SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF ORGANOTIN COMPOUNDS DERIVED FROM ORGANIC ACIDS

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF ORGANOTIN COMPOUNDS DERIVED FROM ORGANIC ACIDS

by

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LIST OF ABBREVIATIONS

Bu = butyl

d = doublet

FT-IR = Fourier-Transform Infrared

HMQC = Heteronuclear Multiple Quantum Correlation

i = *ipso*

KBr = potassium bromide

m = *meta*

m = multiplet

Me = methyl

NMR = Nuclear Magnetic Resonance

o = *ortho*

p = *para*

Ph = phenyl

ppm = part per million

q = quartet

qn = quintet

s = singlet

sp = species

sx = sextet

t = triplet

TBTO = bis[tributyltin(IV)] oxide

TMS = trimethylsilane

SINTESIS, PENCIRIAN DAN AKTIVITI BIOLOGI SEBATIAN ORGANOSTANUM TERBITAN ASID ORGANIK

ABSTRAK

Sejumlah empat puluh satu kompleks organostanum(IV) karboksilat telah disintesiskan dan dikategorikan dalam **Siri A**, **B** dan **C**. Kompleks disintesiskan menerusi tindak balas kondensasi dialkilstanum(IV) oksida, R_2SnO (R= metil dan butil), bis[tributilstanum(IV)] oksida, $(Bu_3Sn)_2O$ atau trifenilstanum(IV) hidroksida, Ph_3SnOH dengan asid organik yang tertentu. Kompleks yang dihasilkan dicirikan melalui analisis unsur CHN dan Sn, serta kaedah spektroskopi seperti inframerah dan resonans magnet nukleus (^{1}H, ^{13}C, ^{1}H-^{13}C HMQC and ^{119}Sn RMN). Kompleks yang dihasilkan menunjukkan takat lebur yang tajam menandakan kompleks yang dihasilkan adalah tulen. Data analisis unsur yang diperolehi bersetuju dengan formula yang dijangkakan juga menunjukkan kompleks yang disintesiskan adalah tulen. Berdasarkan kombinasi kajian spectrum (data FTIR dan RMN), atom stanum bagi kompleks **3A**, **4A**, **7A**, **8A**, **9A**, **10A**, **13A**, **14A**, **21B**, **25B**, **28C**, **30C**, **32C**, **34C** dan **37C** adalah berkoordinatan empat serta berstruktur tetrahedron terherot. Atom stanum bagi kompleks **12A**, **16B**, **17B**, **18B**, **19B**, **20B**, **22B**, **27C**, **29C**, **31C**, **33C**, **35C** dan **36C** adalah berkoordinatan lima serta berstruktur trigon bipiramid terherot manakala atom stanum bagi kompleks **2A**, **5A**, **11A**, **23B**, **26C**, **38C**, **39C** dan **41C** adalah berkoordinatan enam dan bergeometri oktaheron terherot. Kompleks **15B**, **24B** and **40C** terbitan “organodistannoxane dimers” didapati menunjukkan atom stanum berkoordinatan lima dan enam; ini disebabkan anion karboksilat berikatan dengan atom stanum secara bidentat jenis “titian”. Hanya kompleks **1A** saja yang menunjukkan atom stanum berkoordinatan tujuh dan mempunyai struktur geometri pentagon bipiramid terherot. Dalam kajian ini, sebanyak dua puluh kompleks yang diperolehi dalam bentuk hablur tunggal (**2A**, **3A**, **4A**, **8A**, **10A**, **15B**, **16B**, **19B**, **23B**, **25B**, **27C**, **28C**, **29C**, **31C**, **33C**, **34C**, **35C**, **37C**, **39C** dan **41C**) dan menerusi data hablur tunggal kristalografi sinar-X, struktur dan geometri kompleks dapat dicirikan dengan sempurna.

Kebanyakan atom stanum kompleks adalah berkoordinatan empat, lima dan enam. Walau bagaimanapun, hanya atom kompleks **2A** didapati berkoordinatan tujuh. Secara amnya, kompleks organostanum(IV) karboksilat dalam **Siri A**, **B** dan **C** menunjukkan kesan yang memberangsangkan dalam aktiviti biologi berdasarkan penilaian sitotoksik secara *in vitro*, analisis antibakteria dan antifungus yang telah dijalankan. Secara umumnya, kompleks terbitan triorganostanum(IV) didapati menunjukkan aktiviti biologi yang lebih berkesan berbanding dengan kompleks terbitan diorganostanum(IV). Walau bagaimanapun, dalam aktiviti penilaian antibakteria, didapati bahawa kompleks terbitan diorganostanum(IV) (kompleks **1A**, **5A**, **11A**, **18B**, **22B** dan **38C**) adalah lebih aktif berbanding kompleks terbitan triorganostanum(IV) iaitu bertentangan dengan fakta yang diterima secara meluas bahawa penambahan bilangan kumpulan organo akan memberangsangkan lagi aktiviti biologi kompleks organostanum(IV). Pemerhatian ini mungkin disebabkan oleh kebolehan anion karboksilat berfungsi sebagai agen pengangkutan untuk membawa kumpulan aktif kation organostanum(IV) ke tapak aktif sel.

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF ORGANOTIN COMPOUNDS DERIVED FROM ORGANIC ACIDS

ABSTRACT

A total of forty one organotin(IV) carboxylate complexes were synthesized and categorized in **Series A**, **B** and **C**. The complexes were synthesized by the condensation reaction between dialkyltin(IV) oxide, R_2SnO (R= methyl and butyl), bis[tributyltin(IV)] oxide, $(Bu_3Sn)_2O$ or triphenyltin(IV) hydroxide, Ph_3SnOH with the selected organic acids. The complexes were characterized using CHN and Sn elemental analysis as well as spectroscopic methods such as infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (^{1}H, ^{13}C, ^{1}H-^{13}C HMQC and ^{119}Sn NMR). The complexes possess sharp melting points indicating that they were fairly pure. The elemental analytical and calculated values were in agreement with the predicted formula indicating the complexes are pure. Based on combination of spectral studies (FTIR and NMR data), the tin atoms of complexes **3A**, **4A**, **7A**, **8A**, **9A**, **10A**, **13A**, **14A**, **21B**, **25B**, **28C**, **30C**, **32C**, **34C** and **37C** were four-coordinated and possess a distorted tetrahedral geometry. The tin atoms of complexes **12A**, **16B**, **17B**, **18B**, **19B**, **20B**, **22B**, **27C**, **29C**, **31C**, **33C**, **35C** and **36C** were five-coordinated and possess a distorted trigonal bipyramid geometry. Seven complexes have tin atoms which were six-coordinated with a distorted octahedral geometry (**2A**, **5A**, **11A**, **23B**, **26C**, **38C**, **39C** and **41C**). Complexes **15B**, **24B** and **40C** with organodistannoxane structures possess tin atoms which were five- and six-coordinated due to the carboxylate anions being bonded to the tin atoms in a bidentate bridging manner. Complex **1A** is the only complex with a tin atom which was seven-coordinated with a distorted pentagonal bipyramid geometry. In the present study, twenty complexes were isolated as single crystals (**2A**, **3A**, **4A**, **8A**, **10A**, **15B**, **16B**, **19B**, **23B**, **25B**, **27C**, **28C**, **29C**, **31C**, **33C**, **34C**, **35C**, **37C**, **39C** and **41C**) and from the single crystal data, the structures and geometries of these complexes were established. Most of the tin atoms were either four-, five- or six-coordinated. However, only complex **2A** possess a tin atom which is seven-coordinated.

Overall, all the organotin(IV) carboxylate complexes in **Series A**, **B** and **C** showed significant biological activities based on the *in vitro* cytotoxic assays and on the antibacterial and antifungal screening activities. In general, among the tri- and di-organotin(IV) complexes, the triorganotin(IV) derivatives were found to display higher biological activities. However, in antibacterial screening study, diorganotin(IV) derivatives (complexes **1A**, **5A**, **11A**, **18B**, **22B** and **38C**) were found to be more active compared to the triorganotin(IV) derivatives which contradicts with the widely accepted norm that the increase in the number of organo groups enhances the biological activities of the organotin(IV) complexes. This observation may be due to the role of the anionic ligands in facilitating the transportation of the active organotin(IV) cationic group to the active sites of the cell.

CHAPTER ONE

INTRODUCTION

1.1 Tin (Stannum)

In chemistry, tin is referred to as “Stannum” and this element is given the symbol “Sn”. Tin is a member of Group 14 in the Periodic Table along with carbon (C), silicon (Si), germanium (Ge) and lead (Pb) (Cotton *et al.*, 1995). Tin has a relative atomic mass of 118.9, an atomic number of 50 and a covalent radius of 139 pm (Yamin, 1996; Cotton *et al.*, 1995). Tin has an electronic configuration of $[Kr]4d^{10}5s^{2}5p^{2}$ and exists in valence 2 and 4. Hence, the two typical types of oxidation states of a tin atom is +II and +IV (Harrison, 1989). Tin has the largest number of isotopes compared to the other elements in the Periodic Table. Tin has ten stable isotopes and twenty-one unstable isotopes (Harrison 1989). Many unstable isotopes possess half-lives from 132 seconds to 1 x 10^5 years. Among the stable isotopes, ^{115}Sn (μ= 0.9132), ^{117}Sn (μ= -0.9949) and ^{119}Sn (μ= -1.0409), each has a spin quantum number of ½ (Yamin, 1996). Although tin is indisputably a main group element, tin has the transition metal characteristics (Martins *et al.*, 2002). It is well documented that higher coordination numbers for Sn(IV) were possible since the vacant 5*d* orbitals have a suitable/lower energy which may be used in the hybridization or coordination to form stable complexes (Harrison, 1989; Cotton *et al.*, 1995).

1.2 History and the development of organotin complexes

The chemistry of organotin complexes was explored more than a hundred years ago. Lowig prepared the first organotin compound in 1852 (Evans and Karpel, 1985). However, Sir Edward Frankland (1825-1899) carried out the detailed studies of organotin. Sir Edward Frankland prepared diethyltin diiodide (1853) and tetraethyltin (1859) and he gained credit of the first comprehensive study of organotin (Evans and Karpel, 1985; Yamin, 1996). Even after the discovery of organotin nearly a century, the interest and studies of organotins remained as laboratory curiosities.

Organotin complexes were recognized worldwide in conjunction with the PVC industry. Since diorganotin complexes possess the ability to inhibit the degradation of PVC due to heat and ultra-violet light (Blunden *et al.*, 1985; Evans and Karpel, 1985), they were employed as PVC stabilisers in USA (1940s), UK (1951), Europe and Japan (mid-1950s) (Evans and Karpel, 1985). Consequently, the world production of dibutyltin stabilisers in 1957 reached 1000-2000 tonnes (Evans and Karpel, 1985). Due to the large production worldwide, the applications of organotin complexes in industrial areas expanded tremendously especially in wood preservation, antifouling systems, agricultural chemicals, medical uses, catalysts, glass industry, pharmaceuticals and other miscellaneous biocidal uses (Poller, 1970; Evans and Karpel, 1985; Blunden *et al.*, 1985; Harisson, 1989). At the same time, the biological activities of organotin complexes have been stemmed from the systematic study at the Institute for Organic Chemistry, TNO, Utrecht by the International Tin Research Council under Professor G.J.M. van der Kerk and Luijten in 1950 (Evans and Karpel, 1985).

1.3 Organotin(IV) compounds

Organotin compounds can be described as compounds containing at least one direct tin-carbon bond (Sn-C). In general, the tin atom in most organotin compounds has the +4 oxidation state whereas the +2 oxidation state is only common in a few organotin compounds (Evans and Karpel, 1985). In addition, the coordination number of Sn(IV) are four (tetrahedral), five (trigonal bipyramid), six (octahedral) and seven (pentagonal bipyramid). However, Sn(IV) complexes with a coordination number of eight and with a geometry of a hexagonal bipyramid was previously reported but rarely found (Harrison, 1989). Four series of organotin(IV) compounds, monoorganotin(IV) containing of one Sn-C bond; diorganotin(IV) containing of two Sn-C bonds; triorganotin(IV) containing of three Sn-C bonds and finally tetraorganotin(IV) containing of four Sn-C bonds, have been well documented (Evans and Karpel, 1985; Harrison, 1989; Yamin, 1996). They were simplified as $RSnX_3$, R_2SnX_2, R_3SnX and R_4Sn (R= orgono derived from alkyl or aryl; X= halogen or coordinating compounds).

Organotin(IV) compounds act as Lewis acids (Poller, 1970; Graddon and Rana, 1977). The tin atom has *d* orbitals with low energy which enabled it to expand its coordination number beyond four. The phenomenon of organotin(IV) compounds acting as Lewis acids could be explained based on the following two reasons. Most of the organotin(IV) compounds form stable complexes when adducted with Lewis bases and reactions involving nucleophilic attack at the tin atom lower the energy of the transition state (Poller, 1970; Roy and Ghosh, 1978). The ability of tin to form stable complexes depends on the electronegativity of the substituents. As a result, the acceptor strengths of the halides are in the order of $SnCl_4 >> SnBr_4 > SnI_4$ (Poller, 1970). When the chlorine atoms in $SnCl_4$ are substituted with electropositive organic groups, the ability of the acceptor strength in forming complexes are in the descending order of $SnCl_4 > RSnCl_3 > R_2SnCl_2 > R_3SnCl$, $Ph_3SnCl > Bu_3SnCl$ and $PhSnCl_3 > MeSnCl_3 > BuSnCl_3$ (Poller, 1970).

Generally, the tin-carbon bonds are weaker and more polar compared with those in organic compounds of carbon, silicone or germanium. However, the tin-carbon (Sn-C) bonds are stable to water, atmospheric oxygen at normal temperature and are also quite stable to heat. Usually, the cleavage of the Sn-C bonds occurs when strong acids, bases, halogens and other electrophilic reagents are applied (Poller, 1970; Evans and Karpel, 1985; Harrison, 1989; Song *et al.*, 2005). In addition, the cleavage of the Sn-C bonds into non-toxic tin in the environment maybe due to photolysis by sunlight, ultraviolet and biological activities of certain bacteria (Hoch, 2001). In addition, among the four series of organotin(IV) compounds, organotin(IV) complexes with the general formulae of R_2SnX_2 and R_3SnX are easily hydrolyzed. The anions, X^-, would be separated while the Sn-C bond remained stable (Evans and Karpel, 1985).

1.4 Preparation of organotin(IV) carboxylate complexes

Organotin(IV) carboxylate complexes are also known as organotin(IV) esters due to the presence of the O-C=O group in these complexes which are similar to that found in esters generated via organic synthesis (Poller, 1970; Yamin, 1996). In addition, water molecules are produced as the side product when organotin(IV) oxides or hydroxides are introduced during the synthesis of organotin(IV) carboxylate complexes (Win *et al*., 2003; Yip *et al*., 2006). Generally, organotin(IV) carboxylate complexes are isolated as solids with low melting points. Most of all the parent organotin(IV) compounds are colourless, except for organotin(IV) carboxylate complexes which depend on the ligands or acids used in the reaction (Ford *et al*., 1969, Win *et al*., 2003; Win *et al*., 2007b).

Various methods and techniques have been employed in the preparation of organotin(IV) carboxylate complexes (Poller, 1970; Cohen and Dillard, 1970; Roy and Ghosh, 1977; Calogero *et al*., 1977; Yamin, 1996). The reaction between Grignard reagents, containing either aliphatic or aromatic groups, and organotin(IV) halides in dry ethyl ether, usually gives high yields of unsymmetrical organotin(IV) compounds. Moreover, for bulky organo groups, toluene or benzene are used as the solvents in the preparation of the complexes (Ingham *et al*., 1960).

In the present study, simple and economic reactions to synthesize organotin(IV) carboxylate complexes were carried out. Generally, a few simple techniques could be applied. Organotin(IV) carboxylate complexes can be prepared by the esterification of carboxylic acids with organotin(IV) oxide or organotin(IV) hydroxide (Win *et al*., 2006a; Win *et al*., 2007a). Another well known method is the reaction of organotin(IV) halide with respective carboxylic acids (Teoh *et al*., 1996a; Teoh *et al*., 1999). Another important preparation technique is the reaction between organotin(IV) halides and alkali metals or the silver salts of the respective carboxylic acids (Poller, 1970; Yamin, 1996). The general reaction schemes of the preparation of organotin(IV) carboxylate complexes are depicted in Figure 1.1.

$$(R_3Sn)_2O + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O$$

$$R_3SnOH + R'COOH \longrightarrow R_3SnOCOR' + H_2O$$

$$R_4SnCl_{4-n} + (4-n)MOCOR' \longrightarrow R_nSn(OCOR')_{4-n} + (4-n)MCL$$

R= organic groups attached to tin atom
R'= organic groups belong to carboxylic acid
M= metal such as Na, Ag, K, Pb

Figure 1.1: General reaction schemes of the preparation of organotin(IV) carboxylate complexes

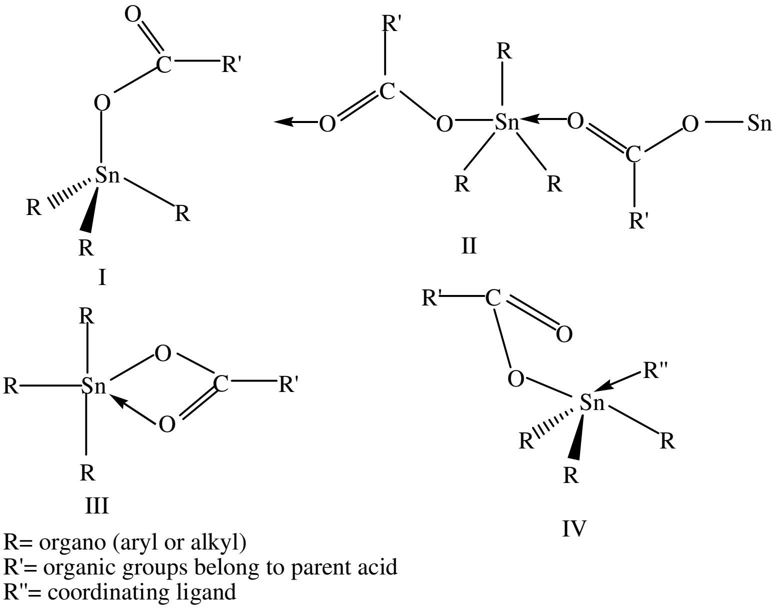
Most of the time, esterification involving the condensation of water is employed for the synthesis of organotin(IV) carboxylate complexes. The water molecules, liberated from the reaction, were easily removed by azeotropic dehydration using the Dean and Stark apparatus (Parulekar *et al.*, 1990; Baul *et al.*, 2001; Win *et al.*, 2006c). In addition, molecular sieves were also employed by some researchers to remove the water molecules (Samuel-Lewis *et al.*, 1992; Win *et al.*, 2003; Win *et al.*, 2006c). Moreover, hydrogen halides (HX) produced during the reaction, were removed by adding amines or pyridine (HX acceptor) (Yamin, 1996).

1.5 Structure of organotin(IV) carboxylate complexes

Various organotin(IV) carboxylate complexes have been well documented as a result of expanding industrial applications as well as its biological activities (Evans and Karpel, 1985; Blunden *et al.*, 1985; Jacques and Poller, 1989; Gielen, 1996; Nath *et al.*, 1999; Nath *et al.*, 2005; Ronconi *et al.*, 2002; Ronconi *et al.*, 2003; Xanthopoulou *et al.*, 2003; Duong *et al.*, 2006). Moreover, the main focus is on the structures of the organotin(IV) carboxylate complex derivatives of triorganotin(IV) and diorganotin(IV). In addition, the structures of the organotin(IV) carboxylate complexes mainly depend on the stoichiometry of the reactions.

1.5.1 Triorganotin(IV) carboxylate complexes

Generally, triorganotin(IV) carboxylate complexes are prepared by a 1:1 stoichiometry reaction between triorganotin(IV) halide or hydroxide [triphenyltin(IV)] and carboxylic acids (Poller, 1970; Ng and Zuckerman, 1983; Sandhu and Verma, 1987b; Yeap and Teoh, 2003; Tian *et al.*, 2005; Win *et al.*, 2006c). Moreover, triorganotin(IV) carboxylate complexes were also isolated from a 1:2 stoichiometry reaction between carboxylic acids and bis[tributyltin(IV)]- or bis[triphenyltin(IV)] oxide (Ng *et al.*, 2000; Pruchnik *et al.*, 2003; Baul *et al.*, 2004b; Win *et al.*, 2006c). Basically, the organic group attached to the tin(IV) atom moiety are aryl such as phenyl or alkyls such as methyl, ethyl, propyl, butyl or octyl (Sandhu and Verma, 1987b; Molloy, 1988; Teoh *et al.*, 1999a; Baul *et al.*, 2004a; Chalupa *et al.*, 2006; Win *et al.*, 2006c). Generally, triorganotin(IV) carboxylate complex derivatives exist either in a polymeric form in which the tin(IV) atom moiety is five-coordinated or in a monomeric structure in which the tin(IV) atom moiety is either four- or five-coordinated (Ford *et al.*, 1969; Baul *et al.*, 2004b; Win *et al.*, 2006c). These two types of structures are dependent on the carboxylate groups attached to the tin(IV) moiety (Molloy, 1988). The general structures of triorganotin(IV) carboxylate complexes are depicted in Figure 1.2.



R= organo (aryl or alkyl)
R'= organic groups belong to parent acid
R''= coordinating ligand

Figure 1.2: General structures of triorganotin(IV) carboxylate complexes

Trialkyltin(IV) carboxylates, existing in a polymeric structure via the carboxylic group has been well documented (Schubert, 1978; Ng *et al.*, 1988; Huber *et al.*, 1989; Linden *et al.*, 2005; Chalupa *et al.*, 2006). One of the C-O groups was bonded to the tin(IV) atom moiety while the adjacent tin(IV) atom moiety was bonded by the C=O group (Huber *et al.*, 1989; Baul *et al.*, 2004b; Win *et al.*, 2006c). As a result, the carboxylate groups served as a bridge in connecting the two tin(IV) atom moieties (Ng *et al.*, 1991a; Baul *et al.*, 2004b; Angiolini *et al.*, 2004). Hence, the tin(IV) atom moieties were five-coordinated and existed in a trigonal bipyramid geometry (Ng *et al.*, 1991c; Baul *et al.*, 2004b; Angiolini *et al.*, 2004). Trialkyltin(IV) carboxylates which naturally occur in a monomeric structure are rarely found. Figure 1.3 depicts the polymeric structure of the bis[trimethyltin(IV)] malonate complex which was isolated by Schubert in 1989 and was found to be similar to Structure II (Figure 1.2). The complex in Figure 1.3 was able to form a polymer structure due to the methyl groups which were small and did not contribute much to the steric effect (Poder and Sams, 1969). In addition, Harrison and Philips, (1979) in their studies on trimethyltin(IV) 2-pyridylcarboxylate monohydrate, also revealed that the title complex was polymeric and similar to Structure II (Figure 1.2).

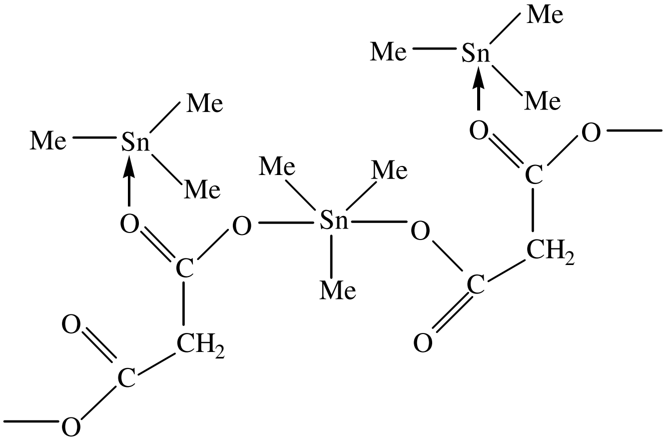


Figure 1.3: Polymeric structure of bis[trimethyltin(IV)] malonate complex

It is not surprising that there are plenty of tributyltin(IV) carboxylate complexes have been well documented (Nádvorník *et al.*, 1984; Ng *et al.*, 1991c; Yoder *et al.*, 1993; Baul *et al.*, 2004b;

Angiolini *et al.*, 2004). Most of the tributyltin(IV) carboxylate complexes were also found to exist in a polymeric structure, with the tin(IV) atom moiety being five coordinated while the carboxylate groups served as bridging bidentate ligands (Nádvorník *et al.*, 1984; Ng *et al.*, 1991c; Yoder *et al.*, 1993; Baul *et al.*, 2004b; Angiolini *et al.*, 2004). It is believed that the bulky butyl groups underwent self arrangement in a planar position in order to enable the carboxylate groups to act as a “bridge” in connecting another adjacent tin(IV) atom moiety (Ng *et al.*, 1991c; Yoder *et al.*, 1993; Angiolini *et al.*, 2004). Generally, the butyl groups occupied the equatorial (basal) position while the carboxylate groups occupied the axial (apical) position (Win *et al.*, 2006c). Figure 1.4 exhibits the polymeric structure of the 2-pyridinecarboxylatotributyltin(IV) complex.

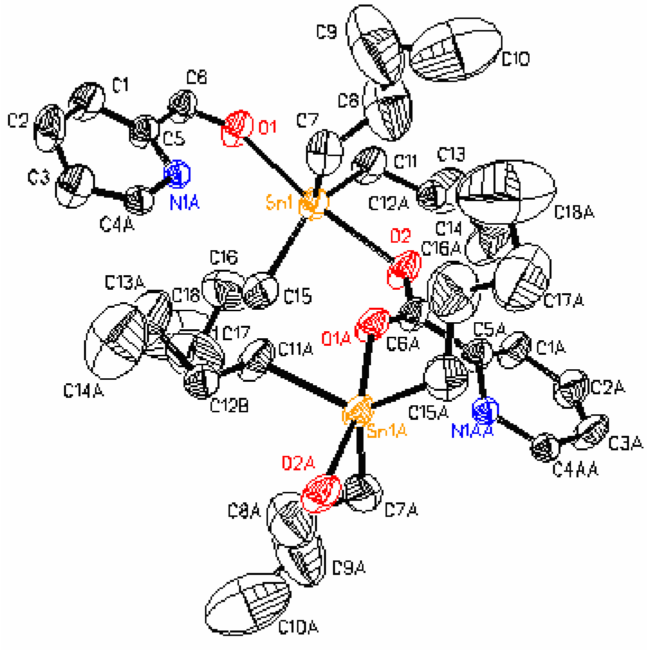


Figure 1.4: Polymeric structure of 2-pyridinecarboxylatotributyltin(IV) complex (Win *et al.*, 2006c)

There has been considerable interest in the structure of triphenyltin(IV) carboxylate complexes. This is due to the ability of triphenyltin(IV) carboxylate complexes existing in the form of either Structure I, Structure II or Structure III (Figure 1.2) (Baul *et al.*, 2001; Yeap and Teoh, 2003; Yin *et al.*, 2005a; Rehman *et al.*, 2005a; Win *et al.*, 2007a; Win *et al.*, 2007e). Interestingly, most of the triphenyltin(IV) carboxylate complexes exist in a four-coordinated monomeric structure with a tetrahedral geometry (Rehman *et al.*, 2005a; Win *et al.*, 2006b; Win *et al.*, 2007a). No doubt, there are some reports indicating that triphenyltin(IV) carboxylate complexes have also been isolated in either a five coordinated monomeric or polymeric structure (Molloy *et al.*, 1984; Ng and Kumar Das, 1993; Yin *et al.*, 2004; Tian *et al.*, 2005; Szorcsik *et al.*, 2006; Win *et al.*, 2007e).

In 1987, Sandhu and his co-workers, in their study indicated that triphenyltin(IV)- and tricyclohexyltin(IV) carboxylate complexes existed in a four-coordinated monomeric structure with a tetrahedral geometry similar to Structure I (Figure 1.2). In addition, Kemmer *et al.* (2001) and Baul *et al.* (2001) in their studies also revealed that their triphenyltin(IV) carboxylate derivatives also existed in a monomeric four-coordinated structure. Generally, the carboxylate anion bonds to the tin(IV) atom moiety via an oxygen atom, resulting in the carboxylate anion exhibiting a monodentate mode of chelation (Samuel-Lewis *et al.*, 1991; Baul *et al.*, 2001; Win *et al.*, 2006b; Win *et al.*, 2007b). Moreover, triphenyltin(IV) carboxylate complexes exist as a four coordinated monomeric structure due to the steric effects of the bulkiness of the phenyl group bonded to the tin(IV) atom, hence prohibiting the formation of the polymeric structure (Baul *et al.*, 2001; Win *et al.*, 2004; Yip *et al.*, 2006). The 2-amino-5-nitrobenzoatotriphenyltin(IV) complex is depicted in Figure 1.5 as a representative structure for the four-coordinated monomeric structure of triphenyltin(IV) carboxylate.

Some of the triphenyltin(IV) carboxylates also occur as a monomeric five coordinated structure with a trigonal bipyramid geometry as depicted in Figure 1.2 (Structure III and IV) which are rarely found. For Structure III, the carboxylate anion is bonded to the tin(IV) atom moiety in a bidentate manner. Win *et al.* (2006b) has reported the 3,5-dinitrobenzoate anion being bonded to the triphenyltin(IV) cation in a bidentate mode. However, from the X-ray crystallography structure determination at 298K, the angle occupied by the tin(IV) atom moiety is a tetrahedral geometry. It is believed that the carboxylate anion exhibited a long-range interaction with the tin(IV) atom via the C=O group. As a result, the 3,5-dinitrobenzoatotriphenyltin(IV) complex remained as a monomeric four-coordinated structure with a long range coordinating from the C=O group. The 3,5-dinitrobenzoatotriphenyltin(IV) complex is depicted in Figure 1.5 as a representative.

In addition, there are a number of well documented literature indicating triphenyltin(IV) carboxylate complexes existing in a monomeric five-coordinated structure like Structure IV (Holeček *et al.*, 1983b; Yin *et al.*, 2005a). The Structure IV indicated that the carboxylate anions in monodentate mode and an extra coordination are contributed from the coordinating ligands (Holeček *et al.*, 1983b). The coordinating ligands may be derivatives of coordinating solvents such as methanol, ethanol and etc. or from pyridine derivatives or amine (Ng *et al.*, 1989b; Ng *et al.*, 1991b; Yeap and Teoh, 2003; Szorcsik *et al.*, 2006; Álvarez-Boo *et al.*, 2006). The 2-methyl-3-aminobenzoatotriphenyltin(IV) methanol solvate complex is depicted in Figure 1.5 as a representative of triphenyltin(IV) carboxylate complexes with a methanol molecule as the coordinating solvent.

There are well documented literature indicating triphenyltin(IV) carboxylates were able to form polymeric structures (Ford *et al.*, 1969; Ford and Sams, 1971; Molloy *et al.*, 1984; Tian *et al.*, 2005). The carboxylate anions act as a bridging bidentate ligand in the bonding to the neighbouring tin(IV) atom moiety resulting in a polymeric structure with a trigonal bipyramid geometry (Molloy *et al.*, 1984; Tian *et al.*, 2005; Yin *et al.*, 2004; Win *et al.*, 2007e). It is believed that the phenyl groups undergo self-rearrangement to reduce the steric effects, hence enabling the carboxylate anions to coordinate to the adjacent tin(IV) atom moiety resulting in the polymeric structure.

As a result, the triorganotin(IV) carboxylate complexes exist either as Structure I, II, III or IV as depicted in Figure 1.2. For triorganotin(IV) carboxylate complexes which possess tetrahedral geometry, the tin atom underwent sp^3 hybridization. Hence, the p_x and p_y orbitals were used for bonding between the tin atom with the aryl or alkyl group while the p_z orbital would be involved in forming the Sn-O bond (Ford *et al.*, 1969). For triorganotin(IV) carboxylate complexes which is five-coordinated with a trigonal bipyramid geometry, the tin atom would be sp^3d hybridized. Consequently, the p_z and d_z^2 would be involved in the formation of the Sn-O bonds (Harrison, 1989; Cotton *et al.*, 1995).

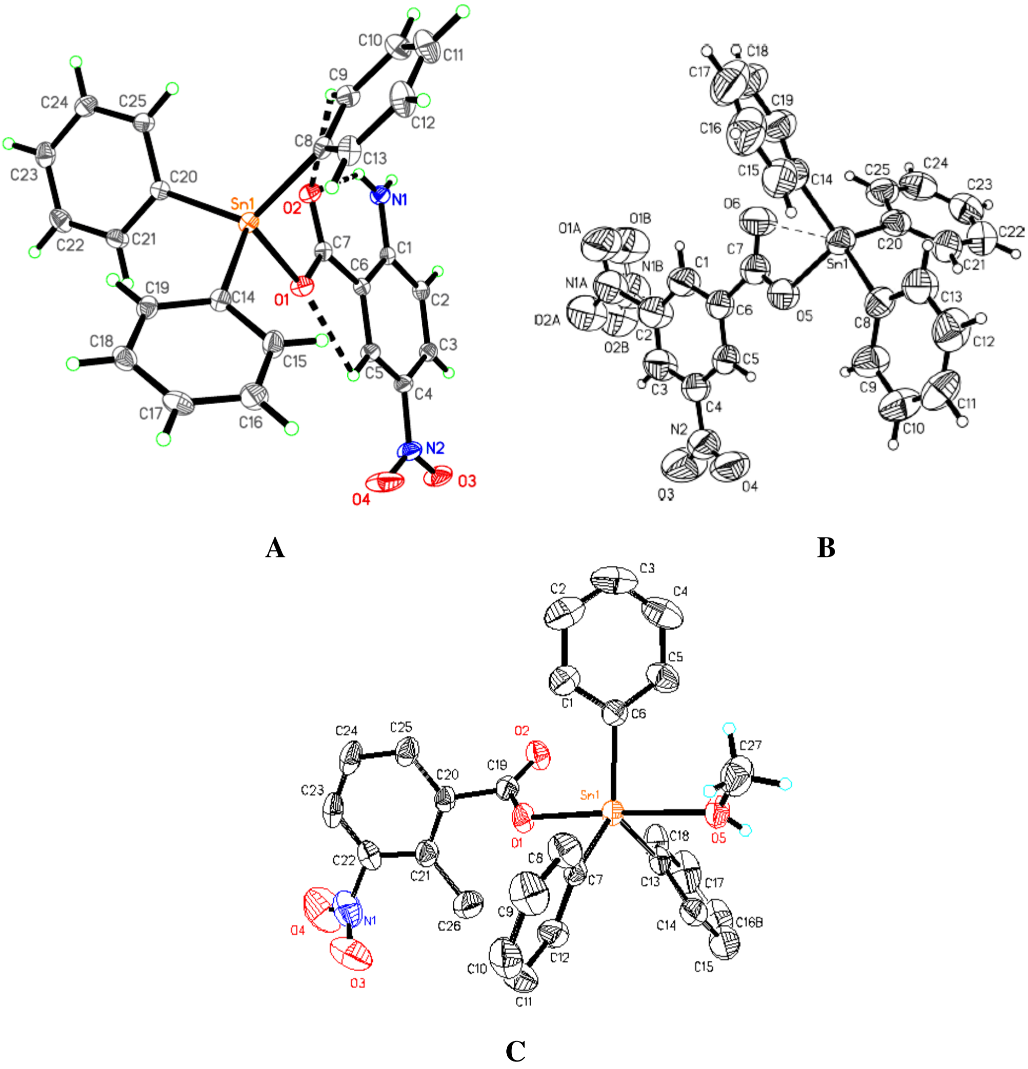
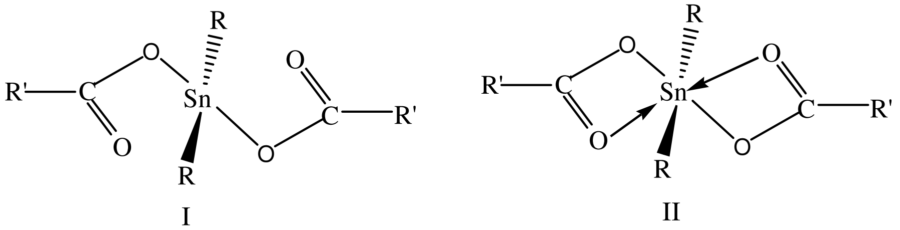


Figure 1.5: (**A**) 2-amino-5-nitrobenzoatotriphenyltin(IV) complex with a four-coordinated monomeric structure (Win *et al.*, 2007b)
(**B**) 3,5-dinitrobenzoatotriphenyltin(IV) complex with a five-coordinated monomeric structure (Win *et al.*, 2006b)
(**C**) 2-methyl-3-nitrobenzoatotriphenyltin(IV) methanol solvate complex with a five-coordinated monomeric structure

1.5.2 Diorganotin(IV) carboxylate complexes

The reaction between diorganotin(IV) and organic acids in a 1:2 stoichiometry reaction yields monomeric diorganotin(IV) dicarboxylate complexes whereas reaction carried out in a 1:1 molar ratio gives a dimeric complex (Ng *et al.*, 1989d; Parulekar *et al.*, 1990; Gielen *et al.*, 1994; Teoh *et al.*, 1996a; Kapoor *et al.*, 2001; Dokorou *et al.*, 2001; Kovala-Demertzi *et al.*, 2001). Generally, diorganotin(IV) dicarboxylate complexes isolated from a 1:2 molar ratio reaction have monomeric structures (Ng *et al.*, 1987; Teoh *et al.*, 1997a; Win *et al.*, 2006a; Win *et al.*, 2007f). The carboxylate anions bonded to the tin(IV) atom either in a monodentate or bidentate mode via the oxygen atoms (Win *et al.*, 2006a; Win *et al.*, 2007c). The structure of the diorganotin(IV) dicarboxylate complexes isolated from a 1:2 molar ratio reaction is depicted in Figure 1.6.



R= organo (aryl or alkyl)
R'= organic groups belong to parent acid

Figure 1.6: Monomeric structure of diorganotin(IV) complexes

The tin(IV) atom moiety would be six-coordinated with a distorted octahedral geometry when both of the oxygen atoms of the carboxylate anions are bonded to the tin atom in a bidentate manner as shown in Structure II (Figure 1.6) (Howard *et al.*, 1985; Sandhu *et al.*, 1991a; Win *et al.*, 2006a; Rehman *et al.*, 2006). Vatsa *et al.*, (1991b) is his studies synthesized $R_2Sn(O_2CC_4H_3S)_2$ and $R_2Sn(O_2CC_4H_3O_2)_2$ (R= methyl, ethyl, propyl and butyl) and found that the structures of these complexes were monomeric, six-coordinated which were analogues to Structure II (Figure 1.6). In addition, complexes $Bu_2Sn(O_2CCH_2SC_6H_5)_2$, $Ph_2Sn(OCOMe)_2$ and $Bu_2Sn(OCOEt)_2$ have tin(IV) atoms which are six-coordinated; two bonds attributed to Sn-C while the other four bonds were attributed to Sn-O (Graddon and Rana; 1977; Sandhu *et al*., 1989). Recently, the crystal structure of bis(2-amino-5-nitrobenzoato)dibutyltin(IV), isolated by Win *et al*., (2006a) also indicated that the structure of the title complex was six-coordinated and tally with documented literature on this type of structures (Ng *et al*., 1987; Teoh *et al*., 1996a; Yahyi *et al*., 2001). The tin(IV) atom underwent sp^3d^2 hybridization and the oxygen atom of the C=O group of the carboxylate anions coordinated to the tin atom due to the vacant *d* orbitals (Harrison, 1989; Cotton *et al*., 1995). The molecular structure of the bis(2-amino-5-nitrobenzoato)dibutyltin(IV) complex is shown in Figure 1.7 as a representative of a six-coordinated monomeric structure.

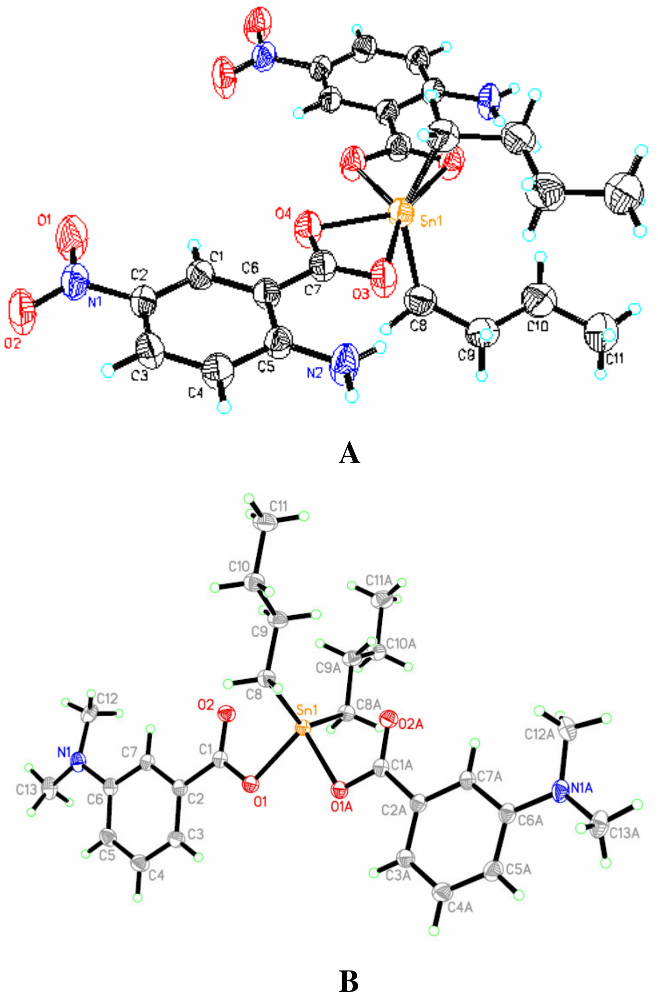
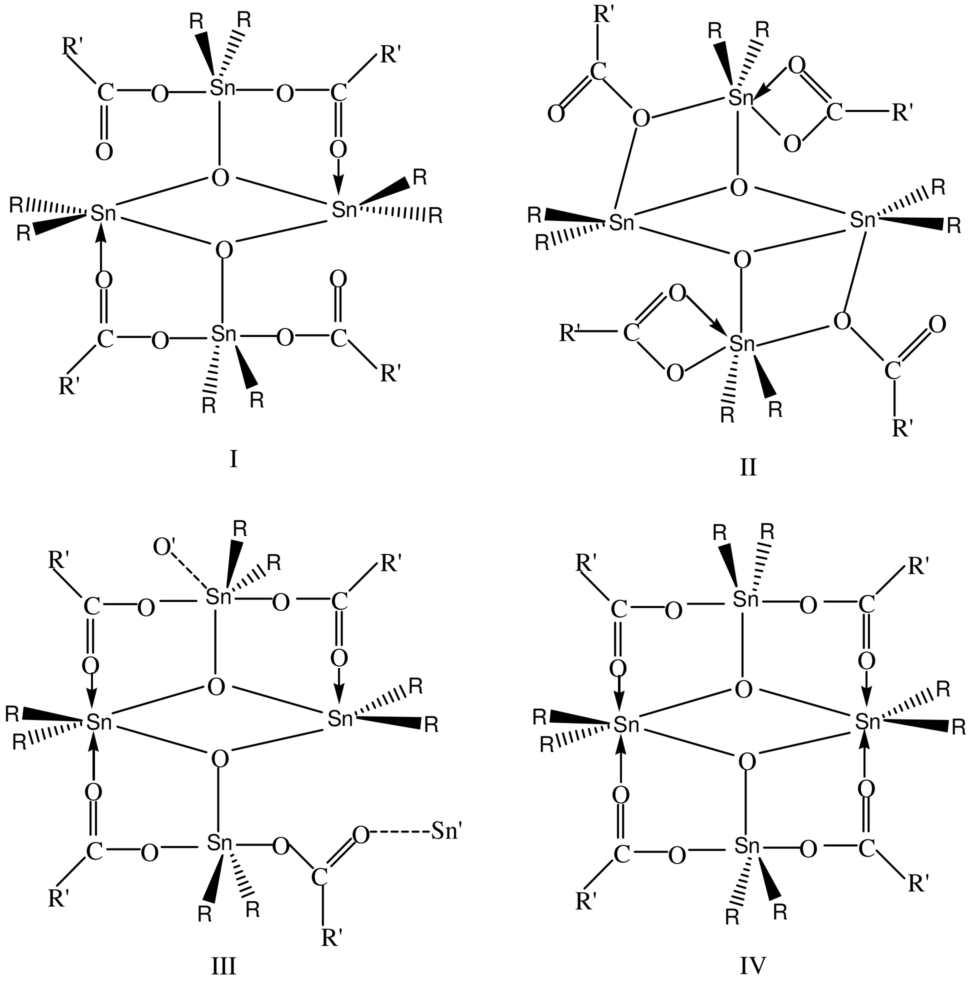


Figure 1.7: (**A**) bis(2-amino-5-nitrobenzoato)dibutyltin(IV) complex with a six-coordinated tin atom moiety (Win *et al*., 2006a)
(**B**) bis{3-(dimethylamino)benzoato}dibutyltin(IV) complex with a four-coordinated tin atom moiety (Win *et al*., 2007c)

There is the possibility of the diorganotin(IV) dicarboxylates isolated from a 1:2 molar ratio reaction to exists in a monomeric four-coordinated structure (Win *et al.*, 2007c; Win *et al.*, 2007d). Even though this kind of structure is rare but it does exist naturally. Recently, Win *et al.*, (2007c) has successfully synthesized the bis{3-(dimethylamino)benzoato}dibutyltin(IV) complex. The X-ray crystallograpic structural study at 273K indicated that the tin atom moiety was four-coordinated with only one oxygen atom from each carboxylate anions coordinating to the tin(IV) atom moiety while the other two bonds were attributed to the Sn-C bonds (Win *et al.*, 2007c). The molecular structure of the bis{3-(dimethylamino)benzoato}dibutyltin(IV) complex is shown in Figure 1.7 as a representative of a four-coordinated monomeric structure.

In general, there are many well-documented structures on complexes isolated from the 1:1 molar ratio reaction between diorganotin(IV) and the respective organic acids. Commonly, this dimeric structure is known as organodistannoxane dimer (Vatsa *et al.*, 1991c; Danish *et al.*, 1995b; Teoh *et al.*, 1996b; Li *et al.*, 2006; Khoo and Hazell, 1999; Parvez *et al.*, 2004). The organodistannoxane dimer type can exist in four common structures but there are other structures which do exist (Candrasekhar *et al.*, 2002). These four common organodistannoxane dimer structures are mainly dependent on the coordination mode of the carboxylate anions which play an important role in the structure elucidation (Candrasekhar *et al.*, 2002). Figure 1.10 represents the major structures of the organodistannoxane dimer types (Candrasekhar *et al.*, 2002).

Vasta *et al.*, (1990) has successfully prepared and characterized the organodistannoxane dimer complexes with a general formulae of $\{[R_2Sn(O_2CR')]_2O\}_2$ (R= Me, Et, ^{n}Pr and ^{n}Bu; R'= thiophene and furan) by using X-ray crystallography. Sandhu *et al.*, (1991a) was also successful in synthesizing some organodistannoxane dimers with the formulae $\{[R_2Sn(A)]_2O\}$ (A = the anion of monochloroacetyl-1-phenylalamine and R = Me, ^{n}Pr, ^{n}Bu and ^{n}Oct). Both researchers revealed that the core geometry of the organodistannoxane dimer complexes consists of a centrosymmetric group planar Sn_2O_2 bonded to the exo- and endocyclic tin(IV) atom moiety via the bridging oxygen atoms so that the oxygen atoms are tri-coordinated. In addition, in 1996 and 2002, Teoh *et al.*, reported on the crystal structures of tetrabutylbis(thiophenegloxylato)distannoxane and tetrabutylbis(3,5-dichloro-4-hydroxybenzoato)distannoxane dimer (Teoh *et al.*, 1996b; Teoh *et al.*, 2002). Both structures revealed the presence of centrosymmetric group planar Sn_2O_2 and have the similar pattern as reported by Sandhu *et al.*, (1991a) and Vatsa *et al.*, (1990).



R= organo (aryl or alkyl)
R'= organic groups belong to parent acid

Figure 1.8: General structures of organodistannoxane dimer type complexes

Moreover, the coordination number of the tin(IV) atom moieties of the organodistannoxane dimers was either five-coordinated with a trigonal bipyramid geometry or six-coordinated with a distorted octahedral geometry (Danish *et al.*, 1995b; Candrasekhar *et al.*, 2002; Win *et al.*, 2008). Obviously, the coordination number of the tin(IV) atom moieties in the organodistannoxane dimers are mainly dependent on the coordination manner of the carboxylate anions which is either monodentate, bidentate or bridging bidentate modes in the molecule which in turn results in the different type of structures obtained (Danish *et al.*, 1995b; Candrasekhar *et al.*, 2002; Win *et al.*, 2008).

1.6 Characterization of organotin(IV) carboxylate complexes

1.6.1 Infrared spectroscopy

Characteristic infrared absorption frequencies (cm^{-1}) can be utilised to investigate the nature of the –COO group coordination mode to the tin atom as well as the characteristic features or functional groups present in the organotin(IV) carboxylate complexes. The C-H stretching region (3340-2700 cm^{-1}) is usually the first region to be diagnosed in the infrared spectral characterization since its reveals the essential structural features present in complexes. Absorption above 3000 cm^{-1} indicates unsaturation or the presence of benzene or phenyl groups. Saturated hydrocarbons have the characteristic C-H stretching frequencies below 3000 cm^{-1}. The methyl group, $-CH_3$, has asymmetric and symmetric C-H stretching frequencies near 2960 cm^{-1} and 2870 cm^{-1} respectively. Moreover, the asymmetric and symmetric C-H stretching bands of the methylene group, $-CH_2-$, are centred at 2930 cm^{-1} and 2850 cm^{-1} respectively (Bellamy, 1975; Colthup *et al.*, 1990; Kamaliah and Noorsaadah, 1997; Pavia *et al.*, 2001; Zou *et al.*, 2001).

It is important to characterize the parent acids or the precursors in order to observe the shifting of the important functional groups before and after complexation. It is an indicator to know if the reaction or complexation was successful or not. As usual, carboxylic acids show a broad ν(OH) stretching absorption due to the carboxylic group (COOH) at 2500-3100 cm^{-1} (Bellamy, 1975; Pavia *et al.*, 2001). The ν(O-H) bands are absent from the infrared spectra of complexes, thus indicating the deprotonation and coordination of the carboxylate anion to the tin atom moiety as reported (Pettinari *et al.*, 1998a; Teoh *et al.*, 1999a; Ma *et al.*, 2006a; Win *et al.*, 2006c). It has been well documented that when an ester is produced from a carboxylic acid, the C=O and C-O bonds are replaced by two equivalent carbon-oxygen bonds of intermediate C=O and C-O bond strengths. This gives rise to the asymmetric and symmetric COO stretching vibrations observed between 1750-1540 cm^{-1} and 1450 -1300 cm^{-1} respectively (Teoh *et al.* 1999a; Win *et al.*, 2003; Yip *et al.*, 2006). The mode of coordination of the carboxylate anion to the tin atom is deduced from the two distinctively strong $\nu(COO)_{as}$ and $\nu(COO)_{s}$ stretching bands observed in the infrared spectra of the complexes.

The magnitude of $\Delta\nu = [\nu(COO)_{as} - \nu(COO)_{s}]$ is an useful indicator in the correlation of the coordination modes of the carboxylate anion to the tin atom in the organotin(IV) carboxylate complexes (Sandhu and Verma, 1987b; Teoh *et al.* 1999a; Szorcsik *et al.* 2004a). Sandhu and Verma (1987b) in their studies have shown that the Δν value of complexes is greater by 65-90 cm^{-1} compared to their sodium salts indicating either asymmetric or monodentate bonding of the carboxylate group to the tin(IV) atom. For complexes with Δν values being comparable or slightly higher by at most 50 cm^{-1} than those of the sodium salts, the carboxylate groups chelate bidentately to the tin atom (Sandhu and Verma, 1987b). The $\nu(COO)_{as}$ of the organotin(IV) carboxylate complexes shifted to lower wave length numbers compare to the parent acids indicating that the coordination took place via the oxygen atoms of the carboxylate anion. Moreover, the are some distinctive characteristics of the Δν value for triphenyltin(IV) carboxylate complexes. Well-documented literature reviews indicate that for complexes derived from triphenyltin(IV) carboxylates, Δν below 200 cm^{-1} would be expected for bridging or chelating carboxylate anions, but for the monodentate bonding carboxylate anions, the Δν is greater than 200 cm^{-1} (Samuel-Lewis *et al.*, 1992; Baul *et al.*, 2001; Yeap and Teoh, 2003; Win *et al.*, 2004).

Further supportive evidence for confirming the formation of complex is the presence of ν(Sn-O), ν(Sn-O-Sn)/ν(O-Sn-O) and ν(Sn-C) stretching bands in the infrared spectra of the complexes (Okawara and Ohara, 1964; Okawara and Yasuda, 1964; Gielen *et al*., 1989; Agarwal *et al*., 1993; Vatsa *et al*., 1990; Teoh *et al*., 1996b; Kovala-Demertzi *et al*., 2001). Based on the literature reviews on diorganotin(IV) carboxylate complexes, the bands at 500-400 cm^{-1} are attributed to the stretching frequency of the Sn-O bond (Sandhu *et al*., 1991a; Rehman *et al*., 2005b; Rehman *et al*., 2006). This provides evidence for the coordination of the oxygen atom of the carboxylate anions to the tin atom moiety during complexation. It is believed that the carboxylate anion is bonded to the tin cation via *p*π-*p*π and *p*π-*d*π during complexation (Poller, 1970). Bonding via *p*π-*d*π occurred due to the transfer of a pair of electrons from the carbonyl group to the vacant 5*d* orbitals of the tin atom (Poller, 1970). The medium absorption band at 679-600 cm^{-1} in the infrared spectra of complexes was ascribed to ν(Sn-O-Sn)/ν(O-Sn-O) which renders an additional supportive evidence for the coordination of the oxygen atoms to the tin atom moiety (Gielen *et al*., 1989; Kapoor *et al*., 2001; Teoh *et al*., 2002). Generally, the ν(Sn-O-Sn) bands fit in the assignment of additional Sn-O in organodistannoxane dimer types since the centrosymmetry of the complexes are occupied by Sn_2O_2 (Sandhu *et al*., 1991b; Sandhu *et al*., 1992a; Rehman *et al*., 2005b). Moreover, for triphenyltin(IV) carboxylate complexes, the ν(Sn-O) bands are centred at 450-445 cm^{-1} as found in literature (Yin *et al*., 2004; Yin *et al*., 2005b; Ma *et al*., 2006a). As a result, *p*π-*p*π is involved in the complexation of tripenyltin(IV) carboxylates (Harrison, 1989).

In the infrared spectra of organotin(IV) carboxylate complexes, there is another significant vibration band attributed to ν(Sn-C) (Ma *et al*., 2004; Costa *et al*., 2005; Yin *et al*., 2006; Szorcsik *et al*., 2005). Okawara and Yasuda (1964) found that trimethyltin(IV) hydroxide exhibited the ν(Sn-C) band at 540 cm^{-1}. In the same year, Okawara and Ohara in their study on trialkyltin(IV) derived from formate showed that the ν(Sn-C) bands were in the range between 552-512 cm^{-1} (Okawara and Ohara, 1964). In addition, Vatsa *et al*., (1990) in their study on

$\{[R_2SnCO_2(R')]_2O\}_2$ (R= Me, Et, ^nPr and ^nBu) reported that the ν(Sn-C) bands were found in the range between 650-570 cm^{-1}. Moreover, the ν(Sn-C) bands are also found in the range between 600-500 cm^{-1} in the infrared spectra of complex derivatives of $\{[R_2SnCO_2CCH_2SPh)]_2O\}_2$ and $R_2Sn(O_2CCH_2SPh)_2$ (R= Me, Et, ^nPr, ^nBu and ^nOkt) (Sandhu *et al.*, 1991b).

Before 1970, there were discrepancies in the assignment of the ν(Sn-C) bands for organotin(IV) carboxylate derivatives of phenyl. Generally, it is better to indicate using ν(Sn-Ph) instead of ν(Sn-C) for organotin(IV) carboxylates containing phenyl groups. Some researchers have proposed that the $\nu(Sn\text{-}Ph)_{as}$ and $\nu(Sn\text{-}Ph)_s$ will be observed at 450 cm^{-1} and 230 cm^{-1} respectively (Srivastava, 1969). However, Ford *et al.*, (1969) suggested that $\nu(Sn\text{-}Ph)_{as}$ should be around 270 cm^{-1} and the $\nu(Sn\text{-}Ph)_s$ should occur in the region less than 250 cm^{-1}. In 1970, Poller proposed that it is reasonable that $\nu(Sn\text{-}Ph)_{as}$ and $\nu(Sn\text{-}Ph)_s$ occur in the range between 280-260 cm^{-1} and 240-225 cm^{-1} respectively in the far infrared region (Poller, 1970). Consequently, in the same year, Srivastava and Tandon in their study on triphenyltin(IV) complexes, revealed that $\nu(Sn\text{-}Ph)_{as}$ and $\nu(Sn\text{-}Ph)_s$ lie in the range proposed by Poller (Srivastava and Tandon, 1970). It is reasonable to observed $\nu(Sn\text{-}Ph)_{as}$ and $\nu(Sn\text{-}Ph)_s$ in the far infrared region since the phenyl groups are much more heavier and bulky.

1.6.2 Nuclear magnetic resonances spectroscopy (NMR)

The ^1H NMR spectra of free carboxylic acids display δ(OH) signal in the range between δ= 10.00-14.00 ppm attributed to the carboxylic proton and upon complexation, the δ(OH) signal will be absent (Sandhu *et al.*, 1991b, Sandhu *et al.*, 1987a). For organotin(IV) carboxylate complexes, the organic groups (methyl, butyl or aliphatic) signal will be observed in the upfield region of the NMR spectra (Win *et al.*, 2006c). For triphenyltin(IV) carboxylate complexes, the proton resonances of the phenyl groups will be centering around δ≈ 7.50 ppm and 7.80 ppm with the integration values of 9:6 respectively (Sau *et al.*, 1980, Sau and Holmes 1981; Willem *et al.*, 1997; Nath *et al.*, 2006). The protons at the *ortho* position are at a lower field while those at the *meta* and *para* positions are located at a higher field, respectively (Sau and Holmes, 1981).

For dimethyltin(IV) carboxylate complexes, there would be two small tin satellites observed in the NMR spectrum (Martin, 2000). These two tiny tin satellites coupling constant, $|{}^{2}J({}^{119}\mathrm{Sn},{}^{1}\mathrm{H})|$ may play an important role in the structure determination and is closely related to the Me-Sn-Me or better known as the C-Sn-C angle (Lockhart and Manders, 1986; Lockhart and Davidson, 1987a; Careri *et al.*, 1989). Lockhart and Manders (1986), found that the C-Sn-C angle could be determined with $|{}^{2}J({}^{119}\mathrm{Sn},{}^{1}\mathrm{H})|$ by applying the following equation:

$$\theta = 0.0161\ |{}^{2}J|^{2} - 1.32\ |{}^{2}J| + 133.4$$

If the θ falls around 106° and the $|{}^{2}J({}^{119}\mathrm{Sn},{}^{1}\mathrm{H})|$ is less than 59.0 Hz, hence there is a possibility that the tin(IV) atom moiety is four coordinated and the ligands possess a monodentate coordination mode (Lockhart and Manders, 1986). In addition, the structure of the dibutyltin(IV) carboxylate complexes could also be determined from the $|{}^{2}J({}^{119}\mathrm{Sn},{}^{1}\mathrm{H})|$ (Howard *et al.*, 1985). However, for dibutyltin(IV) carboxylate complexes there are some difficulties in observing the tiny tin satellites due to the overlapping of the butyl proton multiplicities or even sometimes being hindered by the baseline. Generally, the integration of the peaks concurs with the number of protons postulated from the proposed structures for the complexes implying that the synthesized complexes are in accordance with the predicted molecular structure. In addition, the absence of any peaks arising from impurities in the spectrum significantly shows that the isolated complexes are fairly pure.

In the ^{13}C NMR spectra, the downfield shift of the δ(COO) signals of the free acids upon complexation is an important feature (Vatsa et al., 1991b; Win *et al.*, 2004; Win *et al.*, 2006c;

Yip *et al*., 2006). Parulekar *et al.* (1990) in his studies reported that upon formation of the dibutyltin(IV) carboxylate complexes, the δ(COO) values were shifted downfield to the region between 173.1-174.6 ppm compared to the parent acid, 2-$MeOC_6H_4COOH$ in which the δ(COO) value was 166.3 ppm. Moreover, the δ(COO) value of *o*-anisic acid at 166.3 ppm was shifted downfield to the region between 172.6-174.4 ppm upon complexation to form the organotin(IV) carboxylate complexes (Parulekar *et al*., 1990). This phenomenon was attributed to the decrease in the electron density of the carboxylate anions upon coordination to the tin atom moiety during complexation. The lone-pair electrons of the oxygen atom of the bidentately bonded COO group are transferred to the vacant *d* orbital of the tin(IV) atom. It is believed that at least two different types of carboxylate groups are suppose to be present in the NMR spectra of the complex derivatives of the organodistannoxane dimer. However, only a single δ(COO) resonance is observed. A possible reason could be either due to the magnetic equivalence of both the groups or the lack of resolution between the two sets of resonances (Ma *et al*., 2005a).

In the ^{13}C NMR spectra, the butyl groups of the dibutyltin(IV) derivatives usually exhibit four signals in the range between 13.1-26.3 ppm (Vatsa *et al*., 1991b; Parulekar *et al*., 1990). The butyl groups have also been observed to appear in the range between 26.4-29.7 ppm (Sandhu *et al*., 1987b). Dibutyltin(IV) carboxylate complexes which are derivatives of organodistannoxane dimer types will exhibit two sets of four signals in the upfield region attributed to the butyl groups linked to the exo- and endo-cyclic tin atoms respectively (Parulekar *et al*., 1990; Danish *et al*., 1995b; Rehman *et al*., 2005b). However, in some NMR spectra, only six to seven resonance signals are observed. This is due to the similar environment or the overlapping of the CH_2 groups in the ^{13}C NMR spectra (Danish *et al*., 1995b).

In general, only a sharp resonance signal together with the tin satellites are observed in the ^{13}C NMR spectra of dimethyltin(IV) carboxylate complexes. The coupling constants of the tin satellites $|^{1}J(^{119}\text{Sn},^{13}\text{C})|$ play an important role in the structure determination and is closely related to the C-Sn-C angle (Lockhart and Manders, 1986). Lockhart and Manders (1986), found that the C-Sn-C angle could also be determined from $|^{1}J(^{119}\text{Sn},^{13}\text{C})|$ by applying the following equation:

$$|^{1}J| = 11.4\theta - 875$$

If the calculated θ around 106°, hence there is a possibility that the tin(IV) atom moiety is four coordinated and the ligands possess a monodentate coordination mode (Lockhart and Manders, 1986).

Nádvorník and his coworkers in their studies reported that the tin atom moiety of tributyltin(IV) carboxylate complexes, with a $^{1}J(^{119}\text{Sn-}^{13}\text{C})$ in the range between 326.70-386.70 Hz, has a typical *quasi*tetrahedral arrangement and is four-coordinated (Nádvorník *et al*., 1984). It is believed that sp^3 hybridized orbitals are involved in the bonding of the tin atom to the three *n*-butyl groups (Nádvorník *et al*., 1984). Meanwhile, if the $^{1}J(^{119}\text{Sn-}^{13}\text{C})$ is in the range between 441.9 – 509.0 Hz, the tin atom has a typical *trans*-trigonal bipyramid arrangement and is five-coordinated (Nádvorník *et al*., 1984).

The signals of the phenyl groups attached to the tin(IV) atom moiety are usually observed in the downfield region in the ^{13}C NMR spectra (Ng *et al*., 1989c; Win *et al*., 2004; Yip *et al*., 2006). Four carbon signals of the phenyl groups will be in the range between 128.8-138.1 ppm (Ng *et al*., 1989c). The $\delta(^{13}\text{C})_{\text{ipso}}$, $\delta(^{13}\text{C})_{\text{orto}}$, $\delta(^{13}\text{C})_{\text{meta}}$ and $\delta(^{13}\text{C})_{\text{para}}$ are in the range between 137.1-143.8, 133.9-137.2, 125.5-129.0 and 126.1-135.8 ppm respectively (Kumar Das *et al*., 1986; Baul *et al*., 2001; Win *et al*., 2004; Yip *et al*., 2006). Holeček *et al*., (1983a) found that the $\delta(^{13}\text{C})_{\text{ipso}}$ plays a significant role in the structure determination of the triphenyltin(IV) carboxylate complexes. The $\delta(^{13}\text{C})_{\text{ipso}}$ chemical shifts of the phenyl groups lie in the range between 135.95-138.70 ppm, corresponding to the value shown by a tetrahedrally coordinated

Sn atom (Holeček *et al.*, 1983a, Holeček *et al.*, 1983b, Baul *et al.*, 2001). Hence, the carboxylate anion is bonded to the tin(IV) atom moiety in a monodentate manner with a sp^3 hybridized orbital (Poller, 1970). For five-coordinated triphenyltin(IV) carboxylate complexes, the $\delta(^{13}C)_{ipso}$ will be observed at approximately 4 ppm higher which is 142.0 ppm and above (Baul *et al.*, 2001).

Holeček and his coworkers in their studies have shown that the coordination number of tin in triphenyltin(IV) carboxylates can be determined by the studies of the $^1J(^{119}Sn\text{-}^{13}C)$ coupling constant (Holeček *et al.*, 1983a, Holeček *et al.*, 1983b, Baul *et al.*, 2001). Normally, triphenyltin(IV) compounds with a four-coordinated tin atom will show a coupling in the range between 550-660 Hz (Holeček *et al.*, 1983b; Lyčka *et al.*, 1985; Willem *et al.*, 1997). Meanwhile, triphenyltin(IV) compounds with a five-coordinated tin atom will show a coupling in a range between 600-850 Hz (Holeček *et al.*, 1983b). Basically, the tin atom of triphenyltin(IV) compounds with $^1J(^{119}Sn\text{-}^{13}C)$ values in the range between 750-850 Hz respectively are believed to be five-coordinated with a trigonal bipyramid geometry of the substituents and ligand, Ph_3SnX•L and L is a monodentate ligand (Holeček *et al.*, 1983b). The substituent, X and the ligand, L lie in the axial positions and the three phenyl groups lie in the equatorial positions to form a *trans*-trigonal bipyramid geometry (Holeček *et al.*, 1983b). Generally, the $^nJ(^{119}Sn\text{-}^{13}C)$ (n=1, 2, 3 and 4) displays an usual sequence of $^3J(^{119}Sn\text{-}^{13}C) \gg {}^2J(^{119}Sn\text{-}^{13}C) > {}^4J(^{119}Sn\text{-}^{13}C)$ (Lyčka *et al.*, 1985; Kemmer *et al.*, 2001; Din *et al.*, 2004). The value of $^3J(^{119}Sn\text{-}^{13}C)$ being greater than that of $^2J(^{119}Sn\text{-}^{13}C)$ may be ascribed to the resonances in the phenyl ring and the partial-delocalization of the π-electron of the phenyl ring.

The increase in the coordination number of the tin atom from four to six, causing an increase in shielding, is one of the importance of the ^{119}Sn chemical shift, $\delta(^{119}Sn)$ (Holeček *et al.*, 1983a; Holeček *et al.*, 1983b; Lyčka *et al.*, 1985; Holeček *et al.*, 1986a; Careri *et al.*, 1989). Holeček and his co-workers in their studies have shown that the coordination number of tin in diorganotin(IV) carboxylates can be determined from the δ(^{119}Sn) values (Holeček *et al.*, 1986a). For four-coordinated complexes, the δ(^{119}Sn) value falls in the range between +200 to -60 ppm; for five-coordinated complexes between -90 to -190 ppm and finally between -210 to -400 ppm for six-coordinated complexes. Moreover, for complexes with a seven-coordinated tin species, the δ(^{119}Sn) signal is observed at an upfield region greater than -400 ppm (Harrison *et al.*, 1971; Otera *et al.*, 1980; Hani and Geanangel, 1982; Careri *et al.*, 1989). In addition, for tributyltin(IV) carboxylate complexes, if the δ(^{119}Sn) value falls in the downfield region with a positive value, the tin(IV) atom moiety is four-coordinated (Nádvorník *et al.*, 1984; Yoder *et al.*, 1993; Baul *et al.*, 2004b).

The δ(^{119}Sn) value of triphenyltin(IV) carboxylates lie in a broad range between -40 to -260 ppm (Holeček *et al.*, 1983b). Four-coordinated triphenyltin(IV) carboxylate complexes display the δ(^{119}Sn) value in the range between -40 to -120 ppm (Holeček *et al.*, 1983a; Holeček *et al.*, 1983b). Normally, triphenyltin(IV) compounds with a five-coordinated tin atom will have a δ(^{119}Sn) value in the range between -180 to -260 ppm (Holeček *et al.*, 1983b). Basically, the tin atom of triphenyltin(IV) compounds with a δ(^{119}Sn) value in the range between -200 to -260 ppm are believed to be five-coordinated with a trigonal bipyramid geometry (Holeček *et al.*, 1983b).

Therefore, the ^{119}Sn NMR parameters are very useful in the determination of the coordination number of tin and its geometry and consequently, the molecular geometry of the complexes.

1.6.3 X-ray single crystal structure determination

The structure of organotin(IV) carboxylate complexes can be determined from X-ray single crystal structure determination (Vatsa *et al.*, 1991a; Mokal *et al.*, 1992; Dokorou *et al.*, 2001; Win *et al.*, 2007f; Win *et al.*, 2008). In addition, the geometry, bond lengths and angles of the