CHAPTER 1

INTRODUCTION

1.1 Tin (Group IV)

Tin (Sn) is the element with an atomic number of 50, a member of group IV A of the Periodic Table. It has a atomic weight of 118.70 and with outer electron configuration of ns^2np^2 (Cotton et al., 1999). Along the group IV, it also have carbon (C), silicon (Si), germanium (Ge) and lead (Pb) and these element are remarkable as they are commonly used in the pure form.

Among the group IV elements, Tin has the unusual low melting point of 231.85°C and the unusual high boiling point of 2260, 2270 and 2687°C. This great range makes it easy to form alloys without loss in vaporization. Tin exhibits the oxidation states +2 and +4, like lead. In +2 state is called stannus and the +4 state is called stannic (Cotton et al., 1999).

Tin primarily obtained from mineral cassiterite (SnO_2) which is extracted by roasting cassiterite in the furnace with carbon. Two allotropes of tin occur near room temperature. The first form of tin is called gray tin which is stable at temparature below 13.2°C (Cotton et al., 1999). Above temperature 13.2°C, grey tin will slowly urns into tin's second form, white tin which is normally in metal form.

1.2 Organotin Chemistry

Organotin Chemistry are those compounds that containing at least one bond between tin and carbonIn compounds, Tin have four electrons in the outer electronic shell in the common with other group IV elecments, C, Si, Ge, and Pb. Thus forms compound in which tin has oxidation states of +II and +IV (Kenneth et al., 2002).

Tin can form various compounds, both inorganic and organic. Inorganic tin compounds do not contain a tin-carbon bond, whereas organotin(IV) compounds contain at least one tin-carbon bond with the formula:

$$R_nSnX_{4-n}$$

where, R is usually an aryl or alkyl group and

X is an inorganic species (halide, oxide or hydroxide)

$n = 1 – 4$

In general, tin(IV) compounds are either tetrahedral, trigonal bipyramidal, or octahedral depending on the number and nature of substitutes. For smaller molecules compounds of some combinations of the four substitutes give products that are tetrahedral. When the number is five, the product are trigonal bipyramidal, and when it is six, they are octahedral (Egon et al., 2001). The related basic organotin compound structures were illustrated in Figures 1.1 -1.3.

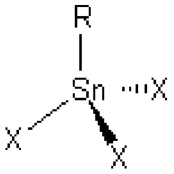

Figure 1.1 Tetrahedral geometry of tin(IV) compound

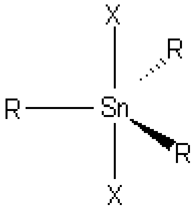

Figure 1.2 Trigonal bipyramidal geometry of tin(IV) compound

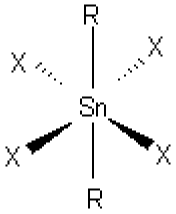

Figure 1.3 Octahedral geometry of tin(IV) compound

1.3 Synthesis of Organotin (IV) Complexes

Tin played an important role in organometallic chemistry which began in 1949, and this was stimulated by the discovery of a variety of applications (Rita et al., 2005). The first organotin compound was prepared over 160 years ago by Sir Edward Frankland in 1849 and described as a side note in a paper devoted largely to the reaction that occurred when ethyl iodide and tin are heated together in a sealed tube that produce the first main-group organometallic compounds, ethyl tin and diethyltin iodide (Rita et al., 2005). Frankland observed that a reaction occurred also with a number of other metals, including tin:

$$2EtI + Sn \rightarrow Et_2SnI_2$$

And in the middle of 1903, Pope and Peachey described the preparation of a number of simple and mixed tetraalkystannanes, and of tetraphenyltin, from Grignard reagents and tin tetrachloride or alkyltin halides, and reactions of this type became the standard route to alky- and aryl-tin compounds (Rita et al., 2005).

Organotin(IV) carboxylate complexes, $R_nSn(O_2CR')_{4-n}$, are most commonly prepared by treating the corresponding oxide or hydroxide with the carboxylic acid (Equations 1.1-1.3), or from the reaction of the corresponding chloride with a metal carboxylate (Equations 1.4), or by cleaving a tin-carbon bond with a carboxylic acid (Equations 1.5), or a mercury(I) or mercury(II), or lead(IV) carboxylate (Equations 1.6) (Yin et al., 2005).

$$R_3SnOH \text{ or } (R_3Sn)_2O + R'CO_2H \rightarrow R_3SnO_2CR' + H_2O \quad (1.1)$$

$$R_2SnO + 2R'CO_2H \rightarrow R_2Sn(O_2CR')_2 + H_2O \quad (1.2)$$

$$RSn(O)OH + 3R'CO_2H \rightarrow RSn(O_2CR')_3 + H_2O \quad (1.3)$$

$$R_nSnCl_{4-n} + 4\text{-}nR'CO_2M \rightarrow R_nSn(O_2CR')_{4-n} + 4\text{-}nMCl \quad (1.4)$$

$$R_4Sn + R'CO_2H \rightarrow R_3SnO_2CR' + RH \quad (1.5)$$

$$R_4Sn + R'CO_2M \rightarrow R_3SnO_2CR' + RM \quad (1.6)$$

1.4 Application of Organotin Compounds

The remarkable variety in the physical, chemical and biological properties of organotin compounds has lead to a great number of industrial applications of the organotin(IV) carboxylate. Basically, There are three main areas in which organotin compounds have product and process utility: (1) heat stabilizers; (2) catalytic agents; (3) biocidal compounds (Ross, 1965). Organotin derivatives account for the fourth largest production of organometallics amounting to about four million pounds per year as compared with about 485 million pounds per year for organolead compounds.

1.4.1 Polyvinyl Chloride (PVC)Heat Stabilizers

Mono- and diorganotins are used extensively as heat stabilizers for processing polyvinyl chloride (PVC). The main purpose of these tin stabilizers is to reduce the polymer backbone degradation of the PVC. They do this by scavenging the HCl lost during processing at high temperatures and stabilizing the unstable chloride sites in the PVC molecule.

There are three major types of tin stabilizers. They are distinguished by their respective alkyl groups: octyl, butyl, and methyl. Octyltin stabilizers have the lowest tin content and are somewhat less efficient. However, they are approved for food contact applications by most regulatory authorities worldwide. Butyltin stabilizers have been the dominant types used until methyltins were introduced. Methyltin stabilizers have a higher tin content and lower raw material cost compared to the other two types. Some formulations (mercaptides) have also been approved for food contact applicationsc (Evan et al., 1985).

The main applications for tin stabilizers are building products, such as pipe and fittings, siding, profiles, packaging, and flexible PVC. It is estimated that between 12 to 13K tons of tin are used annually in tin stabilizers worldwide. This market is expected to grow about 4% annually (European Council of Vinyl Manufacturers, 2000).

1.4.2 Catalysts

Catalysts are used to speed up chemical reactions, especially polymerization. The most common applications for mono-and diorganotin catalysts are in chemical synthesis and the curing of coatings. In chemical synthesis, the organotins are used for the esterification and transesterification of mono- and polyesters. These products are then used for plasticizers, synthetic lubricant manufacturing, and polyester polyol production, as well as some coating applications.

As curing catalysts, one of the largest uses of organotins is in electrocoat (E-coat) coatings. These electrocoating products are sold into a wide range of applications, with the largest being automotive, where they provide excellent rust resistance. The catalysts are also used in urethane coatings as well as polyurethane foam production (Evan et al., 1985).

1.4.3 Biocidal Properties

The biocidal properties of organotins in general were discovered by Van der Kerk at the TNO Institute, Utrecht in the late 1950s. Tributyltin (TBT) is unique among the organotin(IV) in which is used as biocide. The monobutyltins do not exhibit these properties. Tributyltin is normally used as biocide in paint formulations. These paints are applied to protect the underwater surface area of ship’s hull against barnacles, algae, etc. in order to avoid increased fuel consumption and premature dry-docking. Tributyltin(IV) oxide (TBTO) and tributyltin(IV) naphthenate (TBTN) are commercially used in weed industrial for treatment and as preservatives (Kaars et al., 1962).

Since then bactericidal and fungicidal properties in agriculture have been developed. Both triphenyltin(IV) hydroxide and triphenyltin(IV) acetate are used to control fungi that cause potato blight on sugar beets, celery, carrots, onions and rice including tropical plant diseases in peanuts, pecans, coffee and cocoa. As insecticides, triorganotin(IV) compounds have been used against houseflies, cockroaches, mosquito larvae and tobacco budworms (Fargasova, 1955)

1.5 Objectives

In this study, the main objective is to to synthesis new organotin(IV) complexes by reacting the 4-(diethylamino)benzoic acid and with organotin (IV) compounds, which are di-n-butyltin(IV) oxide and triphenyltin(IV) hydroxide.

The coordination number of the tin(IV) atom as well as the coordination mode of the respective ligands to the tin(IV) atom moiety will be study. The complexes obtained will be characterized quantitatively by elemental analysis and melting point determination as well as qualitatively by infrafed spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) to compare the structure with theoretical study.

CHAPTER 2

LITERATURE REVIEW

2.1 The First 1D Tetranuclear Organotin (IV) Complex with N’-acylsalicylhydrazide

The first diorganotin(IV) complex with N’-acylsalicylhydrazide has been successfully synthesized and structurally characterized (Yin et al., 2008). The structure showed that the complex reveals an infinite 1D polymer linked by the Sn–O bonds, and the monomer contains four-tin nuclears with five-coordinated and seven-coordinated tin and an 14-member ring made up of two ligands and two dibutyltin(IV).

In the infrared spectra of the complex, the stretching vibration bands of COO–H and the ArO–H disappear compared with the original ligand suggesting the coordination of carboxyl and phenolate-O oxygen atoms to the organotin(IV) moiety. The absence of the N–H and C=O stretching vibration bands is consistent with the deprotonation of the CONH groups and the coordination to the organotin(IV) moiety in enol form. The characteristic absorptions at 1608 cm^{-1} indicate the presence of C=N–N=C group (Yin et al., 2008).

The ^1H NMR spectrum show that those signal of –COOH, -OH and –CONH protons in the spectrum of the ligand are absent, thus indicate removal of those protons and formation of Sn-O bonds. The ^{119}Sn NMR spectrum spectrum of complex show distint resonance at -187.4 and -296.7 ppm, respectively. The Value of δ ^{119}Sn in the ranges -210 to -400, -90 to -190 and 200 to -60 ppm has been assciated with six- , five- and four-coordinate tin centers, respectively (Holeěek, 1986).

As a conclusion, the tin atoms of the complex in solution are five- and six-coordinated which the sturture of the complex tetranuclesr organotin(IV) complex is shown in figure 2.1.

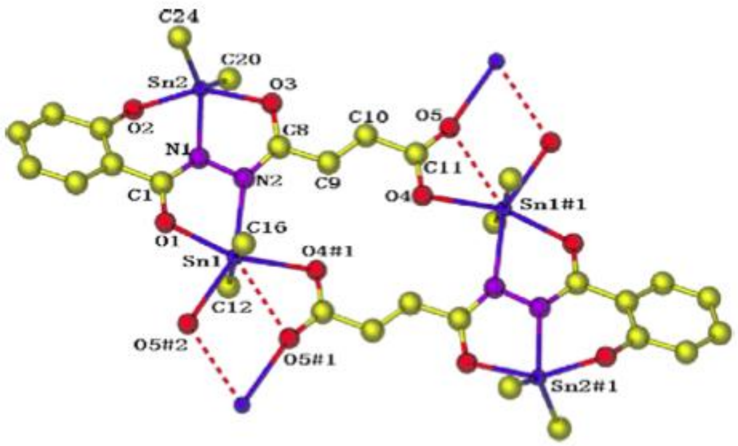

Figure 2.1 The molecular structure of complex tetranuclear organotin (IV) complex with N$^{'}$-acylsalicylhydrazide

2.2 Synthesis, Characterization and Crystal Structure of A Novel 3D Network Tiorganotin(IV) Polymer Containing Two types of Macrocycles

A novel triorganotin(IV) complex has been synthesized by the reaction of sodium ethoxide with tri-n-butytin(IV) chloride in dry ethanol (Hangdong et al., 2008). It is noteworthy that complex contains two types of macrocycles: one is six-tin 24-membered macrocycles, the other is six-tin 36-membered macrocycles. Such large macrocyclic structures appearing in a multidimensional organotin(IV) polymeric system based on covalent interactions are not common and the organotin macrocycles have been extensively studied for their potential industrial application and biological activities (Ma et al., 2005).

The infrared spectra of the complex showed that the absence of bands in the region 3120-2980 cm^{-1}, which appear in the free ligand as COOH stretching vibrations, thus indicating metal-ligand bonding through COO $^{-}$. The typical absorptions for Sn-C, Sn-O, vibrations in complex are located in the normal range 550-586 cm^{-1}and 440-486 cm^{-1} respectively.

The resonances of ^{1}H NMR observed at δ 10.50 ppm, which are absent in the spectra of the complex, indicate removal of the COOH proton and formation of Sn-O bond. The coordination geometry about the tin(IV) atom moiety is distorted trigonal bipyramidal, with the equatorial plane occupied by three n-butyl groups and the axial positions shared by two coordinated oxygen atoms from the ligand (Hangdong et al., 2008).

The β, γ and δ carbon atoms of the butyl groups and the hydrogen atoms have been omitted. All the tin atoms in complex possess the same coordination environment. The coordination about the tin atom is only slightly distorted from a regular trigonal bipyramidal geometry, with the equatorial plane occupied by three n-butyl group and the axial postions shared by two coordinatied oxygen atoms from the ligand.

In short, using a flexible ligand, meso-2,3-di-bromosuccinic acid, a new triorganotin(IV) coordination polymer has been synthesized. The structure of the coordination polymer reveal that the ligand acts as linker to connect four metal centers to give rise to a 3D network structure. The ligand can bond more than one organotin moiety, which will increase the changes for the higher structural dimensionalities assembly, so the selection of organic ligands with appropriate coordination sites is the key to forming metal-organic coordination polymers with fascinating structures(Hangdong et al., 2008). 3D network structure polymer, as indicated in figure 2.2.

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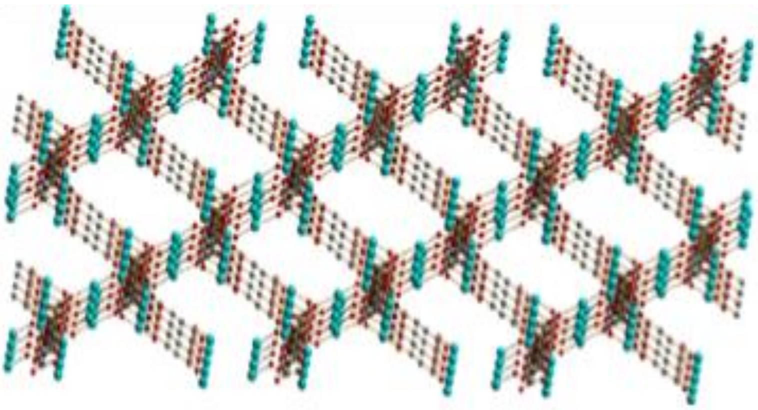

Figure 2.2 The 3D network structure (viewed along to the α axis)

2.3 Di- And Tri-organotin(IV) Complexes of the New sodium bis(1-methyl-1H-imidazol-2-ylthio)acetate Ligand

The new sodium bis(1-methyl-1H-imidazol-2-ylthio)acetate, Na[(S-tim)$_2$CHCO$_2$], has been prepared in ethanol solution using 2-mercapto-1-methylimidazole, dibromoacetic acid and NaOH. Maura et al,. (2008) producing a new class of monoanionic with polyfunctional N,O,S-ligands lead to the high possible considerable coordinative flexibility.

Infrared spectroscopy showed all the expected bands for the ligand and the tin moieties: weak absorptions in the range 3043–3136 cm^{-1} are due to the azolyl ring C–H stretchings and medium to strong absorptions near 1510 cm^{-1} are related to ring ‘‘breathing” vibrations. The presence of the COO moiety in is detected by an intense broad absorption in the range 1639–1656 cm^{-1} and 1308–1335 cm^{-1}, due to the asymmetric and symmetric stretching modes. In the far-IR region medium to strong absorptions appear upon coordination, due to stretching modes of Sn–O, Sn–Cl, Sn–C (Nakatomo, 1997) The absence of Sn–Cl stretching vibrations in the spectra of the triorganotin(IV) derivatives confirms the substitution of the chloride in the complexes formation. The Sn–Cl stretching vibrations fall as broad absorptions near 229–235 cm^{-1} in the diorganotin(IV) derivatives. The Sn–C stretching frequencies fall as medium or strong absorptions in the range 245–275 cm^{-1} for the aryl derivatives; similar stretching vibrations are detected in the range 505–590 cm^{-1} for the alkyl derivatives. In the far-IR spectra absorptions tentatively assigned to Sn–O have been detected in the range 420–455 cm^{-1} in the triorganotin(IV) derivatives.

The resonance for CHCOO group hydrogens occurs at 5.05 and 4.73 ppm are important, in $CDCl_3$ and D_2O solution, respectively, downfield with respect to the decarboxylate analogues $[(S\text{-tim})_2CH_2]$. In the ^1H NMR spectra of complexes, the signals due to the 2-mercapto-1-methylimidazolyl rings are always deshielded with respect to those in the spectra of the free donor, confirming the existence of the complexes in solution; the signals due to the CHCOO group exhibit significant downfield shift (from 5.05 ppm in the free ligand to 5.32–5.42 ppm in the complexes): this is suggestive of a strong bonding of the tin atom to the carboxylate group of the complexes. In the ^1H NMR spectra at room temperature of the decarboxylated derivatives, the resonances due to the bridging methylene protons of the $[(S\text{-tim})_2CH_2]$ ligand appear as singlets at 4.44 and 4.65 ppm, respectively, probably as a result of averaging arising from rapid ring inversion of the puckered eight- membered ring containing the central Sn atom (Maura et al., 2008)

CHAPTER 3

METHODOLOGY

3.1 Reagent and Instrumental

Table 3.1 : List of chemicals for the synthesis of organotin(IV) carboxylate

Chemicals	Supplier
Di-n-butyltin(IV) oxide, $(C_4H_9)_2SnO$, (98.0%)	Fluka Chemie AG
triphenyltin(IV) hydroxide, $(C_6H_5)_3SnOH$,(96.0%)	Aldrich Chemical
4-(diethylamino)benzoic acid, $(CH_3)_2NC_6H_4COOH$, (99.0%)	Aldrich Chemical
Ethanol, C_2H_5OH, (99.8%)	Systerm
Acetonitrile, CH_3CN, (99.5%)	Systerm
Sodium Hydroxide, NaOH, (99.0%)	Systerm

Table 3.2 : List of Instrusments for the analysis of organotin(IV) carboxylate

Instrument	Model
FTIR Spectrophotometer	Perkin Elmer FT-IR System 2000
^{1}H and ^{119}Sn NMR Spctrometer	Bruker AC-P 400MHz
13C NMR SPectrometer	Bruker AC-300MHz
Melting point apparatus	Stuart
Elemental analyzer	Perkin Elmer Series II 2400

3.2 Synthesis Method

3.2.1 Preparation of sodium salt

The sodium salt was prepared by under reflux in 1:1 molar ratio sodium hydroxide, NaOH (4 mmol) with 4-(diethylamino)benzoic acid, $(CH_3)_2NC_6H_4COOH$ (4 mmol) in ethanol (50 mL) for about two hours. After few days, yellow precipitate was obtained.

3.2.2 Synthesis of Bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) Dimer Complex (1)

The reaction of di-*n*-butyltin(IV) oxide, $(C_4H_9)_2SnO$ (2 mmol) and 4-(diethylamino)benzoic acid, $(CH_3)_2NC_6H_4COOH$ acid (2 mmol) and in ethanol (50 mL) was obtained by heating under the refluxed in a 1:1 molar mixture for about two hours. The solution was isolated by filtration. A clear colourless solution was obtained by filtrtion and kept in a bottle. After few days, colourless crystal was collected.

3.2.3 Synthesis of Preparation of 4-(diethylamino)benzoatotriphenyltin(IV) Complex (2)

The reaction triphenyltin(IV) hydroxide, $(C_6H_5)_3SnOH$ (3 mmol) and 4-(diethylamino)benzoic acid, $(CH_3)_2NC_6H_4COOH$ (3 mmol) in acetonitrile (50 mL) was heating under refluxed in a 1:1 molar mixture for two hours. The solution was isolated by filtration. A clear solution was obtained by filtration and a coloured crystal was obtained.

3.3 Charaterization

Complexes was characterized by using four methods:

- Elemental analysis
- Melting point determination
- Fourier Transoform Infrared Spectroscopy
- Nuclear Magnetic Resonance Spectroscopy

All measurements were performed at room temperature.

3.3.1 Elemetal analyzer

Elemental analysis on carbon, hydrogen and nitrogen is the most important investigation performed to charateristize and prove the elemental compostion of the complexes. The compostions of the complexes formed are determined by using Elemental analyzer, Perkin Elmer Series II 2400. The amount of complexes in this analysis is approximate 1.0 to 2.0 mg.

3.3.2 Melting Point Determination

A pure compound will have deifinte melting point, owing to this, the identiy and the purity of complex can be determined by using melting point apparatus, Stuart. The melting point apparatus has a temperature range of 0 to 360 °C. Small amount of sample complex was filled into capillary tub, until about 3 to 4 mm long. The filled capilary tube was inserted into observing chamber and proceed with the heating process. The temperature range at which the complex changesstate from solid to liquid was taken. A pure complex will give a sharp melting point which the temperature fall in between the range 2 to 3°C.

3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The ligand coordination to the tin centre able to clarify by the infrared spectra in the 4000-400 cm^{-1} range. The apparatus was cleaned with absoulute ethanol before preparation of the sample. 1.0 mg sample complex was grinded with potassium bromide (KBr) salt in ratio 1:10 into fine powder using agate mortar and pestle. The sample is compressed in a manual Hydraulic Press by using pressure in the range of 6000 to 8000 psi into a translucent pellet. The sample in a pellet form was placed into the sample holder and ready to be run using FT-IR. The complexes are analyzed with FTIR Perkin Elmer FT-IR System 2000.

3.3.4 Nuclear Magnetic Resonancr Spectroscopy (^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR)

Nuclear Magnetic resonance spectroscopies are the preminent technique for determinning the structure of complexes. ^{1}H and ^{119}Sn NMR Spectrometer were recorded on Bruker AC-P 400 MHz. The ^{13}C NMR Spectrometer data were obtained on Bruker AC-300 MHz. Deuterated dimethly sulfoxode, DMSO-d_6 was used in the sample preparation by dissolve 0.01 g to 0.03 g of complex. Tetramethylsilane, TMS was used as internal standard and the chemical shift of 13C NMR spectra is in the range of 0 to 200 ppm, whereas ^{1}H NMR spcetra in the range of 0 to 12 ppm.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of Complexes

4.1.1 Preparation of Sodium 4-(diethylamino)benzoate

The sodium salt, sodium 4-(diethylamino)benzoate was obtained by heating under reflux a 1:1 molar mixture of sodium hydroxide, NaOH (4 mmol) with 4-(diethylamino)benzoic acid, $(CH_3)_2NC_6H_4COOH$ (4 mmol) in ethanol (50 mL) for about two hours. The water liberated in the reaction was removed by azeotropic dehydration using the Dean-Stark apparatus (Yip *et al.*, 2008). Molecular sieves are used as an adsorbent for water molecules to reducing contaminants. At the end of the reflux, a clear transparent solution was obtained and isolated by filtration. The solution kept in a bottle. After few days some yellowish crystal obtained.

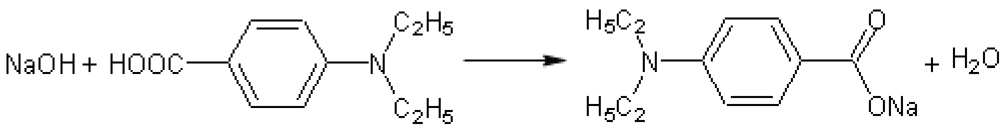

Figure 4.1 Sodium salt formation of 4-diethylamino benzoic acid

4.1.2 Preparation of Bis[4-(diethylamino)benzoato]tetrabutyl distannoxane(IV) Dimer Complex (1)

The title dimer, bis[4-(diethylamino)benzoato]tetrabutyl distannoxane(IV) was obtained by heating under reflux a 1:1 molar mixture of di-*n*-butyltin(IV) oxide, $(C_4H_9)_2SnO$ and 4-(diethylamino)benzoic acid, $(CH_3)_2NC_6H_4COOH$ acid in ethanol (50 mL) for about two hours. The water liberated in the reaction was removed by azeotropic dehydration using the Dean-Stark apparatus (Yip *et al.,* 2008). Molecular sieves are used as an adsorbent for water molecules to reducing contaminants. At the end of the reflux, a clear transparent solution was obtained and isolated by filtration. The solution kept in a bottle. After few days some transparent crystal obtained.

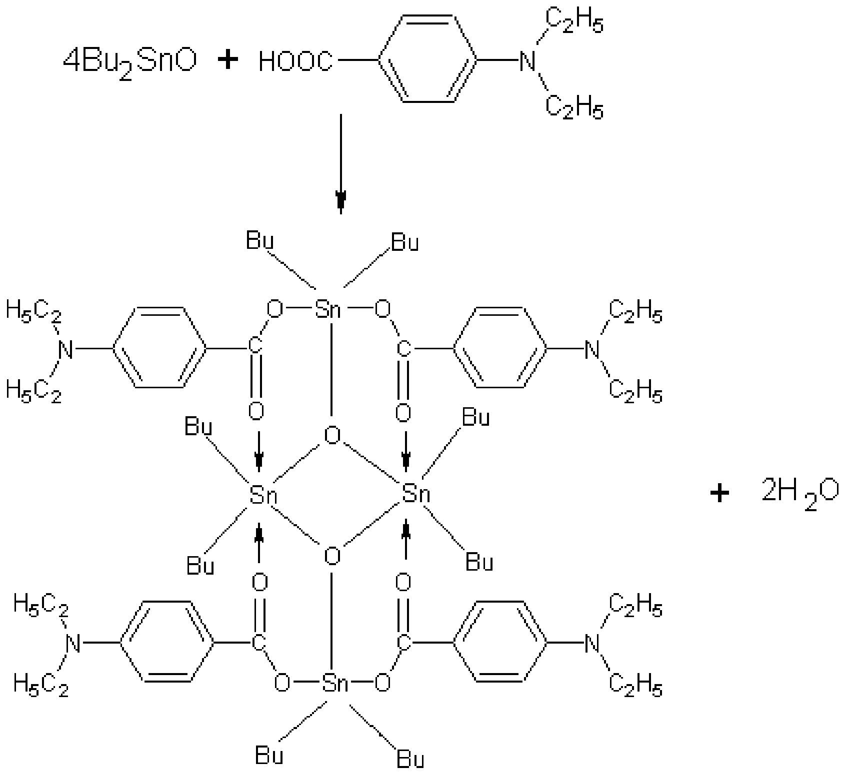

Figure 4.2 Reaction scheme of bis[4-(diethylamino)benzoato] tetrabutyldistannoxane(IV) Dimer Complex

4.1.3 Preparation of 4-(diethylamino)benzoatotriphenyltin(IV) Complex (2)

The title complex, 4-(diethylamino)benzoatotriphenyltin(IV) was obtained by heating under reflux a 1:1 molar mixture of triphenyltin(IV) hydroxide, $(C_6H_5)_3SnOH$ (3 mmol) and 4-(diethylamino)benzoic acid, $(CH_3)_2NC_6H_4COOH$ (3 mmol) in acetonitrile (50 mL) for about two hours. The water liberated in the reaction was removed by azeotropic dehydration using the Dean-Stark apparatus (Yip *et al.*, 2008). Molecular sieves are used as an adsorbent for water molecules to reducing contaminants. At the end of the reflux, a clear transparent solution was obtained and isolated by filtration. The solution kept in a bottle. After few days, some transparent crystal obtained.

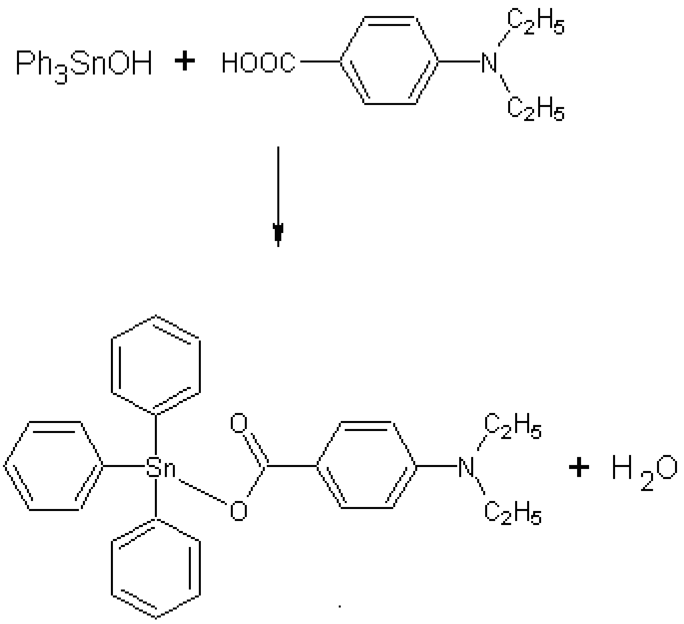

Figure 4.3 Reaction scheme of 4-(diethylamino)benzoate triphenyltin(IV) Complex

4.2 Physical Data and Melting Point

4.2.1 Bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV)Dimer Complex

The bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex **1** was obtained as single fine, shiny and transparent crystals from 1:1 (dibutyltin:acid) reaction. The yield of the complex **1** is 1.13 g (85.20 %). The complex showed a sharp melting point of 219-220 ˚C, which the temperature fall in between the range 1 ˚C indicated the purity of the complex form.

4.2.2 4-(diethylamino)benzoatotriphenyltin(IV) Complex

The 4-(diethylamino)benzoatotriphenyltin(IV) complex **2** was obtained as single fine, shiny and transparent crystals from 1:1 (triphenyl:acid) reaction. The yield of the complex **2** is 0.62g (80.10 %). The complex showed a sharp melting point of 194-195 ˚C, which the temperature fall in between the range 1 ˚C indicated the purity of the complex form.

The data shown that complex **1** have higher melting point than complex **2**. This proved that complex **1** are more stable and have stronger bonding compare to complex **2**. The physical data of these complexes are presented in Table 4.1

Table 4.1 Physical data and melting point.

Complex	Melting Point (^{o}C)	Yield (%)	Molecular weight
Bis[4-(diethylamino)benzoato]tetrabutyl distannoxane(IV) dimer, 1	219-220	85.20	1572.70
4-(diethylamino)benzoatotriphenyltin(IV), 2	194-196	80.10	510.26

4.3 Elemental Analysis and gravimetrik (Sn)

CHN analysis for each complex was obtained from Perkin Elmer Series II 2400 series CHNS-O analyzer. The formula molecular for the complexes was postulated by calculating the percentage weight of compound of carbon, hydrogen and nitrogen present in the complex.

From the CHN analysis, calculated percentage of carbon present in the complex **1** is 52.78 %, the percentage of nitrogen present is 3.19 % and the percentage of the hydrogen is 7.07 %. Thus, molecular formula for the bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex is $[\{4\text{-}[N(C_2H_5)_2]C_6H_4COO\}_2(C_4H_9)_2Sn\}_2O]_2$ and the molecular weight of this complex is 1572.70 g/mol.

For the complex **2**, calculated percentage of carbon, nitrogen and hydrogen compound present in the complex is 64.28 %, 2.68 % and 7.07 % respectively. The molecular formula for the 4-(diethylamino)benzoatetriphenyltin(IV) complex is $4\text{-}[N(C_2H_5)_2]C_6H_4COO(C_6H_5)_3Sn$ and the molecular weight of this complex is 510.25 g/mol.

The differences between the calculated percentage and the theoretical percentage obtained from CHN analysis should not more than 3.0 %. For the complex **1** and complex **2**, the calculated percentage of carbon, nitrogen and hydrogen compared to the data obtained from CHN analysis are below 3.0 %. Table 4.2 and Table 4.3 are elemental analysis results of the complexes.

Table 4.2 **The elemental analytical data (%) of bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer**

Element	Number atom	Molecular Weight	Total Molecular Weight	Analysis Percent (%)	Calculated Percent (%)	Delta (%)
C	76	12.0107	912.8132	52.78	52.68	0.10
H	128	1.00794	129.01632	7.07	7.45	0.38
N	4	14.0067	56.0268	3.19	3.23	0.04
Sn	4	118.71	474.84	27.37	27.41	0.04

Table 4.3 The elemental analytical data (%) of 4-(diethylamino)benzoatotriphenyltin(IV) complex

Element	Number atom	Molecular Weight	Total Molecular Weight	Analysis Percent (%)	Calculated Percent (%)	Delta (%)
C	29	12.0107	348.3103	64.28	64.24	0.04
H	29	1.00794	29.23026	5.00	5.39	0.39
N	1	14.0067	14.0067	2.63	2.58	0.05
Sn	1	118.71	118.71	21.31	21.89	0.58

4.4 Infrared spectroscopy

The IR spectra of the complexes are recorded in the range of 400-4000 cm^{-1}. The spectrums obtained are presented in Figures 4.4, 4.5, 4.6 and 4.7. Infrared spectroscopy is used to investigate the nature of –COO group coordination mode on the tin atom as well as the characteristic features or functional groups present in each complex. The absorptions of interest in the spectra of the complexes are υ(COO), υ(Sn-C) and υ(Sn-O).

The infrared spectrum of the complex **1** and complex **2** shows distinct differences from the acid. The υ(OH) band which appeared in the 2800-3000 cm^{-1} region for the acid, was absent in the infrared spectra of the complexes showing the occurrence of deprotonation prior to coordination of the resulting carboxylate anion in the complex formation (Yip *et al.*, 2008).

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. Strong absorption band that occurred at the wavenumber in between 3000-2700 cm^{-1} from the IR spectra of complex **1** and complex **2** are the characteristic methyl group, $-CH_3$. The methyl group has asymmetric and symmetric C-H stretching frequencies near 2690 cm^{-1} and 2870 cm^{-1} respectively. The asymmetric and symmetric C-H stretching bands of the methylene group, $-CH_2-$, are centered at 2930 cm^{-1} and

2850 cm^{-1} respectively. This result can be confirm that the existence of the long chain butyl group from dibutyltin(IV) in complex **1** and aromatic ring in 4-(diethylamino)benzoate ligand.

In the IR spectra of the complex **1,** the carboxylate bands are observed in the characteristic regions for υ_{asym} (COO) between 1522 and 1603 cm^{-1} and for υ_{sym} (COO) between 1353 and 1393 cm^{-1}. Meanwhile, the complex **2,** the carboxylate bands are observed in the characteristic regions for υ_{asym} (COO) at 1603 cm^{-1} and for υ_{sym} (COO) at 1347 cm^{-1}. υ_{asym} (COO) shifted to lower frequency due to the reduction of electron density. This is an indication to which the complex formation occurred.

The coordination mode of the carboxylate ligand to tin(IV) has been showed by $\Delta v = [v_{asym}(COO)–v_{sym}(COO)]$. When the differences between asymmetric frequency of carboxylate stretching band and symmetric frequency of carboxylate band of the complex is higher than the Δv of sodium ligand, hence the ligand is coordinate monodentate manner. If the Δv of complex is lower than the Δv of sodium salt ligand, then the ligand is conclude that coordinate in bidentate manner. The Δv values of the complex **1** and complex **2** used to compare with the Δv value of sodium salt of 4-(diethylamino)benzoate ligand (223 cm^{-1}). From the calculation, the Δv of the complex **1** was obtained as 210 cm^{-1} and 169 cm^{-1}. Meanwhile, the calculated value of the Δv for the complex **2** is 256 cm^{-1}. Hence complex **1** carboxylic anion is bidentate bonding to the tin atom, meanwhile complex **2** carboxylic anion is monodentate bonding to the tin atom.

Aromatic compounds exhibit one or more C=C stretching of vibration bands in between the region of v_{asym}(COO) and v_{sym}(COO) vibration band at 1600-1400 cm^{-1} (Pavia *et al.*, 2001). Two or more C=C vibration bands can be observed in complex **1** and complex **2** at the frequency region 1600-1400 cm^{-1}. *Ortho*-disubstitution usually shows one very strong peak at 770-730 cm^{-1} (Yip *et al.*, 2008) was found in complex **2**. There are absorption peak that occur in complex 2 at the region 770-690 cm^{-1} that represent as mono-substitution out-of-plane for phenyl group in complex **2**.

The presence of the υ(Sn-O-Sn) in the organotin(IV) compounds in the 600-700 cm^{-1} region displays a strong band, and the presence of υ(Sn-O) in the 450-475 cm^{-1} range indicates deprotonation of the carboxylic acid group and consequent coordination of the carboxylate group with the tin metal as expected. υ(Sn-C) stretching frequencies are observed at 600-500 cm^{-1} (Sandhu *et al.,* 1991). υ(Sn-C) and υ(Sn-O) of complex **1** occurs at 597 cm^{-1} and 467 cm^{-1}, respectively. Meanwhile, υ(Sn-C) and υ(Sn-O) of complex **2** occurs at 505 cm^{-1} and 448 cm^{-1}, respectively. Moreover, the infrared spectrum of the complex **1** displays a strong band at 633 cm^{-1} assigned to the υ(Sn-O-Sn). This band is not observable in complex **2**. The main infrared spectral data are listed in Table 4.4

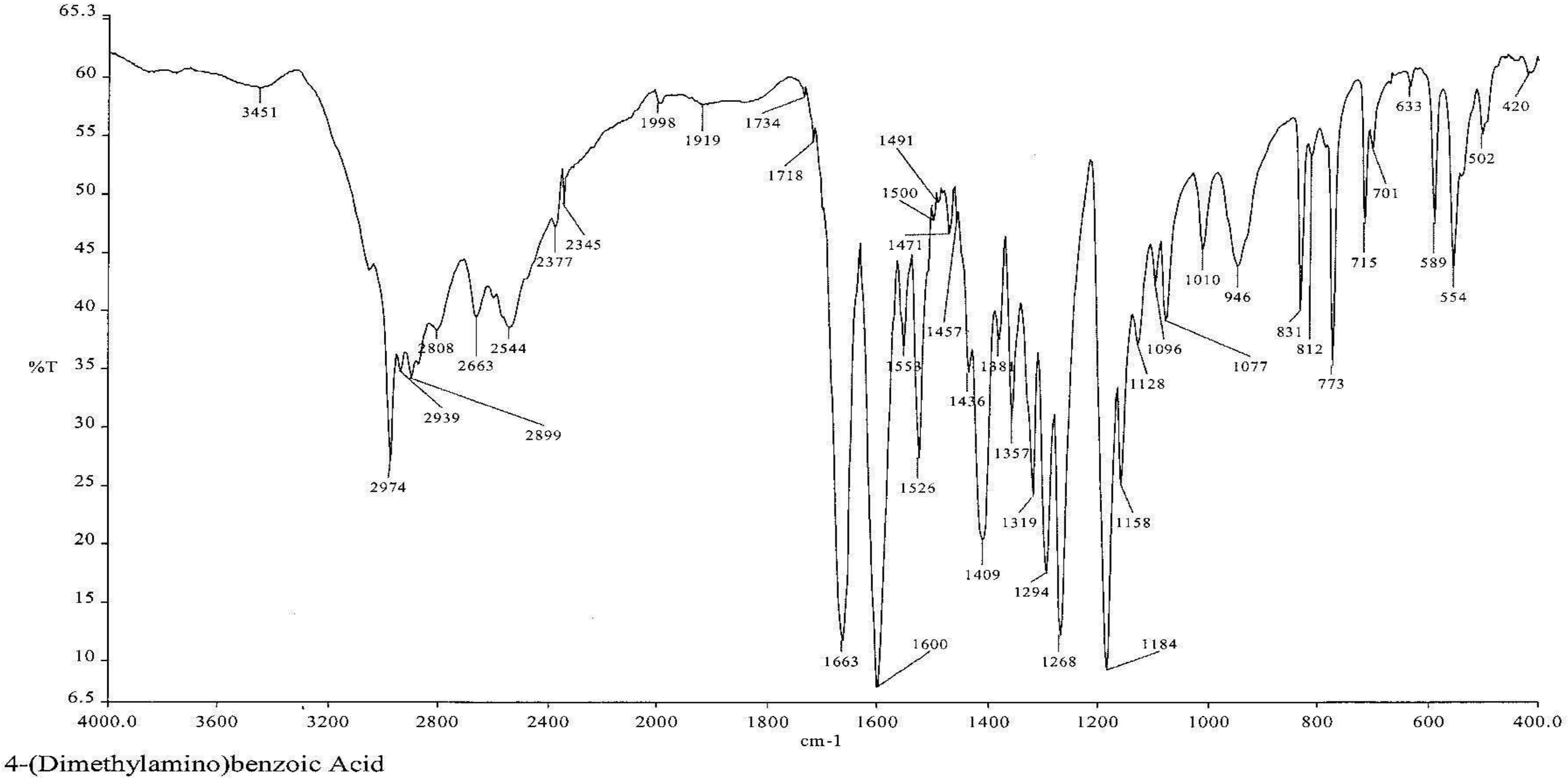

Figure 4.4 The FTIR spectrum of 4-(diethylamino) benzoic acid

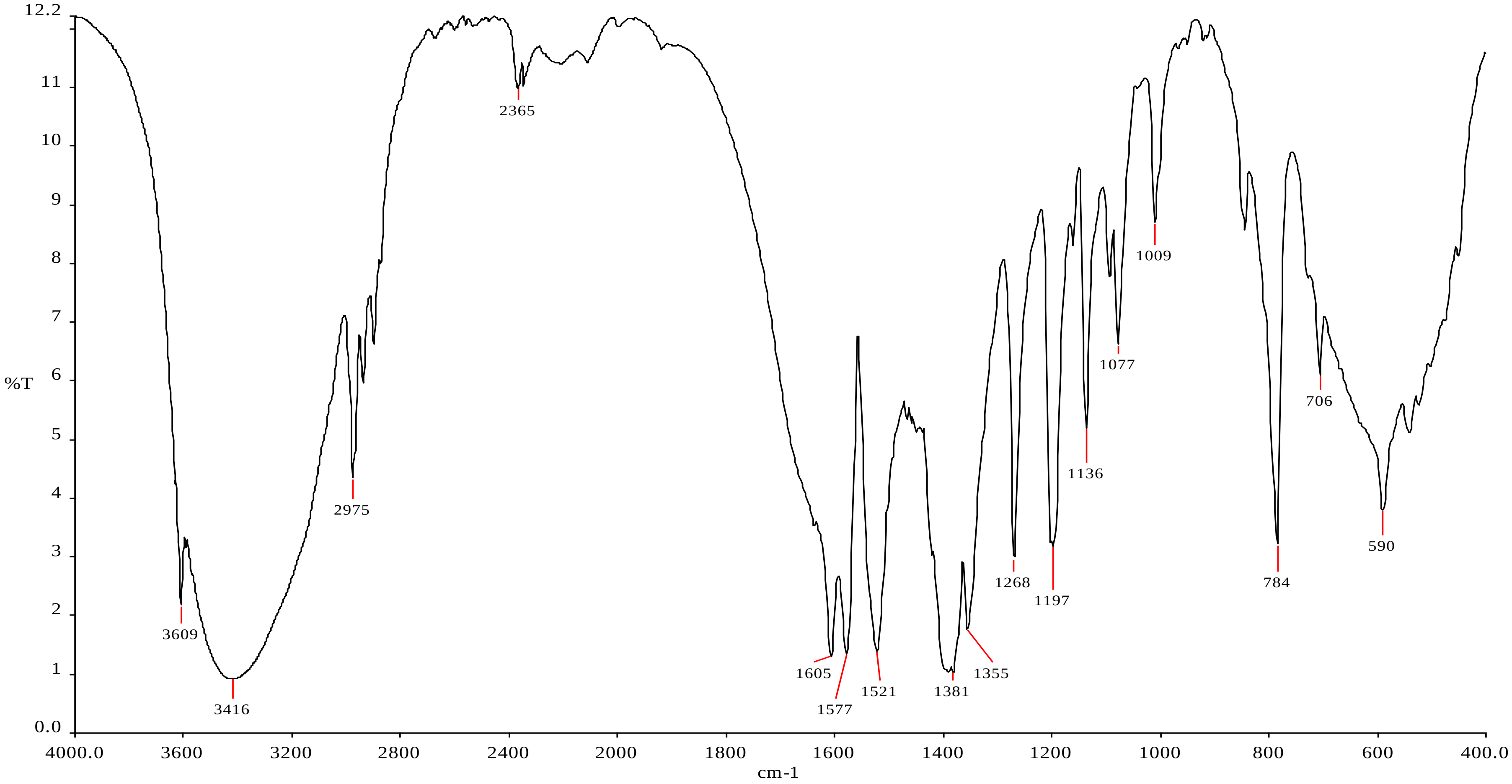

Figure 4.5 **The FTIR spectrum of sodium 4-(diethylamino)benzoate**

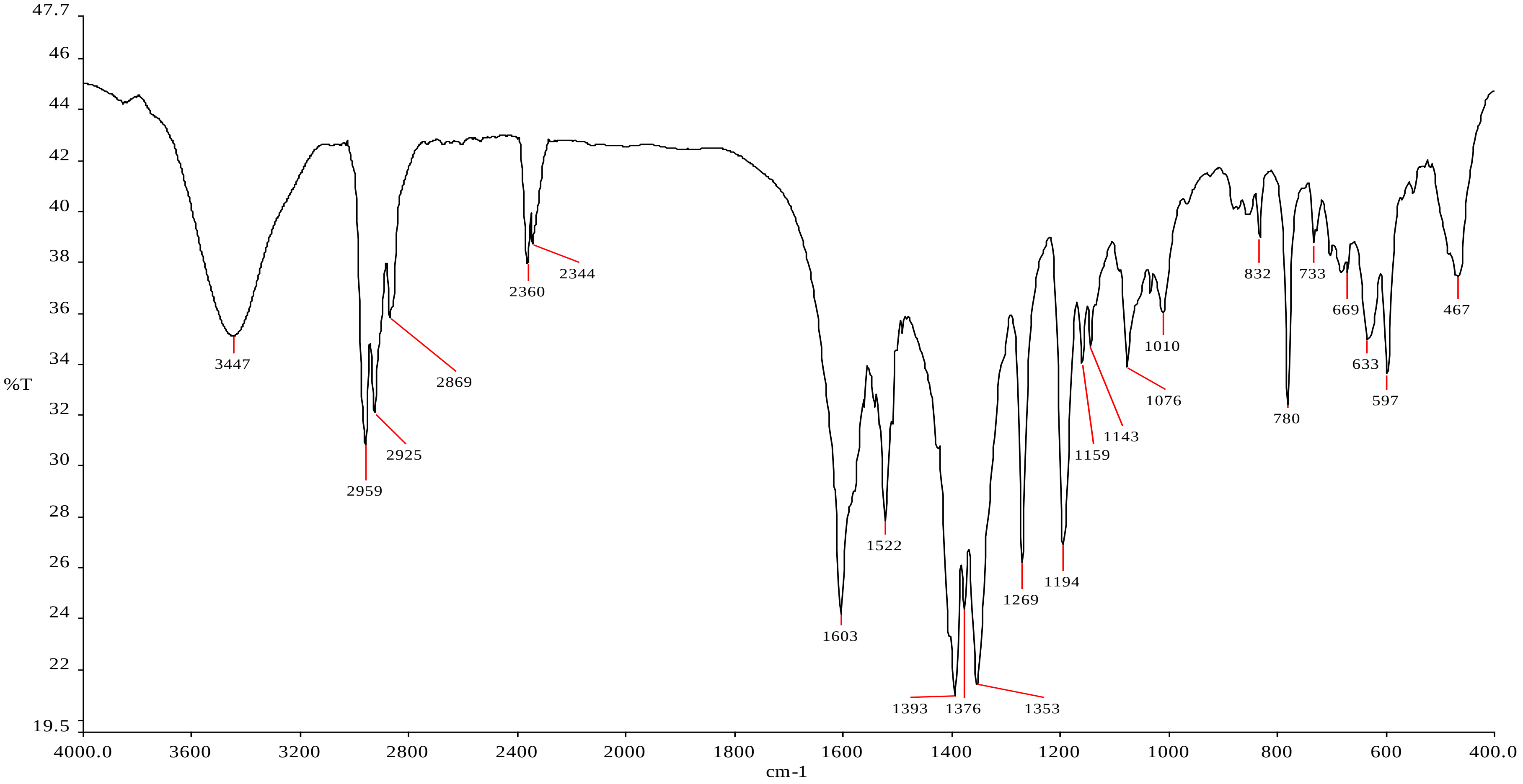

Figure 4.6 The FTIR spectrum of bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex

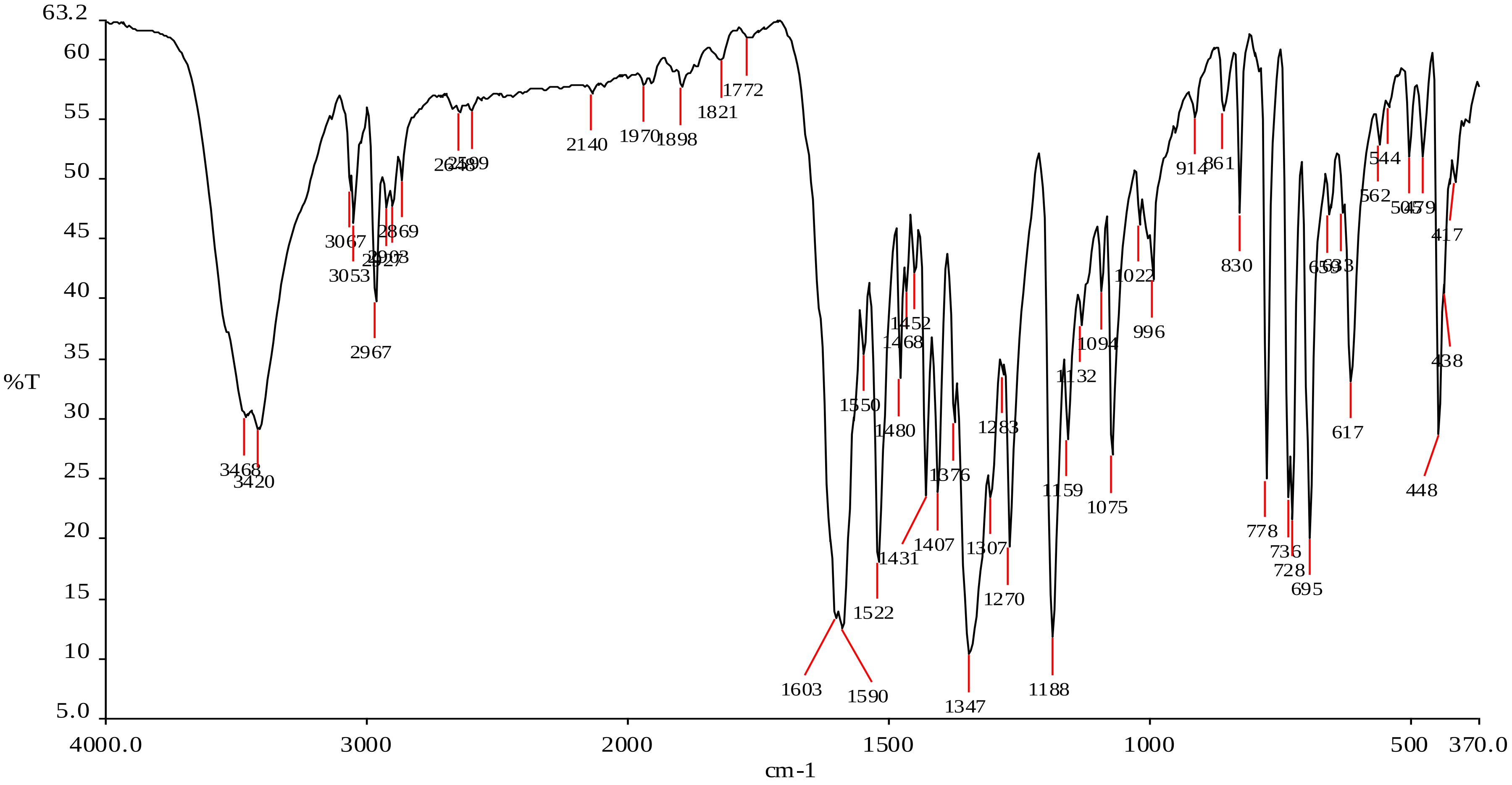

Figure 4.7 **The FTIR spectrum of 4-(diethylamino)benzoatotriphenyltin(IV) complex**

Table 4.4 **The main infrared spectral data in in sodium 4-(diethylamino) benzoate, bis[4-(diethylamino)benzoato]tetrabutyl distannoxane(IV) dimer complex and 4-(diethylamino)benzoatotriphenyltin(IV) complex.**

Compound	υ(COO)			υ(Sn-O)	υ(Sn-C)	υ(Sn-O-Sn)	υ (O-Sn-O)
	υ_{asym}	υ_{sym}	Δ				
Sodium 4-(diethylamino)benzoate	1604 vs	1381 vs	223				
	1603 vs	1393 vs	210				
Complex 1	1522 s	1353 vs	169	467	597	633	669
Complex 2	1603 vs	1347 vs	256	448	505		

***υ = stretching vibrational mode, vs = very strong, s = strong**

Complex 1 - Bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex.

Complex 2 - 4-(diethylamino)benzoatotriphenyltin(IV)complex

4.5 NMR Spectroscopy

Valuable information concerning the structures of the bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV), **(1)** and 4-(diethylamino)benzoatetriphenyltin(IV), **(2)** can be deduced from the ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic studies.

4.5.1 ^{1}H NMR Spectroscopy

The ^{1}H NMR spectroscopy is used to deduce the molecular structure of the complexes by their intensity and multiplicity patterns. The upfield regions of the ^{1}H NMR spectra of complex **1** shows the signals of the butyl protons in the range 0.87-1.10 ppm that appear as triplet, the second signals occur at the region 1.21-1.40 ppm that exhibited as multiplet and the third signal found at the region 1.67-1.73 ppm with doublet splitting. It has been reported that the proton resonances of the di-*n*-butyltin(IV) derivatives occur in the regions of the 0.91–1.91 ppm (Yip *et al.,* 2008). Detailed assignment of each peak is shown in Figure 4.9.

The ^{1}H chemical shift of *ortho* phenyl proton found as multiplet splitting at the region range 7.76-7.80 ppm, whereas, ^{1}H chemical shift of *meta* and *para* observed at the region 7.40-7.50 ppm as multiplet signal (Yip *et al.,* 2008). The ^{1}H NMR spectra of complex **2** shows two signals of phenyl proton of triphenyltin that can be observed at 7.48-7.58 ppm and 7.78-7.88 ppm. Multiplet splitting at the region 7.48-7.58 ppm which assigned as ^{1}H chemical shift of *meta* and *para* phenyl proton, whereas, ^{1}H

chemical shift of *ortho* phenyl proton found as multiplet splitting at the region range 7.78-7.88 ppm. Detailed assignment of each peak is shown in Figure 4.10.

In the spectrum of acid (Figure 4.8), the benzene protons of the acid ligand appear in the downfield region in the range 6.53-8.18 ppm. 4-diethylamino benzoic acid ligand shows the signal 6.53-6.94 ppm and 7.76-8.18 ppm that having spin splitting as doublet of doublet, whereas, in the region 7.21-7.33 ppm appear as singlet in the spectrum. Complex **1** shows ^{1}H chemical shift of benzene proton signals at the region range 6.64-6.66 ppm and 7.21-7.33 ppm. Chemical shift for aromatic proton signals of complex **2** at the region range 6.65-6.66 ppm, 7.42-7.58 ppm and 7.78-7.88 ppm. The carboxylic acid proton signal that resonated at 8.18 ppm and 8.05 ppm in the ^{1}H NMR spectrum was invisible in the spectra of ^{1}H NMR complex **1** and complex **2** respectively. This disappearing of carboxylic acid indicates to the deprotonation of carboxylic acid proton and formation of complex (Zhang *et al.*, 2008).

As a conclusion, the perfect matching of the number of protons for each fragment of the predicted molecular structure corresponding signals in the ^{1}H NMR spectrum implies the complexes synthesized fits well with the predicted molecular structure. The disappearance of carboxylic acid proton in the ^{1}H NMR spectrum of complex **1** and complex **2** is another confirmation to the deprotonation of carboxylic acid proton. In addition, the absence of any impurity peaks in the ^{1}H NMR spectrum is indicative of an experimentally pure complexes thus prepared. ^{1}H NMR chemical shift values of 4-(diethylamino) benzoic acid, and the complexes synthesised were tabulated in Table 4.5.

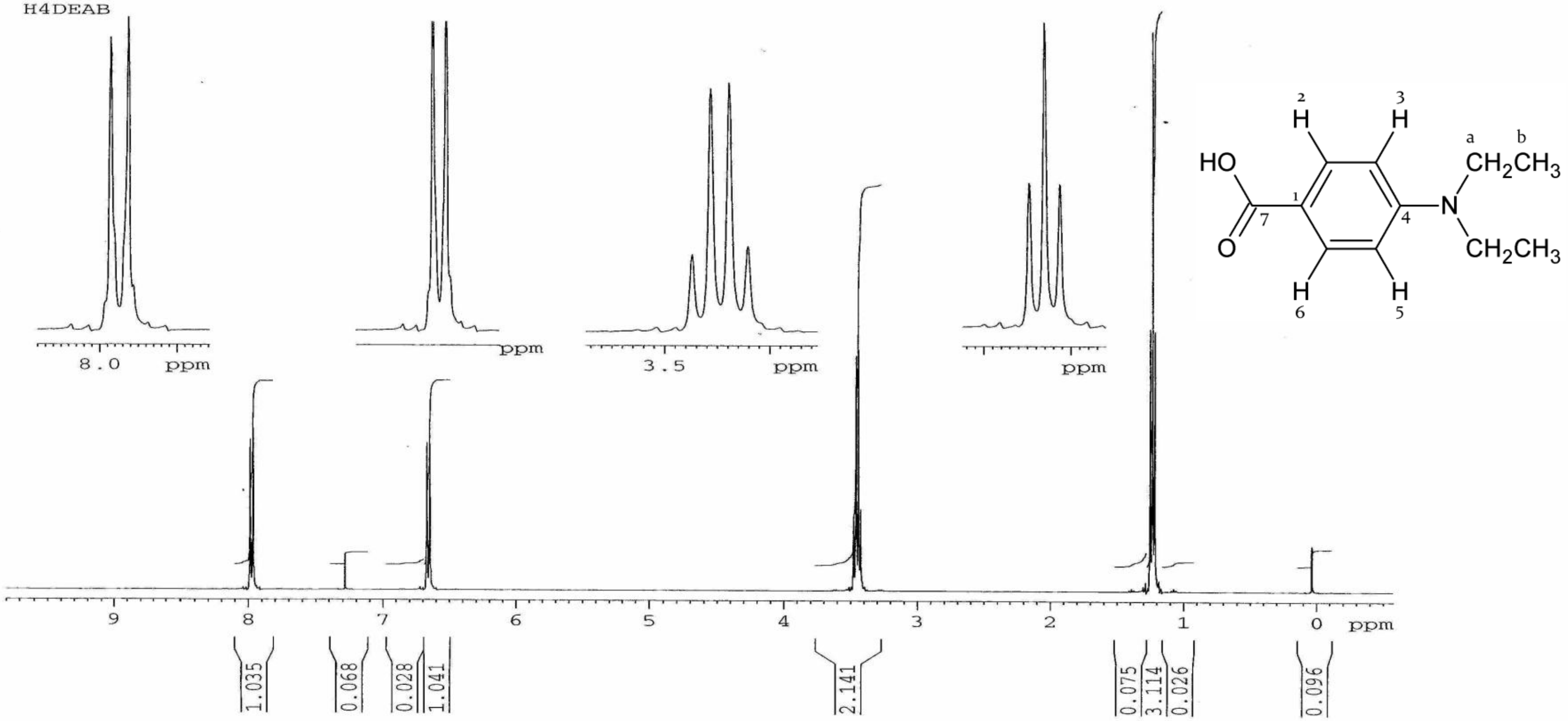

Figure 4.8 ^{1}H NMR spectrum of of 4-(diethylamino) benzoic acid

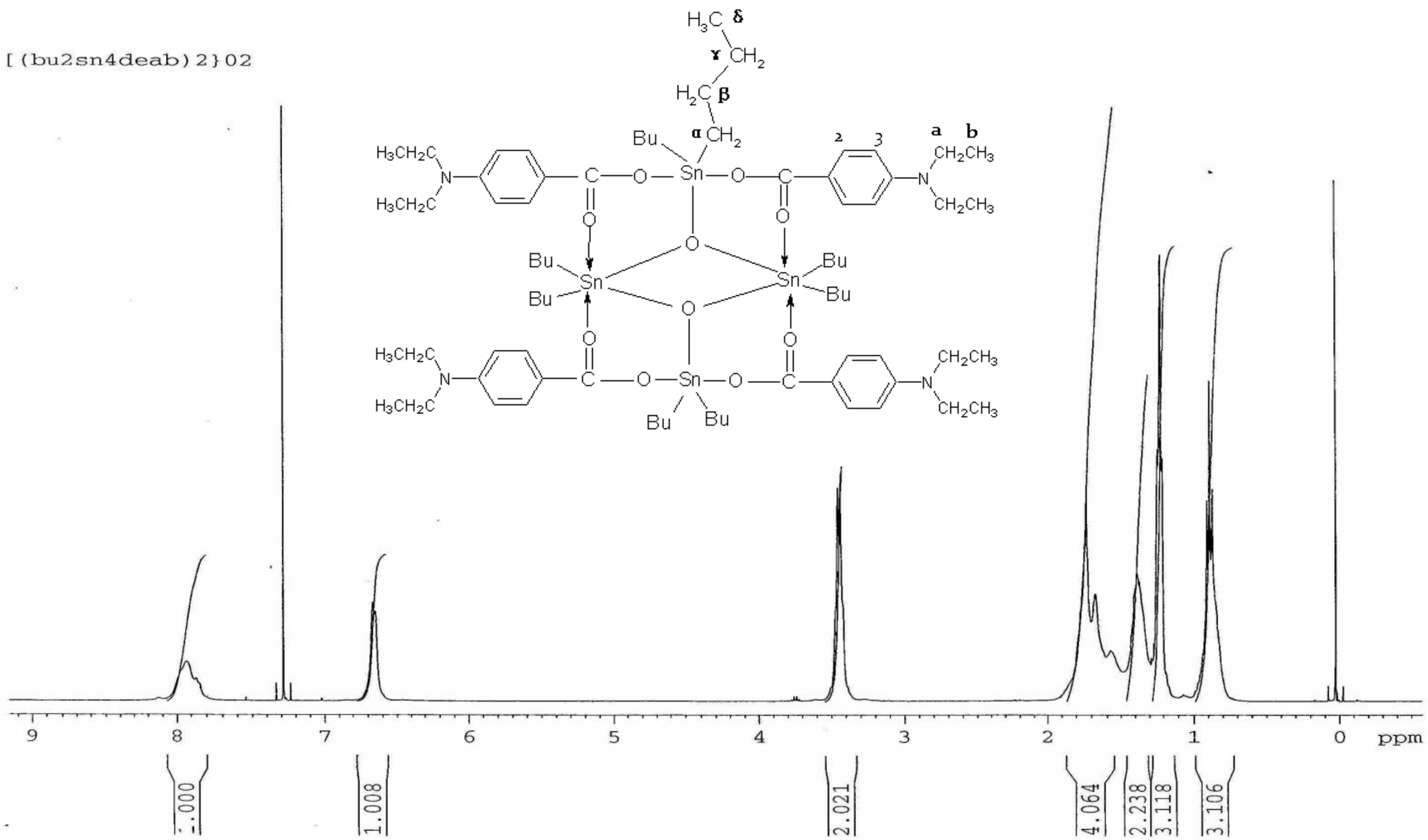

Figure 4.9 ^{1}H NMR spectrum of bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex

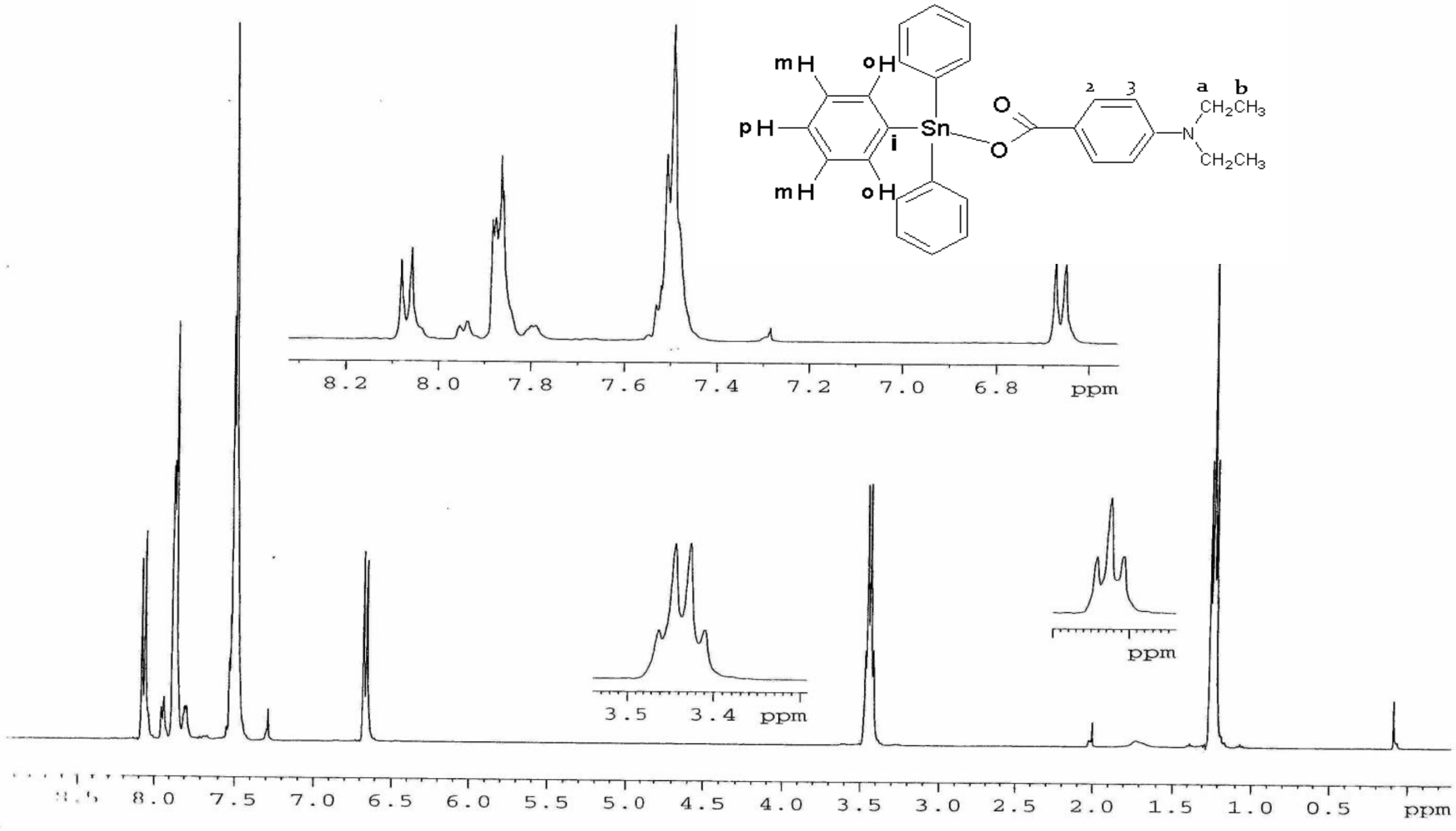

Figure 4.10 ^{1}H NMR spectrum of 4-(diethylamino)benzoatotriphenyltin(IV) complex

Table 4.5 **The major ^{1}H NMR chemical shift data in complex 1, 2 and acid ligand.**

Complex	Chemical shift (ppm)
4-(diethylamino) benzoic acid	H_2= 8.15-8.18 (d), H_3= 6.94-6.97 (d); H_a= 3.40-3.51 (t), H_b= 1.05-1.15 (t)
Complex 1	H_2= 8.72 (d), H_3= 6.51-6.83 (d); H_a= 3.40-3.51 (t); H_b= 1.05-1.15 (t)
	H_δ= 0.81-0.93 (m), 6H; H_γ= 1.28-1,47 (m), 4H; H_α H_β= 1.47-1.80 (m), 8H
Complex 2	H_2= 8.73-8.74 (d), H_3= 6.51-6.73 (d)
	H_a= 3.40-3.51 (t); H_b= 1.05-1.15 (t); H_m H_p= 7.53-7.59 (m), 9H; H_o= 7.87-7.97 (m), 6H

***d=doublet, t=triplet, q=quartet**

Complex 1 - Bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex.

Complex 2 - 4-(diethylamino)benzoatotriphenyltin(IV) complex.

4.5.2 ^{13}C NMR Spectroscopy

Evidence of the formation of the complexes is clearly displayed in the ^{13}C NMR spectrum. In the ^{13}C NMR data explicitly resolved the resonance of all the distinct type of carbon atoms present in the complex. The ^{13}C NMR spectrum of free ligand (Figure 4.11), complex **1** (Figure 4.12) and complex **2** (Figure 4.13) are obtained. The downfield regions of the ^{13}C NMR spectrum of complex **1** show a sharp peak carbon signal at 173.43 ppm. This signal is assigned to the $\delta(COO^-)$ chemical shift. Moreover, the ^{13}C NMR spectrum of complex **1** shows that the chemical shift $\delta(COO^-)$ signals is shifted downfield compared to that of the acid (173.02 ppm) indicating the carboxylate anion is bonded to tin upon complexation. The occurrence of six resonances in the range 109.13-150.78 ppm in the ^{13}C NMR spectrum of the complex **1** and acid are due to the presence of benzene carbons. In the upfield region of ^{13}C NMR spectrum, the complex **1** shows the occurrence of CH_3 and CH_2 in the range 13.17-13.97 and 23.84-29.62 ppm, respectively. The butyl group of the di-*n*-butyltin derivatives in $CDCl_3$ solution exhibit four signals in the upfield region of 13.1-26.4 ppm (Yip *et al.,* 2008). In addition, the complex **1** exhibited two sets of butyl signals in ^{13}C NMR spectrum. This attributed to the butyl groups linked to the exo- and endo-cyclic tin atom respectively (Danish *et al.*, 1995).

The chemical shift for the aromatic carbons for the ^{13}C NMR spectrum of complex **2** (in $CDCl_3$ solution) appear in the downfield region of 116.29-151.41 ppm (Shandu *et al.,* 1991). The $\delta(COO^-)$ signal of carboxyl carbon occur at 173.95 ppm. The chemical shift $\delta(COO^-)$ signals is shifted downfield compared to that of the acid

(173.02 ppm) indicating the carboxylate anion is bonded to tin upon complexation. The carboxylate carbon being attached to two electron-withdrawing oxygen atoms, is more deshielded and its signal appears slightly downfield in the region (Parulekar *et al.,* 1990).

The phenyl group of the triphenyltin derivatives in $CDCl_3$ solution exhibit in the downfield region of 128.43-136.41 ppm. This occurrence is due to the effect of anisotropic and hybridization of benzene group. The chemical shift of the $\delta(^{13}C)_{ipso}$ is found at region 137.1-143.8 ppm, whereas the chemical shift of $\delta(^{13}C)_{ortho}$, $\delta(^{13}C)_{meta}$, $\delta(^{13}C)_{para}$ are found in the region 133.9-137.2 ppm (Pruchnik *et al.,* 2003). In the ^{13}C NMR spectrum, the complex **2** shows the occurrence of $\delta(^{13}C)_{ipso}$, $\delta(^{13}C)_{ortho}$, $\delta(^{13}C)_{meta}$ and $\delta(^{13}C)_{para}$ in the range 139.75 ppm, 137.07 ppm, 133.24 ppm and 128.71, respectively. Additionally, The chemical shift of the $\delta(^{13}C)_{ipso}$ is useful to determine the coordination of tin atom, when the $\delta(^{13}C)_{ipso}$ chemical shift occur at about 138 ppm and 142 ppm, hence the tin atom is said to be four and five coordinated respectively (Pruchnik *et al.,* 2003). Hence can conclude that the $\delta(^{13}C)_{ipso}$ chemical shift occur at 139.75 ppm the tin atom is four coordinated. The ^{13}C NMR data of free ligand and complexes are determined and tabulated in Table 4.6.

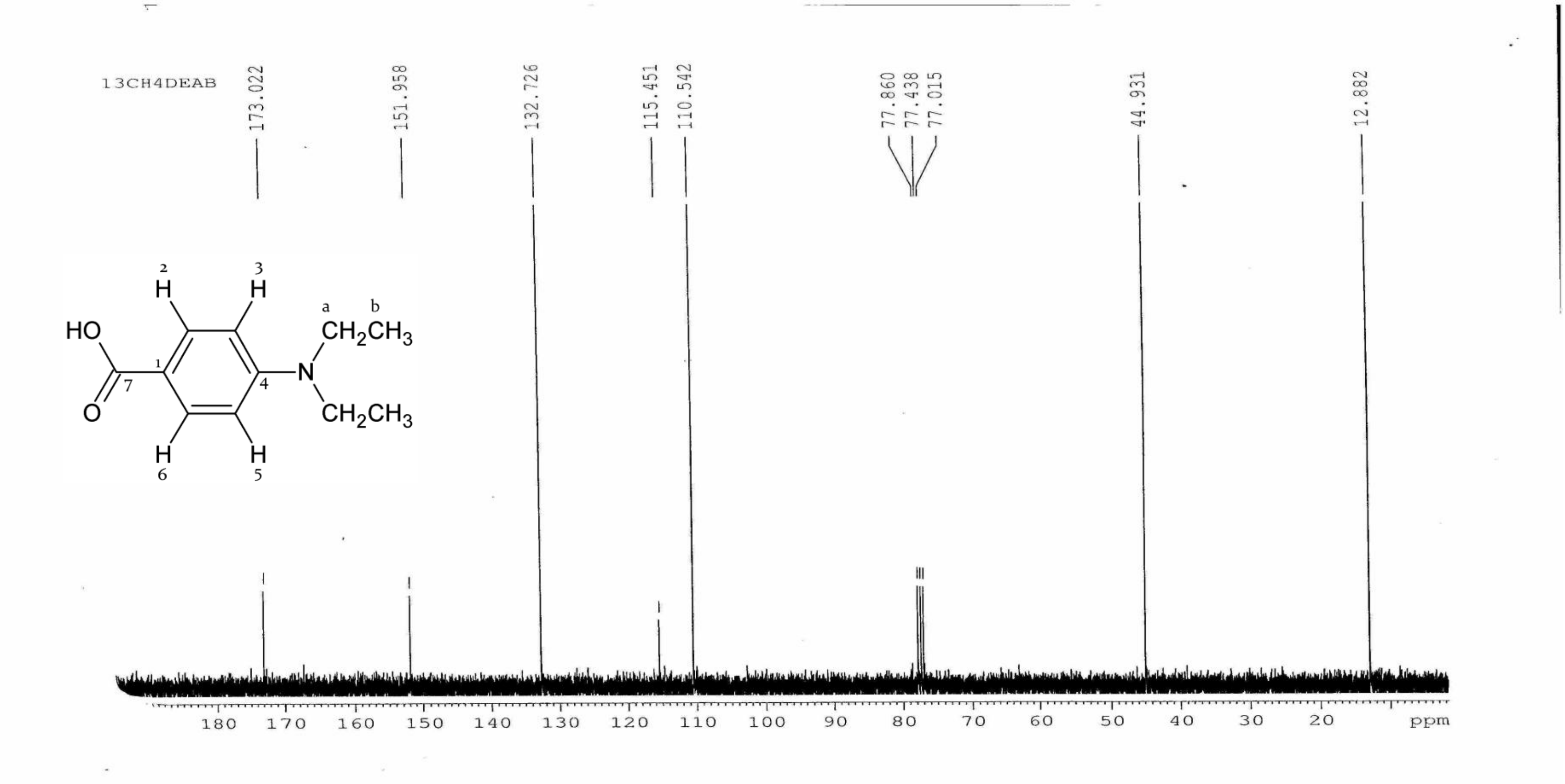

Figure 4.11 ^{13}C NMR spectrum of of 4-(diethylamino) benzoic acid

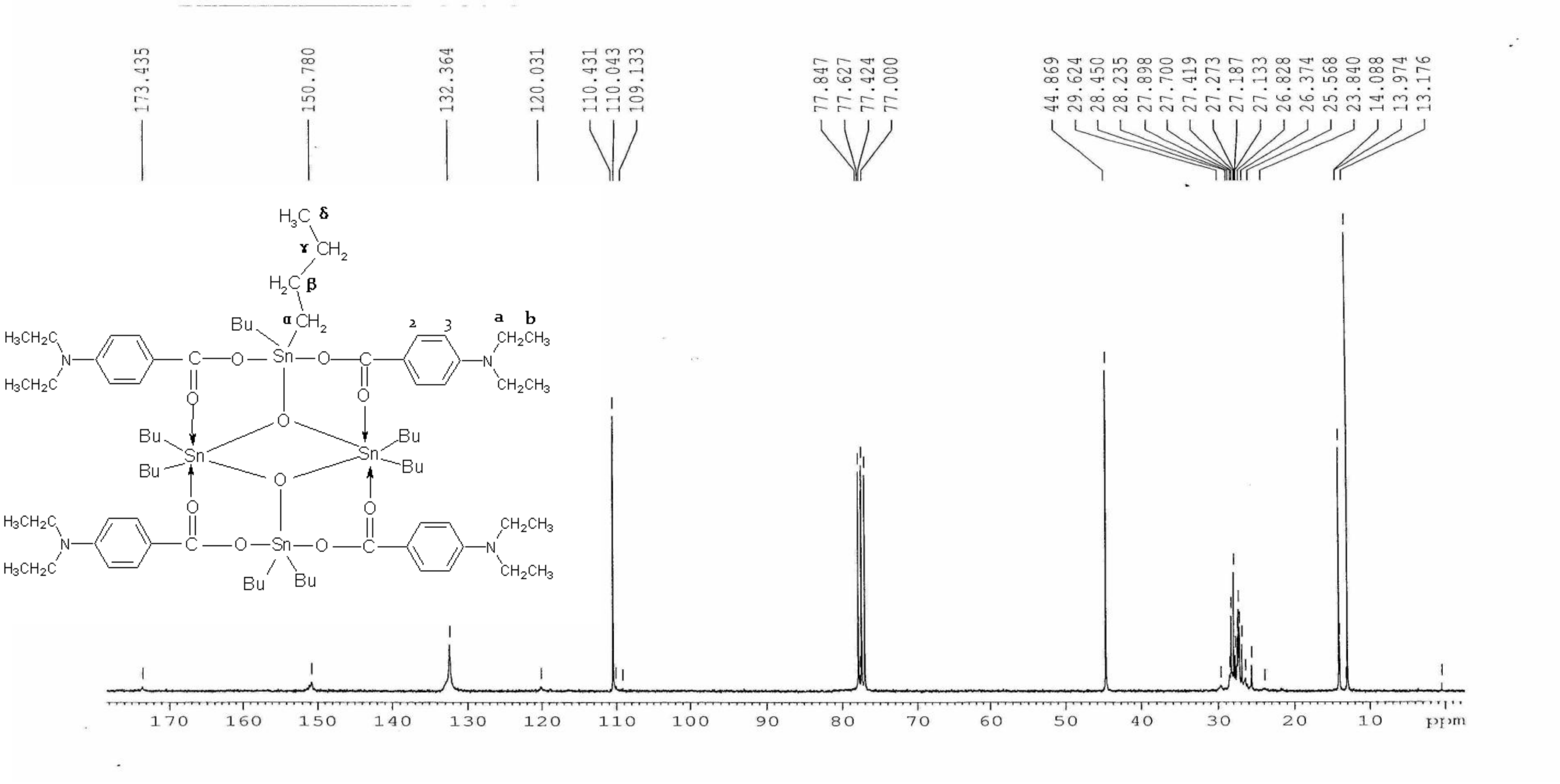

Figure 4.12 ^{13}C NMR spectrum of bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex

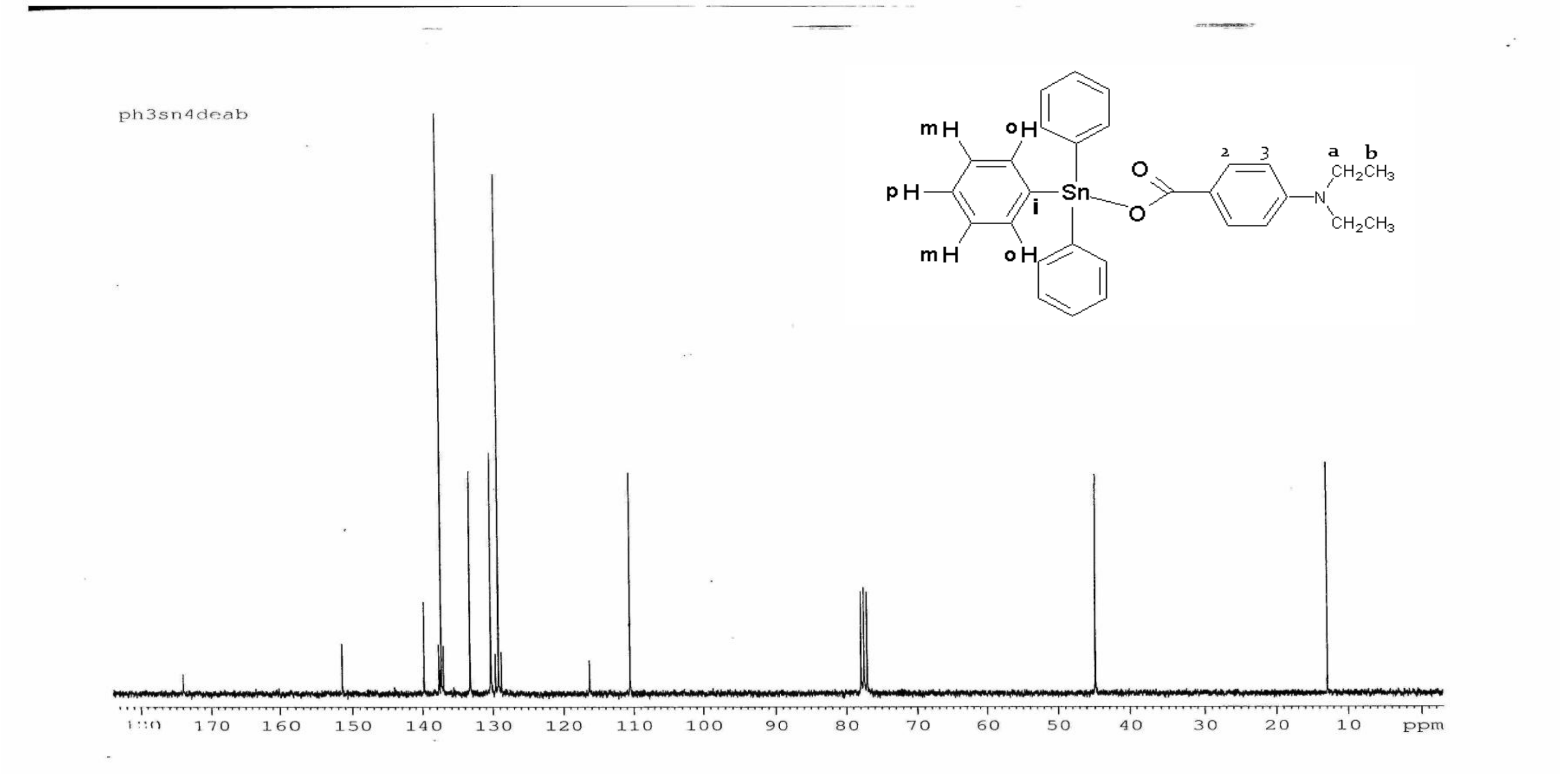

Figure 4.13 ^{13}C NMR spectrum of 4-(diethylamino)benzoatotriphenyltin(IV) complex

Table 4.6 The major ^{13}C NMR chemical shift data in complex 1, 2 and acid ligand.

Complex	Chemical shift (ppm)
4-(diethylamino) benzoic acid	C_1= 109.31, C_2= 136.99, C_3= 117.34, C_4= 151.58, C_7= 172.95; C_a= 46.31, C_b= 11.99
Complex 1	C_1= 109.27, C_2= 136.49, C_3= 119.50, C_4= 152.47, C_7= 173.55; C_a= 48.49, C_b= 12.11; C_δ= 13.71-13.91; C_γ C_α C_β= 26.09-27.29
Complex 2	C_1= 110.77, C_2= 135.92, C_3= 117.75, C_4= 152.97, C_7= 173.89; C_a= 48.72, C_b= 12.52; C_m= 128.43, C_p= 129.03, C_o= 142.87, C_i= 142.87

Complex 1 - Bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex.

Complex 2 - 4-(diethylamino)benzoatotriphenyltin(IV) complex

4.5.3 ^{119}Sn NMR Spectroscopy

It has been reported that in alkyltin carboxylates, four-coordinate tin has δ^{119}Sn value raging from +200 to -60 ppm, five-coordinate tin from -90 to -190 ppm and six-coordinate tin from -210 to -400 ppm (Mahmood *et al.*, 2003; Tao *et al.*, 1996; Holecek *et al.*, 1986). The complex **1** showed two well separated resonances of $\delta(^{119}$Sn) at -171.646 ppm and -221.432 ppm, respectively. These two well separated resonances, respectively, are attributed to the endocyclic and exocyclic tin atoms in the distannoxane dimer (Danish *et al.*, 1995). The resonances of $\delta(^{119}$Sn) at -171.646 ppm lie in the lower range of values for five-coordinated tin atom, whereas, the resonances of $\delta(^{119}$Sn) at -221.432 ppm lie in the upper range of values for six-coordinated tin atom. The existence of two resonances of $\delta(^{119}$Sn) is due to fast exchange in the coordination behaviour of carboxylate groups attached to endo and exo-cyclic tin atoms as reflected by different butyl signals (Khan *et al.*, 2004). Detailed assignment of each peak is shown in Figure 4.14.

On the basis of the values of the chemical shifts $\delta(^{119}$Sn) of the triphenyltin(IV) compounds examined vary over a wide range, from -44.7 ppm up to -257.2 ppm. Although the chemical shift $\delta(^{119}$Sn) lie in a broad range from -40 to -120 ppm, they never exceed the maximum value of -128.1 ppm (tetraphenyltin) are known to form tetrahedral molecules with a four-coordinate tin atom in the solid state (or at least in a solution) (Zuckerman *et al.*, 1970). The compounds with higher $\delta(^{119}$Sn) values shifts from -180 to -260 ppm involve molecules with trigonal-pyramid geometry around five-coordinate tin atom (Carpino *et al.*, 1980). There is a sharp and strong $\delta(^{119}$Sn) signal found in the ^{119}Sn NMR spectra of complex **2**, the signal occur at chemical shift -127.329 ppm, and hence we can conclude that the tin atom of complex **2** is a four-coordinate tin atom. Detailed assignment of each peak is shown in Figure 4.15.

Therefore, ^{119}Sn NMR parameters are very useful for the determination of the coordination number of tin and its geometry and consequently, the molecular geometry of the complexes thus prepared (Mahmood *et al.,* 2003). The signals of complex **1** are given in two well separated signals peaks which confirm as endocyclic and exocyclic tin respectively, the two signals giving two types of coordination number of tin atom as five and six-coordinated whereas, ^{119}Sn NMR spectra of complex **2** shows only a single strong peak that indicate as four-coordinated tin atom. This indicates that only one bond between tin atom with anion carboxylate in complex **2**. All of the Sn chemical shifts gained from the complexes are tabulated in Table 4.7.

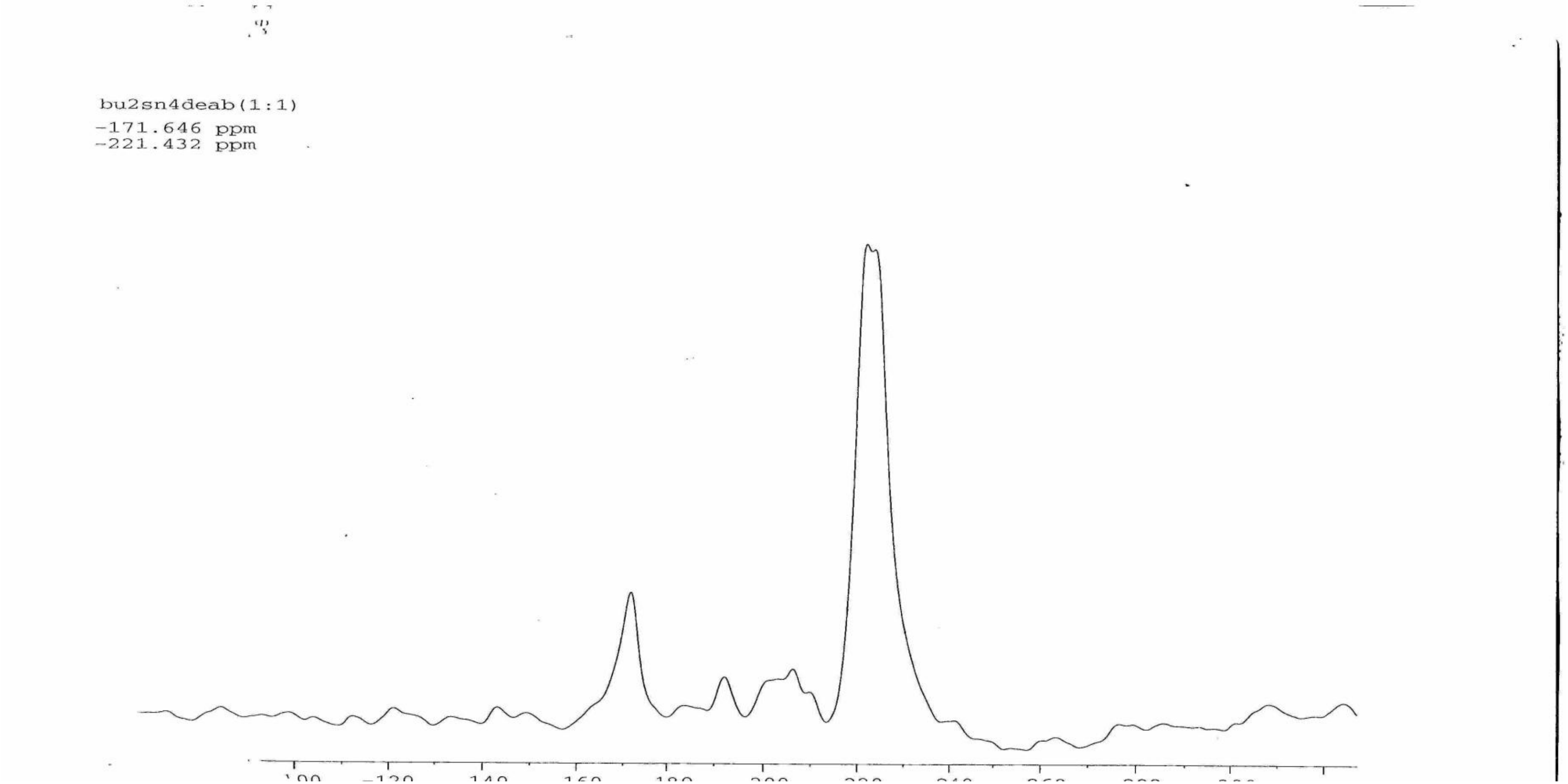

Figure 4.14 ^{119}Sn NMR spectrum of bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex

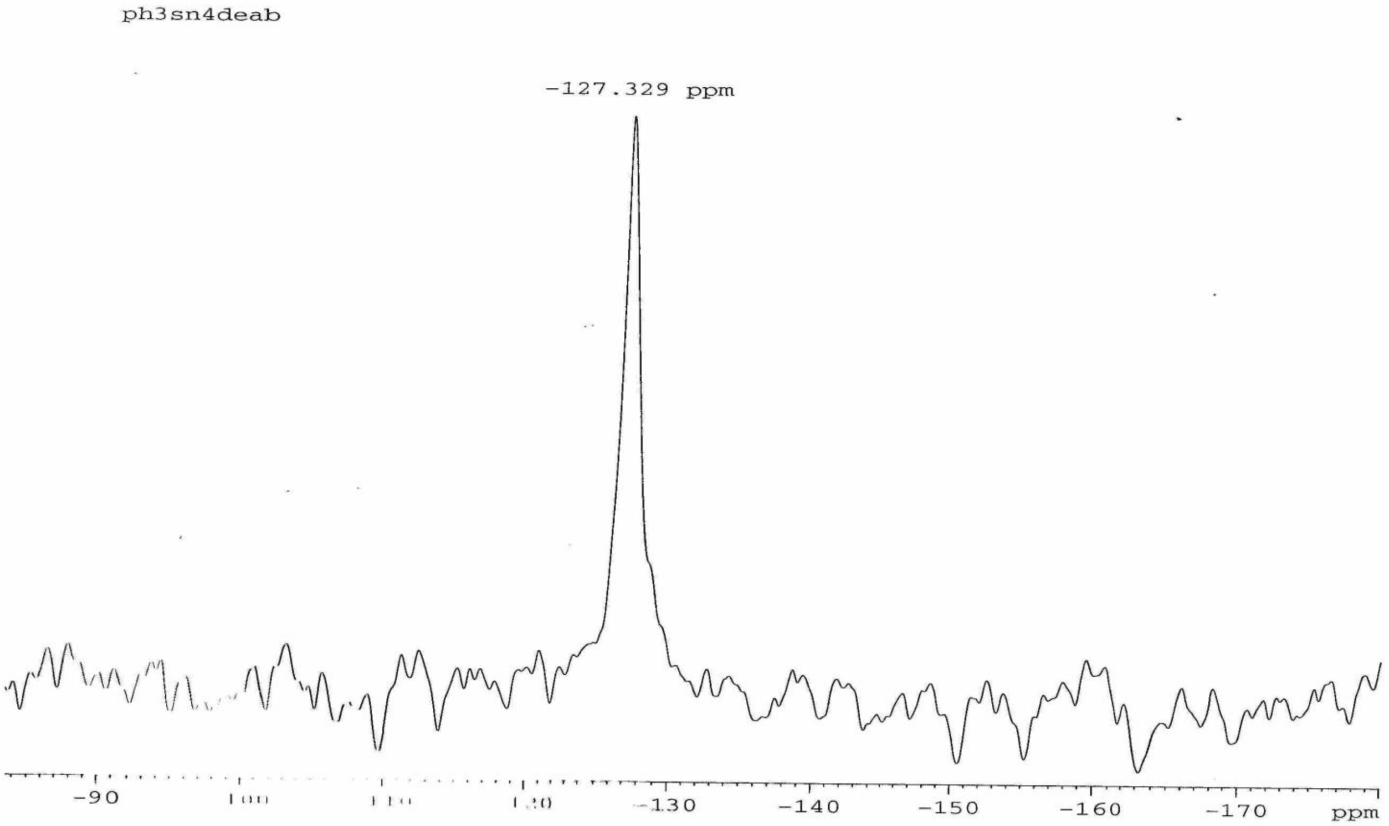

Figure 4.15 ^{119}Sn NMR spectrum of 4-(diethylamino)benzoatotriphenyltin(IV) complex

Table 4.7 The major ^{119}Sn NMR chemical shift data in bis[4-(diethylamino)benzoato]tetrabutyldistannoxane(IV) dimer complex and 4-(diethylamino)benzoatotriphenyltin(IV) complex.

Complex	**Chemical shift (ppm)**
Bis[4-(diethylamino)benzoato]tetrabutyl distannoxane(IV) dimer complex	**-171.646** **-221.432**
4-(diethylamino)benzoatotriphenyltin(IV) complex	**-127.329**

CHAPTER 5

CONCLUSION

The bis[4-(diethylamino)benzoato]tetrabutyl distannoxane(IV) dimer complex **1** and the 4-(diethylamino)benzoatotriphenyltin(IV) Complex **2** are success synthesised and fully charaterized.

For the complex **1** and complex **2**, the calculated percentage of carbon ,nitrogen and hydrogen compared to the data obtained from CHN analysis are below 3.0 %. The differences between the calculated percentage and theoretical percentage obtained from CHN analysis are not much varied. Both complex **1** and **2** giving the sharp melting point. The analysis data can deduced that the purity of the complexe that has been successfully synthesized. Elemental analysis result of the complex **1** and **2** were agreement with the predicted formula.

The infrared spectrum of the complex **1** and **2** showed distinct differences from the acid ligand. The υ(OH) band which appread in the acid, was absent in the infrared spectra of the complexes showing the occurrence of the deprotonation prior to cooridnation of the resulting carboxylate anion in the complex formation. The presence of the υ(Sn-O-Sn) , υ(Sn-O) and υ(Sn-C) indicates coordination of the carboxylate group with the tin metal.

The differences [$\upsilon\Delta$)], between υ_{asym}(COO) as and υ_{sym}(COO) is important to determine the coordination of the carboxylic groups boding to the tin atom. From the FTIR spectra of the complex **1** υ_{asym}(COO) vibraional peaks has shifted to higher frequency which complex **2** shift to the lower frequency, whereby will causes the electron density of the carboxyl group tend to donate to the d acceptor of the tin atom.

NMR spectroscopy provided valuable information about the structure of complex **1** and **2**. The number of protons for each fragment of the predicted molecular structure corresponding signals in the ^{1}H NMR spectrum implies the complex **1** and **2** synthesized fits well with the predicted molecular structure. The disapperance of the carbxylic acid proton in 1H NMR spectra of the complex **1** and **2** is the another confirmation to the deprotonation of carboxylic acid proton.

The chemical shift δ(COO^{-}) signal of complex **1** and **2** is shifted downfield compared to that of the acid indicating carboxylate anion is bonded to tin upon complexation. In addition, the absence of any impurity peaks in the ^{1}H NMR and ^{13}C NMR spectrum is indicative of an experimentally pure complexes thus prepared.

The signal of ^{119}Sn NMR spectra of complex **1** is given in two well separated signal peak which confirmed as endocylic and excocylic tin respectivetely, the two signals giving two types of cooridnation number of tin atoms as five and six-cooridnated whereas, ^{119}Sn NMR spectra of complex **2** shows only a single strong peak that indicate as four-coordinated tin atom. This indicates that only one bond between tin atom which anion carboxylate in complex **2**.

As a conclusion, all the value and data obtained from the qualitative and quantitative analysis are well defined and proven that both of the complex **1** and complex **2** were in agreement with the predicted formula and structure. The structure of the complex **1** and **2** are shown in Figure **1** and **2**.

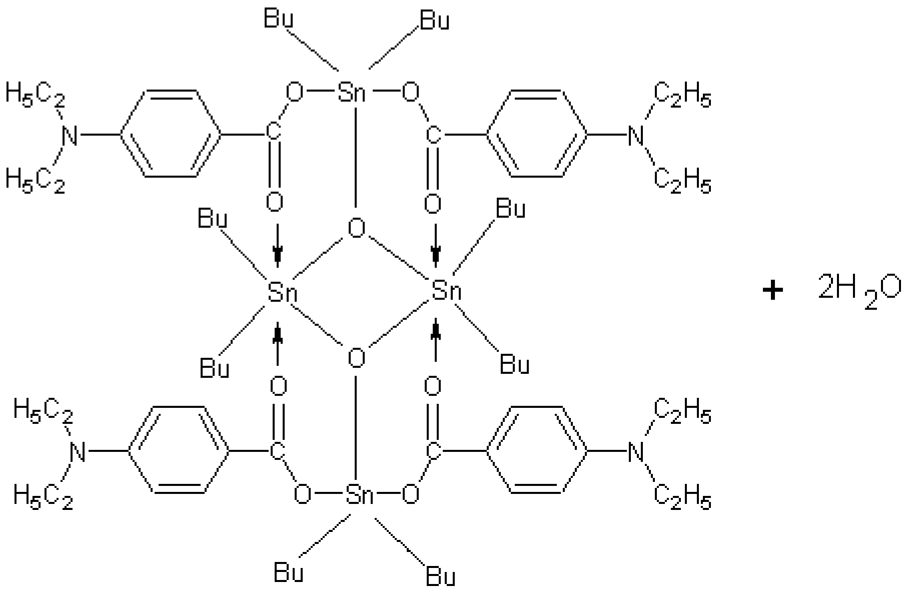

Figure 5.1 The strucure of bis[4-(diethylamino)benzoato] tetrabutyldistannoxane(IV) Dimer Complex

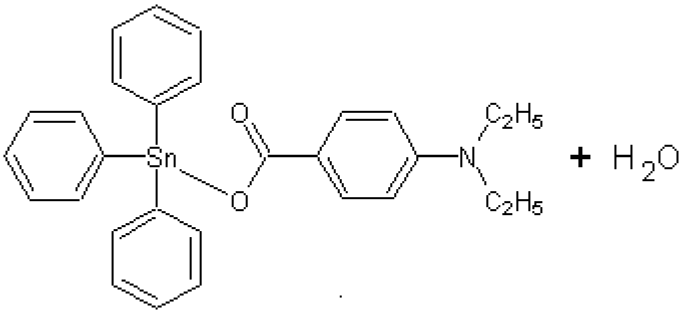

Figure 5.2 The structure of of 4-(diethylamino)benzoate triphenyltin(IV) Complex