institute for Higher Education, Glasnevin, Dublin 9 (Ireland)

and I.W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB (Great Britain) (Received January 2nd, 1985)

Summary

The crystal and molecular structure of dicyclohexyltin dichloride has been solved by heavy atom methods in conjunction with least-squares data collected on a two-circle automatic diffractometer. Crystals are orthorhombic, space group *Pbcm*, cell dimensions a 6.671(5), b 9.445(6), c 24.203(12) Å, U 1525.0 Å³ and Z = 4. The structure was refined using 1527 reflections to final discrepancy factors of R = 0.047and R' = 0.058. The local geometry at tin is a severely distorted *trans*-R₂SnCl₄ octahedron. Chlorine atoms serve as bridging groups to link sub-units into a one dimensional polymer along b.

Introduction

Our interest in the structural chemistry of organotin compounds which either possess [1] or have the potential to exhibit [2] biocidal properties has caused us to focus attention on derivatives of phenyl- and cyclohexyl-substituted tin. Compounds of these two classes are highly active as fungicides [3] and acaricides [4,5] respectively, while showing low mammalian toxicity, and $(C_6H_5)_3SnO_2CCH_3$, $(C_6H_5)_3SnOH$, $(C_6H_{11})_3SnOH$ and $(C_6H_{11})_3Sn-1,2,4$ -triazole are all commercially exploited agrochemicals. Surprisingly, the structural chemistry of these two types of organotin,

* For part IV see ref. 2.

** Address for correspondence.

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and particularly the cyclohexyltins, is substantially less well evaluated than that of their methyltin counterparts [6], and the unpredictable effects that the bulky cyclohexyl groups will render on the stereochemistry of the metal make extrapolation of this latter data at best tentative.

The organotin halides are of importance both as structural models for other more complex systems, and also as the starting point for most synthetic work in the field. To complement existing reports on the complete range of tricyclohexyltin halides [7,8], we herein report our findings on the structure of dicyclohexyltin dichloride, and correlate these results with our previous inferences based upon variable temperature Mössbauer spectroscopic data [9].

Experimental

Dicyclohexyltin dichloride was prepared by a redistribution reaction between equimolar quantities of tetracyclohexyltin and stannic chloride. Crystals suitable for X-ray crystallography were obtained by slow evaporation of an ether solution. Analysis: Found, C, 40.36; H, 6.55; $C_{12}H_{22}Cl_2Sn$ calcd.: C, 40.50; H, 6.23%. M.p. 88–89°C, lit. [10] 88–89°C.

Crystal data

TABLE 1

 $C_{12}H_{22}Cl_2Sn$, M = 355.9, orthorhombic *Pbcm*, $a \ 6.671(5)$, $b \ 9.445(6)$, $c \ 24.203(12)$ Å, $U \ 1525.0$ Å³, Z = 4, $D_c \ 1.55 \ Mg \ m^{-3}$, $\mu(Mo-K_{\alpha}) \ 18.4 \ mm^{-1}$, $F(000) \ 712$.

Data collection and reduction

A crystal of approximate dimensions $0.42 \times 0.35 \times 0.24$ mm was used for data collection. 1722 unique reflections were collected on a Stöe Stadi-2 two circle diffractometer, of which 1527 were considered observed $[I \ge 3\sigma(I)]$ and used for subsequent analysis. Corrections were made for Lorentz and polarisation effects; no absorption corrections were included due to the low $\mu(Mo-K_{\alpha})$ coefficient.

Structure determination and refinement

Structure analysis was initially conducted in the non-centrosymmetric space

| Atom | x | у | Z | |
|---------------|-----------|----------|---------|--|
| Sn | 7507(6) | 14109(4) | 25000 | |
| C l(1) | 2404(2) | 3676(2) | 2500 | |
| Cl(2) | - 2522(2) | 2391(2) | 2500 | |
| C(11) | 1388(7) | 651(5) | 3319(2) | |
| C(12) | 193(13) | 1483(8) | 3753(3) | |
| C(13) | 631(2) | 911(4) | 4336(3) | |
| C(14) | 2889(13) | 874(10) | 4458(3) | |
| C(15) | 3991(9) | 73(1) | 4033(3) | |
| C(16) | 3618(8) | 595(7) | 3447(2) | |

FRACTIONAL POSITIONAL PARAMETERS ($\times 10^5$ for Sn, otherwise $\times 10^4$) WITH e.s.d.'s IN PARENTHESES

| TA | BI | E. | 2 |
|----|----|----|---|
| | _ | | _ |

| Bond distances | | | |
|--------------------|-----------|------------------|-----------|
| Sn-Cl(1) | 2.407(2) | C(14)–(15) | 1.473(11) |
| Sn-Cl(2) | 2.371(1) | C(15)-C(16) | 1.523(8) |
| Sn-Cl(1') | 3.332(2) | C(16)–C(11) | 1.520(7) |
| Sn-Cl(2') | 3.976(1) | | |
| Sn-C(11) | 2.151(4) | | |
| C(11)-C(12) | 1.535(7) | | |
| C(12)-C(13) | 1.540(10) | | |
| C(13)-C(14) | 1.535(10) | | |
| Bond angles | | | |
| Cl(1)-Sn-Cl(1') | 168.1(1) | Cl(2')-Sn-Cl(1) | 135.5(1) |
| Cl(1)-Sn-Cl(2) | 94.3(1) | Cl(2')-Sn-Cl(2) | 130.3(1) |
| Cl(1) - Sn - C(11) | 101.9(1) | Cl(2')-Sn-Cl(1') | 56.5(1) |
| Cl(2)-Sn-Cl(1') | 73.8(1) | Cl(2')-Sn-C(11) | 67.8(1) |
| Cl(2)-Sn-C(11) | 108.2(1) | C(11)-Sn-C(11') | 134.4(2) |
| Cl(1')-Sn-C(11) | 82.3(1) | | |
| Sn-C(11)-C(12) | 110.9(3) | | |
| Sn-C(11)-C(16) | 113.1(3) | | |
| C(12)-C(11)-C(16) | 112.8(5) | | |
| C(11)-C(12)-C(13) | 110.4(5) | | |
| C(12)-C(13)-C(14) | 111.7(6) | | |
| C(13)-C(14)-C(15) | 111.6(7) | | |
| C(14)-C(15)-C(16) | 113.7(6) | | |
| C(15)-C(16)-C(11) | 111.2(5) | | |
| | | | |

BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES ^a

^a Primed atoms are related to their unprimed counterparts (x, y, z) by: (')-x, y = 0.5, z; ('')x, y, 0.5 = z.

group $Pca2_1$, [a 9.445(6), b 6.671(5), c 24.203(12) Å]. The structure was solved using conventional Patterson and Fourier methods to final value of R = 0.046 and R' = 0.054. The presence of an apparent mirror plane perpendicular to c through the Sn and Cl atoms (relating the two cyclohexyl groups) led us to impose exact mirror symmetry and to refine the structure in the centrosymmetric space group *Pbcm* (Z = 4). Although the final R values were marginally higher (R = 0.047, R' = 0.058), this is to be expected given that imposition of exact mirror symmetry reduces the number of independent variables. Refinement in *Pbcm* did lead to a significant improvement in the bond distances and angles associated with the cyclohexyl group and hence we feel the centrosymmetric space group to be the more appropriate. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were localised in ideal positions and given a common isotropic temperature factor which finally refined to $U \ 0.131(9) Å^2$. Scattering factors were calculated using an analytical expression [11] and the weighting scheme employed was $w = 1.0000/[\sigma^2(F_0) + 0.007(F_0)^2]$.

Final positional parameters for the non-hydrogen atoms are given in Table 1, bond distances and angles in Table 2. The asymmetric unit with atomic labelling is shown in Fig. 1. Tables of hydrogen atom positions, thermal parameters and structure factors are available upon request from the authors (I.W.N.).



Fig. 1. Part of the polymeric structure of $(C_6 H_{11})_2 \text{SnCl}_2$, showing atomic labelling. Hydrogen atoms have been omitted for clarity. Primed and double-primed atoms are related to their unprimed counterparts by the symmetry operations -x, y - 0.5, z and x, y, 0.5 - z respectively.

Discussion

The structure of dicyclohexyltin dichloride consists of sub-units intermediate in geometry between cis- R_2SnCl_3 and trans- R_2SnCl_4 linked by chlorine bridges into a one-dimensional polymer. The complexities of this arrangement will be considered in two parts: the intramolecular geometry about tin and the spacial distribution of monomers from which the polymer is constructed. The local geometry about tin can be best understood in terms of a two-step reaction between a tetrahedral R_2SnCl_2 and two chlorine atoms (Fig. 2). The first step involves intermolecular approach of Cl(1') towards the C(11), C(11''), Cl(2)-triangular face of the tetrahedron, to produce a cis-R₂SnCl₃ trigonal bipyramidal (tbp) geometry at tin with Cl(1) and Cl(1') in the axial positions. The significant results in terms of bond angles about tin are the closing of those angles between Cl(1) and each of C(11), C(11") and Cl(2) from 109° 28' towards the ideal tbp value of 90° [101.9(1), 101.9(1) and 94.3(1)°, respectively]. The corresponding angles involving Cl(1') are all less than 90° [82.3(1), 82.3(1), 73.8(1)°], and the magnitude of the Cl(1'): \rightarrow Sn interaction, while relatively weak [3.332(2) Å], is clearly significant. Indeed, in comparison with Sn-Cl bond lengths in other diorganotin dichloride structures [12-15, Table 3], the intra- and inter-molecular Sn-Cl(1') bonds [2.407(2), 3.332(2) Å] are the longest and shortest respectively of their types yet reported. Only in solid (CH₃)₃SnCl are the two analogous bonds more similar in length [2.430(2), 3.269(2) Å] [16]. Further comparison for this primary mode for coordination expansion at tin in $(C_6H_{11})_2SnCl_2$ can be made with $(C_6H_{11})_3$ SnCl, in which the stereochemical arrangement of tin and chlorine atoms along c is suggestive of lattice association [7]. The two Sn-Cl bond lengths here [2.407(5), 3.30 Å] are almost identical with those in the title compound. In each of these organotin chlorides, the arrangement of bond lengths (and angles, vide supra)



Fig. 2. The formation of the coordination sphere about tin, depicted schematically in terms of the sequential approach of chlorine atoms to an initially tetrahedral $(C_6H_{11})_2SnCl_2$ molecule.

is totally consistent with a re-distribution of the chlorine bonding electrons between two, rather than one, bonds to tin and the intramolecular Sn–Cl bond is always longer than in tetrahedral $(C_6H_5)_3$ SnCl (2.32 Å; [17]).

The second intermolecular tin-chlorine interaction, step two of the reaction shown in Fig. 2, is markedly weaker and more subjective in its significance. Cl(2') approaches tin in the plane of the metal and the three halogen atoms, from below the equatorial plane of the tbp and between the two carbon atoms C(11) and C(11''). The final intermolecular Sn-Cl(2') distance is long [3.976(1) Å] and in excess of the

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TABLE 3

OMBADATIVE STRUCTUDAT

| COMPARATIVE STRUCTURAL | DATA FOR OROANOTIN CITLORIDES | |
|------------------------|-------------------------------|--|
| | | |

| Compound | Sn-Cl | Sn · · · Cl | C-Sn-C | Structure ^b | Ref. |
|---|-----------------------|-------------|--------------------|------------------------|-----------|
| | (Å) | (Å) | (°) | type | |
| $(C_6H_{11})_2$ SnCl ₂ | 2.407(2) | 3.332(2) | 134.4(2) | 3c | this work |
| | 2.371(1) | 3.976(1) | | | |
| $(CH_3)_2 SnCl_2$ | 2.40(4) | 3.54(5) | 123.5(4.5) | 3d | 12 |
| $(C_2H_5)_2$ SnCl ₂ | 2.385(3) | 3.483(4) | 134.0(6) | 3d | 13 |
| | 2.384(3) | 3.440(4) | | | |
| (ClCH ₂) ₂ SnCl ₂ | 2.37(2) | 3.71 | 135.0(6) | 3c | 14 |
| $(C_6H_5)_2$ SnCl ₂ | 2.336 ° | 3.77 | 125.5 ° | 3a ^d | 14, 15 |
| | 2.355 ° | | | | |
| (CH ₃) ₃ SnCl | 2.351(7) ^e | | 114.9(1.6) | tetrahedral | 23 |
| | 2.430(2) | 3.269(2) | 117.1 ^f | tbp | 16 |
| $(C_6H_5)_3$ SnCl | 2.32 | | 112.3 | tetrahedral | 17 |
| $(C_6H_{11})_3$ SnCl | 2.407(5) | 3.30 | 115.0(6), | | |
| | | | 119.0(5) | tbp | 7 |

^{*a*} X-ray diffraction unless stated otherwise. ^{*b*} See Fig. 3 for representations of 3a-d. ^{*c*} Mean value for two molecules in the asymmetric unit. ^{*d*} See also ref. 19. ^{*e*} Gas phase electron diffraction data. ^{*f*} Mean value of the three independent C-Sn-C angles.



Fig. 3. Structural variations in diorganotin dihalide chemistry: (a) tetrahedral monomer, (b) 2-d polymer, (c) 1-d polymer with bridging/chelating chlorine atoms, and (d) 1-d polymer with purely bridging chlorine atoms. For each of structures (b)–(d), the R groups lying above and below the polymer plane have been omitted for clarity.

Van der Waals radii sum of 3.85 Å [18] generally taken as the limit of meaningful electronic interactions between these atom types. The proximity of Cl(2') to tin does however, manifest itself in angular distortions about that atom which do imply a real, albeit very weak interaction. The most relevant of these angular changes occurs at C(11)-Sn-C(11") which is opened to 134.4(2)°, and C(11)-Sn-Cl(2), C(11")-Sn-Cl(2) which close to 108.2(1)°, all three of which would be 120° in a regular tbp geometry and all of which have altered in a manner consistent with the formation of a distorted six-coordinate, octahedral *trans*-R₂SnCl₄ geometry at tin in which the idealized angles would be 180 and 90° for the each of the two angular types. It is notable that in $(C_2H_5)_2SnI_2$ the intermolecular Sn-I interaction at 4.284(5) Å is also in excess of the sum of the tin and iodine Van der Waals radii (4.08 Å [18]), but still results in a C-Sn-C of 130.2(11)° [13]. Accordingly, we prefer to describe the structure of $(C_6H_{11})_2SnCI_2$ in terms of distortions of an octahedral rather than tbp geometry, a distinction which has chemical and not merely semantic significance.

The second structural feature of interest is the stereochemical relationship of bonds which give rise to polymer formation. The various known senarios on this theme in diorganotin dihalide chemistry are depicted in Fig. 3, while the nature of the polymer architecture for $(C_6H_{11})_2 \text{SnCl}_2$ can be seen in the simplified diagram of cell contents in Fig. 4. In addition to a tetrahedral monomer such as $(C_6H_5)_2\text{SnCl}_2$ [19], three types of polymer are known which embody a *trans*-R₂SnX₄ geometry at tin. In the unique case of $(CH_3)_2\text{SnF}_2$ (Fig. 3b), all the Sn-F bonds are equivalent, the polymer is two-dimensional, and the Sn-F-Sn residue is linear [20], a situation that we have termed a "Class 1" type polymer in as much as the bridging is as rigid as possible [9]. Two other arrangements are known, which incorporate two distinct types of Sn-X bond, and where the spacial arrangement of the Sn-X-Sn unit is zig-zag or "Class 2" (less rigid) type: the halogens which form the longer, bridging



Fig. 4. Unit cell viewed along c, showing the nature of polymer propogation. Only the α -carbon of the C₆H₁₁ ring above the polymer plane has been included for clarity.

bonds to tin can be from the same molecule (Fig. 3c; e.g. $(C_2H_5)_2SnI_2$ [13]) or different molecules (Fig. 3d; e.g. $(CH_3)_2SnCI_2$ [12]). The title compound adopts a 3(c) type structure with the Cl(1')-Sn(1')-Cl(2') unit both bridging and chelating Sn(1), although the mode of chelation is markedly anisobidentate. While it would not have been possible to predict which of the two types of Class 2 polymer would be formed by dicyclohexyltin dichloride, we have previously indicated a preference for this Class of polymer rather than that of Class 1, based upon variable temperature Mössbauer spectroscopic studies [9].

Compounds such as $(C_6H_{11})_2 \text{SnCl}_2$ are often used as models for correlating spectroscopic properties and structure. In the case of organotin chemistry in which Mössbauer spectroscopy plays a prominent role, two parameters – the quadrupole splitting (QS) and the temperature coefficient of the recoil free fraction $(a = -d \ln f/dT)$ – are often cited and it is of interest to review the significance of these parameters within the context of the present structure.

The QS is a function of the electric field gradient at tin, and a model exists [21] which correlates this value with C-Sn-C in six-coordinate diorganotin compounds using a point charge approach:

$$|QS| = 4\{R\} [1 - 3\sin^2\theta \cos^2\theta]^{1/2}$$

where $\{R\}$ = partial quadrupole splitting for R (-1.03 for C₆H₁₁ [22]) and C-Sn-C = 2θ . On this basis, for an experimentally observed QS value of 3.40 mm s⁻¹ [9], the calculated C-Sn-C is 139°, in good agreement will the observed value of 134.4(2)°, particularly in the light of the assumptions made in the model, namely that contributions to the QS are negligible for ligands other than R.

The temperature coefficient of the recoil-free fraction, a, is a measure of the rigidity of the lattice as experienced by the Mössbauer active atom, tin. In short, a

TABLE 4

VARIABLE TEMPERATURE MÖSSBAUER SPECTROSCOPIC DATA FOR SELECTED CYCLOHEXYLTIN HALIDES a

| Compound | $10^2 a (\mathrm{K}^{-1})$ | |
|-----------------------------------|----------------------------|--|
| $(C_6H_{11})_3$ SnI ^b | 1.60 | |
| $(C_6H_{11})_3$ SnBr ^b | 1.64 | |
| $(C_6H_{11})_3$ SnCl | 1 40 | |
| $(C_6H_{11})_2$ SnCl ₂ | 1.13 | |
| $(C_6H_{11})_3$ SnF | 0.91 | |

^a Data taken from ref. 9 unless stated otherwise. ^b Ref. 8.

diminishes as the lattice stiffens, usually with the onset of polymerisation in one or more directions. Data for representative cyclohexyltin compounds are given in Table 4. By comparison, the tin is held in the lattice with rigidity similar to the associated (Class 1) halides (C_6H_{11})₃SnX (X = Cl, F), and more tightly so than the non-interacting lattices of the corresponding bromide and iodide [7,8]. However, the bridging bonds in tricyclohexyltin fluoride and chloride are relatively long, so it seems reasonable to assume that if (C_6H_{11})₂SnCl₂ were also a polymer of Class 1 type [cf. (CH₃)₂SnF₂] it would show a substantially lower value for *a* than either triorganotin halide, even if one or both of the bridging bonds is weak. On this basis, we have previously suggested the likely structure for the title compound to be a polymer of Class 2 type (zig-zag), a proposal which is now substantiated by the present work.

Acknowledgements

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Organotin Biocides. Part 2.¹ Variable-temperature ¹¹⁹Sn Mössbauer Study of Phenyl- and Cyclohexyl-tin Compounds

Kieran C. Molloy * and Kieran Quill

National Institute for Higher Education, Glasnevin, Dublin 9, Ireland

The temperature dependence of the recoil-free fraction ($a = -d \ln f/dT$) for 13 phenyl- and 11 cyclohexyl-tin compounds has been investigated, and the results interpreted in terms of the lattice structures of the compounds. This interpretation is aided by a classification of organotin polymers based upon the stereochemical disposition of tin and the bridging groups. Lattices based upon non-interacting units, or polymers which are helical (Class 4) or 'S'-shaped (Class 3), show the highest *a* values. The value of this parameter is generally reduced for zigzag (Class 2) polymers, while the most rigid lattices (lowest *a*) are based upon a rod-like (Class 1) architecture.

The current depth of understanding of solid-state organotin chemistry owes much to the availability of a battery of physical techniques which can be brought to bear on the structural problem. In the absence of definitive X-ray crystallographic data, indirect spectroscopic probes must suffice, and amongst the available techniques Mössbauer spectroscopy has assumed a particular prominence. From the single-temperature (78 K) experiment, conventional isomer shift (i.s.) and quadrupole splitting (q.s.) data can yield both the oxidation state and coordination number at tin, and under favourable circumstances distinguish between alternative geometric isomers.² Less clear cut under these experimental conditions are situations in which potential association within the solid can generate either monomeric or polymeric compositions, as exemplified by compounds (1) and (2) for a triorganotin (SnR_3) derivative of a bidentate ligand (L-L). Q.s. data for the two geometries can often be too close to permit unambiguous resolution, and the situation is exacerbated by distortions from ideal geometry. Furthermore, no distinction can be made on the basis of q.s. data alone between short chain, cyclic oligomers (2; n up to ca. 10) and true polymers (2; n up to ∞).

Such situations can potentially be resolved by variabletemperature Mössbauer spectroscopy (v.t.M.s.), in which the mean-square amplitude of vibration of the tin, $\langle x(T)^2 \rangle$, is related to the recoil-free fraction of the absorber, f(T) [equation (1)], where π is the wavelength of the Mössbauer transition

$$f(T) = \exp[-\langle x(T)^2 \rangle / \hbar^2]$$
(1)

divided by 2π . In the high-temperature limit ($T \ge \theta_D/2$), the Debye model for solids is applicable and hence we obtain equation (2), where E_R is the Mössbauer recoil energy, k the

$$\frac{\mathrm{d}f(T)}{\mathrm{d}T} = \frac{\mathrm{d}\,\exp\left(-6E_{\mathrm{R}}T/k\theta_{\mathrm{D}}^{2}\right)}{\mathrm{d}T} \tag{2}$$

Boltzmann constant, and θ_D the Debye temperature for the lattice. For 'thin absorbers' ($N\sigma_0 < 1$, where N = number of absorber atoms per cm², and $\sigma_0 =$ resonant absorption cross-section for ¹¹⁹Sn), A(T), the area under the spectral envelope, and f(T) are linearly related and plots of $\ln [A(T)/A(78)]$ vs. T are linear. Normalisation of data to 78 K is merely to facilitate inter-sample comparison. The temperature coefficient of f derived from these plots, $a = -d \ln A(T)/dT$, characterises the



tightness with which the tin atom is bound into the lattice, and hence the degree of molecular association.

Most previous work in this area³ has broadly elucidated a/structure systematics for methyltin derivatives. These systematics are not necessarily applicable to phenyl- and cyclohexyl-tin compounds where both steric bulk and a structured nature to the hydrocarbon can lead to different lattice dynamics. Understanding the v.t.M.s. behaviour of these two classes of organotins is a prerequisite to application of the methodology to structure determination of novel compounds of interest for their high biocidal activity, which is exploited commercially in a number of tin-based agrochemicals.^{4a} We herein report our findings in this area.

Experimental

Organotin reagents and ligands were purchased from normal commercial sources (usually Aldrich or Merck) and were used in syntheses without further purification. Samples of tetraphenyltin (Aldrich) and triphenyltin chloride (Merck) used for Mössbauer spectra were recrystallised from toluene or diethyl ether. Triphenyltin hydroxide, tricyclohexyltin hydroxide, and diphenyltin oxide were gifts from the International Tin Research Institute (Greenford); the two SnR₃(OH) compounds were recrystallised from cold acetone and toluene, respectively. Diphenyltin dichloride (BDH) was recrystallised from toluene. Tetracyclohexyltin was prepared from cyclohexylmagnesium chloride and tin(IV) chloride in diethyl ether⁵ and recrystallised from toluene. Dicyclohexyltin dichloride was obtained by a redistribution reaction between tetracyclohexyltin and tin(IV) chloride (1:1) under established conditions⁶ and purified by recrystallisation from diethyl ether.

The remaining organotin compounds used in this study were largely prepared by standard metathesis reactions, involving either an organotin hydroxide and a protonated form of the ligand, with the water formed in the reaction removed azeotropically in a Dean and Stark apparatus (route 1), or from an organotin halide and an alkali-metal (Na or K) salt of the ligand (route 2). Route 1 was employed to prepare the

^{*} Present address: School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY.

| Table | 1. | Analy | /tical | data ^a | for | phenyl | - and | cyclohexy | vl-tin | com | pound | s |
|-------|----|----------|--------|-------------------|-----|--------|-------------|-----------|--------|-----|-------|---|
| | | L BAABBA | | | | P | Are 1 4 4 4 | | | | | ~ |

| | | Analysis (%) | | | | |
|--|---------------|----------------------------|--------------|--------------------------------------|-------------|-------------|
| Compound | С | Н | N | M.p. (°C) ^b | i.s. ' | q.s. ' |
| SnPh ₄ | | | | 224-226 (224-225) | 1.27 (1.27) | 0.00 |
| SnPh ₃ F | 58.70 (58.60) | 4.00 (4.10) | | 320 (decomp.) (357, decomp.) | 1.30 (1.25) | 3.62 (3.53) |
| SnPh ₃ Cl | CC 10 (CC 00) | 2 70 (2 70) | 2 20 (2 45) | 104-106 (105.5-107) | 1.35 (1.37) | 2.53 (2.45) |
| SnPh ₃ (NCS) | SO.TU (SS.90) | 3.70 (3.70) | 3.20 (3.45) | 162—164 | 1.40 (1.35) | 3.44 (3.54) |
| SnPh ₃ (OH) | | | | 119-120(119-120) | 1.18 (1.24) | 2.82 (2.98) |
| $(Ph_3Sn)_2O$ | 59 25 (59 70) | 4 40 (4 45) | | 123 - 124 (124) 120 121 (121 122) | 1.10 (1.07) | 1.37(1.03) |
| $SnPn_3(O_2CMe)$ | 38.33 (38.70) | 4.40 (4.45) | | 120-121(121-122) | 1.28 (1.20) | 3.33 (3.30) |
| $S_{n}Ph_{3}(O_{2}Ch)$ | 57.00 (57.75) | 4.00 (4.10) | | 200-207(201) | 1.40 (1.57) | 3.46 (3.36) |
| $SnPh_{3}(O_{2}FFI_{2})$ | 56 50 (57 45) | 4.70 (4.43) 3.75 (4.10) | 0.00 (10.05) | 260 (decomp.) 306308 | 1.25 | 2.35 |
| $S_n Ph O$ | 50.50 (57.45) | 5.75 (4.10) | 3.30 (10.03) | 300 | 0.80 (0.05) | 1.00 (1.87) |
| SnPh_Cl_ | | | | 47-44 (47-44) | 141(140) | 2 85 (2 80) |
| SnPh ₂ Cl ₂ ·0.75 pvz | 44 40 (44.60) | 3.25 (3.25) | 5.15 (5.20) | 114-115 | 1.37 (1.32) | 3.08 (3.00) |
| $Sn(C_2H_{1,1})$ | 63.50 (63.85) | 10.0 (9.30) | | 263-264 (263-264) | 1.46 (1.57) | 0.00 |
| Sn(C _c H ₁₁) ₂ F | 55.55 (55.85) | 8.65 (8.60) | | 310 (decomp.) (305, decomp.) | 1.47 (1.56) | 3.71 (3.96) |
| Sn(C ₆ H ₁₁) ₃ Cl | 53.75 (53.55) | 8.20 (8.25) | | 127—129 (129—130) | 1.68 (1.64) | 3.52 (3.49) |
| $Sn(C_6H_{11})_3(OH)$ | 56.35 (56.10) | 9.05 (8.90) | | 198—202 (220—222) [*] | 1.41 (1.40) | 2.99 (2.99) |
| $Sn(C_6H_{11})_3(O_2CMe)$ | 56.45 (56.25) | 8.45 (8.50) | | 61-63 (61-63) | 1.59 (1.57) | 3.35 (3.27) |
| $Sn(C_6H_{11})_3(O_2CH)$ | 55.25 (55.25) | 8.65 (8.30) | | 152—153 | 1.59 | 3.79 |
| $Sn(C_6H_{11})_3(iaa)$ | 62.20 (62.00) | 7.75 (7.65) | 2.50 (2.60) | 150—152 | 1.54 | 3.00 |
| $Sn(C_6H_{11})_3(O_2PPh_2)$ | 61.50 (61.55) | 7.45 (7.40) | | 300 (decomp.) | 1.56 | 3.93 |
| Sn(C ₆ H ₁₁) ₃ (triaz) | 55.00 (55.10) | 8.20 (8.10) | 9.45 (9.65) | 202—205 (218) ^f | 1.51 | 3.26 |
| $Sn(C_6H_{11})_2Cl_2$ | 40.35 (40.50) | 6.55 (6.25) | | 88-89 (88-89) | 1.78 (1.76) | 3.40 (3.47) |
| $Sn(C_6H_{11})_2F_2$ | 43.60 (44.60) | 7.30 (6.85) | | 275 (278) | 1.37 | 3.31 |

^a Required values given in parentheses. ^b Literature values (in parentheses) are taken from R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 1960, 60, unless stated otherwise. ^c Literature values (mm s⁻¹) in parentheses are taken from ref. 2 and J. N. R. Ruddick, *Rev. Silicon, Germanium, Tin, Lead Comp.*, 1976, **2**, 115. ^d B. F. E. Ford, B. V. Liengme, and J. R. Sams, *J. Organomet. Chem.*, 1969, **19**, 53. ^eC. A. Kraus and R. H. Bullard, *J. Am. Chem. Soc.*, 1929, **51**, 3605. ^f Ref. 41.

triphenyltin derivatives of 1,2,4-triazole, diphenylphosphinic, formic, and acetic acids, and the tricyclohexyltin derivatives of 1,2,4-triazole, diphenylphosphinic, formic, acetic, hydrochloric, and indol-3-ylacetic⁷ acids. Triphenyltin fluoride and isothiocyanate, tricyclohexyltin fluoride, and dicyclohexyltin difluoride were all prepared by route 2. Bis(triphenyltin) oxide was obtained by dehydration of SnPh₃(OH) in boiling toluene under the conditions used in route 1. The pyrazine (pyz) adduct of diphenyltin dichloride precipitated from a 1:1 mixture of the reagents in light petroleum b.p. 40–60 °C, and was recrystallised from the same solvent.⁸

All the compounds subjected to v.t.M.s. analysis were confirmed by i.r., m.p., and (in most cases) C, H, and N microanalyses (microanalytical service, University College, Dublin). Mössbauer i.s. and q.s. data (Table 1) are in good agreement with published values.

Details of our Mössbauer spectrometer, method of data collection and manipulation have been described elsewhere.¹ Samples were utilised as finely ground powders (to minimise orientation effects), with up to 2 mg ¹¹⁹Sn per cm² to comply as fully as possible with the criteria for a 'thin sample' while maintaining the viability of the experimental method, *i.e.* goodquality spectra accumulated in ca. 12 h. In certain instances, quantities of absorber in excess of 2 mg were used (up to a maximum of 4 mg), usually at elevated temperatures for species with relatively non-rigid lattices, leading to a curvature in the ln A vs. T plots. In such cases it was found that a range of equally valid 'best straight lines' was possible (as judged by the correlation coefficient, r) depending on the temperature range over which the linear relationship was assumed to hold. In reporting these results, we quote a single value for the slope for the complete data set, followed in parentheses by maximum and minimum slopes for segments of the data which could be considered to obey a linear relationship, and which do not show

any significant reduction in correlation coefficient. Data for which only a single fit are given show no appreciable deviation from a linear relationship, from which it may be concluded that vibrational anharmonicity within the lattice is also absent. The quoted correlation coefficients are related to the complete data set for a given compound.

Discussion

Variable-temperature Mössbauer spectroscopic data for phenyland cyclohexyl-tin compounds are given in Tables 2 and 3 respectively. For both series we have concentrated our efforts on a study of compounds of known (X-ray crystallographic) lattice structure, or whose structure can be reliably assumed from their formulation and ancillary spectroscopic data. This has posed some restrictions on the range of compounds available, since relatively few crystallographic studies have been made on these two classes of organotins, particularly for polymeric arrangements.⁹ Tables 2 and 3 also contain compounds of uncertain crystal structure, and v.t.M.s. data from other laboratories for comparison.

It is worth prefacing our analysis of these data with a note of caution. The temperature dependence of f is only a theoretically linear function for a 'thin sample,' in the high-temperature limit $(T \ge \theta_D/2)$ for the Debye model of solids upon which the systematics are based. Deviations from a linear function are not uncommon in both our own experience (Figure 1) and that of others,¹⁰ and even in cases where a 'thin absorber' is rigorously employed, non-linearity of plots of ln *A vs. T* can arise from lattice vibrational anharmonicity.¹¹ Where relatively minor curvature occurs, linear fits remain acceptable as judged by *r*, the correlation coefficient, but do not represent a totally reliable value for d ln f/dT. Correlation of data from a number of sources, which inevitably introduces variations in sample

| Compound | $10^2 a/K^{-1}$ | -r (T range/K, points) | Structure |
|---|---|---|-----------------------------------|
| (3) (Ph ₂ Sn) ₆ | 2.80 % | | Monomer ⁴ |
| (4) {Ph ₂ Sn[(CH ₂)C ₄ H ₄ (CH ₂) ₂]}, | 2.72 ^ª | | Polymer $(3 \text{ or } 4)^{d,e}$ |
| (5) (Ph_Sn)_Sn | 2.42 ^b | | Monomer |
| (6) $\operatorname{SnPh}_{2}(C_{c}F_{c})_{2}$ | 2.37 " | | Monomer |
| (7) [Ph_Sn(C, H_CHCH_)]. | 2.30 ^d | 0.991 (77-130, 14) | Polymer ^{d,f} |
| (8) SnPh_[S_P(OPr ^{n}),] | 2.19# | (78—110, 5) | Monomer ^h |
| (9) $SnPh_{H_{2}}$ | 2.19* | (,.,., | Monomer |
| (10) SnPh ₂ (C,F ₂) | 217 | | Monomer |
| (11) $Ph_SnO_C(CH_s)$ -C(O)Me | 217 | | Polymer $(3 \text{ or } 4)^{e,h}$ |
| (12) Ph.SnO. $CC(Me)CH$. | 2136,1 | | Monomer ^h |
| (12) $\operatorname{SnPh}_{(O, PPh_{-})}$ | $209(209-143)^{j}$ | 0.985(78-150, 12) | Polymer (3) |
| (14) Ph. SnSnPh. | 2.09 (2.05) 1113) | 0.000 (10 100, 12) | Monomer |
| (15) (Ph Sp) NCN | 2.08* | | Polymer (4) ^{e,h} |
| (16) $S_{n}Ph H$ | 2.01 | | Monomer |
| (10) SnPhC1 | 1 97 * | | Monomer ^h |
| (12) SnPhCl AH salen | 1 94 | 0.995(78-115.4) | Polymer $(3)^{e,h}$ |
| (10) Shi h Ci_3 · i_2 salch (10) S ₂ Db [S P(OEt)] | 1.07# | (78-145, 8) | Monomer ^c |
| (19) $SnPh_{2}[S_{2}P(OL)_{2}]_{2}$ (20) $SnPh_{2}(OCM_{2})$ | 1.92 | (78-145, 8) | Polymer (3) ^{e,m} |
| (20) $\operatorname{Shi} \operatorname{h}_3(\operatorname{O}_2\operatorname{CMC})$ (21) $\operatorname{Ph} \operatorname{SpON}(\operatorname{Ph})C(\operatorname{O})\operatorname{Ph}$ | 1.857 | 0.000 (76-140, 6) | Monomer ^c |
| (21) $\prod_{3,3} (1,1) \subset (0,1)$ | 1.05 | 0.007 (78-110.7) | Polymer (3) ⁶ |
| (12) Shifting (NCS) (13) SpBh (ONC H) | 1.07 | 0.337 (76—110, 7) | Monomer [#] |
| (23) $\sin n_3(ONC_6n_{10})$ (24) $\operatorname{SpBh}(Cl_{10}, 0.75 \operatorname{prot})$ | 1.02 | 0.008 (78 205 13) | Monomer polymer (2) Se |
| (24) SIF $\Pi_2 \subset \Pi_2^{-10}$, $(3p)$ (25) (So Dh. COD(S)(ODh) (10H) | 1.75 | 0.998 (78-203, 13) 0.995 (77-160, 6) | Dimer ^c |
| (25) $\{S_{1}, F_{1}, C_{1}, C_{2}, C$ | 1.70 | 0.995(77-100,0) | Manamar ^h |
| $(20) \text{ ShPh}_3(CN)$ | 1.73 | | Delumer (2 or 4) 6/ |
| $(27) Pn_2 SnOC_6 H_4 O$ | 1.73 | | Monomore ^h |
| (28) $Pn_3SnO_2CC_6H_4(0-N_2R^2)$ | 1./1* | | Monomer |
| (29) $Pn_3SnO_2CC_6H_4(0-N_2K^2)$ | 1.607 | | Monomer |
| $(30) \operatorname{Ph}_3 \operatorname{SnO}_2 \operatorname{CC}_6 \operatorname{H}_4(0 - \operatorname{N}_2 \operatorname{K}^2)$ | 1.59" | 0.000 (78 145 6) | Monomer |
| (31) ShPh ₃ Ci | 1.50 (1.50-1.43) | 0.998(78-145, 0) | Monomer |
| $(32) (Pn_3Sn)_2O$ | 1.56 (1.56-1.38) | 0.996 (78-145, 7) | Monomer |
| $(33) \operatorname{SnPh}_2 \operatorname{Ui}_2$ | $1.54 (1.54 - 1.39)^{3^{\prime\prime}}$ | 0.998 (78—145, 7) | Monomer |
| (34) $Ph_3SnO_2CC_6H_4(o-N_2R^2)$ | 1.53* | 0.000 (78 1.00 12) | Monomer ^P |
| (35) SnPh ₃ F | 1.495.3 | 0.999(78-160, 13) | Polymer (2) |
| $(36) \operatorname{SnPh}_3[S_2P(OEt)_2]$ | 1.43 | 0.999(77-150, 7) | Monomer |
| $(37) \operatorname{SnPh}_3[S_2P(OPr')_2]$ | 1.40' | 0.998(77-155,9) | Monomer" |
| $(38) \operatorname{SnPh}_4$ | 1.377 | 1.000 (78—140, 6) | Monomer |
| $(39) \{ SnPh_3[O_2P(OPh)_2] \}_6$ | 1.37 | 0.984(77-170, 6) | Cyclic hexamer |
| (40) $\text{SnPh}_2\text{Cl}_2 \cdot \text{H}_2\text{salen}$ | 1.27* | 0.995(78-140,7) | Polymer (2) |
| (41) $\operatorname{SnPh}_2(\operatorname{trop})_2$ | 1.20 | | Monomer" |
| $(42) \operatorname{SnPh}_{3}(O_{2}CH)$ | $1.15 (1.15 - 1.03)^{7}$ | 0.997 (78—145, 7) | Polymer" |
| (43) SnPh_2O | 1.15 (1.15-0.94) | 0.996 (78-200, 8) | Polymer (2) ^e |
| (44) $\operatorname{SnPh}_3(OH)$ | $1.10(1.10-1.08)^{5}$ | 0.998 (78145, 6) | Polymer $(2)^{r,e}$ |
| (45) $\text{SnPh}_2[\text{S}_2\text{P}(\text{OPr}')_2]_2$ | 1.06 % | (78-160, 9) | Monomer |
| (46) $\text{SnPh}_3(\text{triaz})$ | 1.04 | 1.000 (78—145, 6) | Polymer (2) en |
| (47) $SnPh_2Cl_2$ ·dppoe | 1.04 ~ | (77—110, 6) | Polymer (1) ^{en} |
| (48) $SnPh_2[OP(S)(OMe)_2]_2$ | 0.97 | 0.972 (77—170, 6) | Monomer" |
| (49) SnPhCl ₃ •pyz | 0.90* | 0.999 (79—150, 5) | Polymer (1) ^e |

^{*a*} Abbreviations: H₂salen = N,N'-ethylenebis(salicylideneimine); pyz = pyrazine; R¹ = 4-hydroxynaphthyl; R² = 2-hydroxynaphthyl; R³ = 4dimethylaminophenyl; R⁴ = 2-hydroxy-5-methylphenyl; trop = tropolonate (2-hydroxycyclohepta-2,4,6-trien-1-onate); triaz = 1,2,4-triazol-1-yl; dppoe = 1,2-bis(diphenylphosphoryl)ethane; ONC₆H₁₀ is cyclohexanone oximate. ^{*b*} Ref.43. ^c From X-ray crystallographic data (see ref. 9 and Discussion section). ^{*d*} Ref. 39a. ^{*e*} Figures in parentheses define the polymer class (see Figure 2 and Discussion section). ^{*f*} Ph₃Sn pendant to polymer chain. ^{*e*} J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, M. Curtui, C. Guta, and D. Ruse, *Inorg. Chem.*, 1980, 19, 2861. ^{*h*} On the basis of v.t.M.s. and other spectroscopic data. ^{*i*} H. Sano and R. Kuroda, *Chem. Phys. Lett.*, 1971, 11, 512. ^{*j*} This work. ^{*k*} A. J. Rein and R. H. Herber, Proceedings of the 5th International Conference of Raman Spectroscopy, eds. E. D. Schmid, J. Brandmeuller, and W. Kiefer; Hans Ferdinand Schultz Verlag, Freiburg (F.R.G.), 1976, p. 66; *Chem. Abstr.*, 1978, **88**, 14527. ^{*i*} Ref. 10. ^{*m*} Ref. 1; also quoted as 2.17 × 10⁻² K^{-1. *b*} ^{*n*} Ref. 24. ^{*o*} F. A. K. Nasser and J. J. Zuckerman, *J. Organomet. Chem.*, 1983, **244**, 17. ^{*p*} Ref. 19. ^{*a*} Also quoted as 1.53 × 10⁻² K^{-1. *k*} Also quoted as 2.21 × 10⁻² K^{-1. *k*} Also quoted as 1.33 × 10⁻² K^{-1. *b*} ^{*i*} J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, C. Guta, and D. Ruse, *Inorg. Chem.*, 1980, **19**, 1662. ^{*a*} A. J. Rein and R. H. Herber, *J. Chem.*, *Phys.*, 1975, **63**, 1021. ^{*b*} Also quoted as 1.30 × 10⁻² K^{-1. *b*} P. G. Harrison, N. W. Sharpe, C. Pelizzi, G. Pelizzi, and P. Tarasconi, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 921. ^{*x*} E. Rivarola, A. Silverstri, and R. Barbieri, *Inorg. Chim. Acta*, 1978, **28**, 223.

thickness and the subjectivity of what is an acceptable linear range for the data, is *potentially* unreliable, particularly if too much is read into minor variations in *a*. In this light, our discussion is restricted to trends within the body of data as a whole, although on the basis of our conclusions we do draw inferences on the structures of specific, structurally uncharacterised compounds. *Phenyltin Compounds.*—Of the compounds studied, those which are known to have lattices made up of non-interacting units comprise the monomers (3),¹² (14),¹³ (19),¹⁴ (21),¹⁵ (31),¹⁶ (32),¹⁷ (33),¹⁸ (34),¹⁹ (36),²⁰ (38),²¹ the dimer (25),²² and the cyclic hexamer (39)²³ and on the basis of spectroscopic evidence also include (5), (6), (8), (10), (16), (29), (30), and (37); all show a large value of a, (1.37–2.80) × 10⁻² K⁻¹, reflecting

 Table 3. Variable-temperature ¹¹⁹Sn Mössbauer data for cyclohexyltin compounds

| Compound ^a | $10^2 a^b/K^{-1}$ | -r (T range/K, points) | Structure |
|---|-------------------------------|------------------------|--------------------------|
| (50) $Sn(C_6H_{11})_3(iaa)$ | 1.75 (1.75-1.45) | 0.996 (78-165, 6) | Polymer (3) ^d |
| (51) $Sn(C_6H_{11})_3Br$ | 1.64 ^e | 0.999 (77-175, 6) | Monomer ^f |
| (52) $Sn(C_6H_{11})_3I$ | 1.60 ^e | 1.000 (77-175, 5) | Monomer ^f |
| (53) $Sn(C_6H_{11})_3(O_2CMe)$ | 1.59 | 0.997 (78-145, 7) | Polymer (3) ^e |
| (54) $Sn(C_6H_{11})_3(O_2PPh_2)$ | 1.58 (1.96-0.82) | 0.988 (78-200, 8) | Polymer (3) |
| (55) $Sn(C_6H_{11})_3Cl$ | 1.40 (1.40-1.28) ^g | 0.998 (78-145, 7) | Polymer (1) ^f |
| (56) $Sn(C_6H_{11})_3(triaz)$ | 1.31 (1.31-1.10) | 0.993 (78-145, 6) | Polymer (2) |
| $(57) \operatorname{Sn}(C_6H_{11})_3O_2CC_6H_4(o-N_2R)$ | 1.30 | (78-175, 9) | Polymer (3) ^h |
| (58) $Sn(C_6H_{11})_2F_2$ | 1.23 | 0.999 (78-160, 11) | Polymer (2) ^h |
| (59) $Sn(C_6H_{11})_4$ | 1.14 | 0.996 (78-165, 9) | Monomer ^h |
| (60) $Sn(C_6H_{11})_2Cl_2$ | 1.13 (1.130.94) | 0.996 (78-160, 7) | Polymer (2) ^h |
| (61) $Sn(C_6H_{11})_3F$ | 0.91 (0.91-0.79) | 0.996 (78-145, 6) | Polymer (1) |
| (62) $Sn(C_6H_{11})_3(O_2CH)$ | 0.93 | 0.992 (78-150, 10) | Polymer ^g |
| (63) $Sn(C_6H_{11})_3(OH)$ | 0.66 | 0.999 (78-135, 6) | Polymer (1) ^h |

^{*a*} Abbreviations: iaa = indol-3-ylacetate; R = 2-hydroxy-5-methylphenyl. ^{*b*} This work unless specified otherwise. ^{*c*} Figures in parentheses (also in Table 2) define the polymer class (see Figure 2 and Discussion section). ^{*d*} Ref. 7. ^{*e*} Ref. 28. ^{*f*} X-ray crystallographic data (see ref. 9 and Discussion section). ^{*a*} Also quoted as $1.60 \times 10^{-2} \text{ K}^{-1}$. ^{*e*} h On the basis of v.t.M.s. and other spectroscopic data. ^{*i*} Quoted as $1.78 \times 10^{-2} \text{ K}^{-1}$.



Figure 1. Representative variable-temperature Mössbauer data: (\Box) , $Sn(C_6H_{11})_3(OH)$, linear over whole T range $(a = 0.66 \times 10^{-2} \text{ K}^{-1})$; (\blacksquare) , $Sn(C_6H_{11})_3(\text{triaz})$, showing mild curvature (78—145 K); the range of 'best straight lines' is given by — (1.31 × 10⁻² K⁻¹, all data) and $---(1.10 \times 10^{-2} \text{ K}^{-1})$, three points); (\bigcirc, \bigcirc) , $SnPh_3(O_2PPh_2)$, showing a marked deviation from linearity over the whole T range. For the latter, data correspond to two separate data sets $(\bigcirc, 1 \text{ mg}^{119}Sn \text{ per cm}^2)$, $O, 4 \text{ mg}^{119}Sn \text{ per cm}^2)$ collected over a time interval of 4 months. The point \triangle (78,0.00) is common to all plots shown

the relative vibrational freedom of the tin atom in each case. This range of values of *a* embraces (in part) data for compounds whose lattices are strengthened by hydrogen bonding,²⁴ suggesting that with regular, well structured groups bonded to tin, *e.g.* C_6H_5 , packing factors can play an important part in determining lattice dynamics.

Phenyltin compounds which are known to have polymeric structures fall into two groups: $(44)^{25}$ $(a = 1.10 \times 10^{-2} \text{ K}^{-1})$ and (20),¹ (22),²⁶ and $(24)^{8}$ $(a ca. 1.80 \times 10^{-2} \text{ K}^{-1})$. The lower value of a for (44) relative to the non-associated lattices discussed above is in consonance with the restrictions imposed on the vibrational motion of the tin when it is incorporated into a polymer chain. Such a simple rationale is clearly not



Figure 2. Schematic classification of organotin polymers: (a) Class 1 (rod), (b) Class 2 (zigzag), (c) Class 3 ('S'), and (d) Class 4 (helical)

applicable for the second group of polymers, whose *a* values are all in the 'non-polymeric' region of the systematics.

In order to understand the behaviour of organotin polymers under the conditions of the v.t.M.s. experiment, it is necessary to understand fully the architecture of the polymer, which we define as having three layers of complexity: the *primary structure*, which is related to the monomer from which the polymer is built, its co-ordination number, geometry, stereochemistry, *etc.*; the *secondary structure* we will use to describe the dimensionality of the polymer, one-, twodimensional, chain, sheet, *etc.*; and the term *tertiary structure* which covers the three-dimensional disposition of secondary structure. While the primary and secondary structures play a major role in defining the characteristics of the polymer, they do not alone necessitate a restriction in the vibrational motion of the atoms incorporated into the polymer, as evidenced by the v.t.M.s. data for the second group of phenyltin polymers. The role of the polymer's tertiary structure must therefore be considered more fully, a pre-requisite for which is a classification of existing structures, which we present here for the first time in a collective form.

The tertiary structure of the polymer can be classified in terms of the relative spacial disposition of the R_nSn and bridging ligand (X) sub-units. We have identified four classes of tertiary structure which will serve as a framework for the analysis, and these are depicted schematically in Figure 2. For simplicity, we have excluded polymeric structures arising from hydrogen bonding due to the presence of lattice water, and confined ourselves to instances where X is covalently bound to R_nSn, as well as bridging to an adjacent tin moiety. Class 1 is a rod wen as bridging to an adjacent in molecty. Class 1 is a rod polymer, in which the Sn and X groups are collinear, *e.g.* $Sn(C_6H_{11})_3X$ (X = Cl²⁷ or F²⁸), $SnMe_3(CN)$,²⁹ or Me₃- $SnO_2CCH_2NH_2^{30}$ (where the bridging group straddles the Sn ··· Sn vector) all of which have a one-dimensional secondary structure, and $SnMe_2F_2^{31}$ which is two-dimensional. Class 2 is a zigzag arrangement, exemplified by SnPh₃(OH).²⁵ SnMe₃Cl,³² SnMe₂Cl₂,³³ and Bu₂SnO(CH₂)₃O,³⁴ all of which are one-dimensional, the first two with single and the latter two with double bridges. Where the group X contains several atoms, the structure expands and becomes more flexible (Class 3, 'S'shaped). The compound SnPh₃(NCS)²⁶ is placed in Class 3, although the tin atoms remain collinear and together with the rigid NCS group the overall tertiary structure retains some Class 2 character. Where more flexible groups X are involved, and particularly where the tin atoms are no longer collinear along the chain, the 'S'-shape becomes more pronounced, e.g. $\text{SnPh}_3(\text{O}_2\text{CMe})$,¹ $\text{Sn}(\text{C}_6\text{H}_{11})_3(\text{O}_2\text{CMe})$ (one-dimensional),^{19,35} and $\text{SnMe}_2(\text{SO}_3\text{F})_2$ (two-dimensional).³⁶ As the extent of coiling of the polymer increases, a clearly helical structure is reached (Class 4), e.g. a-SnMe₃[O₂P(Ph)OH],³⁷ and SnMe₃(O₂SMe).³⁸ In such cases, the bridging group X may embody complete primary units, and the only tin atoms shown in Figure 2 are the starting points of the unique repeating coil section.

In terms of the v.t.M.s. experiment, the lattice rigidity decreases as (a) the strength of the bridging bond $(X \cdots Sn)$ decreases or (b) as the bridging mass is progressively displaced away from the Sn · · · Sn vector (Class 1 - \rightarrow Class 4), or some combination of these factors. Class 2 polymers, e.g. (44), do reduce the vibrational motion of the tin relative to a noninteracting lattice. More flexible arrangements, as in the Class 3 polymers (20) and (22), on the other hand, afford a vibrational freedom to the tin akin to a non-polymeric structure. In the light of this assessment it must be concluded that the tertiary structure of compound (4) $(a = 2.72 \times 10^{-2} \text{ K}^{-1})$ must be severely coiled (Class 4, or an irregular variation thereof). Compound (24) must be reviewed independently to the other phenyltin polymers. The structure consists of both 2SnPh₂Cl₂·pyz monomers and the (SnPh₂Cl₂·pyz), polymer.⁸ The latter is of Class 2 type, accentuated by the large (but rigid) pyrazine bridge. It is plausible that this lengthy bridge would increase the value of a from ca. 1.1 × 10⁻² K⁻¹ [the value for compound (44)] in its own right, but in any case the experiment is measuring the average rigidity of the two types of tin site, which are indistinguishable in their Mössbauer q.s. values. On this basis the measured value of $a (1.79 \times 10^{-2} \text{ K}^{-1})$ is not anomalous.

Two other features of these phenyltin data have been noted previously, but are worth reiterating in the generality of this treatment. First, compound (7) in which a Ph_3Sn group is pendant to a polymer chain, has the vibrational characteristics of a monomer, irrespective of the tertiary structure of the polymer.³⁹ Secondly, monomeric (45) packs in the lattice very regularly in a pseudo-one-dimensional, doubly bridged, Class 3 polymer⁴⁰ (of which there are no genuine organotin

examples ⁹), reducing the *a* value to 1.06×10^{-2} K⁻¹ and underlining the potential influence of packing forces on these experimental data.

Cyclohexyltin Compounds.—V.t.M.s. data for 11 cyclohexyltin compounds are given in Table 3, and can be interpreted in a similar fashion to those of the phenyltin compounds. The monomers (51) and (52) both show high values for a (ca. $1.60 \times 10^{-2} \text{ K}^{-1}$), as does the weakly polymeric (Class 3) (53).^{19,35} The tricyclohexyltin ester of indol-3-ylacetic acid (50) is also of Class 3 type, but in this case the polymer arises from hydrogen bonding between C=O···H–N units onto which an essentially four-co-ordinate tin is appended,⁷ and this is reflected in a slight increase in a (1.75 × 10⁻² K⁻¹) relative to the true Class 3 polymer (53). On the basis of these systematics, the value of a for Sn(C₆H₁₁)₄ (59) is remarkably low, and can only arise from packing factors within the lattice, underlining the warnings outlined above.

The triazole (56) is a polymer of Class 2 type,⁴¹ and this reflected in a reduction of the *a* value to $1.31 \times 10^{-2} \text{ K}^{-1}$. Similarly, data for the two lightest tricyclohexyltin halides (55) and (61) reflect the onset of formation of the rigid Class 1 polymer lattice,^{27,28} relative to the random orientation of molecules in the solid bromide (51) and iodide (52).²⁸ Other workers have 28 found a similar value for *a* for all four $Sn(C_6H_{11})_3X$ (X = halide) (ca. 1.60 × 10⁻² K⁻¹), but in our work we observe a sequential stiffening of the lattice from the chloride $(1.40 \times 10^{-2} \text{ k}^{-1})$ to the fluoride $(0.91 \times 10^{-2} \text{ K}^{-1})$. No detailed assessment of intermolecular bond strengths can be made in terms of the available crystallographic data²⁸ which suffer from crystal decomposition in the X-ray beam, and result in R factors in excess of 0.1. However, our data are entirely consistent with the widely held belief that the strength of the intermolecular bond should increase in parallel with electronegativity of the bridging atom. Furthermore, the relatively low value of a for compound (61) suggests that Class 1 polymers do indeed produce more rigid lattices than similar Class 2 polymers, a phenomenon which has a direct bearing on our initial structural data for $Sn(C_6H_{11})_3(OH)$ (see below).

Compounds of Unconfirmed Structure.—Included in Tables 2 and 3 are structural assignments for lattices for which crystallographic evidence is lacking, based entirely on indirect, spectroscopic measurements, including v.t.M.s. These inferences are largely in accord with those of the original authors, but it is pertinent to comment here both on those compounds for which v.t.M.s. data are recorded for the first time, and where alternative structural possibilities to those offered previously suggest themselves in the light of the present work.

The compound $\text{SnPh}_3(\text{CN})$ (26) ($a = 1.73 \times 10^{-2} \text{ K}^{-1}$) must be monomeric, given that any lattice association would be of Class 1 type. Of the organotin halides (35), (58), and (60), SnPh₃F is presumed to be a polymer on the basis of q.s. data (3.53 mm s⁻¹)⁴² which specify a five-co-ordinated, *trans*-R₃SnX₂ geometry at tin. Since this polymer will be of Class 2 type, we conclude that the intermolecular bond is relatively weak (anisobidentate bridging), resulting in a comparatively high *a* value (1.49 × 10⁻² K⁻¹) for this polymer class. In the case of the two dicyclohexyltin dihalides (58) and (60), v.t.M.s. data suggest polymeric formulations, which are probably doublybridged Class 2 (*cf.* SnMe₂Cl₂⁻³³) rather than Class 1 (*cf.* SnMe₂F₂⁻³¹) in construction.* The two polymeric oxygen-

^{*} Despite the fair analytical data and a m.p. in agreement with the literature value, we are concerned about the authenticity of our $Sn(C_6H_{11})_2F_2$ sample. The q.s. (3.31 mm s⁻¹) seems unreasonably low, particularly when compared to the corresponding chloride (3.40 mm s⁻¹). Moreover, a lower value of *a* than observed would be anticipated on the basis of our results for the tricyclohexyltin halides.

bonded diphenyltin compounds $Ph_2SnOC_6H_4O$ (27) (presumably of *para* stereochemistry), and $SnPh_2O$ (43) both have higher *a* values $(1.73 \times 10^{-2},^{43} 1.15 \times 10^{-2} \text{ K}^{-1})$, respectively) than might have been expected. It seems reasonable then that the former polymer belongs to Class 3 or 4, facilitated by a tetrahedral geometry at tin, and the latter to Class 2, but with little or no cross-linking between chains. Bulky groups on tin are known to reduce the degree of association of diorganotin oxides,^{4b} and in this respect the steric effect of the C₆H₅ groups seems to generate a polymer similar to $SnPr_{12}^{i}S_{12}^{i4}$ rather than a sheet polymer as proposed for $SnMe_2O^{4b}$ ($a = 0.87 \times 10^{-2}$ K⁻¹).²⁴ The compound $SnPh_3(triaz)$ (46) can also be assigned a Class 2 polymer structure ($a = 1.04 \times 10^{-2}$ K⁻¹) corroborated by a *trans*-R₃SnN₂ primary structure as specified by the q.s. data (2.89 mm s⁻¹), and isostructural with $Sn(C_6H_{11})_3(triaz)$.⁴¹

The situation is less clear cut for three pairs of compounds (28) and (57), (42) and (62), and (13) and (54). Of the two triorganotin arylazobenzoates, the triphenyltin derivative (28) has been assigned a monomeric, mer-R₃SnON geometry on the basis of q.s. (3.06 mms⁻¹) and v.t.M.s. ($a = 1.71 \times 10^{-2} \text{ K}^{-1}$) data.¹⁹ That no precedent for this geometry in organotin chemistry exists,⁹ and the acknowledged lack of rationale for the structure change in the light of the structure of the related compound (34),¹⁹ prompts us to offer two alternative structural possibilities. First, a trans-R₃SnO₂ geometry with a Class 3 tertiary structure for the resulting polymer is consistent with both data (despite being previously discounted) and would follow the normal structure adopted by associated organotin carboxylates. This would, however, still fail to explain the reason for the change in structure from that of compound (34). Secondly, a highly distorted six-co-ordinate, mer-R₃SnO₂(OH) geometry, in which the only intermolecular interaction is a long Sn · · · OH bond, which, in conjunction with a Class 2 or 3 type tertiary structure, would maintain the high a value. This latter type of bonding scheme would be plausible, in that the 4-hydroxynaphthyl group in compound (28) would, on steric grounds, be free from the intramolecular hydrogen-bonding role played by the 2-hydroxyphenyl moiety in (34). The general features of this second architecture, which we prefer of the two alternatives, have recently manifest themselves in the structure of $Ph_3SnO_2CC_6H_4(OH)$ -o.⁴⁵ In the case of (57), the tricyclohexyl homologue of (34), the first of the above two alternatives was proposed in the original report to explain the Mössbauer data (q.s. = 3.35 mm s⁻¹, $a = 1.30 \times 10^{-2} \text{ K}^{-1}$).¹⁹ The *a* value however, seems too low for this rationale [*cf*. $Sn(C_6H_{11})_3(O_2CMe)$, $a = 1.59 \times 10^{-2} \text{ K}^{-1}$], unless the lattice receives additional stabilisation, possibly via intermolecular hydrogen bonds.*

The two formates (42) and (62) both show distinctly more rigid lattices ($a = 1.15 \times 10^{-2}$ and 0.93×10^{-2} K⁻¹ respectively) than their acetate counterparts (20) and (53) ($a = 1.91 \times 10^{-2}$ and 1.59×10^{-2} K⁻¹ respectively), and enhanced q.s. values. We have no definitive explanation for these data at present, but speculate that the Class 3 polymer may receive stabilisation involving a more symmetrical six-co-ordinate, *mer*-R₃SnO₃ primary structure than seen in SnPh₃(O₂CMe).¹ We hope to report a crystallographic rationale in the near future.

Still less can be inferred structurally from the v.t.M.s. data alone about the two diphenylphosphinates (13) and (54), which show ln *A vs. T* plots which are markedly curved over the whole temperature range (Figure 1), irrespective of the quantities of sample used in the experiments. Q.s. data for the compounds (3.33 and 3.93 mm s⁻¹ respectively) specify a coordination number at tin greater than four, and the fact that J. CHEM. SOC. DALTON TRANS. 1985



Figure 3. Classification of a values according to lattice type for phenyl-(----) and cyclohexyl-tin compounds (---)

both compounds decompose without melting at *ca.* 300 °C suggests lattice association. The *a* values when the majority of data points are included in the analysis are *ca.* $1.50 \times 10^{-2} \text{ K}^{-1}$ for both compounds (lower values of *a* arising from the effect of the data at 78—110 K) which would suggest polymeric Class 3 structures akin to that of SnPh₃(O₂CMe)¹ and isostructural with SnMe₃[OP(S)Me₂] and SnMe₃(O₂PMe₂).⁴⁶

Finally, we turn our attention to tricyclohexyltin hydroxide (63), one of the commercially marketed organotin agrochemical miticides,^{4a} and which exhibits the lowest *a* value (0.66×10^{-2} K⁻¹) recorded in this study. The compound is unquestionably polymeric, with a *trans*-R₃SnO₂ primary structure (q.s. = 2.99 mm s⁻¹), and in comparison with the analogous Class 2 polymer (44) (Sn-O-Sn 137.8°)²⁵ the lattice is significantly more rigid. Extrapolation of the crystallographic and v.t.M.s. data for compounds (55) and (61) leads us to believe that Sn(C₆-H₁₁)₃(OH) is a Class 1 polymer, in which Sn-O-Sn is *ca.* 180°. Such a structure is consistent with the steric demands of the hydrocarbon groups pendant to the polymer backbone, which must be greater for the chair C₆H₁₁ group than the planar C₆H₅ ring, and suggests that Class 1 polymers are a common feature of tricyclohexyltin chemistry.

Conclusions

Despite the fact that v.t.M.s. a values for different lattice types do not fall into discrete, non-overlapping bands, the interpretation of such data can be aided by consideration of the nature of the (potentially) bridging group(s) and the tertiary structure of any viable polymeric arrangements. A guide to the application of v.t.M.s. data applied to phenyl- and cyclohexyltin compounds can be derived from Figure 3, which collates the available data into groups based upon the different classes of lattice type. The ranges in a values for each class will undoubtedly change as further crystallographic and v.t.M.s. data become available, and in any case only reflect the subjective opinion of the authors as to where the cross-over between an ordered array of non-interacting units and a weakly associated polymer can be drawn.

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^{*} We have observed a parallel trend in the organotin derivatives of indol-3-ylacetic acid, where *a* for SnMe₃(iaa) is $1.35 \times 10^{-2} \text{ K}^{-1}$ (K. C. Molloy and T. G. Purcell, unpublished work).

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